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of
Process- and Aerosol Measurement Technology Division

Prof. Dr.-Ing. H. Fissan

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1. Preface

This documentation is designed to give the reader insight into the activities of our department.

The teaching activities of the department are mainly in the fields of measurement and process technology. In research we are concentrating on the material system aerosol, liquid and/or solid particles suspended in a gas.

Of equal interest for us are unwanted aerosols emitted from technical processes and distributed in the atmosphere and wanted product aerosols.

The work related to emission and immission of aerosols is mainly concentrating on the implications of the introduction of new EU particulate matter (PM$_x$) Standards. Nanostructured materials and devices can be made using several synthesis technologies. We are concentrating on the synthesis of particles in the gas phase as a very promising route. We develop nanostructured materials with exiting properties, e.g. quantum dots in semiconductors and sensor materials.

As the application of aerosols are manifold the research activities of our department have been directed towards various other fields of application. Research priorities at our department are to be found in clean technology, filtration, aerosol measurement technology, physical and chemical characterization of aerosols, synthesis, transport behavior as well as characterization of properties of particles.

I would like to acknowledge and convey my gratitude to all those who contributed to the aerosol research work over the last year enabling the successful work of our department.

Duisburg, July 2002                  Prof. Dr.-Ing. H. Fissan
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Kokoszka, Dominik
Özbas Hayar
Shadmani, Mohtashim
Top Sezgin
### 3. Curriculum

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<td>Sensorik und Aktorik 2</td>
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<td>Kruis &amp; scientists</td>
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* L = Lecture, E = Excercise, P = Practical study
4. Research

4.1 Research Areas and Projects

Basic Research:

Physical Properties: - Size and Shape
- Charge Level
- Particle Concentration Measures

Physical Behavior: - Light Scattering
- Particle Transport in Flows
- Particle Deposition onto Surfaces
- Aerosol Dynamics

Application Areas:

Aerosol Measurement Technology:
- Test and Calibration of Aerosol Instruments
- Sampling and Conditioning Processes
- Development of Aerosol Measurement Technology
- Characterization of Aerosols in Technical Processes

Clean Technology: - Contamination Risk Analysis
- Particle Control Concepts
- Quality Assurance of Filter Elements
- Particle Transport and Deposition in Clean Areas
- Development of Particle Flux and Deposition Meter

Process Gas and Air Cleaning:
- Analysis of the Structure of Fibrous Filter Media
- Effect of Filter Media Inhomogeneities on Filter Performance
- Optimization of Pleated Filter Media
- Collection of Agglomerates in Fibrous Filter Media
- Collection Efficiency of Fibrous Filter Media with Electric Fields

Nanostructured Materials:
- Nanoparticle Generation Technology
- Transport of Aerosols with Nanoparticles
- Deposition of Nanoparticles
- Characterization of Nanoparticles

Ambient Aerosols: - Characterization of Ambient Particles
- Ambient Air Monitoring
- Source Apportionment
- Analysis of Factors Influencing Ambient Aerosol Concentration and Compositions
4.1.1 Physical Properties and Behavior of Particles in Aerosols

Mixing of Nanoscale Particles by Electrical Bipolar Aggregation

SPP 1062 (Handling Highly-Dispersed Powders) of the DFG

Dr.rer.-nat. A. Maisels, Dr.-Ing. F.E. Kruis

Nanoscale materials are promising for modern technologies, but their production is complicated. The aim of this work is to investigate the ability for aggregation of particles carrying opposite charges in bicomponent aerosols mixture because composite powder cannot be produced as a result of classical mechanical mixing. Opposite charge polarities on particles of different kinds lead to enhancement of attraction between different particles and in the same time to repulsion between particles of the same kind.

In experiments with oppositely charged aerosols the value of coagulation coefficient is extremely important. However, some uncertainty about this value can be found in the literature. Thus, coagulation coefficient for singly oppositely charged particles was determined experimentally. For this purpose two aerosols with oppositely charged quasi-monomodisperse Ag and PbS particles have been mixed. The mixture was led to an aggregation tube and after some time, determined by the volume of aggregation tube used, the particle ensemble was studied. The fact that the initial aerosols contained only particles with charges of the same magnitude but opposite polarities with respect to each other allows to separate Ag and PbS particles by electrostatic filtering using their electrical neutrality. The number concentration of electrically neutral aggregates was determined by the condensation nuclei counter (CNC). The increase of this fraction with the time allowed to determine the value of the coagulation coefficient. The influence of the particle size and morphology on coagulation coefficient was studied by altering the voltage on DMA (differential mobility analyser) and the sinter temperature. From these experiments coagulation coefficients for size-selected singly oppositely charged particles were determined and compared with analytically calculated ones. The approach we take here to calculate the coagulation coefficients of non-spherical particles is based on the use of both the volume-equivalent and mobility-equivalent diameters which were obtained experimentally. Experimental measurements of the coagulation coefficient are in good agreement with Fuchs’ theory when accounting for the particle non-sphericity.

In order to check the proposed calculation of the coagulation coefficient in a mixture of two polydisperse, partly charged aerosols of aggregates of different materials, the time-evolution of the resulting size distribution was measured. Good agreement of numerical simulations with experimental results leads to conclusion that the Fuchs’ theory corrected for non-sphericity is applicable for such a complex system. The variations of dimensionless particle number concentration and geometric mean diameter could be described by simple expressions, valid for either the initial or the later stages of aggregation.

From numerical simulations of aggregation process follows that homogeneity of the component distribution within aggregates depends on the initial charge distribution in aerosols mixed. Highly unipolarly charged aerosols produce by mixing highly homogeneous aggregates with respect to the internal component distribution. Thus, a unipolar charger with high charging efficiency is required. The initially used radioactive charger is not sufficiently efficient, and a UV-lamp was taken as alternative charger. Charge distributions obtained by photocharging depend, however, on aerosol parameters, like particle number concentration,
size and material as well as on parameters of the lamp irradiation (photon energy, irradiation intensity). In dependency of these parameters were obtained either bipolar or unipolar size distributions.

Theoretical description of the photocharging process was carried out on basis of the system of differential equations, balancing different charge fractions. This system can be solved numerically and, after some simplifying assumptions, analytically. Comparison of both solutions shows that the analytical one is accurate for aerosols with mean particle charges larger than one. On basis of the analytical solution the influence of different initial parameters on the aerosol charge distribution can be clarified. Numerical solution is useful outside of the validity range of the analytical solution, for example in the case of highly concentrated aerosols.

Publications


Controlled Deposition of Nano-Particles from the Gas Phase

ESF Nano-Program

Co-operation with the Division of Solid State Physics, Lund University, Sweden

Dipl.-Ing. T. Krinke

The increasing knowledge about the properties of nanostructured materials is a source of ideas for the improvement of existing and the development of new electronic or opto-electronic devices. One approach is the implementation of nanoparticles as building blocks. Among other synthesis routes, different kinds of gas phase synthesis have been developed which open the possibility to produce nanoparticles with defined properties like chemical composition, crystal structure, shape and size distribution. In order to make use of these properties, the particles have to be transferred from the three dimensional distribution in the gas phase to a two dimensional arrangement on a carrier material, for instance a substrate surface. The first goal of the investigation is to describe the microscopic aspects of the deposition process of nanoparticles in the size range between 5 nm and 100 nm at ambient pressure and temperature, under the condition that the particle density (which is the number of particles per unit area) on the substrate surface is below one monolayer. For this purpose, a computer simulation program has been developed, which calculates the particle trajectory that results from the balance of forces on the particle. It takes into account the interaction of incoming individual particles with the substrate surface as well as the interactions with already deposited particles. A parameter study has been carried out in order to point out how the particle arrangement on the substrate depends on the deposition parameters. The results obtained by the computer simulations are compared with experimental results. The parameters varied were the particle diameter, the particle charge, the number of particles per unit area, the substrate properties and the electric field strength.

The second goal of the investigation is the structured deposition of nanoparticles from the gas on oxidized silicon substrates by direct deposition from the gas phase of an aerosol. The particles are attracted onto charge patterns created on the plane surface by contact charging. The basic principle of which is that charges cross the interface between an insulator and a metal brought into contact. After the metal is removed, charges retain on the insulator. The charge patterns can either be transferred by a sharp metal tip which is allowed to slide over the substrate surface or by a metal stamp which is pressed on the substrate surface. In the second case even complex structures may be transferred. The resolution of the patterns obtained with these methods is in the order of below 100 nm.

Publications

T.J Krinke, H. Fissan, K. Deppert, M.H. Magnusson, L. Samuelson,

T.J. Krinke, K. Deppert, M. H. Magnusson, F. Schmidt and H. Fissan,
Microscopic Aspects of the Deposition of Nanoparticles from the Gas Phase.
J. Aerosol. Sci. in press
4.1.2. Aerosol Measurement Technology

Development of a Gas Particle Partitioner (GPP) for Highly Efficient Separation of Gas and Particle Phase with Minimal Changes in the Gas Phase

Industry

Dipl. Ing. C. Asbach
Dr. rer. nat. T. A. J. Kuhlbusch
Dipl. Ing. F. Jordan

Measurements of particle mass concentrations in ambient air can be performed by manual and automatic samplers. In manual samplers, the air is pumped through a filter and the particles are deposited on the filter. If the total air flow through the filter is known, the particle mass concentration may be determined by weighing the filter in a conditioned room prior to and after filter loading. In automatic online samplers, the air gets pumped through a filter and the change of filter mass is measured simultaneously. To avoid meteorological influences, the aerosol is heated inside the automatic sampler. This leads to an underestimation of particle mass concentration, due to loss of volatile and semivolatile material. The differences of particle mass concentrations measured by automatic and manual samplers reach up to 30%.

To avoid these discrepancies, the temperature inside the automatic sampler has to be reduced. Therefore a set up has been developed, containing a diffusion dryer, a GPP and a TEOM® automatic sampler. The GPP (patent pending) is developed and evaluated in this project. It is a device that separates gas and particles with no or minimal effect on the thermodynamic properties and gas composition of the aerosol. Inside the GPP, particles get charged due to a corona discharge and deflected by means of electrostatic forces. The total aerosol flow is split into two flows, the sample flow and an excess air flow, which is used to dry the aerosol in the downstream diffusion dryer. By switching the corona and deflection voltage on, the sample air stream will be particle free, though maintaining all of its thermodynamic properties, such as pressure, gas composition, temperature and relative humidity. When no voltages are applied to the GPP, it acts as an ideal flow splitter, i.e. the total flow is divided into the sample flow and the excess flow with no changes to the particle size distribution.

To determine the artefacts, leading to the described underestimation of particle mass, the TEOM® is alternately operated with particle laden and particle free air, i.e. with and without voltages applied to the GPP. When operated with particle free air, the filter mass will decrease due to loss of semivolatile material. Provided the thermodynamic properties remain unaltered, the loss of mass is comparable to that when operating with particle laden air. By subtracting the negative mass difference, obtained with particle free air, from the positive mass change, obtained with particle laden air, the real particle mass concentration can be determined.

Two prototypes of the Gas Particle Partitioner have been developed and investigated. The GPP has proven to be a reliable instrument for the separation of gas and particles.
Evaluation of the Effects of a Dryer on Particle Sampling and Mass Determination with a TEOM®

Industry

Dipl.-Ing. U. Drosten
Dr. rer. nat. T. A. J. Kuhlbusch

The discussion about the particulate matter measurement is revived by the information that an increasing fine particle concentration in the atmosphere increases the mortality rate. The new PM (Particulate Matter) standards for the measurement of particles less than 10µm, 2,5µm or even less than 1µm will be discussed in European countries. The development of standards towards smaller particle sizes increases the importance of eviting artifacts during sampling and conditioning.

Atmospheric aerosols consist of a combination of different substances such as organic and for a considerable part, in view of the mass concentration, of inorganic particulate matter. The artifact characteristics depends for volatile and hygroscopic salt particles on temperature and humidity. Ammonium nitrate and sulfate are representative in this study for theoretical and experimental modeling of volatilization characteristics during sampling and conditioning. Ammonium nitrate is of volatile nature while both of them are of hygroscopic nature.

All standards up to now recommend to collect particles with a filter at the thermodynamic state of atmospheric aerosols, to condition it at a certain temperature and relative humidity and to weight it off-line. In such a method the aerosol concentration is changed because of evaporation taking place at the filter and further changes during conditioning. The latter ones can be avoided by using a quasi on-line measuring balance like the Tapered Element Oscillating Microbalance-TEOM®. Since the thermodynamic state of the aerosol may change during sampling the measured aerosol concentration can be different depending on the history of the thermodynamic state during sampling.

First basic research experiments have shown that a zero point drift can be seen depending on different values of relative humidity. This tendency has to be investigated in more detail by several experiments. For this reason a laboratory setup has been build up to get defined thermodynamic conditions for long time experiments.

A suitable way to reduce the influence of relative humidity on artifacts is the use of a diffusion dryer. In this work experimental investigations show the efficiency of a Dryer-TEOM® system with regard to the stationary and dynamic behaviour of the drying process. The criterion of a successful drying operation is that the relative humidity level in the system is below the deliquescent point of important atmospheric substances. Under defined conditions in the laboratory experiments with particle free air give information about the limits of the drying process for several TEOM® operation modes. For practical applications further investigations with several aerosols should be done to show possible limits for particle mass concentration measurements in field measurements.

A further existing zero point drift has to take into consideration by a correction procedure. After we got informations about dynamic behavior, losses and chemical behavior in our overall measuring system we should be able to design an online system for particle mass concentration measurements.

Publications:

4.1.3 Process Gas and Air Cleaning

Enhanced Filtration Efficiency in High Quality Fibrous Filters with Low Voltage Electric Fields

AIF-FLT

Dr.-Ing. F. Jordan

The filtration efficiency of fibrous filters shows in the submicron particle regime a bold reduction. The reason for this behavior is the transition from interceptional to diffusional particle capture. Particle size dependent filtration mechanisms cause a minimum in filtration efficiency at particle sizes about 0.2 micrometer. Previous investigations have shown that a reduction of particle penetration, i.e. enhancement of filtration efficiency due to variation of the filterstructure (diameter of fibres, packing density, depth of filterlayer) results in a higher resistance to flow and causes a higher pressure drop.

Another way to improve filtration efficiency without changing the filter structure is the use of additional electric particle capture mechanisms. The main advantage is the higher filtration efficiency without increasing the pressure drop.

Today electric particle capture mechanisms are mainly applied in electret filters, which consist of electric inhomogeneous charged fibres. However, the fibres of electret filters loose their charge with time and particle loading. The electric field inside the filter layer will be neutralized so that filtration efficiency decreases.

To avoid this disadvantage a new type of filter can be used, in which dielectric fibres become polarized by an external electric field. This field maintains an inhomogeneous electric field inside the filter layer. Aim of this project is the development of a new filter, which will be optimized for filtration efficiency without increased pressure drop in conjunction with external electric fields.

The new filter will be produced with alternating thin translucent conducting layers and filterlayers of dielectric fibres. In that way it will be possible to obtain strong electric fields at low applied voltages inside the filter layers. The applied voltage should be in the range of 220V. The flow direction is perpendicular to the layers and parallel to the direction of the electric field.

Publications
Maisels, A.; Jordan, F.; Fissan, H.
Dynamics of the Aerosol Particle Photocharging Process

Jordan, F.; Fissan, H.
Loading Behavior of Electrified Fibrous Filters

Jordan, F.
Untersuchungen zum Partikelabscheideverhalten submikroner Partikel in Faserfiltern im elektrischen Feld
Dissertation, Universität Duisburg, 2002
4.1.4. Nanostructured Materials

Synthesis of Semiconducting Nanoparticles

SFB 445 - A7 / NRW

Dr.-Ing. F.E. Kruis
Dr. K. Nanda

Nanostructured materials are receiving increasingly interest as building blocks for nanotechnological applications, such as nanoelectronics, quantum electronics, sensor technology, non-linear optics and solar technology. Our synthesis technique consists of modified standard aerosol technologies to generate monodisperse size fraction. In a furnace a specific solid material is heated, and during the cooling of the vapor, nanometer-sized particles are formed. A specific size-fraction is selected based on the size-dependent electrical mobility (Differential Mobility Analyzer). In a second furnace, the particles which might consist of aggregated primary particles, can be sintered in order to reach a more spherical form. An electrostatic precipitator is used to bring the particles on a specific surface, e.g. a TEM grid, mica, glass etc.

We have developed a laser ablation set up for the synthesis of nanoparticles. Present investigations focus on the synthesis of GaN and FeNi nanoparticles by laser ablation and Indium nanoparticles by thermal evaporation. A new radial DMA for three different size ranges has also been developed for the operation at low pressures. The radial DMA have been successfully employed for analyzing the size of Indium nanoparticles.

We have also investigated the size-dependent evaporation of free-spherical PbS nanoparticles by in-flight sintering of size-classified aerosols. The temperature at which the particle size decreases due to evaporation is found to be size-dependent and decreases with decreasing particle size. A linear relationship between the evaporation temperature and the inverse of the particle size is obtained as is the case of size-dependent melting of nanoparticles. This gives a direct evidence of the Kelvin effect and allows to estimate the surface energy of nanoparticles.

Publications


Preparation Of Nanostructured SnO$_2$ Thin Films For Gas Sensor Applications

DFG SFB 445/ Project C1

Dipl.-Ing. M. K. Kennedy
Dr.- Ing. F.E. Kruis

In recent years there has been an increasing interest in the study of nanostructured thin films, because these films possess special electrical, optical, chemical and magnetic properties. Tin oxide is one of the most important semiconducting materials for gas sensors. Its electrical properties change as a result of the adsorption of gases onto the surface. In view of the high specific surface and activity of nanocrystalline tin oxide thin films, considerable improvement in sensing properties is expected. In order to understand the relationship between behaviour and particle size better it is necessary to generate monosized nanoparticles, because a distribution of particle sizes will decrease the special properties and complicate the interpretation of the experimental results. The most important parameters of the particle preparation are crystallinity, stoichiometry, particle size and morphology of the deposited particles. The deposited nanoparticles should be sintered to generate a contact between the particles. The dependence on the electrical properties of the parameters mentioned above provides the opportunity to optimise the sensorical properties of the films. The set-up to produce the SnO$_2$ nanoparticles was developed in the project A7. In this project C1 the deposition of the nanoparticles will be optimised. In addition, the sintering processes must be examined. The stoichiometry will be measured by using AES/XPS/UPS,EDX and with RBS. The depth profile will also be investigated by means of RBS, the crystallinity by X-ray diffraction analysis and the morphology by TEM/AFM and SEM. An apparatus for measuring the gas-sensing properties, such as response time, charged carrier concentration and electron mobility has been built. Gas concentrations from 10ppm to 10000 ppm can be adjusted by applying mass flow controllers (MFC). Accordingly the electrical properties of thin films of different particle sizes were investigated. Examination of the time-dependent change of conductivity while changing the gas type or the gas concentration were taken place. First van der Pauw measurements with monosized particles were done to obtain information about the conductivity of the sensor material. Furthermore, first impedance spectroscopy measurements were performed. Hall-measurements are going to be performed because of their ability to measure the charged carrier concentration and the mobility of these charged carriers separately in the thin films.

Publications

Laterally Controlled Nanoparticle Deposition from the Gas Phase

DFG

Co-operation with the Solid-State Electronics Department, University of Duisburg, Prof. Tegude and T. Krinke, K. Deppert, Lund University, Sweden

Dipl.-Ing. F. Otten

Producing small structures (d< 50 nm) by high resolution lithography reaches the economical and physical limits. The use of simpler nanopatterning techniques result in loss of structure control and engineering design. The goal of this research project is to implement the gas-phase synthesis of nanostructures into a microelectronic technology to fulfill the design control. Here, lead sulfide (PbS) nanoparticles are synthesised by aerosltechniques in the gase-phase and are deposited in an electrostatic precipitator on planar substrates. Electrostatic lenses formed by charged and patterned photoresist are employed to control the deposition process of the nanoparticles.

Publications

CVS of Nanocrystalline Metaloxide Films by Means of Pyrolysis of Molecular Metalsiloxides

Co-operation with Lehrstuhl für Anorganische Chemie I, Ruhr-Universität Bochum

DFG

Dr.-Ing. F.E. Kruis
Dr. Abhijit Roy

Semiconductor nanocrystals have attracted much attention due to their fundamental importance in bridging the gap between bulk matter and molecular species. The small size of nanoparticles, which is responsible for unusual electrical, optical and magnetic properties of nanoparticles and nanostructured materials, makes them suitable for new technological applications. Zinc Oxide (ZnO) is a very important semiconducting material because of its applications in gas sensors, catalysts, varistors, photoluminescent device, and optical wave guides. In view of these technological applications and fundamental research, it is necessary to prepare size-classified nanocrystalline ZnO particles and thin films.

In this project nanocrystalline ZnO and Zn were prepared from a single source molecular precursor by a chemical vapour synthesis (CVS) process. The decomposition pathways of the volatile precursor, siloxy-substituted tetranuclear heterocubane (cubane), were studied in the gas phase and in the solid state. In the CVS process, the volatile solid precursor was vaporized in a tube furnace and then carried to another tube furnace using nitrogen as a carrier gas. Decomposition of the precursor and sintering of the formed particles took place in the second furnace at different temperatures. The particles formed after decomposition remain in the gas phase and were then passed through a radioactive $\beta$-source ($^{241}$Am) to electrically charge the particles. This polydisperse charged particles were then either deposited directly using a electrostatic precipitator or passed through a DMA for size classification and then deposited on a desired substrate. The detail characterization of the deposited nanoparticles were made using XRD, TEM. The results showed that at low temperatures ($300{}^\circ$C) decomposition of the pure precursor in the gas phase leads to the formation of ZnO. At $750{}^\circ$C the same precursor yields nanoparticles of Zn. These can further grow and give rod and belt like morphology when deposited on the furnace wall.

Further measurements to identify different gas phase decomposition by-products of the precursor using online Mass spectrometer are in progress. A thorough investigation will also be done on the deposited thin film of ZnO for its application as a gas sensor and optoelectronic material.

Publications


Surface Chemistry and Impedance Studies on Aerosol Films of Tin Oxide Nanoparticles

Humboldt-Stiftung

Co-operation with Dept. of Physics, University of Duisburg, Prof. Lorke

Dr. R. Ramamoorthy

The advancement of the nanomaterials science has been well realized in the past two decades in the fields of quantum electronics, energy storage devices, (e.g. batteries, fuel cells), sensors, and catalysis etc. In the field of gas sensors, metal oxide semiconductors such as \( \text{SnO}_2, \text{ZnO}, \text{TiO}_2 \), etc. are widely used both in bulk and thin film forms. The high surface area of the nanoparticles of such materials leads to an enhancement in the sensitivity of the sensor devices especially when the particle size is very homogeneous. Our aim is to study the electrical resistivity/conductivity behaviors of the thin/ultrathin films of size classified semiconducting tin oxide (\( \text{SnO}_2 \)) nanoparticles. Impedance analysis is an interesting technique to study the resistive behavior of the materials at different frequencies. It gives an insight over different mechanisms of the electrical conduction in polycrystalline materials. This technique is employed on the thin films of tin oxide nanoparticles. The \( \text{SnO}_2 \) aerosol thin films comprising nanometer sized (10 – 50 nm) particles are deposited on different substrates by a gas phase technique. The chemical compositional analysis, of the particle surface, is being carried out by Auger electron spectroscopy. The sensitivity and the selectivity of these films for different gases are under study by their frequency response of the conductance and hence a correlation between the grain size and the sensing properties will be established.
Determination of distributed properties of solid particles by means of Monte-Carlo simulations

NRW

Dipl.-Inform. E. Bollow
Dipl.-Ing. T. Weber
Dr.-Ing. F. E. Kruis

In certain chemical processes, solid particles are formed which can change their properties by subsequent chemical and physical processes. These properties are, however, distributed as probability density functions. The simulation is complicated by the fact that usual several properties are relevant, e.g. particle size, chemical composition, charge level, morphology, etc. The modelling of these properties-changing processes by means of sectional population balances is very programming-intensive and is usually limited to only one property. As an example, in coagulation processes the particle size distribution is determined. For particles with different chemical composition the composition of the coagulated particles can only be modelled with a complicated model. The complexity does not allow the application in industrial praxis. The simultaneous modelling of several properties-changing processes is possible by means of Monte-Carlo processes. The main effort is now shifted from the programmer to the computer, at the same time increasing the CPU time.

Our experience in particle-dynamic processes is used in setting up suitable simulations models on the basis of Monte-Carlo methods which are able to track the development of several properties. These processes are particle-dynamical processes such as particle formation, aggregation, crystal growth, milling, etc, but also processes which refer to single particles such as chemical reactions in droplets, catalytic reactions at particle surfaces or mass transfer. The model will allow the utilization for different chemical engineering operations under knowledge of process-specific and known kinetic constants. The in chemical engineering well-known method of combining several process steps as combination of unit operations will be applied here.

Publications
Developement of a Method for the Measurement of Particle Number Size Distributions in Industrial Processes for the Production of Nano-scale Powders

Deutsche Forschungsgemeinschaft / Industrie

Dr.-Ing. F. E. Kruis
Dipl.-Ing. P. Müschenborn

Nanotechnology is expected to become one of the key technologies of the very near future. In order to make the results of recent research on properties of nano-scale particles available for commercial applications, appropriate techniques for the control of processes and measurement have to be developed.

In cooperation between the DFG and DEGUSSA a so-called "Projekthaus Nanomaterialien" has been established, where the university of Duisburg as one of 9 universities takes part.

We have been developing a method to measure the particle number size distributions under the conditions of industrial production of nanopowders. These are namely:

- Low pressures (down to about 200mBar)
- High temperatures (up to about 1500°C)
- Presence of very corrosive gases (HCl, H₂O)
- very high number concentrations (up to about 10^{12} ccm⁻³)

We have built a measuring system basing on the differential mobility analyzer DMA. Since already available systems do not work under the mentioned conditions, modifications of the single components of ordinary differential mobility particle sizers are neccessary. These modifications concern charger, DMA and electrometer, which have to be vacuum-tight and resistant against corrosion. Besides, careful considerations as to the materials, tube connections, valves, etc. have to be made.

The measurement system is controled by a computer and runs fully automatically. Therefore we have developed adequate software and interfaces.

The work in the laboratory is completed by phases of investigations and tests at the research plants of DEGUSSA in Hanau.

Publications

4.1.5. Ambient Aerosols

Characterization of Fine Airborne Particles at Carbon Black Working Places in Industry

Dr. T.A.J. Kuhlbusch
Dipl.-Ing. S. Neumann

Carbon Black is an industrial product for use in e.g. tyres and Xerox machines. It nearly consists of pure elemental carbon with only minute amounts of trace elements and organic carbon and has an amorphous structure. The primary Carbon Black particle size is around 10 nm. The particle size of the processed particles range from around 1-10 µm depending on the later use.

Black Carbon or elemental carbon in ambient aerosols is of similar origin as industrial Carbon Black. These kinds of carbon are produced by all incomplete combustion processes, e.g. the combustion of diesel in cars. Black carbon, in contrast to Carbon Black, is always associated with relatively high amounts of organic carbon such as PAH’s. The main particle size range of Black Carbon in ambient aerosols ranges from 30 nm to about 1 µm. Airborne Black Carbon, in Europe mainly emitted by diesel engines, is currently discussed to be a health hazard.

Three field measurements at different Carbon Black factories will be conducted to study the influence of Carbon Black production, processing and packaging on particle concentrations at corresponding working places.

Particle characterization will be conducted by means of Differential Mobility Particle Sizer (DMPS), Scanning Mobility Particle Sizer (SMPS), and Aerodynamic Particle Sizer (APS) to determine influences on particle number size distributions (0.02-10 µm aerodynamic diameter) and number concentrations. Especially the employment of the DMPS and SMPS will allow the determination of influences of the working area on particles in the size range below 300 nm. Mass concentrations of the size fractions PM 1, PM 2.5, and PM 10 will be measured with manual and automatic systems parallel to the particle number concentrations. These data will be used to study influences of the working process on mass concentrations. The laden filters of the manual samplers will be analyzed for Black Carbon and organic carbon to also study possible influences of the working process on the chemical composition of the aerosols.
**Evaluation and Comparison of manual and automatic PM$_{2.5}$ Filtration Samplers for the European Harmonisation of Air Quality Assessments**

Europe, CEN

Dr. T.A.J. Kuhlbusch

PM$_{2.5}$ beside PM$_{10}$ was set as a new standard in the 1$^{st}$ daughter directive related to ambient air quality of the European Union. No European standard for PM$_{2.5}$ currently exists and a working group for setting a standard measurement method for PM$_{2.5}$ was established within the European harmonisation agency (CEN). To evaluate and establish a European standard for PM$_{2.5}$, field measurements have to be conducted at different sites in Europe. A six month field campaign comparing 8 different manual and 4 automatic filtration samplers for PM$_{2.5}$ is conducted. Soot, particulate nitrate, PM$_{10}$, and all meteorological conditions are measured along with PM$_{2.5}$ to assess the quality of the data and investigate possible influences on PM$_{2.5}$ mass concentration measurements by various factors.

**Source apportionment of the fine dust fraction**

MUNLV

Dr. T.A.J. Kuhlbusch
Dr. U. Quass

On behalf of the North Rhine-Westphalian ministry of environment a project is carried out which comprises a comprehensive physical and chemical characterisation of the ambient aerosol.

Data are collected at the site of Duisburg university throughout a one-year period and at two sites located upstream and downstream of the main wind direction for two periods of each 40 days in different seasons. High volume and low volume samplers are used to collect filter samples for PM10, PM2.5 at all sites and for PM1 at the university site. These samples are analysed for six heavy and four light metals, six PAHs, anions (sulfate, nitrate, chloride) and ammonia. Simultaneously, continuous and semi-continuous detectors collect information on particle mass, particle size distribution, soot and aerosol nitrate. Additionally, a three-stage impactor equipped with a PM10 sampling head and with cut-off diameters of 2.5, 1 and 0.2 $\mu$m is used to sample particle fractions on quartz disks for multi-element analysis with total reflection x-ray fluorescence.

By analysing the obtained data with statistical methods (factor analysis, positive matrix factorisation) it is attempted to set up a source apportionment with respect to source groups like traffic, industry, households, secondary aerosols etc. Such information is needed by the environmental authorities to initiate measures in order to keep the new PM10 emission limits which are in force in the EU since 2001.

The project is carried out in close collaboration with the Institute of Energy and Environmental Technology (IUTA e.V.), Duisburg, the North Rhine-Westphalia State Environment Agency (LUA NRW), Essen, and Ecofys GmbH, Cologne.
4.2 PhD Theses

Jordan, Frank
Untersuchungen zum Partikelabscheideverhalten submikroner Partikel in Faserfiltern im elektrischen Feld

Universität Duisburg, 2002

Referent: Prof. Dr.-Ing. H. Fissan
Korreferent: Prof. Dr.-Ing. G. Kasper

Faserfilter werden technisch genutzt, um Partikel aus Gasströmen abzuscheiden. Große Partikel werden aufgrund der Siebwirkung an der Oberfläche des Filters abgeschieden, wogegen kleinere Partikel in den Filter eindringen und durch unterschiedliche Kraftwirkungen auf Filterfasern transportiert werden. Treffen submikron Partikel auf Filterfasern, so bleiben diese dort in der Regel haften und gelten als abgeschieden.


Die Ergebnisse der Beladungsexperimente zeigen, daß der Einfluß elektrischer Felder auf die Filtrationseigenschaften besonders deutlich bei unbeladenen bzw. schwach beladenen Filtern ist. Sind die Partikel elektrisch geladen, ist es möglich die Filtergüte eines Filters durch Anlegen eines elektrischen Feldes mehr als zu verdoppeln. Die größten Verbesserungen der Filtrationseigenschaften durch Anlegen eines elektrischen Feldes sind bei Filtern mit offener Struktur (geringe Packungsdichte), bei groben Fasern mit Durchmessern > 5µm mit möglichst hoher Polarisierbarkeit ($\varepsilon_r >2$) zu erzielen. Zudem sollten die Partikel möglichst hoch elektrisch aufgeladen und die Anströmgeschwindigkeit des Filters möglichst gering (< 5cm/s) sein.


Daraufhin wurde ein Verfahren entwickelt, das auf der lokalen Aufladung von Siliziumsubstraten, die eine definierte Oxidschicht tragen, basiert. Durch die Oberflächenladungen werden mikroskopische elektrische Felder erzeugt, durch die eine konsolidierte Deposition der Partikel ermöglicht wird. Es konnte gezeigt werden, daß die elektrischen Felder eine fokussierende Wirkung auf die Partikel haben und dadurch die Anordnung der Partikel auf der Substratoberfläche durch die Ladungsmuster bestimmt wird. Das Verfahren wurde zum Patent angemeldet und ermöglicht es Partikel gezielt mit einer Auflösung im Nanometerbereich abzuscheiden.
John, Astrid

Probenahme und chemische Analytik von korngrößenfraktionierten Immissions- und Emissionsaerosolen

Universität Duisburg, 2002

Referent: Prof. Dr. A. Golloch
Korreferent: Prof. Dr.-Ing. H. Fissan

Vor dem Hintergrund der neuen Partikel-Immissionsstandards PM 10 und PM 2.5 wurden im Rahmen dieser Arbeit unterschiedliche Probenahmeeinrichtungen für Immissions- und Emissionsmessungen entwickelt und im Feldeinsatz getestet. Die Geräte bzw. die erarbeiteten Methoden ermöglichen eine umfassende chemische und physikalische Charakterisierung der PMx-Aerosole. Unter "PM 10" ist dabei die Partikelgrößenfraktion zu verstehen, die "einen grösstenslektiven Einlaß passiert, der einen 50 % cut-off bei 10 µm aerodynamischen Durchmessers aufweist". Mit "PM 2.5" werden analog Partikel kleiner als 2.5 µm aerodynamischen Durchmessers bezeichnet. Die Bestimmung der Massenkoncentrationen dieser Größenfraktionen zusammen mit PM 1 hat inzwischen den Gesamtschwebstaub als Meßgröße abgelöst.

Für die Immissionsmessungen wurde ein PM 1-Vorabscheider für einen vorhandenen High-Volume Filtriersammler neu entwickelt und nach der theoretischen Auslegung und Konstruktion im Labor kalibriert. Die Kalibrierung des sogenannten cut-off d(α50) wurde mit monodispersen Polystyrol-Latexpartikeln durchgeführt und zeigte bei einer Partikelgröße von 1,01 µm aerodynamischen Durchmessers eine Abscheidung von (50,5 ± 4,0) %. Der (D16/D84)0,5-Wert als Maß für die Steilheit der Abscheidekurve liegt mit 1,39 innerhalb der in der Literatur mit 1,14 bis 1,45 veröffentlichten Werte. Der Volumenstrom von 385 l/min erlaubt aufgrund der relativ hohen Partikelmasse, die dadurch auf dem Filter abgeschieden wird, auch für diese kleine Korngrößenfraktion die parallele Bestimmung von elementarem und organischem Kohlenstoff, Anionen und Kationen, Schwermetallen sowie PAHs von derselben Probe. Das neu entwickelte Gerät wird inzwischen von der Firma Digitel kommerziell vertrieben und wurde bereits während weiterer Feldmessungen erfolgreich eingesetzt.

Zur weiterführenden Charakterisierung der Immissionsaerosole wurde die Totalreflexions-Röntgenfluoreszenzspektrometrie (TXRF) als Multielementanalyseverfahren mit niedrigen Nachweisgrenzen ausgewählt. Zur Reduzierung der normalerweise erforderlichen, aufwendigen Probenvorbereitung wurde ein Gerät speziell für die Sammlung von PM 10-, PM 2.5- und PM 1-Stäuben und die nachfolgende Direktanalyse mit der TXRF entwickelt. Dieses Immissionsprobenahmesystem (ISP) besteht aus dem US EPA-PM 10-Einlaß und einem Kaskaden-impaktor, in dem die Partikelfraktionen 10 -2.5 µm und 2.5-1 µm direkt auf den TXRF-Probenträgern impaktiert werden. Das Problem des Einsatzes eines Backup-Filters zur Sammlung der Partikel < 1 µm konnte durch die Verwendung eines Elektrostatischen Präzipitators (ESP) vermieden werden, da das Aerosol hier ebenfalls direkt auf den TXRF-Impaktoren abgeschieden wird. Das ISP wurde ebenfalls auf der Basis der theoretischen Grundlagen konstruiert und im Labor experimentell überprüft. Die Kalibrierung zeigte eine sehr gute Übereinstimmung der PM 2.5-Abscheidekurve mit derjenigen des WINS-Impaktors (der US-Referenzmethode). Die ermittelten cut-offs des entwickelten Impaktors liegen bei 1,02 µm bzw. 2,44 µm und zeigen damit Abweichungen von lediglich + 2,0 % bzw. –3,0 % zu den mit Hilfe der Impaktortheorie berechneten cut-offs von 1,0 µm bzw. 2,5 µm. Europäische Normen für die Partikelgrößenfraktion PM 2.5 sowie Standards für PM 1 existieren zur Zeit noch nicht.
Der im Immissionsprobenahmesystem eingesetzte Koronaauflader und der ESP wurden vor den Feldmessungen ebenfalls im Labor kalibriert. Dabei zeigte sich mit (97 ± 2) % eine nahezu vollständige Sammlung sogar für die Partikelgröße 0,5 µm, bei der aufgrund der verhältnismäßig geringen elektrischen Mobilität mit schlechten Abscheideeigenschaften zu rechnen war. Problematischer sind in diesem Zusammenhang die Partikelverluste von 30 %, die im Korona-Auflader auftreten. Diese sind zwar rechnerisch zu korrigieren, für zukünftige Messungen sollte jedoch geprüft werden, ob inzwischen durchgeführte Neuentwicklungen im Fachgebiet Prozeß- und Aerosolmeßtechnik für die Aufladung submikroner Partikel im vorliegenden ISP eingesetzt werden können.


Nach der Überprüfung im Labor wurden die neu entwickelten Probenahmegeräte zusammen mit kommerziell erhältlichen Meß- und Sammelgeräten im Feld eingesetzt. Während der Meßkampagne an der Verkehrsstation in Düsseldorf (04/11-01/12/99) wurden Massenkonzentrationen von 45 µg/m³ (PM 10), 32 µg/m³ (PM 2.5) und 26 µg/m³ (PM 1, mit dem neu entwickelten Vorabscheider) ermittelt. Mit Hilfe der Daten der Filteranalytik wurde die chemische Zusammensetzung der PMx-Immissionen bestimmt. Dabei stellte sich heraus, daß die Stäube an der Verkehrsstation Düsseldorf fast zur Hälfte aus kohlenstoffhaltigen Verbindungen (organischer und elementarer Kohlenstoff) bestanden. Ionische Inhaltsstoffe wie Sulfat, Nitrat und Ammonium trugen zu etwa einem Drittel der Masse bei, und ca. 20 % konnten mit den zur Filteranalytik eingesetzten Methoden nicht identifiziert werden. Weitere Bestandteile wie Metalle oder Polyzyklische Aromatische Kohlenwasserstoffe waren mit Ausnahme von Eisen für die Zusammensetzung der Stäube hinsichtlich der Partikelmasse nicht relevant.

Bei der Elementbestimmung der Aerosole, die mit dem ISP gesammelt und anschließend mittels TXRF detektiert wurden, ergaben sich Mittelwerte der relativen Standardabweichungen der Einzelmessungen für die bestimmten Elemente von (3,2 ± 1,2) %. Das Verhältnis Blindwert/Meßwert lag meistens unterhalb von 10 %. Bei der Bestimmung einiger Metalle in der Größenfraktion 10-2.5 µm traten jedoch Probleme auf, die auf Kontaminationen durch Materialabrieb zurückzuführen sind. Aus diesem Grund sind für weitere Messungen die Verwendung eines modifizierten Probenahmerohres sowie von Verschraubungen aus Kunststoff anstelle von Metall zu empfehlen. Die Abweichungen, die beim Vergleich der mittels ISP/TXRF bestimmten Konzentrationen und den Gehalten auftraten, die für einige Elemente gleichzeitig von den Filterproben mit Ionenchromatographie oder Atomabsorptionsspektrometrie bestimmt wurden, liegen im Bereich der in der Literatur veröffentlichten Werte für die chemische Analytik bei paralleler Probenahme.

Die während der Meßkampagne mit ISP/TXRF analysierten Elementkonzentrationen liegen in der gleichen Größenordnung wie an anderen belasteten Standorten. Die Literaturdaten
 zeigten darüber hinaus auch, daß Messungen atmosphärischer Aerosole mit TXRF bislang fast ausschließlich für Reinluftgebiete wie beispielsweise die Nordsee durchgeführt wurden. Die Verhältnisse PM 1/PM 10 und PM 2.5/PM 10 geben Hinweise darauf, ob der Immissionsstaub bzw. ein bestimmter Inhaltsstoff eher aus Verbrennungsprozessen und Gas-zu-Partikel-Umwandlung stammt und damit hauptsächlich im Feinstaub zu finden ist, oder ob er durch Windaufwirbelung oder mechanische Prozesse entstanden ist und damit verstärkt im Grobstaubanteil vorliegt. Die PMx/PM 10-Verhältnisse wurden für alle bestimmten Substanzen sowohl für die Filteranalytik als auch die TXRF-Proben durchgeführt. Während beispielsweise elementarer Kohlenstoff (hauptsächlich aus der Quelle "Verbrennung/Dieselruß") mit 94 % (PM 2.5/PM 10) fast ausschließlich im Feinstaub vorliegt, ist dieser Anteil bei Erdkrustenmaterialien wie Calcium oder Silizium kleiner als 20 %.

Im Rahmen der Meßkampagne in Düsseldorf konnten auch Proben mit einer höheren Zeitauflösung als die normalerweise in der Luftqualitätsüberwachung üblichen 24 h gesammelt werden. Die Analysen für die Probenahmen von 6 Uhr morgens bis 8 Uhr abends und von 8 Uhr abends bis 6 Uhr am nächsten Morgen zeigten, daß für nahezu alle Inhaltsstoffe tagsüber höhere Werte gemessen wurden als nachts. Das bedeutet, daß Quellen oder Prozesse vorhanden sind, die tagsüber aktiver sind als nachts. Weiterhin müssen die Partikel in der Nähe der Meßstelle entstehen, da keine Tag/Nacht-Schwankungen zu beobachten wären, wenn die Aerosole erst über längere Strecken transportiert werden müßten. Diese Tatsache ermöglicht es, die Konzentrationsunterschiede zur Berechnung des Beitrages lokaler Quellen heranzuziehen.

Die Meßkampagne zeigte mit einer durchschnittlichen PM 10-Massenkonzentration von 45 µg/m³ sowie einer Anzahl von 125 Überschreitungen (auf 365 Tage hochgerechnet) des Tagesgrenzwertes von 50 µg/m³, daß die neuen Grenzwerte von 40 µg/m³ (Jahresgrenzwert) sowie von maximal 35 Überschreitungen des Tagesgrenzwertes an dieser Station voraussichtlich nicht eingehalten werden können. Daraus ergibt sich die Notwendigkeit zur Erstellung von sogenannten Maßnahmeplänen, die Schritte festlegen, die zur Reduktion der Partikelmassenkonzentrationen zu ergreifen sind. Zur Festlegung von effektiven Minderungsstrategien ist eine Kenntnis der Quellen notwendig, die zu den PMx-Konzentrationen den hauptsächlichen Beitrag liefern. Eine Methode zur Quellenidentifizierung ist das Fingerprintmodelling. Darüber können bei Kenntnis der korngrößenabhängigen Zusammensetzung der wichtigen Quellen die Beiträge der einzelnen Emittenten(gruppen) zu der Immissionsbelastung eines Meßstandortes berechnet werden.

Zur effektiven Quellenzuordnung sind Kenntnisse über die PMx-Konzentrationen auch in der Emission notwendig. Ein geeignetes Meßgerät zur Bestimmung dieser Partikelfraktionen, die im Immissionsschutz die alte Meßgröße "Gesamtschwebstaub" abgelöst haben, stand für Emissionsmessungen nicht zur Verfügung und wurde im Rahmen dieser Arbeit neu entwickelt. Dieser Impaktor (GMU-Impaktor johnas) trennt das Emissionsaerosol in die Fraktionen > 10 µm, 10-2.5 µm und < 2.5 µm. Die Auslegung erfolgte ebenfalls nach der Impaktortheorie, wobei sich das Design stark an dem Aufbau des bisher zur Gesamtschwebmuss verwendeten Planfilterkopfes orientierte, um eine gute Vergleichbarkeit mit diesem Standardgerät zu erreichen und auch die peripheren Komponenten zur Probenahme wie beispielsweise die Ansaugsonden übernehmen zu können. Die Kalibrierung ergab eine gute Übereinstimmung der Abbaukurven mit den US-Standards hinsichtlich PM 2.5 und PM 10. Nach der Überprüfung im Labor wurde der Impaktor vom Landesumweltamt NRW an der Emissionssimulationsanlage der Hessischen Landesanstalt für Umwelt in Kassel getestet und anschließend an unterschiedlichen industriellen Anlagen zur Bestimmung der PM 10- und PM 2.5-Emissionen eingesetzt. Die Standardabweichungen von Doppelbestimmungen mit dem Impaktor lagen bei 3,4 % (PM 2.5) bzw. 3,1 % (PM 10). Im Vergleich dazu betrug die Standardabweichung von Doppelbestimmungen mit dem
Planfiltergerät 5,7 %. Parallele Messungen mit dem Emissionsimpaktor und dem Planfiltergerät ergaben Verhältnisse von durchschnittlich 49,1 % für den Anteil von PM 2.5 am Gesamtstaub (TSP) und von 78,3 % PM 10/TSP, wobei diese Anteile jedoch für unterschiedliche Anlagen stark schwankten.

Nach der gravimetrischen Auswertung wurden einige Filter von Impaktor- und Planfilterkopf-Messungen vom Landesumweltamt NRW für die chemische Analytik zur Verfügung gestellt. Proben von TSP sowie den Impaktorstufen > 10 µm, 10-2.5 µm und < 2.5 µm, die an zwei unterschiedlichen industriellen Prozessen während der Stahlherstellung gesammelt worden waren, wurden aufgeschlossen und mit TXRF bestimmt. Bereits die gravimetrische Analyse zeigte große Unterschiede, sowohl in der Konzentration als auch der Korngrößenverteilung, zwischen den beiden Prozessen. Die Messungen mittels TXRF verdeutlichten die unterschiedlichen Emissionen auch hinsichtlich der Elementgehalte und zeigten einen charakteristischen "Fingerprint" der Emissionen.


Für die in Zukunft relevante umfassende und detaillierte Quellenzuordnung ist die Charakterisierung der chemischen Zusammensetzung der korngrößenfraktionierten Immissionsaerosole sowie diejenige der wichtigen Emittenten notwendig. Mit Hilfe dieser Informationen ist dann eine Identifizierung und Quantifizierung des Beitrages unterschiedlicher Quellen für bestimmte Immissionsstandorte möglich.

Mit den Geräte- und Methodenentwicklungen der vorliegenden Arbeit wurde die Grundlage für die PMx-Immissions- sowie Emissionsmessungen einschließlich chemischer Analytik geschaffen. Sowohl der PM 1 High-Volume Sampler und das Immissionsprobenahmesystem als auch der Emissionsimpaktor werden in nachfolgenden Projekten zur Charakterisierung der Immissions- und Emissionsaerosole eingesetzt. Mit Hilfe der bereits vorhandenen und noch zu ermittelnden Daten können nun quantitative Quellenzuordnungen zur Erstellung effektiver Minderungsstrategien für die Reduzierung der PMx-Belastung erfolgen, die aufgrund der 1. Tochterrichtlinie für diverse Standorte in Europa notwendig werden.
4.3 MSc Theses

**Butt, Saif Ali**
Entwicklung und Aufbau eines CAN Netzwerks für Peripheriesensoren optischer Partikelzähler
April 2001


**Giesen, Klaus**
Nummerische Untersuchungen zum Beladungs-verhalten elektrisch unterstützter Filter
Juni 2001

In technischen Prozessen treten häufig mit Partikeln kontaminierte Gase auf. Um die Partikel aus der Gasphase abzuscheiden, werden Faserfiltermedien verwendet. Aus experimentellen Untersuchungen ist bekannt, dass die Abscheideeffizienz bei Zuschaltung eines elektrischen Feldes zunimmt, ohne eine Vergrößerung des Druckabfalls über dem Filter zu verursachen.


Im Gegensatz zu diesen theoretischen Untersuchungen wurden in der hier durchgeführten Diplomarbeit das zweidimensionale Geschwindigkeits- und Druckfeld und das zweidimensionale elektrische Feld numerisch berechnet. Dazu wurde eine rechteckige Zellenform gewählt in der die NAVIER-STOKES-Gleichungen in Zylinderkoordinaten gelöst wurden. Die rechteckige Zellenform ermöglichte die Bildung von periodischen Randbedingungen und durch die numerische Lösung der Differentialgleichungen in

Um in dieser Arbeit den Druckabfall in Abhängigkeit zunehmender Beladung zu untersuchen, wurden 3 unterschiedliche Beladungsfunktionen angenommen. Es konnte gezeigt werden, dass die Entwicklung des Druckabfalls bei zunehmender Beladung vom Depositionsort der Partikel um die Faser abhängt. 


van Aken, Thomas
Entwicklung und Aufbau eines automatisierten Messplatzes zur Bestimmung der Ladungsverteilungen von Aerosol-Aufladern
Juni 2001


4.4 Student Reports

Top, Sezgin
Aufbau und Bestimmung der Vergleichbarkeit von manuellen PM 2.5 Filtriersammlern
November 2001

In Anlehnung an die europäische Norm zur Bestimmung der PM$_{10}$ Fraktion wurden in Duisburg an der Gerhard-Mercator Universität auf dem Parkplatz des BA Gebäudes Feldmessungen im Rahmen einer europäischen Norm zur Bestimmung der PM$_{2.5}$ Massenkonzentrationen durchgeführt. Es wurden Filtriersammler von verschiedenen Firmen aus Europa und den USA aufgestellt. Die Filtriersammler unterscheiden sich in ihren Fraktionierungs- und Messmethoden. Es wurden manuelle, sequentielle und automatische Filtriersammler verwendet. Die Geräte wurden mit Filtern verschiedener Größen und Materialien betrieben, welche im Reinraum vorher und nachher gewogen wurden. Um eine qualitative Aussage zu den erzielten Ergebnisse machen zu können, wurden neben den Filtriersammlern auch meteorologische Daten mittels einer Wetterstation, ein Aethalometer (Rußbestimmung) und ein Nitratanalysator zur Bestimmung des partikelgebundenen Nitrats (semivolatilen) hinzugezogen. Die Feldmessungen wurden vom 27.03.2001 bis zum 07.07.2001 durchgeführt.

Anhand der Daten aus den Filtriersammlern, der Wetterstation und den Filterdaten wurden die Geräte auf ihre Vergleichbarkeit und ihrer Reproduzierbarkeit untersucht. Im allgemeinen wiesen die Geräte gute Reproduzierbarkeiten auf, wobei Geräte A bessere Reproduzierbarkeit der Massenkonzentration geliefert hat als Gerät B. Gerät C wies eine qualitativ sehr schlechte Reproduzierbarkeit auf, welches auf Fehler des Gerätes zurückzuführen war. Die Vergleichbarkeit der Geräte verbesserte sich erheblich wenn die Werte des Nitratanalysators hinzugezogen wurden. Auf Basis der Annahme, dass Gerät D (Aktas, 2001) keine semivolatile Substanzen verliert, ergab sich die beste Vergleichbarkeit für Gerät B bei 100% Verlust an semivolatilem Substanzen und für Gerät A bei 60% Verlust. Hierbei änderte sich der Regressionskoeffizient R$^2$ (Gerät A zu D) von 0,95 auf 0,95 und die Steigung von 0,81 auf 0,97. Die Änderungen für Gerät B zu D (100% NH$_4$NO$_3$) waren 0,90 zu 0,90 (R$^2$) und 0,65 zu 0,92 (Steigung). Gerät c) wurde nicht mit anderen Geräten verglichen, da das Gerät c) aufgrund der schlechten Reproduzierbarkeit keine Basis zur Vergleichbarkeit lieferte.

Aktas, Tamer
Aufbau und Bestimmung der Vergleichbarkeit von sequentiellen manuellen PM 2.5 Filtriersammlern
November 2001

In Anlehnung an die europäische Norm zur Bestimmung der PM$_{10}$ Fraktion wurden in Duisburg, an der Gerhard-Mercator Universität, Feldmessungen vom 27.03.2001 bis zum 07.07.2001 im Rahmen einer europäischen Norm zur Bestimmung der PM$_{2.5}$ Fraktion durchgeführt. Filtriersammler von verschiedenen Firmen und Ländern wurden aufgestellt. Es gab drei verschiedene Arten von Geräten, die manuellen, die sequentiellen manuellen und die automatischen Filtriersammler. In der vorliegenden Arbeit wurden die sequentiellen manuellen Filtriersammler untersucht. Obwohl diese Geräte über einen automatischen
Filterwechsler verfügen, wurden sie aber nur als manuelle Filtriersammler betrieben, d. h. dass die Filterwechsel parallel zu allen anderen Geräten manuell durchgeführt wurden, um eine Vergleichbarkeit der Sammelzeiten und Bedienung zwischen allen Filtriersammlern zu gewährleisten.

Außer den Filtriersammlern wurden auch eine Wetterstation, ein Aethalometer und ein Nitratsammler, zur Bestimmung der semivolatilen Stoffe, aufgestellt, um eine bessere Interpretation der von den Geräten gewonnenen Daten zu ermöglichen. Die mit diesen Geräten erhaltenen Daten wurden dann hinsichtlich der Vergleichbarkeit und der Reproduzierbarkeit untersucht und ausgewertet.

Alle Gerätepaare wiesen eine sehr gute Reproduzierbarkeiten auf (R²: 0,96-0,99; Steigungen: 1,00-1,06). Analog zu der Arbeit von Sezgin (2001) wurden die Ergebnisse der Filtriersammler mit den Ergebnissen zu einem willkürlichen Referenzgerät (Gerät D) verglichen.

### Tabelle 1: Vergleich der sequentiellen manuellen Filtriersammler zu Gerät D

<table>
<thead>
<tr>
<th>Gerät</th>
<th>R²</th>
<th>Steigung</th>
<th>Ammoniumnitrat addiert</th>
<th>R²</th>
<th>Steigung</th>
<th>% NH4NO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gerät E</td>
<td>0.92</td>
<td>0.78</td>
<td>0.92</td>
<td>0.99</td>
<td>80%</td>
<td></td>
</tr>
<tr>
<td>Gerät F</td>
<td>0.94</td>
<td>0.91</td>
<td>0.94</td>
<td>0.99</td>
<td>30%</td>
<td></td>
</tr>
<tr>
<td>Gerät B</td>
<td>0.90</td>
<td>0.65</td>
<td>0.90</td>
<td>0.92</td>
<td>100%</td>
<td></td>
</tr>
</tbody>
</table>

Özbas, Haydar
Aufbau und Bestimmung der Vergleichbarkeit von automatischen PM 2,5 Filtriersammlern
November 2001

Zur Erstellung einer einheitlichen europäischen Norm zur Bestimmung der PM<sub>2.5</sub> Massenkonzentrationen werden Feldmessungen an verschiedenen, europäischen Standorten mit unterschiedlichen Quellprofilen und meteorologischen Bedingungen durchgeführt. Einer der ersten Standorte war Duisburg (Ruhrgebiet) als eine Station mit städtisch/industriell geprägten Hintergrund. Die Feldmessung umfasste 90 Messtage, um statistisch abgesicherte Aussagen bezüglich der verschiedenen eingesetzten Messgeräte machen zu können.

In Rahmen dieser Studienarbeit wurde die Vergleichbarkeit der automatischen Geräte zu dem manuellen Gerät D, sowie eventuelle Einflüsse semivolatiler Substanzen auf die Massenkonzentrationsbestimmung untersucht.


Außerdem wurden die Massenkonzentrationen an partikelgebundenen Nitrat und Ruß kontinuierlich bestimmt und die lokalen meteorologischen Bedingungen aufgezeichnet.

Anhand der ermittelten Daten wurden die automatischen Geräte, in Anlehnung an die Richtlinie EN-12341 für PM<sub>10</sub>, mit dem manuellen Filtriersammler D verglichen. Die erste Untersuchung der automatischen Geräte zu D zeigten, daß die automatischen Geräte I und J deutliche Minderbeträge aufwiesen (Tabelle 1). Für das Gerät H ergaben sich im Vergleich zu den anderen Messgeräten deutlich bessere Werte für die Steigung (0,88) und den Korrelationskoeffizienten (0,92). Die beste Steigung zeigte das Gerät G aber mit einem sehr schlechten Korrelationskoeffizienten.

Tabelle 1: Korrelationen der automatischen Geräte mit Gerät D

<table>
<thead>
<tr>
<th></th>
<th>R²</th>
<th>Steigung</th>
<th>Achsenabschnitt</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0,79</td>
<td>0,52</td>
<td>4,40</td>
</tr>
<tr>
<td>J</td>
<td>0,83</td>
<td>0,46</td>
<td>5,26</td>
</tr>
<tr>
<td>H</td>
<td>0,92</td>
<td>0,88</td>
<td>0,03</td>
</tr>
<tr>
<td>G</td>
<td>0,73</td>
<td>0,97</td>
<td>-0,72</td>
</tr>
</tbody>
</table>

+ Ammoniumnitrat

<table>
<thead>
<tr>
<th></th>
<th>R²</th>
<th>Steigung</th>
<th>Achsenabschnitt</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0,94</td>
<td>0,76</td>
<td>2,94</td>
</tr>
<tr>
<td>J</td>
<td>(100%)</td>
<td>0,93</td>
<td>2,92</td>
</tr>
<tr>
<td>H</td>
<td>(45%)</td>
<td>0,93</td>
<td>-2,45</td>
</tr>
<tr>
<td>G</td>
<td>(100%)</td>
<td>0,80</td>
<td>-2,51</td>
</tr>
</tbody>
</table>
4.5 Publications

Borggréfe, P.; Trampe, A.; Fissan, H.
Quantitative Characterization of Noise in the Measurement Chain of an Optical Particle Counter

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**Development of a PM 10/Pm 2.5 Cascade Impactor and In-Stack Measurements**

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Jordan, F.; Fissan, H.
**Loading Behavior of Electrified Fibrous Filters**

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5. Selected publications

5.1 Tailored nanoparticle films from monosized tin oxide nanocrystals: particle synthesis, film formation, and size-dependent gas-sensing properties


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ABSTRACT

In order to investigate the change of gas-sensitive properties of undoped tin oxide nanoparticle films depending on particle size, a new thin film synthesis technique has been developed. Well-defined tin oxide nanoparticles have been prepared using a gas-phase condensation method. Pure SnO was used as starting material and was evaporated at $T = 820 \degree C$. The resulting particles were sintered and crystallized in-flight at $T = 650 \degree C$. Size-selected nanoparticles ranging from 10 to 35 nm were produced to form a nanoparticle film by means of electrostatic precipitation or low pressure impaction. The effect of in-flight oxidation, sintering and crystallization on the structure, size and size distribution of nanoparticles have been studied in detail. The samples show n-type semiconductors behavior like bulk SnO$_2$. The influence of particle size on gas sensitivity and response behavior is investigated for C$_2$H$_5$OH at operating temperatures 200-300 $\degree C$ using silicon substrates having an interdigitated contact pattern and an integrated heating system. In the range of 10-35 nm it has been shown unambiguously for the first time that decrease the particle size of tin oxide particles leads to an increase of the sensitivity and a more rapid response on changing gas conditions. The effect is especially clear for films with particle size of 20 nm or smaller.
I. INTRODUCTION

It has been known for a long time that the adsorption of gas on the semiconductor surface can cause a significant change in the electrical resistance of the material.\textsuperscript{1} This effect initiated the development of commercial gas sensors which are based on semiconductors whose surface properties are very sensitive to changes in the gas atmosphere, especially small amounts of hydrocarbons and hydrogen. The change in surface properties leads to easily detectable changes in the conductivity. Tin oxide (SnO\textsubscript{2}), which is a n–type semiconductor material, is one of the most studied materials, because SnO\textsubscript{2} sensing elements in the form of a porous material offer high sensitivity at a low operating temperature.\textsuperscript{2} The gas sensing mechanism depends, in a complicated way, on the chemical and electronic properties and on the three-dimensional ordering of both the bulk and the surface material. As a result, gas sensor development is at present still being done empirically.

SnO\textsubscript{2} gas sensors are one of the first examples of functional materials where the use of nanoparticles was shown to lead to improved properties. In 1981, the sensitivity of dense nanoparticle films was compared with that of porous films with mean grain sizes in the order of 7-12 nm.\textsuperscript{3,4} The greatly increased sensitivity of the latter structure was explained on the basis of Hall measurements, which showed that the carrier mobility is no function of the concentration of ethanol in case of the dense film but is strongly dependent on the ethanol concentration for the porous nanocrystalline films.\textsuperscript{5} A clear relationship between grain size and sensitivity was shown by numerous examples that decreasing the grain size by the addition of sinter-inhibiting metals leads to an increase in sensitivity, specially below 6 nm.\textsuperscript{6} The gas sensing mechanism can be described as an adsorption/desorption process of oxygen on the surface of the sensing material.\textsuperscript{7,8} At temperatures below 100 °C oxygen is physisorbed at the surface. At higher temperatures (>100 °C) oxygen acts via a chemisorption process as electron acceptor. The formation of oxygen adsorbates (O\textsuperscript{2–}, O\textsuperscript{−} or O\textsuperscript{2−}) leads to a space charge region on the surface of the metal oxide, resulting in an electron - depleted surface layer due to electron transfer from the surface to oxygen.\textsuperscript{9} This can also be explained from a shift of the edges of the conduction and valence band towards higher energies, so that the potential barrier to electronic conduction increases. If the sensing material is exposed to a reducing atmosphere such as CO, C\textsubscript{2}H\textsubscript{5}OH, H\textsubscript{2} or CH\textsubscript{4} containing air, surface reactions will lead to a lower surface coverage of oxygen adsorbates. During this process the electrons return to the metal oxide, leading to a decreased resistance.\textsuperscript{10} The ratio of the resistance in air (R\textsubscript{a}) and the resistance in the reducing atmosphere (R\textsubscript{g}) is defined as the sensitivity S and is one of the main sensor characteristics. The depth of the space-charge layer was estimated to be 3 nm.\textsuperscript{5} Therefore significant changes of the sensitivity are expected for a material composed of very small SnO\textsubscript{2} particles with sizes similar to the depth of the space charge layer. The effect is due not only to the fact that a large part of the conductivity is located in this surface layer, but also because the depletion layer can extend into the interparticle connections.

The studies which determined both the SnO\textsubscript{2} particle size and the sensitivity of the corresponding nanoparticle film gas sensor are shown in Table 1. The most popular synthesis methods can seen to be sol-gel and gas-phase condensation. Note that it is not possible to correlate directly particle size and sensitivity from these studies, because other parameters which influence the electrical properties of the metal-oxide gas sensor are not shown. As an example, the film thickness has a great influence on the sensitivity.\textsuperscript{15} For an objective comparison between different sensor structures, not only the particle size but also the nanoparticle film dimensions have to be identical. Otherwise it is difficult to compare results.
in order to obtain information about the influence of the microstructure on gas sensing properties. These synthesis methods, however, suffer from one essential drawback when one strives to understand the effect of grain size on gas sensing characteristics: the change in grain size is accompanied by the change in other microstructural features. As illustration, the grain size was changed by changing the partial pressure of O\textsubscript{2} during the synthesis\textsuperscript{3} so that the stoichiometry of the films with different particle sizes will be clearly different. The grain size was varied by adding different metals to the SnO\textsubscript{2} before sintering the films at 700 °C, so that the effect of dopant and that of grain size are difficult to distinguish.\textsuperscript{6}

In general, single-step synthesis procedures have only very limited control over grain size and structure. In an ideal process for synthesis of tailored nanoparticle structures, it should be possible to control grain size, chemical composition, film thickness and porosity independently. Clearly, a process comprising several independent but controllable steps will allow a better control than single-step synthesis procedures. Well-known nanoparticle film deposition processes are the Gas-deposition Method (GDM) and Energetic Cluster Impact (ECI). The deposition system developed is more flexible than the one used in the so-called Gas-Deposition Method\textsuperscript{24} and which can also be used for studying electrical transport in nanoparticle films.\textsuperscript{25} In GDM, particles formed in a high-pressure chamber are extracted from the central part of an evaporation zone through a transfer pipe into a low-pressure chamber where they deposit by impaction. The degree of control obtained in the GDM is far less than in the process described here and does not allow a size-selection, the film deposition rate is however higher. In the Energetic Cluster Impact method clusters are expanded in a high vacuum and can be accelerated by means of an electric field towards a substrate.\textsuperscript{26} The main parameter here is the impact velocity which can be varied by changing the electrical field strength. No size selection takes place, however.

In this work, we have developed a synthesis procedure to obtain tailored nanoparticle films from monosized SnO\textsubscript{2} nanocrystals. This is a multi-step synthesis method, in which various particle and film characteristics can be independently controlled. The present study is aimed at investigating the size-dependent gas-sensing properties of SnO\textsubscript{2} nanoparticle films.

II. EXPERIMENTAL PROCEDURE

A. Gas-phase synthesis setup

In this work, SnO is used as an evaporation material for the synthesis of SnO\textsubscript{x} as it has significant advantages over Sn or SnO\textsubscript{2}. In case SnO\textsubscript{2} is used, large particles are formed above 1650 °C. Below this temperature SnO is formed by the disproportionation reaction 2 SnO\textsubscript{2}(s) ⇔ 2 SnO(g) + O\textsubscript{2}(g).\textsuperscript{26} Evaporation of Sn is only feasible at high evaporation temperatures due to the low vapour pressure of Sn. Also it requires costly high-vacuum equipment as traces of oxygen will lead to the formation of SnO. The change in the composition of the evaporant, both with SnO\textsubscript{2} and with Sn, leads to unreproducible and unstable results. Alternatively, SnO has a higher vapour pressure than either Sn or SnO\textsubscript{2}, so that a lower evaporation temperature can be used. This is advantageous because less impurities from the furnace walls will be incorporated in the condensed phase. It necessitates, however, a subsequent oxidation step to SnO\textsubscript{2}.
A gas-phase synthesis method originally devised for the synthesis of PbS nanoparticles was modified for the preparation of crystalline, quasi-spherical, monodisperse SnO\(_x\) particles by introducing an additional oxidation step.\(^{27}\) The method is based on particle formation by homogeneous nucleation induced by cooling down of a SnO vapor and subsequent aggregation by Brownian motion, followed by a size-fractionation step and a sintering/crystallization step. The experimental setup is depicted in Figure 1. It contains six elements: a nanocrystal source in the form of a sublimation furnace, a radioactive \(\beta^-\) source (Kr\(^{85}\)) which acts as bipolar aerosol charger, a Differential Mobility Analyzer (DMA) used as a size-classifier, a second tube furnace for sintering and crystallization of the SnO aggregates, a deposition chamber and a particle size measurement system consisting of a DMA and a condensation nucleus counter (Model 3025, TSI, Minneapolis, USA). Nitrogen obtained from evaporating liquid nitrogen and purified by passing it through a getter (MonoTorr PS4-MT3-N2, SAES Getters, Cologne, Germany) is used as carrier gas. The total gas flow is kept at 1.5 slm by means of a mass flow controller (MFC) and the system is operated at atmospheric pressure. In the second half of the sintering/crystallization furnace a flow of O\(_2\) is added in order to oxidize the SnO nanoparticles to SnO\(_x\) nanoparticles, with \(x > 1\).

In a Differential Mobility Analyzer the charged particles are size-selected on the basis of their electric mobility, which is a function of their charge level, mass and shape. The DMA (NANO-DMA, TSI, Minneapolis, USA) is capable of delivering monodisperse aerosols with sizes adjustable between 2 and 50 nm and geometric standard deviations as small as \(\sigma_g = 1.05\), depending on the flow conditions in the apparatus.\(^{28}\) In our studies, the flow ratio was chosen to get a theoretical distribution in diameter of \(\pm 0.1 \ D_m\). The second DMA connected to the nucleus counter allows to detect on-line the change in mobility diameter due to the passage through the second furnace and the width of the particle size distribution after size-fractionation can also be checked.

B. Nanoparticle deposition

For film deposition, two methods are used. An electrostatic precipitator enables the aerosol to be deposited with nearly 100% efficiency on a substrate placed in a high-voltage field.\(^{29}\) The distance between the nanoparticle inlet and the substrate placed on the electrode, which is at \(\sim 5 \text{ kV}\), is 4 cm and the area for uniform deposition is 1 cm\(^2\). This method is used to deposit films for characterization methods requiring larger areas such as XRD and RBS and for depositing nanoparticles in submonolayer thicknesses for TEM analysis. For the measurements of the gas-sensitive properties, interdigitated structures having an active area of \(\sim 1 \text{ mm}^2\) are used. For his purpose, a method was developed for a more localized deposition than is possible with the electrostatic precipitator. The electrostatic precipitator can be changed into a low-pressure impactor by adding a nozzle with an inner diameter between 0.5 mm and 2 mm and positioned 2 mm above the substrate, and evacuating the deposition chamber down to 3 mbar. The inertial focusing of the nanoparticle aerosol results in a deposition spot as small as 200 \(\mu\text{m}\) when using the 0.5 mm nozzle, so that films with a thickness above 100 nm can be formed rapidly. The combined electrostatic precipitator/low-pressure impactor is shown in Figure 2.
C. Characterization of gas-sensitive properties

A substrate with interdigitated electrodes was developed in cooperation with the Fraunhofer Institut, IMS, Duisburg, Germany. In order to enable electrical measurements of the gas-sensitive properties of the deposited SnO\textsubscript{x} nanoparticle films having higher resistivities, a 1 mm\textsuperscript{2} structure consisting of 160 interdigitated fingers with a width of 2 µm and an identical separation was fabricated on a chip of 3x3 mm size. The electrodes are buried in phosphor-doped silicate glass (PSG) which has a high resistance and suitable viscous behavior during processing. When the electrodes are not buried, they influence the particle deposition and a region of low particle concentration appears close to the electrodes.\textsuperscript{30} This would also hinder the electrical transport. A schematic of the structure is shown in Figure 3(a) and 3(b). The resistance of the structure without deposited film is more than 1000 GΩ. The structures are bonded to a DIL8 chipcarrier. A poly-Si layer is imbedded in the structure and serves as heating element, allowing a maximum surface temperature of 350 °C at these conditions. A thermoelement close to the interdigitated electrodes allows the measurement of the temperature of the substrate surface. Resistance measurements are carried out in an automated gas sensor set-up using a Picoameter with internal voltage source (model 487, Keithley, Germering, Germany). The gas species and gas concentrations are controlled via a battery of mass flow controllers having suitable ranges and automated valves. The gas flow systems allows a control of the gas concentrations between 50 ppm up to 10000 ppm (volume-based) of the measured gas in synthetic air (20 % O\textsubscript{2}, 80 % N\textsubscript{2}). The measurement cell has a volume of 120 cm\textsuperscript{3} and the gas flow was kept at 150 ml/min. The temperature controller, the valves in the gas flow system and the resistance measurements are controlled by a PC.

D. General characteristics of the procedure to deposit tailored nanoparticle films

In view of the fact that the method used in the present study to grow nanoparticle films with tailored properties has not been described in the literature, an overview of the general characteristics of this new and novel film formation method is given below. The basic principle followed is that in order to attain maximum control, the process has to be divided into individually controllable multiple steps. As already mentioned, the method is divided in two main parts: particle formation and film formation.

The particle formation steps are shown schematically in Figure 4(a). Here, the particle formation is understood in terms of tailoring particle properties such as size and shape. The size-fractionation step is an important step in the particle formation process. By means of a cylindrical DMA, the mean electrical mobility of the particles $Z$ can be selected according to:\textsuperscript{31}

$$Z = \frac{Q \ln(R_2/R_1)}{2\pi L V}$$

with $Q$ as volumetric flow rate, $R_2$ and $R_1$ as diameter of the two electrodes, $L$ as electrode length and $V$ as voltage applied between the two electrodes. Usually the voltage is varied to select the particle mobility. The electric mobility of a particle is related to its diameter $d$ by:

$$Z = \frac{neC(d)}{3\pi\mu d}$$
where \( n \) is the charge level, \( C \) is the slip correction \(^{31}\) and \( \mu \) is the gas viscosity. In case of particles smaller than 50 nm the particle are singly charged \((n = 1)\) or uncharged. The particle diameter calculated using equation (2), assuming a spherical shape, is called mobility-equivalent diameter. A second important parameter can be easily controlled by using the DMA is the width of the particle size distribution. The width be decreased by increasing the ratio of sheath gas flow to aerosol flow.\(^{31}\) Measurements using a second DMA showed that the geometric standard deviation of the mobility-equivalent diameter can be varied between 1.05 and 1.25.

In-flight sintering and crystallization is the third important step in the particle formation process. This is done in a furnace immediately after the size-selection step. Quasi-spherical monocrystals have to be formed in order to obtain a well-defined particle system, therefore it is important to avoid aggregation. In the size-selection step, the particle concentration gets reduced roughly by two decades. With the number concentration reduced to \(10^6\) cm\(^{-3}\), the number of particles aggregating would be only 0.7 %, in case of a particle diameter of 10 nm and a residence time of 10 s. The original number concentration of \(10^8\) cm\(^{-3}\), however, would lead to a concentration which is 13 % of the initial, so that each original particle is contained in an aggregate of some 8 particles. This is the main reason why this step takes place after the size-selection. This step is often combined with an in-flight oxidation step, which can be used to change the stoichiometry of the SnO particles formed.

Most commercial gas sensors are doped with metals in order to improve the sensitivity. Although not a part of the present study, the process in principle can be used for preparing metal-doped nanoparticles and metal-semiconductor composite nanoparticles. When the SnO vapor cools down in presence of a metal vapor (in form of atoms or clusters), heterogeneous nucleation on metal clusters or ions will lead to metal-doped SnO nanoparticles. Another possibility is the addition of a metal nanoparticle-aerosol to the SnO\(_x\) aerosol. This can also be highly controlled, e.g. by the use of preferential coagulation of oppositely charged particles, which we already used to synthesize PbS-Ag nanoparticle pairs.\(^{33}\) The formed two-component aggregates can be transformed in a composite particle by inducing a diffusion process by means of a thermal treatment. When this is done in flight with the number concentration such that no collisions occur, the volume concentration of metal can be adjusted over the ratio of the two initial particle diameters.

The different steps possible in the film formation are shown schematically in Figure 4(b). As usual, the film thickness depends directly on the deposition time. The film porosity can be changed by means of the impact velocity of the nanoparticles. This has been demonstrated by Molecular-Dynamics simulations for charged clusters accelerated towards a substrate.\(^{34}\) In our case, the deposition velocities can be varied from a few m/s when using the electrostatic precipitator to a few hundred m/s in case of the low-pressure impactor.

Annealing of the deposited films is essential to form conducting necks between individual particles while maintaining the initial particle size. The neck growth rate \( \dot{x} \) is a complicated function of material constants such as surface tension \( \gamma \), solid-state diffusion coefficient \( D \), initial particle radius \( a \) by the expression:\(^{35}\)

\[
\frac{\dot{x}}{a} = \frac{CD\gamma}{RTa^m} \left( \frac{x}{a} \right)^{-n}
\]

where \( C \) is a constant, the exponent \( m \) is 3 for lattice diffusion and 4 for surface diffusion and the exponent \( n \) is 3.78 and 5, respectively.\(^{35}\) The neck growth rate is thus a function of
the primary particle size. The use of equal-sized particles ensures that the necks between the particles will be of comparable sizes. The extent of necking can be controlled over the annealing time and temperature. The annealing temperature can be relatively low in comparison to other methods where the crystallite size is increased by annealing. This is advantageous when, as in our case, one is using prefabricated microelectronic structures like interdigital structures or heating circuits. A further improvement in the stoichiometry of the film can be obtained by addition of O₂ at elevated temperatures. This step can be combined with the annealing step.

Although not shown in this study, the method allows to deposit a film composed of clearly distinct metal and SnOₓ nanoparticles by mixing the two (size-fractionated) aerosols shortly before the deposition chamber. The possibility to localize the metal either as distinct particle contacting the SnOₓ or as dopant atom inside the SnOₓ will allow to investigate whether the improved selectivity of metal-doped SnOₓ gas sensors is due to a catalytic reaction or a direct change in the transport properties of the material.

III. RESULTS AND DISCUSSION

A. Measurements of particle size distributions in the gas phase

The evaporation-condensation mechanism for synthesis of SnOₓ nanoparticles was first tested with respect to its stability as function of time. It was found that the number concentration of particles produced was stable within 10 % for several consecutive days. The evaporation material in the evaporation boat can be used for weeks without refilling due to the small evaporation rate which is necessary to produce particles in the nanometer size range. The evaporation temperatures which were found to be necessary for obtaining aggregates in the desired size range were in the range 700 – 900 °C. In Figure 5 the yield of nanoparticles measured using the DMA is shown as function of the mobility-equivalent diameter \( D_m \) for different temperatures in the evaporation furnace. Note that these curves are, in the strict sense of the word, not equivalent to particle size distributions, as the charging efficiency of the radioactive charger, the transfer function of the DMA and the particle losses are all included. Relevant for our purposes, however, is only the yield of size-fractionated particles. The mobility diameter with the largest yield shifts to larger values with increasing temperature due to the increased vapor pressure. It is also clear that there exist a temperature, which maximizes the yield for each particle size.

The effect of the sintering and crystallization of SnO particles in-flight in the second furnace is shown in Figure 6. The figure shows the yield of size-fractionated particles of initial mobility-equivalent diameter 25 nm at several temperatures, as measured with a Differential Mobility Particle Sizer (DMPS). It can be seen that the width of the size distribution is indeed very narrow, in reality it is still narrower due to the fact that the convolution of two DMA transfer functions is shown. As the sintering temperature increases, the mobility-equivalent diameter decreases due to the compaction caused by the sintering of several primary particles in the aggregates. The model for solid-state sintering may be applicable to nanoparticles. The development of a bimodal distribution at 690 °C and above is due to the partial evaporation and subsequent secondary nucleation of the SnO nanoparticles. The sintering temperature of 650 °C was chosen for subsequent synthesis of nanoparticles in order to maintain monodispersity. The reduced yield of particles at this
temperature compared to room temperature is due to the fact that the heating and cooling cycle induces a radial temperature distribution inside and just after the furnace which leads to particle losses due to thermophoresis.

B. Structural characterization

TEM, electron diffraction and XRD investigations were used to study the effect of in-flight sintering, size-fractionation and oxidation on the particle size, crystal structure and morphology. Figure 7(a) shows the morphology of SnO particles immediately after the evaporation furnace. The particles are aggregates with a low degree of crystallinity, which is confirmed by diffused rings in the electron diffraction. Figure 7(b) shows that during in-flight sintering of unfractionated particles at 650 °C, an improvement in particle nature and crystalline quality is obtained. However, the particles have a relative broad size distribution. Best results are obtained, as expected, using size-fractionation and subsequent sintering/crystallization (Figure 8). Quasi-spherical morphology and a narrow size distribution are reached for particles with an initial mobility-equivalent diameter below 30 nm, larger particles can be seen to be not completely sintered and crystallized within the residence time of 0.5 s. This can be explained by looking at the characteristic coalescence time \( \tau \), which is a function of the radius of the primary particles, the sintering mechanism and temperature-dependent parameters such as surface tension and solid-state diffusion coefficient can be estimated by:

\[
\tau = \frac{1}{16} \frac{k_B T a^3}{D \gamma_m v_m}
\]

where \( k_B \) is the Boltzmann constant and \( v_m \) is the molecular volume. The formula indicates that the characteristic coalescence time increases rapidly with increasing particle radius \( a \), so that larger aggregates (composed of larger primary particles at an intermediate stage) will need a much longer residence time at the same temperature in order to get completely coalesced. This is indeed confirmed by the experiments. At a later stage we will show that for our sensor application particles with diameters over 30 nm are not useful, so no further experiments at increased residence times with the goal to obtain coalesced particles of that size were carried out. In Figure 9, the particle size distribution determined from the TEM micrographs shown in Figure 8(a) and 8(b) is depicted. It can be seen that a relatively narrow size distribution is obtained, which is slightly broader for the smaller particles. This is caused by the diffusional broadening of the transfer function the DMA, which is more significant for the smaller particles. The width can, in principle, be reduced further by changing the operating conditions of the DMA or by using a second DMA after the sintering.

X-ray diffraction (Philips Pb1710, country, using Co - K\(_\alpha\) radiation, \( \lambda = 1.7902 \) nm) was carried out on SnO\(_x\) films composed of size-fractionated nanoparticles with mobility-equivalent diameter of 25 nm before sintering and 15 nm after sintering (Figure 10). Without addition of O\(_2\) in the sintering and crystallization furnace (Figure 10a), the predominant peaks at 20 = 21.11° (d = 4.88 Å), 20 = 34.4° (d = 3.002 Å), 20 = 38.88° (d = 2.689 Å) and 20 = 43.13° (d = 2.435 Å) observed correspond to the (001), (101), (110) and (002) plane of the tetragonal SnO (romarchite) phase. No XRD peaks corresponding to SnO\(_2\) are detected. When 0.15 slm of O\(_2\) is added with the furnace temperature being 650°C, the XRD peaks shown in Figure 10(b) at 20 = 31.04° (d=3.34 Å), 20 = 39.63° (d = 2.64 Å) and 20 = 44.27° (d = 2.375Å) clearly point to the (110), (101) and (200)-planes of the tetragonal SnO\(_2\) phase.
Interestingly, the weaker peak at $34.4^\circ$ indicates that also some tetragonal SnO phase is present. Apparently the oxidation is not yet completed. From the line-broadening of the (101) peak of the SnO phase and (110) peak of the SnO$_2$ phase, a crystallite size of $14 \text{ nm} \pm 2 \text{ nm}$ was determined by means of the Scherrer equation, which is in good agreement with the mean value from the TEM measurement (Figure 8(b)) of $13 \text{ nm} \pm 2 \text{ nm}$ and the mobility-equivalent diameter after sintering, $15 \text{ nm}$.

The surface topography of the unannealed nanoparticle film is shown in the SEM micrograph in Figure 11. The regular grain size, the uniform particle deposition, the porous structure and the connectivity between the particles can be qualitatively recognized. No difference could be seen by means of SEM between the nanoparticle film which was annealed for many hours at $300 \text{ }^\circ\text{C}$ shown in Figure 12 and the unannealed nanoparticle film. This was supported by XRD measurements, which did not detect a change in crystallite size for the annealed film. The formation of the sintering necks, which unfortunately cannot be seen in the SEM due to insufficient resolution, is thus possible without changing the particle size. Eq. (3) describes the development of the ratio of the sinter neck width and the particle diameter $x/a$, which is valid for constant $a$, constant temperature and for the initial stages of the sintering ($x/a < 1$). It can easily be derived that $(x/a)$ is a function of $t^{1/(n+1)}$, so $t^{-1/5}$ or $t^{-1/6}$ respectively. Therefore, after a very rapid initial increase of the neck width the neck width develops much more slowly. This ensures that sinter necks can develop without substantially changing the particle dimensions. The stability of the film against grain growth is probably due to the fact that the particles did already undergo a high-temperature treatment. Furthermore, the uniform grain size ensures a similar neck formation rate for all particles without substantially changing the grain size.

C. Gas-sensing properties

This section describes the gas-sensing characteristics of SnO$_x$ nanoparticle films prepared from monosized nanoparticles synthesized using the method described above. Three nanoparticle films samples (NF10, NF20 and NF35) were prepared from nanoparticles having mobility diameters after sintering $D_{ms} = 10$, 20 and 35 nm. Further particle and film properties are described in Table 2. It can be seen that the diameters as determined from TEM $D_T$ (9, 20 and 34 nm for samples NF10, NF20 and NF35, respectively) matches very well with $D_{ms}$. The deposition conditions were chosen such that the estimated film thickness of all samples was equal. The nanoparticles were deposited on substrates with interdigitated electrodes as described in the experimental section.

The gas-sensing properties in terms of sensitivity and dynamic behavior were determined by measuring the time-dependent changes in resistance on changing the gas environment in the measurement cell at substrate temperature varying from 100 to $300 \text{ }^\circ\text{C}$. The sensitivity ($S$) is determined by the ratio of the resistance of the metal oxide in air ($R_a$) and the resistance in a reducing atmosphere ($R_g$):

$$S = \frac{R_a}{R_g}$$

(5)

The time constant $\tau$ is determined from the measured dynamic behavior by determining the time at which the sensor attains $63\%$ of the stabilized value of the electrical resistance after changing the concentration of the reducing gas.
Prior to gas-sensing measurements, SnO\textsubscript{x} nanoparticle films were annealed at a temperature of 300 °C for about 2 hours in 1000 ppm ethanol in synthetic air. The annealing will lead to the formation of sintering necks. This is supported by the fact that during the annealing process the resistance of SnO\textsubscript{x} nanoparticle samples decreased by several orders. Results for sample NF35 show that resistance, initially 700 kΩ, reaches a stable value of 1 kΩ after heating for 2 hours. This annealing procedure was also carried out for the other particle sizes, the resulting values of the resistance are shown in Table 2. Clearly, the resistance increases steeply for smaller particle sizes.

In order to investigate the chemisorption process of O\textsubscript{2} on the surface, the temperature dependence of resistance at different oxygen concentrations in N\textsubscript{2} was measured for sample NF10 (Figure 13). The measurements were done by heating the sample from room temperature up to 300 °C at a constant heating rate of 6 °C/min. At all oxygen concentrations, a decrease in resistance with increasing temperature is observed up to 150 °C. Above 150 °C, an increase in the resistance is observed, which is more prominent for higher O\textsubscript{2} concentrations. This behaviour is similar to that observed in literature for temperature-dependent physisorption and chemisorption processes at the surface of a n-type semiconductor. Below 100 °C, oxygen molecules are physisorbed, which does not affect the electrical properties of the semiconductor material and thus the observed decrease in the resistance corresponds to the decrease in the resistance of a n-type semiconductor material with increase in temperature.\textsuperscript{38} This is supported by the observation that these changes are not dependent on the O\textsubscript{2} concentration. Above 100 °C, chemisorbed oxygen acts as an electron acceptor and creates O\textsubscript{2}\textsuperscript{-} species on the surface. Electrons from the semiconductor surface are removed to the adsorbed oxygen species due to a charge transfer mechanism. The negative charge generates a depletion layer and a Schottky potential barrier is formed on the metal oxide surface.\textsuperscript{1} By means of electron paramagnetic resonance (EPR) investigations together with conductance measurements, it was shown that at $T > 150$ °C, O\textsubscript{2}\textsuperscript{-} desorbs and an O\textsubscript{2}\textsuperscript{-} to O\textsuperscript{-} transformation takes place.\textsuperscript{9} Upon increasing the temperature from 200 to 280 °C, the concentration of the O\textsuperscript{-} species decreases, which was assumed to be due to the transformation into O\textsubscript{2}\textsuperscript{2-}.

In the present study the change of resistance was measured as function of oxygen partial pressure in nitrogen at different temperatures. The steady-state values of $1/R$ for sample NF10 are depicted in a log-log plot as a function of $p(O_2)$ at 200, 250 and 300 °C (Figure 14). The behaviour can be described by the formula:

$$\frac{1}{R} \sim \frac{1}{R_0} \cdot p(O_2)^{-\frac{n}{2}}$$  \hspace{1cm} (6)

The nature of the oxygen species determines the value of $n$. A value of 4 indicates corresponds to singly ionized vacancies. If a n-type semiconductor is heated under decreasing oxygen pressure, it loses spontaneously surface oxygen anionic species O\textsubscript{2}\textsuperscript{-} followed by the formation of anionic vacancies. If the sample is thermally treated the neutral anionic vacancy can lose an electron which is followed by a decrease of the resistance. A value of 2 indicates O\textsuperscript{-} surface species.\textsuperscript{17} The positive value of $n$ shows the n-type behavior of the SnO\textsubscript{x} nanoparticle samples.\textsuperscript{38} From the graphs, a value of $n = 2.6\pm0.1$ is observed. The resistance of the SnO\textsubscript{x} nanoparticle films increases with increasing oxygen partial pressure $p(O_2)$. This means that a larger amount of oxygen interacts with the metal oxide surface and therefore more charge carriers are removed. The value $n = 2.6$ indicates that both O\textsubscript{2}\textsuperscript{-} and O\textsuperscript{-} are involved in the chemisorption process.
Addition of ethanol will lead to a surface reaction which causes a decrease in the surface coverage of the oxygen species and, as a consequence, a decrease in resistance. The catalytic oxidation reaction with the reducing gas also decreases the Schottky barrier height. This gas-sensitive behavior was studied for the different samples in Table 2. Typical resistance transients observed for sample NF20 at 300 °C are shown in Figure 15. The ‘on’-state shown in the graph corresponds to the introduction of 1000 ppm ethanol diluted in synthetic air and the ‘off’-state to the introduction of pure synthetic air. The measured change of the resistance on introduction of ethanol has a time constant \( \tau \) of 38 s and the introduction of synthetic air has \( \tau = 400 \) s. The actual time constant will be slightly lower, as the time needed for exchanging the gas atmosphere in the measurement cell (~8 s) is included in the measured value. As can be seen from the graph, the resistance transients are reproducible. Decreasing the ethanol concentration from 1000 to 100 ppm leads to a decrease of the sensitivity from 2.7 to 1.9 and an increase of the time constant from 38 to 63 s.

Figure 16 compares the response transients of nanoparticle films (NF10, NF20 and NF35) at 300 °C having \( D_{ms} = 10, 20 \) and 35 nm at an ethanol concentration of 1000 ppm. It can be clearly seen that the sensitivity to ethanol increases as the particle size decreases. Furthermore, the value of \( \tau \) decreases with decreasing particle size, \( \tau = 10 \) s for NF10 and \( \tau = 38 \) s for NF20. For sample NF35, it was difficult to estimate \( \tau \) due to insignificant change in the resistance on gas exposure.

Figure 18 describes the sensitivity of the nanoparticle films as a function of particle size in the range 200-300 °C. It can be seen that the sensitivity increases with decreasing particle size. Increasing the temperature leads also to an increase in the sensitivity. Similar results were also obtained by changing the mean particle size between 5 and 32 nm via the calcination temperature and by using metal additives. In addition to wide particle size distribution observed in these samples, the process parameters responsible for size control must have caused microstructure and composition variations. On this account the conclusion about size dependence of gas sensitivity could be misleading in the above investigation. It may be emphasized again that in our studies the size distribution was narrow and the particle size was the only variable. Also, the microstructure of the films of different particle sizes was comparable and did not change due to the annealing. It is clear that the variation of \( S \) and \( \tau \) observed in the present study is a purely a consequence of nanoparticle size dependence. As mentioned earlier, a sharp increase of the resistance value is observed for sample NF10 having a particle size of \( D_{ms} = 10 \) nm in comparison to samples NF20 and NF35 with \( D_{ms} = 20 \) and 35 nm (Table 2). Similar behavior were obtained as the resistance of SnO\(_2\) in dry air at 300 °C increases steeply for crystallite size below 6 nm. From these investigations, \( L \) was estimated to be 3 nm, in agreement also with the results from Hall measurements. In the present study, the Debye length seems to have a larger value (approximately 7-8 nm). This is supported by the fact sensitivity is a function of particle size in 10-20 nm size range. At smaller particle sizes (D less that 2L), particle core is the major resistance controlling part of the chain and the sensitivity is known to be a sensitive function of nanoparticle size. As the size becomes small, concentration and energy position of absorption sites in the band gap of the semiconductor are also affected significantly. Together, these factors result in an improved response of the nanoparticle films to the gas molecules in terms of higher sensitivity and low response time at smaller particle sizes (below 20 nm).
IV. CONCLUSIONS

In order to investigate the dependence of gas-sensitive properties of undoped tin oxide nanoparticle films on particle size, a new thin film synthesis technique has been developed. This process, comprising several independent but controllable steps, allows a better control over particle and film properties than single-step synthesis procedures. These steps include particle size-fractionation and in-flight crystallization and oxidation. Monocrystalline tin oxide nanoparticles are formed with mean crystallite sizes adjusted between 10 and 35 nm and a relatively narrow size distribution. Subsequently, they are deposited at room temperature on a substrate with interdigitated electrodes, forming a thin porous film. This experimental procedure guarantees that particles of different sizes have undergone the same thermal and chemical treatment. This is in contrast with the usual practice to vary the grain size by means of the synthesis conditions or by changing the annealing temperature. Annealing of the film in O\textsubscript{2} in these experiments does not change the crystallite size but decreases the (room-temperature) resistance over several orders of magnitude. It is surmised that sintering necks are formed which facilitate the electrical transport and that due to the in-flight temperature treatment and the uniform particle size the nanoparticle film is stable against grain growth. The particle layers show the well-known temperature-dependent behavior of the resistance of a n-type tin oxide in O\textsubscript{2}-atmosphere, indicating that both O\textsuperscript{2-} and O\textsuperscript{-} surface species are involved in the chemisorption process which leads to a charge depletion of the particle surface. The gas sensing properties of SnO\textsubscript{x} films composed of different particle size and equal film thickness were measured in the temperature range 200-300°C. For the first time, it has been shown unambiguously that using smaller tin oxide particles in size range 10-35 nm leads to higher values of the sensitivity (defined as the ratio of the resistance in air and in a reducing tracer gas) for ethanol vapour and a more rapid response on changing gas conditions. The effect is especially clear for particle of 20 nm or smaller.

ACKNOWLEDGEMENTS

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Figure captions

Fig. 1. Experimental setup for the synthesis of monodisperse tin oxide nanoparticle films.

Fig 2. Combined electrostatic precipitator/low-pressure impactor.

Fig. 3. Schematics of interdigitated electrodes with integrated heating: (a) cross section and (b) top view.

Fig. 4. Schematics of the procedure to deposit tailored nanoparticle films having individually controllable multiple steps: (a) particle formation and (b) film formation.

Fig. 5. Yield of SnO nanoparticles as function mobility-equivalent particle diameter as selected by the DMA for different temperatures (caption) in the evaporation furnace.

Fig. 6. Yield of size-fractionated SnO particles having initial mobility-equivalent diameter 25 nm after in-flight sintering and crystallization at different temperatures indicated in the caption.

Fig. 7. TEM micrographs of unfractionated SnO nanoparticles (a) after evaporation in the first furnace and (b) after subsequent sintering and crystallization at 650 °C.

Fig. 8. TEM micrographs of size-fractionated SnO nanoparticles having initial mobility diameters (a) 10 nm, (b) 20 nm, (c) 30 nm and (d) 45 nm. They were all sintered and crystallized in flight at 650°C for 0.5 s.

Fig 9. Histogram of the particle size of SnO nanoparticles taken from TEM-micrographs with initial particle size \( D_{mi} \) of 10 nm and 20 nm. The geometric standard deviation \( \sigma_{ge} \) is indicated.

Fig. 10: \( \Theta - 2\Theta \) scans of a nanoparticle film composed of size-fractionated SnO\(_x\) nanoparticles with \( D_{mi} = 25 \) nm and \( D_{ms} = 15 \) nm (a) without addition of O\(_2\) in the second furnace and (b) with addition of 10 vol % O\(_2\). The solid lines denote the position of the Bragg peaks for tetragonal SnO and the dashed lines for tetragonal SnO\(_2\).

Fig. 11. SEM micrograph of a nanoparticle film composed of size-fractionated as-deposited SnO nanoparticles.

Fig. 12. SEM micrograph of a nanoparticle film composed of size-fractionated SnO\(_x\) nanoparticles. The film has been annealed at 300°C for 1000 hrs under O\(_2\) and C\(_2\)H\(_5\)OH.

Fig. 13: Resistance \( R \) of sample NF10 as function of temperature at different oxygen concentrations (heating rate 6 °C/min)

Fig. 14: Inverse resistance of sample NF10 as function of the O\(_2\) partial pressure at different temperatures.

Fig. 15: Response transients of sample NF20 on switching the ethanol flow on and off (\( T = 300 \) °C, ethanol concentration 1000 ppm).

Fig. 16: Response transients of samples NF10, NF20 and NF35 on switching the ethanol flow on (\( T = 300 \) °C, ethanol concentration 1000 ppm).

Fig. 17: Sensitivity as function of the particle size at different temperatures (1000 ppm Ethanol). The film thickness for all the samples is 1.5 µm.
Table 1: Overview of different nanoparticle synthesis methods

<table>
<thead>
<tr>
<th>synthesis method</th>
<th>size-variation method</th>
<th>smallest, largest particle size (nm)</th>
<th>Sensitivity</th>
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<tr>
<td>Gas-phase condensation</td>
<td>varying oxygen pressure</td>
<td>3, 15</td>
<td>1-10</td>
</tr>
<tr>
<td>sol-gel</td>
<td>annealing</td>
<td>3, 15</td>
<td>1-100</td>
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<td>laser ablation</td>
<td>different targets, annealing</td>
<td>4, 46</td>
<td>1-200</td>
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<tr>
<td>reactive sputtering</td>
<td>unknown</td>
<td>4, 16</td>
<td>1.5-20000</td>
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<tr>
<td>sol-gel</td>
<td>annealing, doping</td>
<td>5, 32</td>
<td>10-360</td>
</tr>
<tr>
<td>hydrothermal treatment</td>
<td>solution concentration</td>
<td>5, 32</td>
<td>up to 2000</td>
</tr>
<tr>
<td>sol-gel</td>
<td>----</td>
<td>6</td>
<td>100-630</td>
</tr>
<tr>
<td>sol-gel</td>
<td>calcination</td>
<td>7, 15</td>
<td>2-10</td>
</tr>
<tr>
<td>Gas-phase condensation</td>
<td>----</td>
<td>9</td>
<td>----</td>
</tr>
<tr>
<td>sol-gel</td>
<td>----</td>
<td>11</td>
<td>1-18</td>
</tr>
<tr>
<td>gas phase condensation</td>
<td>varying furnace temperature</td>
<td>12, 100</td>
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<td>sol-gel</td>
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<td>20, 110</td>
<td>1.5-40</td>
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<td>decomposition of organo-metallic precursor</td>
<td>----</td>
<td>20</td>
<td>7-80</td>
</tr>
<tr>
<td>decomposition of organo-metallic precursor</td>
<td>----</td>
<td>20</td>
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</table>

Table 2: Characteristics of deposited SnO₂ particles in form of nanoparticle films used for gas-sensing investigations.

<table>
<thead>
<tr>
<th></th>
<th>$D_{mi}$</th>
<th>$D_{ax}$</th>
<th>$\sigma_{S,ms}$</th>
<th>$D_f$</th>
<th>$\sigma_{S,T}$</th>
<th>surface density</th>
<th>number of particle layers $^*$</th>
<th>film thickness</th>
<th>$R^{**}$</th>
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<tbody>
<tr>
<td></td>
<td>[nm]</td>
<td>[nm]</td>
<td>[nm]</td>
<td>[µm$^2$]</td>
<td></td>
<td></td>
<td></td>
<td>[µm]</td>
<td>[Ω]</td>
</tr>
<tr>
<td>NF10</td>
<td>15</td>
<td>10</td>
<td>1.12</td>
<td>9</td>
<td>1.19</td>
<td>1.99E+06</td>
<td>152</td>
<td>1.52</td>
<td>2.0E+06</td>
</tr>
<tr>
<td>NF20</td>
<td>33</td>
<td>20</td>
<td>1.08</td>
<td>21</td>
<td>1.15</td>
<td>2.48E+05</td>
<td>76</td>
<td>1.52</td>
<td>4.0E+03</td>
</tr>
<tr>
<td>NF35</td>
<td>75</td>
<td>35</td>
<td>34</td>
<td>34</td>
<td>4.54E+04</td>
<td></td>
<td>43</td>
<td>1.5</td>
<td>1.0E+03</td>
</tr>
</tbody>
</table>

$^*$ number of particle layers assuming a closed packed system

$^{**}$ measured for 1000 ppm ethanol at 250°C
Buried interdigitated structure
Width: 2 µm
Distance: 2 µm

1000 µm

Heating

Thermocouple
size-fractionation: mean diameter

size-fractionation: width of size distribution

sintering and crystallization in flight

oxidation in flight

(not shown in this study)

doping with metal atoms by heterogeneous nucleation

composite particles by mixing in flight
deposition time: film thickness

impact velocity: film porosity

annealing temperature: particle contact, necking

SnO_x

SnO_y

further oxidation

(Not shown in this study)

SnO_x

M

Simultaneous deposition of nanoparticles of SnO_x and metal (M)
5.2 Nanostructured Deposition of Nanoparticles from the Gas Phase

submitted to Particle and Particle Characterisation

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Abstract

For many applications, nanoparticles from the gas phase are of interest due to their physical properties. Especially for electronic or opto-electronic applications, the transfer from their random distribution in the gas phase onto flat substrate surfaces has to be controlled, because the particles are needed in exactly defined areas on the substrate. We demonstrate a parallel process for the transfer of charge patterns on oxidized silicon surfaces followed by the deposition of monodisperse singly charged nanoparticles, which allows the creation of particle arrangements reaching from 100 nm resolution up to structures in the upper micrometer range. The charge patterns are transferred using a polydimethylsiloxane (PDMS)-stamp, which is covered with a metal layer. By applying different voltages to the stamp, negative or positive charges can be transferred. Thus, nanoparticles of different polarities can be guided to certain places.
1 Introduction

The design of future electronic and opto-electronic devices is based on the ability to combine different materials like insulators, semiconductors and metals on a nanometer scale. An improvement of these skills will open ways for the production of new devices, which can not be produced with conventional methods, like UV-lithography and epitaxy. One example is the utilization of monodisperse nanocrystals from the gas phase. Their physical properties, which can be adjusted by varying the particle material, their size or shape, make them important candidates for a number of applications. For instance, films of monodisperse SnO$_2$-particles can be used for sensor applications [1]. Closed lines of metal nanoparticles like Au or Ag or Cu may be used as nanowires for the power supply of electronic devices. Single nanoparticles can be used for single electronic transistor applications [2]. Arrangements of single nanoparticles might be used for data storage [3] or light emitting devices [4] or even new kinds of logic circuits [5]. Au nanoparticles as catalysts allow selective growth of nanowhiskers [6]. All these examples depend on the ability to guide nanoparticles from the random distribution in the gas phase to locally defined areas on a flat substrate surface. As has been shown before [7], this transfer is possible with a resolution better than 100 nm. Here, charge patterns on oxidized silicon surfaces are applied by contact charging with a stainless steel needle that is allowed to slide over the substrate surface. The basic principle of which is that charges cross the interface between an insulator and a metal brought into contact. After the metal is removed, charges retain on the insulator [8]. During the deposition process in a special deposition chamber, oppositely charged particles are attracted from the gas phase due to Coulomb interactions and are deposited exactly were the surface charges reside on the substrate. The drawback of this method is that this kind of “charge writing” is a serial process, which is too slow for the transfer of complex patterns. Subsequently, a parallel process which allows the printing of charge patterns on a large scale has been developed. It is based on the principle of soft lithography where a PDMS (polydimethylsiloxane) stamp is used to apply chemicals on substrate surfaces in a printing process. Feature sizes down to 80 nm can be realized [9]. Jakobs and Whitesides have shown that the transfer of charge patterns to 3 nm thick PMMA-layers on silicon substrates is possible with metalized PDMS-stamps [10]. In this paper, we demonstrate our results on the theoretical and experimental investigation of the nanostructured deposition of nanoparticles after charge printing using metalized PDMS-stamps on oxidized silicon surfaces.

2 Experimental Setup

The experimental setup [11] used to generate the test aerosols is shown schematically in fig. 1. The particle material is evaporated in a tube furnace and carried out of the
furnace by ultra pure nitrogen. During the cooling process behind the furnace, homogeneous nucleation of the vapor takes place. Afterwards, particle growth starts with homogeneous condensation and continues with coagulation of primary particles, which leads to a polydisperse aerosol containing agglomerates. After charging the aerosol with a UV-charger, a monodisperse fraction of negatively or positively singly charged particles is selected by a differential mobility analyzer (DMA). In a second tube furnace, a reshaping step by heating takes place, which is necessary to get a spherical shape of the particles. A second DMA is used to narrow the size distribution. Afterwards, the particles are deposited in an electrostatic precipitator (ESP). We used 30 nm indium or gold particles as test aerosol for our experiments [12]. The particle concentration in the gas phase was in the order of $5 \cdot 10^5$ #/cm³. At this concentration, further agglomeration of particles in the gas phase can be neglected.

The ESP used [13] is a cylindrical chamber designed to remove charged particles from the gas flow by means of a homogeneous electric field. The bias is applied between the top plate, where the aerosol enters the ESP, and a horizontally arranged electrode, 30 mm in diameter, on which the substrate is placed. The aerosol jet enters the ESP at the inlet with a velocity of 3 m/s and a stagnation point flow is built up.

![Diagram](image-url)

*Fig. 1: Scheme of the experimental set up.*
At a distance of 3.5 mm beside the stagnation point, the gas flow is parallel to the electrode. When the homogeneous electric field is applied, the charged particles are pulled towards the substrate surface. In combination with the drag forces parallel to the substrate, this leads to a circular deposition spot on the substrate. The spot has for our conditions a diameter of 15 mm, determined by scanning electron microscope (SEM) investigation and calculation of the particle trajectory starting on the outer streamline. Due to the combination of flow field and electric field in the ESP, the particle distribution is macroscopically homogeneous over the whole sample area.

In order to investigate the structured deposition of particles on oxidized silicon substrates, charge patterns were applied on the substrate surface by contact charging with different PDMS-stamps. The two main aspects were to show, on the one hand whether it is possible to transfer complex charge patterns with a stamp onto oxidized silicon substrates, and on the other hand, whether the charge density within these patterns is sufficient to selectively deposit nanoparticles on the desired areas of the substrate. In order to realize a good contact between stamp and substrate surface without applying a strong pressure, it turned out that the stamp has to be flexible. For this reason, polydimethylsiloxane (Sylgard 184, Dow Corning) was used as stamp material. For the processing of the stamps, oxidized silicon substrates were used as masters. They were patterned using standard processes either using UV-lithography or e-beam lithography. On top of the master, a stainless steel cylinder was placed, into which the viscous PDMS was poured. After polymerization of the PDMS at 60°C for 5 h, the master was stripped off the stamp. The size of the stamps varied between a diameter of 5 mm to 5 cm. The stamping area has to be metalized to allow contact charging. This was realized by evaporating a 5 nm thin layer of chromium followed by a 80 nm thick layer of gold. A steel plate was fixed with silver glue on the back side of the stamp, which was used to attach the stamp to a magnetic holder. The principle of charge printing is visualized in Fig. 2. The stamp was moved gently up and down by a piston in order to touch the substrate without applying pressure. The substrates were silicon (100), p+ doped with 0.01 to 0.02 Ω·cm resistivity, with thermally-grown wet oxide and a planar surface. The oxide thickness was chosen to be either 500 nm or 50 nm. During contact between the metal layer of the stamp and the substrate, charges cross the interface between the two materials. As deposition experiments with positively charged particles show, the substrate is charged slightly positively in case of a contact between SiO₂/Au. In order to be able to control the charge transfer and to enhance the charging effect, a voltage of ± 20 V was applied between the stamp and the back side of the substrate, depending on whether negative
Fig. 2: Principle of contact charging with a stamp.

or positive charge patterns should be created. The charging procedure was carried out in a glove box flooded with ultra clean nitrogen, in which the ESP is installed as well. Thus, contact of the substrate with ambient air during and after charging is avoided.

3 Results
In order to show that deposition patterns in the micro- to millimeter size range can be obtained by deposition of monodisperse particles from the gas phase on charge patterns, a stamp with a microscopic finger structure was used. The fingers were approximately 1.6 mm in length and, as the sketch in fig. 3 shows, 10 µm in width, with a pitch of 40 µm. The stamp had a diameter of 5 cm. A bias of –20 V was applied to the stamp during charging a substrate with a 500 nm thick oxide layer. After charging, the substrate was put on a heating plate inside the glove box, and heated to 250°C for 5 min. The sample was placed in the ESP and 30 nm indium particles, which were carrying a single positive charge were deposited for 120 min. An additional homogeneous electric field of 50 kV/m was applied in the ESP to enhance the particle deposition. As the left SEM-image in fig. 3 shows, the particles were deposited in parallel line patterns which correspond to the structure of the
Fig. 3: SEM-images of finger structures consisting of 30 nm indium particles and sketch of stamp structure.

stamp, which was in contact with the substrate. Between these lines no deposition of particles takes place. Due to the heat treatment of the substrate after charging, the charges were allowed to diffuse to distribute more homogeneously, leading to a homogeneous particle distribution within the charge patterns. Even after the heat treatment, the charge density is high enough to attract particles from the gas phase. The SEM-image shows only a small fraction of the whole pattern, which was repeated over the whole stamping area. The right image in fig. 3 shows a clipping of the left image at a magnification of 5000. The width of the line is approximately
83

8 µm, which can be explained by the rounded shape of the contact area as illustrated in fig. 3. The particles are distributed homogeneously over the whole width of the line. At the edges of the line the particle density decreases to zero within a narrow transition zone of less than 1 µm width.

Fig. 4 demonstrates that the deposition of continuous lines of nanoparticles is possible even in the nanometer range. The experiment has been carried out as described before with a substrate with an oxide thickness of 50 nm. After the charging no heat treatment was carried out. The deposition time was 60 min. A sketch of the stamp is shown in fig. 4. It had 500 nm wide lines with a pitch of 2 µm. From the deposition pattern that were obtained follows that the amount of charges transferred to the substrate is sufficient to attract enough particles to form closed nanowires. The width of the nanowires is in the order of 200 nm. Their sharp edges show that the particle deposition is focused on the charged regions of the substrate. Again the width of the particle patterns is smaller than the width of the line structure of the stamp due to a rounded shape of the contact area.

The SEM-image in fig. 5 shows discontinuous line patterns of particles. The image demonstrates that the deposition of single particles with a resolution better than 100 nm is possible and even on this small scale particle deposition only occurs onto
charged areas. In this case the stamp consisted of lines with a width of 1 µm and a pitch of 1.5 µm. As the sketch in fig. 5 illustrates, the contact area of the lines was different from the previous examples. Instead of a cushion like contact area as before, here the edges of the lines were in contact with the substrate leading to narrow contact areas of widths below 300 nm.

The ability to create attractive and repulsive regions on the substrate surface by charging defined areas either positively or negatively, will open the possibility to deposit different kinds of particles like particles of different materials and/or sizes on defined areas close to each other. Depending on whether a positive or negative voltage is applied to the stamp, positive or negative charges are transferred to the substrate. In fig. 6, the influence on the deposition patterns is demonstrated. Fig. 6A shows a SEM-image of the stamp used for these experiments. It is an array of pillars 1 µm in diameter. As can be seen from the image, the metal layer on top of the PDMS is not smooth but has cracks. Thus, parts of the metal layer will not have electrical contact. This causes yet unsolved problems in the transfer of continuous lines in the sub-micrometer range over larger areas. Fig. 6B and fig. 6C show the
Fig. 6: Influence of the voltage applied to the stamp during contact charging: Image A shows the stamp. –20 V leads to negative charged regions the corresponding deposition pattern is shown in image B, and +20 V leads to positive charged regions as the deposition pattern in image C illustrates. 

particle arrangement in case of +20 V (B) and –20 V (C) applied to the stamp during charging. The substrate used for these experiments had an oxide thickness of 50 nm. No heat treatment was carried out after charging. An electric field strength of 150 kV/m was applied in the ESP during the deposition of 40 min duration. The particles deposited were 30 nm gold particles carrying one positive charge. As the deposition pattern in fig. 6B shows, the particles were attracted by the charge patterns in case of a negative voltage applied to the stamp. Thus, the substrate has been charged negatively. From the particle arrangement follows that only the edges of the pillars came into contact with the substrate. Furthermore, the contact was not
continuous over the whole perimeter. On the other hand, the arrangement of the particles proves that the charge patterns clearly determine the particle motion and the particle deposition is focused on the charged areas of the substrate. The deposition mechanism in this case is characterized by attractive Coulomb forces which increase quadratically with decreasing distance, resulting in a strong acceleration towards the charge pattern. On the contrary fig. 6C shows the inverse pattern due to the repulsive interaction between the incoming particles and the charge patterns. Thus, the substrate has been charged positively by applying a positive voltage to the stamp. The deposition mechanism differs from the case of attractive interaction. As follows from fig. 6B the charge patterns can be regarded as rings. Due to the repulsive interaction between the incoming particles and the charges on the substrate, a circular zone around each of these rings exists, where particle deposition is impossible. The diameter of this zone depends (at given homogeneous electric field and particle charge) on the size of the charge pattern and the charge density. As fig 6C shows, most of the particle free areas all have a more or less similar circular shape with a diameter of approximately 2 µm. Thus, the form of the patterns and the charge density must be the same. The particles are deposited between these areas, were the repulsive Coulomb force due to the charges on the substrate is overcome by the attractive Coulomb force due to the homogeneous electric field of the ESP. This results in a even distribution of the particles because the microscopic particle arrangement is determined by the particle-particle interactions and not by attractive Coulomb forces.

4 Conclusions
From the results of the investigation on the structured deposition of nanoparticles from the gas phase on charge patterns applied by metalized PDMS-stamps the following conclusions can be drawn. The parallel transfer of charge patterns with resolutions from the upper micrometer range down to the 100 nm range is possible on oxidized silicon substrates. The influence of the oxide thickness has not been investigated in detail yet, but first results show that the resolution improves with decreasing oxide thickness. The charge density of the charge patterns obtained with the described method is sufficient to attract enough particles even to form closed films. The resolution of the deposited particle patterns obtained is better than 100 nm. The investigation has shown that the stamp material has to be flexible in order to transfer charge patterns reliably over large areas. PDMS seems to be a good material for the creation of stamps because it is easy to handle. Nevertheless, the metal layer, which is necessary to obtain the charging effect, has to be improved. Two aspects are of importance. First, the adhesion between the PDMS and the metal has to be improved in order to make the stamp more robust. The second aspect is that the gold layer cracks while using the stamp, which leads to a non-uniform charge
transfer. A solution to these problems might be the use of alternative metals. First experiments with silver and nickel top layers have been carried out.

7 Acknowledgements
This work was carried out at the Nanometer Consortium in Lund and was supported by the ESF program NANO and the EU-TMR project CLUPOS. The authors would like to thank Mariusz Graczyk, Lena Timby and Eva-Lena Sarwe for their help during the investigations.

8 References

NUMBER SIZE DISTRIBUTION, MASS CONCENTRATION, AND PARTICLE COMPOSITION OF PM$_1$, PM$_{2.5}$ AND PM$_{10}$ IN BAGGING AREAS OF CARBON BLACK PRODUCTION

Submitted to A I H A J

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Keywords: Carbon Black, working place exposure assessment, particle number concentrations, PM, chemical composition, ultrafine

Abstract
Particle number size characteristics and PM$_{10}$ mass concentrations of particles emitted during the bagging of various kinds of carbon blacks were measured online in the bagging areas of three carbon black plants and in parallel at an ambient comparison site. PM$_{10}$, PM$_{2.5}$, and PM$_1$ were also determined discontinuously with manual filtration samplers in the bagging areas. The loaded filters were then analysed for elemental and organic carbon. Comparisons of the measured number size distributions and mass concentrations during bagging activities with those measured parallel at the ambient site and with those determined during non-working periods in the working area enabled the characterization of emitted particles. PM$_{10}$ mass concentrations were always elevated (up to a factor of 20) during working periods in the bagging area. Detailed analysis revealed that the carbon black particles released by bagging activities have a size distribution starting at $\approx 400$ nm aerodynamic diameter ($d_{ae}$) with modes around $1 \mu$m $d_{ae}$ and $> 8 \mu$m $d_{ae}$. Ultrafine particles (< 100 nm $d_{ae}$), when found in the bagging areas, could clearly be attributed to non carbon black production sources such as forklift and gas heater emissions.

Introduction
It is generally known that excess exposure of workers to airborne particulate matter may cause adverse health effects. Therefore occupational exposure guidelines at working places are recommended by organizations like the American Conference of Governmental Industrial Hygienists, the American Industrial Hygiene Association, and the MAK Commission/Germany. Limit
values by these organisations are based on mass concentrations. Some recent epidemiological studies on the other hand show higher associations of some negative health effects with ultrafine particle (UFP, < 100 nm) number concentrations than with particle mass concentrations \(^1\). UFP may contribute to health effects due to their high number concentration and surface area, a high deposition efficiency in the pulmonary region, and a high propensity to penetrate the epithelium. Even though the mechanisms and particle characteristics causing negative health effects are heavily debated, it is necessary to determine all particle characteristics at various locations, e.g., in ambient air and working areas to enable detailed toxicological studies and to produce a data base for particle exposure assessments.

So far no studies have been conducted to our knowledge to assess the particle exposure to particle number size distributions at working places in the carbon black industry. Therefore a comprehensive study was started with the aim to characterize the potential fine (PM\(_{10}\), PM\(_{2.5}\), PM\(_1\); mass concentration) and ultrafine particulate (number concentration) exposure to workers in the carbon black industry. Within this study particle number size distributions, particle mass concentrations, and chemical composition with respect to the carbon fractions were determined. This paper reports on measurement results in the bagging area of carbon black plants. The mass concentration reported here were determined a) to assess the mass size distribution of possible particle sources and b) to enable a comparison with other studies at carbon black working places.

Elemental and organic carbon were also determined from the loaded filters to evaluate the composition of the particles.

**Descriptions of the investigated processes and sites**

The carbon black manufacturing process consists of three process steps: Reactor, Pelletizing, Bagging. In the first process step, the reactor, the chemical reactions take place to produce the primary carbon black particles. They are formed by gas-to-particle conversion processes during incomplete combustion of carbon containing fuels. Primary particle sizes can range from 1-500 nm (nm \(= \ 10^{-9}\) m) with the most commonly produced being in the range from 10 nm to 100 nm. These primary particles very rapidly form aggregates due to the high particle number concentrations in the closed reaction area. Aggregates are the primary structural entity of carbon black. Aggregates are highly branched strings made up of roughly spherical nodules (primary particles) fused rigidly to one another. Aggregates may be made up of a few to many tens of nodules. The forces of adhesion, which arise because of interactions between electrons in two very nearby particles, are particularly strong for electrically conductive materials such as carbon black \(^2,3\). The strength of particle attraction between conducting carbon black is about 8 times larger than it would be if the material were an insulator \(^2\). These forces between surfaces are called “London Forces”, “Dispersion Forces”, or most commonly “Van der Waal’s Forces”.

\[ \text{nm} = 10^{-9} \text{m} \]
As aggregates suspended in air move around under the influence of Brownian motion, they come in contact, and various aggregates stick together with several points of contact and adhesion. These entities, composed of several to many aggregates are called “agglomerates”. While they can be dispersed back to the individual aggregates from which they formed with sufficient energy, they are really quite stable. It is very difficult to disperse carbon blacks back to the single aggregate state, since the actual state of agglomeration is a balance between the collision process, which forms agglomerates, and any redispersion forces that may be acting. It is not uncommon to find agglomerates of carbon black that are made up between ten and a thousand aggregates suspended in air.

In many carbon black processes, the second process step (pelletizing) is the formation of very large agglomerates called “pellets”. These may be made by tumbling the newly made carbon black in a drum for a period of time and taking out the large pellets that are formed, or by spraying water on the carbon black in a pin mixer in such a way that the water ends up facilitating the aggregation process. These pellets are then dried to make the final pellets. Thus carbon black comes in three forms for various applications, fluffy – which has not been pelletized, dry pellets made by tumbling without water, and wet pellets. Carbon black is mostly shipped as wet-formed pellets for greater ease of handling.

Measurement methods

Measurements discussed in this paper, were conducted at two locations in each bagging area of three carbon black plants. The bagging equipment, ventilation, size of the bagging halls, and local wind fields were quite diverse and significantly influenced the determined particle concentrations and characteristics.

Particle size distributions were measured with a Scanning Mobility Particle Sizer (SMPS; TSI 3065) which determined the size distributions in the size range of 15-734 nm (d_{St}, Stokes diameter). The determined particle size distributions were converted to the aerodynamic diameter (d_{ae}) by assuming a particle density of 1.75 g/cm³. A particle size distribution was determined every five minutes. Two SMPS were employed at plant 2 and plant 3 to simultaneously determine the ambient and work environment particle size distributions. The two SMPS systems were compared to each other prior to each measurement campaign and were found to be equivalent within a factor of two over the whole particle size range (Figure 1).

An Aerodynamic Particle Sizer (APS, TSI 3310) was employed in the working areas to determine and classify airborne particles in the range from 0.5-15 µm (d_{ae}, aerodynamic diameter). The aerosol is drawn through a nozzle accelerating the particles. The velocity of the particles, determined in the APS, depends on the aerodynamic diameter of the particle. The APS was calibrated with latex particles of certified aerodynamic diameters prior to the measure-
ment campaign. The flow rate was checked regularly and adjusted if necessary. Average particle size distributions were recorded every 5 minutes.

Two automatic instruments (TEOM®, R&P, USA) were used as online PM$_{10}$ mass concentration monitors running parallel in the working areas and at the ambient comparison site. The measurement principle of the TEOM® is based on the oscillating tapered element. The tapered element is kept at a constant temperature of 50°C to reduce any influences of changes in ambient conditions on the mass determination. PM$_{10}$ mass concentrations were averaged and recorded every 5 minutes.

PM$_{10}$ mass concentration ratios between the two samplers (Inside, Outside) ranged between 0.83 and 1.19. Taking into account the results of the above comparison and a safety margin due to the frequent change of sampling location for TEOM Inside, determined mass concentrations can be viewed to be significantly different between inside and outside by factors $> 2$.

Manual filtration samplers, two LVS 3 (Derenda, Germany) and one DHA 80 (DIGITEL, Switzerland) equipped with PM$_{10}$, PM$_{2.5}$, and PM$_{1}$ inlets, respectively, were used in this study to determine the mass size fraction and chemical composition of the different size fractions. The PM$_{10}$ and PM$_{2.5}$ inlets are in accordance with ambient air quality standards in the US and Europe (5-7).

The volume flow of the filtration samplers was checked and inlets cleaned regularly.

All filters (before and after sampling) used in the campaigns were equilibrated to 20±1°C and 50±5% relative humidity for at least 48 hours, then weighed at least 2-3 times with 12-24 hours between each weighing. Weighing was conducted in a climatized clean room, with loaded filters transported frozen in petri dishes or wrapped carefully in aluminium foil. Filters were refrozen directly after the last weighing of the loaded filters to avoid losses during storage prior to the carbon analysis.

Filters were analyzed for elemental and organic carbon to assess and quantify the magnitude and proportion of the carbon fractions of the total particulate matter throughout the manufacturing process. The purpose of this analysis was to determine whether identified ultrafines and particle mass concentrations could be attributed to carbon black. Elemental carbon (EC) and organic carbon (OC) were analyzed from preheated quartz fiber filters by a method developed by Cachier et al.(8) and Kuhlbusch(9) briefly described herein. Filters are divided into several aliquots. One aliquot of the filter is combusted at 900°C in pure oxygen and the evolving CO$_2$ representing the total carbon (TC) is quantitatively determined by an NDIR-spectrometer. The other aliquot of the filter is exposed to 340°C pure oxygen for 2 hours to remove the OC from the filter by oxidation and volatilization. The remaining carbon, termed EC, is quantified as described for TC by combustion of the aliquot at 900°C. OC is derived by subtracting EC from TC.

An Aethalometer was used as a real-time technique for the determination of black carbon (BC) (10,11). The term Black Carbon (BC) is used for data obtained with the Aethalometer and refers to the optically absorbing carbon fraction.
The term elemental carbon refers to the inert carbon fraction determined by thermal analysis. Since the Aethalometer determines the light-absorbing fraction of carbon it does not clearly differentiate between elemental carbon (EC) and organic carbon (OC). Some organic carbon may well be quite dark and hence will be determined as black carbon. Thus, values given by the Aethalometer are semi-quantitative. They are used here to identify short-time changes in BC mass concentrations due to any discontinuous source processes. The Aethalometer measures Black Carbon by determining changes in the light transmittance through a filter with time while the filter is loaded with airborne particles with a flow rate of about 3 l/min. A specific attenuation cross section \((\sigma)\) of \(19 \text{ m}^2 \text{ g}^{-1}\) is internally used by the Aethalometer to convert the change in light absorption to the mass of black carbon \(^{10,12}\). The internal mass flow meter of the Aethalometer was checked every two days and calibrated when necessary.

All instruments were checked and calibrated in the laboratory prior to each measurement campaign. Additionally, all instruments were co-located prior and after the working place measurements at an ambient comparison site to verify the comparability of the instruments. Sampling locations within the plants were selected on the basis of proximity to appropriate production activity and were not personal breathing zone samples. All reported mass concentration data have been standardised to 0°C and 1.013 hPa.

**Results and Discussion**

Number size distributions, mass concentrations and the results of the carbon analysis are presented and discussed separately. The first two sections discuss the number size distributions and mass concentrations in order to assess the presence of particle sources. Generally two methods were used to determine specific sources in the bagging areas. Discontinuous processes leading to enhanced particle concentrations could be determined by comparison of the online data prior or after the start of the processes with the one determined during the ongoing activity. Discontinuous and continuous sources could be investigated by comparing the ambient particle characteristics with the ones determined in the working area.

The third section presents the results of the carbon analysis and is discussed in view of carbon black as a possible source for any observed increases in PM\(_X\) mass concentrations. Both, the mass concentrations and carbon fractionation will be compared to results of a study by Kerr et al.\(^{13}\).

**Number Size Distributions**

**Plant 1**

Particle number concentrations for three size classes (10-100 nm, 200-700 nm, and 1-10 µm) were calculated from the determined number size distribution to
visualize changes with time in these relevant size classes. Figure 2 shows exemplarily for all measurement campaigns such a graph. This kind of graph was chosen to identify periodic changes and changes going along with working processes. Information on working processes such as bagging, breaks, welding activities etc. were recorded manually. The periods termed “event” (Figure 2) were periods with elevated coarse mode (> 1 µm d_{ae}) particle number concentrations. These “events” were observed in all working areas and at the ambient site at plant 1 and have to be attributed to a source outside of plant 1. Looking at the number concentrations of the size classes 200-700 nm and > 1 µm in Figure 2 the start, break, and end points can clearly be seen where as no significant changes can be observed for the UFP. This kind of graph was also used to identify the time periods for size distributions during working and non-working periods. Figure 3 shows exemplarily the number size distribution determined during bagging N550 in Plant 1. N550 and similar alpha-numeric designations are ASTM designations for types of carbon black. The ratio of particle number concentrations during work to break (Figure 3) start to increase at about 400 nm d_{ae} with modes at ≈ 1 µm and > 8 µm. This comparison analysis was conducted for several break periods and for the start and end of working periods. All analysis showed very similar results with increases in particle number concentrations starting at about 400 nm. Plant 2 Figure 4 shows typical number size distributions determined in the closed bagging area during bagging small bags (ca 25 kg) of E570 and during a non-working night time period along with parallel measured outside size distributions. The ratio work/ambient starts to increase at about 400 nm d_{ae} and reaches a maximum 1.2 µm and > 10 µm d_{ae}. This increase is most likely due to the packing. Also a slight increase of the number concentration ratio below 50 nm can be observed showing no maximum. The same ratio for the non-working period during the night (inside/ambient at night, not shown in Figure 4) does not show these differences in the size distribution. The second ratio shown in Figure 4, the ratio of the size distribution inside between working and night period, shows a similar change in the size distribution as the ratio In/Out during the working period indicating a source of particles < 100 nm. The increase of the number of particles > 400 nm is also evident in this ratio. The ratios in this size range are very similar to the ones determined in Plant 1 indicating a strong source of coarse mode particles due to bagging activities. Figure 5 shows the number size distribution during the bagging of big bags (super sacks, ca. 1000 kg) of fluffy carbon black (E325). The number size distributions determined with the APS (0.7-14 µm d_{ae}) do not overlap with that of the SMPS. The difference is due to the local wind fields and the different locations of the two instruments. Regular peaks in the number concentrations below 100 nm were observed going along with the packing intervals of the big bags. A detailed analysis of the
bagging process and comparison with the manual records of activities enabled us to differentiate the time periods while the big bags were filled and while a change of bags took place. The shown distributions (bag change, filling) and ratios are representative of 22 bag changes and fillings measured.

The average size distribution ratio in Figure 5 shows a similar feature as the one in Figure 4. A maximum around 30-40 nm $d_{ae}$ in the number concentration ratios can be observed in the UFP size range comparing the size distributions of bag change with filling and ambient. The ratio (filling/ambient and bag change/ambient) also increases at about 400 nm towards larger particle sizes.

The increase in particles $> 0.4$ µm is most likely due to the packing process (c.f. Figure 3 and Figure 4) and thus carbon black particles. The maxima in the UFP size range depicted in Figure 4 and Figure 5 were also seen during other packing periods comparing ‘Inside/Outside’ and ‘working/break’. No such maxima were determined in Plant 1. From Figure 5 it can also be depicted that the UFP maxima were only determined during the working period when the bags were changed but not during the filling process.

A feature also observed in Plant 2 was that the peaks in the UFP range did not always correspond to the actual packing activity, meaning filling of the bags. This became especially evident analysing the size distributions determined during the bagging of the big bags. The maxima in the UFP range were only determined during the change of the big bags but not during the filling of the bags itself (Figure 5, maximum for ratio change/filling but not for ratio filling/ambient). Fork lifts were active when the big bags were changed but were not used during the filling of the bags. Hence we made some measurements with only a forklift running but with no ongoing bagging activities.

Figure 6 shows the number size distributions determined during a break and during a single forklift (running on propane) driving near the instruments. There were no other activity changes from the break time to the running fork-lift time.

The size distribution comparison in Figure 6 clearly shows an increase in the UFP size range 20-50 nm $d_{ae}$ but also in the coarser particle size range ($> 1$ µm). Both emissions can be attributed to the forklift activity since there were no other ongoing working activities. The particles in the UFP size range are emitted with the exhaust of the engine whereas the coarser particles are most likely resuspended particles due to air turbulence from the motion of the forklift.

**Plant 3**

Figure 7 shows number size distributions determined in the bagging area and at the ambient comparison site in Plant 3 as an example. Two different time periods were chosen. The first was during bagging of N550 in small bags (ca. 25 kg) and the second during the break just prior to the bagging of N550. The size distribution ratios of inside bagging to break and break inside to outside are given.
Figure 8 shows number size distributions obtained during bagging of big bags N339 (ca. 1000 kg) and a break prior to bagging. The ratio shown in this case is the one of bagging / break time. Figure 7 and Figure 8 show two modes during bagging one around 30-50 nm and a second for particles > 400 nm and > 1 µm, respectively. The latter mode agrees well with the ones determined in Plant 1 and Plant 2 and can be attributed to particle emissions due to bagging activities. The mode (maximum) around 30-50 nm (comparison Bag In/Out and work/break) is well pronounced with ratios of about 20. The increase of these particles in the UFP size range was consistently determined only during ongoing bagging activities. A source of particles in this mode was investigated by recording forklift activities in close proximity to the measurement platform. The forklifts used in Plant 3 run on diesel. Figure 9 shows number size distributions during test run with forklifts running near the instruments and a break period (each about 15 minutes). The ambient size distribution shown is the average during both test runs. The break was 2 hours after the test runs. The comparison ratios shown in the same figure clearly demonstrate that the emissions of particles with a mode around 30-50 nm determined during bagging stem from forklift activities.

Figure 10 shows an example of the number size distributions measured inside and outside during longer periods without any activities in the bagging hall. The number concentration ratio shown in this figure indicate a source of particles with a mode < 30 nm and a concentration ratio of > 10. This feature can also be seen in Figure 7 for the ratio break In/Out and was consistently observed during longer periods without any activities. Since this increase could only be observed during longer break periods, but then consistently over the whole time, a permanent process must be the source of these UFPs. The source is expected to be close to the measurement equipment since the ratio increases down to the lower detection limit (17 nm d_{50}) of the instrument. The most likely source for these particles are the butane space heaters used for comfort heating of the bagging area. One of these burners was placed about 5-10 m away from the measurement platform.

**Summary Particle Number Size Distributions**

Particle number size distributions were measured in ambient air and in bagging areas of three carbon black manufacturing plants. Size distribution characteristics of particles emitted in the bagging areas were determined by comparisons with size distribution measured during non-working periods or measured parallel at the ambient site. Particle emissions due to bagging activities of various kinds of carbon blacks were determined. The number size distribution comparisons showed in all cases emissions of particles > 0.4 µm d_{50}. Particle emissions in the ultrafine particle range (< 100 nm) were determined in Plant 2 and 3 but not in Plant 1. Detailed analysis of the online data revealed that emissions and detection of UFP’s did not always correlate with bagging activities hence indicating a different source. Electric forklifts were used in Plant 1,
propane fuelled ones in Plant 2, and diesel forklifts in Plant 3. Comparisons of crude size distribution forklift emission measurements with size distributions determined in the bagging areas showed good agreements, explaining the determined increases in UFP number concentrations. Additionally a continuous source of ultrafine particles was observed in Plant 3 which could be attributed to the gas heaters. Hence, carbon black particles emitted during bagging have size characteristics with particle sizes starting at \( \approx 0.4 \mu m \) in aerodynamic diameter with modes at particle sizes of 1-2 \( \mu m \) and > 8 \( \mu m \).

Mass Concentrations

Plant 1

Ambient PM 10 mass concentrations during the measurement campaign in Plant 1 were on average 45±31 \( \mu g/m^3 \) (TEOM® data, Max: 291 \( \mu g/m^3 \)). Table 1 gives an overview of the mass concentrations determined at the ambient site and the different bagging areas with the automatic device (TEOM®) and the manual filtration samplers. The maximum PM 10 mass concentrations determined with the TEOM® in the bagging area was 670 \( \mu g/m^3 \). PM10 mass concentration ratios working places to ambient are given in Table 2 (2nd column). Comparing the mass concentration ratio of the ambient comparison to bagging night/ambient (no work under way), no significant increase in PM10 mass concentration indoors were observed. Columns 3 and 4 in Table 2 give the PM2.5/PM10 and PM1/PM10 mass concentration ratios. These ratios indicate the size fraction of a source when significantly different from the ambient values. Taking the bagging area ground level as an example. Here significant PM10 mass concentration increases (indoor/outdoor) were observed and the PM2.5/PM10 and PM1/PM10 ratios significantly decrease to 33% and 16%, respectively. The latter result indicates that mainly coarse particles (> 2.5 \( \mu m \) diameter) lead to the observed increased PM10 mass concentrations in the bagging area during ongoing work. The continuous mass concentration readings clearly showed the correlations between packing and break times indicating that the mass concentration changes are due to the working process (Figure 2). The PM1/PM10 and the PM2.5/PM10 mass concentration ratio shows the lowest value for the bagging area during the time with higher mass concentrations (Table 2). This indicates that the higher mass concentrations in the bagging area are due to mainly coarse mode particles (> 1 \( \mu m \)) in agreement with the measurements of the number size distributions.

Plant 2

Ambient PM 10 mass concentrations during the measurement campaign in Plant 2 were quite low averaging 14±11 \( \mu g/m^3 \) (TEOM® data, Max: 59 \( \mu g/m^3 \)). Table 3 gives an overview of the mass concentrations determined in the different working areas with the automatic device (TEOM®) and the manual filtra-
tion samplers. The maximum PM$_{10}$ mass concentrations determined with the TEOM® in the bagging area was 335 µg/m$^3$ and 500 µg/m$^3$ for pelletized and fluffy carbon black, respectively.

Table 2 gives an overview of the PM$_{10}$ mass concentration ratios working places to ambient as well as the mass concentration ratios PM$_{2.5}$/PM$_{10}$ and PM$_{1}$/PM$_{10}$.

Comparing the mass concentration readings during the ambient comparison, and between bagging night to ambient no significant increase in PM 10 mass concentrations were observed.

High mass concentration increases were determined in the bagging area. The continuous mass concentration readings clearly showed the correlations between packing and break times indicating that the mass concentration changes are due to the working process.

The PM$_{1}$/PM$_{10}$ mass concentration ratio shows the lowest value for the times with higher mass concentrations. No clear trend is evident from the PM$_{2.5}$/PM$_{10}$ ratios. The former ratio indicates that the higher mass concentrations are due to mainly coarse mode particles (> 1 µm$_{w}$).

### Plant 3

Ambient PM 10 mass concentrations during the measurement campaign in Plant 3 were quite low averaging 13±7 µg/m$^3$ (30 min TEOM® data, Max: 51 µg/m$^3$). Table 4 gives an overview of the mass concentrations determined in the different working areas with the automatic device (TEOM®) and the manual filtration samplers. The maximum PM$_{10}$ mass concentrations determined with the TEOM® in the bagging area was 300 µg/m$^3$ and 730 µg/m$^3$ for bagging small and large bags respectively.

Table 2 shows the PM 10 mass concentration ratios of working places to ambient as well as the mass concentration ratios PM$_{2.5}$/PM$_{10}$ and PM$_{1}$/PM$_{10}$. A clear mass concentration increase with decreasing PM$_{2.5}$/PM$_{10}$ mass ratios can be seen for the bagging area. This indicates that mainly the coarse fraction (> 2.5 µm) contributes to the elevated mass concentrations.

### Summary PM$_X$-Mass Concentrations

Table 5 gives an overview of the average PM$_{10}$ mass increase in the different working areas for all three investigated carbon black plants. The ambient measurements are comparisons and show that the two TEOM® used in these studies show comparable PM$_{10}$ mass concentrations.

Emissions of particles were determined in the bagging areas of all three investigated carbon black plants. Time series plots could clearly show the correlations between elevated PM$_{10}$ mass concentrations and bagging activities. Hence it is shown that bagging activities are the major source of the increased PM$_{10}$ mass concentrations in the bagging area.

The increases in mass concentrations can be attributed mainly to coarse mode particles (> 2.5 µm) in all cases. This conclusion is drawn from the comparison of the PM$_{1}$/PM$_{10}$ and PM$_{2.5}$/PM$_{10}$ mass concentration ratios for periods
with elevated mass concentrations and comparing those ratios to the ones determined at the comparison site or in areas where no emissions were detected. This result compares well with Kerr et al.\(^{13}\) and the results obtained from the number size distribution measurements which showed that particle number concentrations start to increase for particles > 0.4 \(\mu m\) ae with a small mode around 1 \(\mu m\) ae and another mode > 2.5 \(\mu m\) ae.

**Carbon Fractionation**

The filters used for the PM\(_X\)-mass concentration measurements in the previous section were also analyzed for organic and elemental carbon to identify if the production of carbon black could be the source of any elevated concentrations. Table 6 gives a summary of the PM\(_X\) and organic, elemental and total carbon concentrations determined in the bagging areas of Plants 1-3. The PM\(_{10}\) non-carbon fraction was calculated by subtracting the mass of total carbon (TC) determined from the corresponding particle mass. Comparing the values in the bagging areas for the non-carbon fraction with those determined at the corresponding comparison site it can be seen that they are quite similar. This indicates that carbon is the main source of the additional mass concentrations determined.

Calculating the additional PM and carbon mass by subtracting the ambient concentrations from the concentrations measured in the bagging area we can compute the contribution of elemental carbon to the additional mass. From this calculation we derived that elemental carbon explains (90±9) %, (92±25) %, and (81±12) % of the additional PM\(_{10}\), PM\(_{2.5}\), and PM\(_1\) mass, respectively. Hence the product particles carbon black are identified as the likely source of the elevated mass concentrations in the bagging areas. This results agrees well with the results obtained from the number size distribution and PM mass concentration measurements which correlated with the bagging activities.

The EC/TC ratios determined in all areas are summarized in Table 7. The average ratios and ratio range of the EC/TC and TC/PM\(_{10}\) measured by Kerr et al.\(^{13}\) agree well with the results obtained during this study.

**Summary and Conclusions**

Measurements in the bagging areas of three plants enabled the characterization of the particle number size distributions of particles being released by bagging activities. Detailed analyses of the comparisons of size distributions in the bagging area to those at the ambient site or of the comparison of size distributions during work to break periods showed two particle modes. Particle number concentrations start to increase for particles > 400 nm with modes around 1 \(\mu m\) and a mode > 8 \(\mu m\). Ultrafine particle emissions (< 100 nm \(\mu m\) ae) detected in the bagging areas could be attributed to forklifts running either on propane or diesel. Another source of ultrafine particles determined were gas heaters in plant 3.
PM$_{10}$ mass concentration changes due to bagging activities could similarly be determined by the two TEOM®, one placed inside of the working area and the other at a comparison site outdoors. Both, number size distribution and mass concentration changes could clearly differentiate working from break periods. Comparisons of the ambient to bagging area PM$_{10}$ mass concentrations showed increases by factors of 4-8.

PM$_{10}$, PM$_{2.5}$, and PM$_{1}$ were also measured with manual filtration samplers in the bagging areas and before and after the campaign at the comparison site. From the comparison of the PM$_{1}$/PM$_{10}$ and PM$_{2.5}$/PM$_{10}$ mass concentration ratios for periods with elevated mass concentrations and comparing those to the ones determined at the comparison site it is concluded that most of the additional mass concentration measured in the bagging area were due to particles > 2.5 µm d$_{ae}$. This result agrees well with the determined number size distributions of particles being released by bagging activities.

The filters used for the PM$_X$-mass concentration measurements were also analyzed for organic and elemental carbon. Calculating the additional PM and carbon mass by subtracting the ambient concentrations from the concentrations measured in the bagging area we computed the contribution of elemental carbon to the additional mass. From this calculation we derived that elemental carbon explains (90±9) %, (92±25) %, and (81±12) % of the additional PM$_{10}$, PM$_{2.5}$, and PM$_{1}$, mass, respectively. Hence manufactured carbon black can be identified as the source of the elevated mass concentrations in the bagging areas.

Kerr et al.$^{(13)}$ measured PM$_X$, EC, and TC mass concentrations at three different plants and found a) that increases in the inhalable mass concentrations were mainly due to coarse particles (> 2.5 µm d$_{ae}$), b) that the mass concentrations were always elevated in the bagging areas, and c) that the EC/TC and TC/PM$_{10}$ mass ratio was also always elevated in the bagging areas. Their results agree well with the ones presented here. Hence we can conclude that the plants investigated in this study can be viewed as being representative for bagging areas in the carbon black production industry.

**Acknowledgement**

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**References**


Tables

Table 1: Mass concentration data of Plant 1 as determined at the different working places (standardized to 0°C and 1.013 hPa)

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<tr>
<th>Location</th>
<th>Start Time</th>
<th>End Time</th>
<th>TEOM® PM10 µg/m³</th>
<th>PM10 µg/m³</th>
<th>PM2.5 µg/m³</th>
<th>PM1 µg/m³</th>
<th>PM2.5 / PM10</th>
<th>PM1 / PM10</th>
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<td>27.06.00 14:05</td>
<td>27.06.00 22:35</td>
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<td>28.06.00 08:58</td>
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<td>28.06.00 18:00</td>
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<td>20.06.00 14:55</td>
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<td>80.7</td>
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<td>40.2%</td>
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<td>21.06.00 10:15</td>
<td>216.3</td>
<td>202.8</td>
<td>73.7</td>
<td>39.7</td>
<td>36.4%</td>
<td>19.6%</td>
</tr>
<tr>
<td>Bagging Area N234</td>
<td>21.06.00 10:35</td>
<td>21.06.00 16:48</td>
<td>369.8</td>
<td>230.9</td>
<td>69.8</td>
<td>40.7</td>
<td>30.2%</td>
<td>17.6%</td>
</tr>
<tr>
<td>Bagging Area N550</td>
<td>22.06.00 09:17</td>
<td>22.06.00 15:12</td>
<td>256.2</td>
<td>339.5</td>
<td>112.6</td>
<td>35.1</td>
<td>33.2%</td>
<td>10.3%</td>
</tr>
</tbody>
</table>

Numbers in bold indicate values influenced by power failure
Table 2: Average mass concentration ratio working place to outside and average mass size ratios at Plant 1-3

<table>
<thead>
<tr>
<th>Plant 1</th>
<th>TEOM® In/TEOM® Out</th>
<th>PM$<em>{2.5}$/PM$</em>{10}$</th>
<th>PM$<em>{1}$/PM$</em>{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td>97%</td>
<td>56%</td>
<td>(1)</td>
</tr>
<tr>
<td>Bagging Area 1st Floor</td>
<td>69%</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td>Bagging Area Ground Level Night</td>
<td>103%</td>
<td>46%</td>
<td>50%</td>
</tr>
<tr>
<td>Bagging Area Ground Level</td>
<td>620% (max 2000%)</td>
<td>33%</td>
<td>16%</td>
</tr>
<tr>
<td>Plant 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient</td>
<td>119%</td>
<td>75%</td>
<td>70%</td>
</tr>
<tr>
<td>Bagging E 570, BP 460</td>
<td>809% (max 1100%)</td>
<td>68%</td>
<td>49%</td>
</tr>
<tr>
<td>Bagging Night</td>
<td>119%</td>
<td>45%</td>
<td>52%</td>
</tr>
<tr>
<td>Bagging Fluffy (2)</td>
<td>418% (max 1200%)</td>
<td>58%</td>
<td>32%</td>
</tr>
<tr>
<td>Plant 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient</td>
<td>94%</td>
<td>85%</td>
<td>67%</td>
</tr>
<tr>
<td>Bagging small bags</td>
<td>797%</td>
<td>66%</td>
<td>71%*</td>
</tr>
<tr>
<td>Bagging big bags</td>
<td>662%</td>
<td>43%</td>
<td>471%*</td>
</tr>
</tbody>
</table>

Max refers to manual filter time intervals, (1) sampler malfunction
(2) depending on packing small or big bags, *too close to source
Table 3: Mass concentration data of Plant 2 as determined at the different working places (standardized to 0°C and 1.013 hPa)

<table>
<thead>
<tr>
<th>Location</th>
<th>Start Time</th>
<th>End Time</th>
<th>TEOM® PM$_{10}$</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>PM$_{1}$</th>
<th>PM$<em>{2.5}$/PM$</em>{10}$</th>
<th>PM$<em>{1}$/PM$</em>{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td>19.09.00 10:10</td>
<td>19.09.00 17:07</td>
<td>21.1 µg/m³</td>
<td>37.8 µg/m³</td>
<td>23.6 µg/m³</td>
<td>16.2 µg/m³</td>
<td>62.5 %</td>
<td>42.9 %</td>
</tr>
<tr>
<td>Ambient</td>
<td>19.09.00 17:23</td>
<td>20.09.00 05:22</td>
<td>9.6 µg/m³</td>
<td>13.1 µg/m³</td>
<td>11.6 µg/m³</td>
<td>12.7 µg/m³</td>
<td>88.2 %</td>
<td>97.1 %</td>
</tr>
<tr>
<td>Site 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bagging E 570, BP 460</td>
<td>20.09.00 06:18</td>
<td>20.09.00 15:58</td>
<td>83.5 µg/m³</td>
<td>72.6 µg/m³</td>
<td>56.0 µg/m³</td>
<td>32.8 µg/m³</td>
<td>77.1 %</td>
<td>45.2 %</td>
</tr>
<tr>
<td>Bagging Night</td>
<td>20.09.00 18:02</td>
<td>21.09.00 05:50</td>
<td>19.1 µg/m³</td>
<td>27.0 µg/m³</td>
<td>12.1 µg/m³</td>
<td>14.2 µg/m³</td>
<td>44.8 %</td>
<td>52.5 %</td>
</tr>
<tr>
<td>Bagging E 570, E 410</td>
<td>21.09.00 06:28</td>
<td>21.09.00 12:42</td>
<td>99.3 µg/m³</td>
<td>94.0 µg/m³</td>
<td>54.6 µg/m³</td>
<td>47.2 µg/m³</td>
<td>58.1 %</td>
<td>50.2 %</td>
</tr>
<tr>
<td>Site 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bagging Fluffy</td>
<td>21.09.00 17:53</td>
<td>22.09.00 09:21</td>
<td>55.0 µg/m³</td>
<td>84.9 µg/m³</td>
<td>53.3 µg/m³</td>
<td>20.2 µg/m³</td>
<td>62.7 %</td>
<td>23.8 %</td>
</tr>
<tr>
<td>Bagging Fluffy</td>
<td>22.09.00 09:38</td>
<td>22.09.00 15:42</td>
<td>125.6 µg/m³</td>
<td>137.4 µg/m³</td>
<td>71.4 µg/m³</td>
<td>36.8 µg/m³</td>
<td>52.0 %</td>
<td>26.8 %</td>
</tr>
<tr>
<td>Bagging Fluffy</td>
<td>22.09.00 16:15</td>
<td>23.09.00 05:22</td>
<td>90.6 µg/m³</td>
<td>36.1 µg/m³</td>
<td>20.7 µg/m³</td>
<td>21.7 µg/m³</td>
<td>52.0 %</td>
<td>(1)</td>
</tr>
<tr>
<td>Bagging Fluffy</td>
<td>23.09.00 05:40</td>
<td>23.09.00 08:16</td>
<td>37.8 µg/m³</td>
<td>40.0 µg/m³</td>
<td>23.2 µg/m³</td>
<td>18.2 µg/m³</td>
<td>58.0 %</td>
<td>45.5 %</td>
</tr>
</tbody>
</table>

*: power failure problems; (1): unknown error
Table 4: Mass concentration data of Plant 3 as determined at the different working places (standardized to 0°C and 1.013 hPa)

<table>
<thead>
<tr>
<th></th>
<th>Start Time</th>
<th>End Time</th>
<th>TEOM® PM$_{10}$</th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>PM$_{1}$</th>
<th>PM$<em>{2.5}$/PM$</em>{10}$ %</th>
<th>PM$<em>{1}$/PM$</em>{10}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td>14.11.00 14:46</td>
<td>14.11.00 20:26</td>
<td>10</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>75%</td>
<td>57%</td>
</tr>
<tr>
<td>Ambient</td>
<td>14.11.00 20:53</td>
<td>15.11.00 07:48</td>
<td>9</td>
<td>*</td>
<td>8</td>
<td>6</td>
<td>95%</td>
<td>77%</td>
</tr>
<tr>
<td>Ambient</td>
<td>22.11.00 16:23</td>
<td>23.11.00 08:42</td>
<td>15</td>
<td>14</td>
<td>12</td>
<td>95%</td>
<td>77%</td>
<td></td>
</tr>
<tr>
<td>Site 1</td>
<td>Bagging N550</td>
<td>15.11.00 13:32</td>
<td>15.11.00 21:29</td>
<td>130</td>
<td>63</td>
<td>31</td>
<td>46</td>
<td>49%</td>
</tr>
<tr>
<td>Site 1</td>
<td>Bagging N339</td>
<td>15.11.00 21:44</td>
<td>16.11.00 08:53</td>
<td>71</td>
<td>76</td>
<td>64</td>
<td>52</td>
<td>84%</td>
</tr>
<tr>
<td>Site 2</td>
<td>Bagging N339, HV3396</td>
<td>16.11.00 12:59</td>
<td>16.11.00 22:24</td>
<td>165</td>
<td>53</td>
<td>28</td>
<td>280</td>
<td>52%</td>
</tr>
<tr>
<td>Site 2</td>
<td>Bagging HV 3396</td>
<td>16.11.00 22:39</td>
<td>17.11.00 08:40</td>
<td>45</td>
<td>44</td>
<td>14</td>
<td>181</td>
<td>33%</td>
</tr>
</tbody>
</table>

*: readings negative or filter overloaded; values in **bold**: PM$_{1}$ elevated due to location of the sampler too close to the source.
Table 5: Averaged PM$_{10}$ mass concentration factors between inside and outside

<table>
<thead>
<tr>
<th></th>
<th>Ambient</th>
<th>Bagging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant 1</td>
<td>1.0</td>
<td>6.2</td>
</tr>
<tr>
<td>Plant 2</td>
<td>1.2</td>
<td>4.2-8.1</td>
</tr>
<tr>
<td>Plant 3</td>
<td>0.9</td>
<td>6.6-8.0</td>
</tr>
</tbody>
</table>

Ambient: Comparison of the two TEOM®; Bagging: ratio inside/outside
Table 6: PM<sub>x</sub> carbon fractionation in Plant 1-3

<table>
<thead>
<tr>
<th></th>
<th>PM&lt;sub&gt;10&lt;/sub&gt;</th>
<th>PM&lt;sub&gt;10&lt;/sub&gt; carbon</th>
<th>TC/PM&lt;sub&gt;10&lt;/sub&gt;</th>
<th>EC/PM&lt;sub&gt;10&lt;/sub&gt;</th>
<th>PM&lt;sub&gt;2.5&lt;/sub&gt;</th>
<th>TC/PM&lt;sub&gt;2.5&lt;/sub&gt;</th>
<th>EC/PM&lt;sub&gt;2.5&lt;/sub&gt;</th>
<th>PM&lt;sub&gt;1&lt;/sub&gt;</th>
<th>TC/PM&lt;sub&gt;1&lt;/sub&gt;</th>
<th>EC/PM&lt;sub&gt;1&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Plant 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient</td>
<td>45</td>
<td>28</td>
<td>38±2</td>
<td>12</td>
<td>25</td>
<td>57±4</td>
<td>14</td>
<td>Sampler defect</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bagging top</td>
<td>118</td>
<td>43</td>
<td>64</td>
<td>46</td>
<td>81</td>
<td>79</td>
<td>40</td>
<td>47</td>
<td>68</td>
<td>30</td>
</tr>
<tr>
<td>Bagging ground</td>
<td>258</td>
<td>20</td>
<td>92±5</td>
<td>79</td>
<td>85</td>
<td>99±2</td>
<td>75</td>
<td>39</td>
<td>92±5</td>
<td>52</td>
</tr>
<tr>
<td>Bagging night</td>
<td>49</td>
<td>26</td>
<td>47</td>
<td>20</td>
<td>22</td>
<td>74</td>
<td>35</td>
<td>24</td>
<td>62</td>
<td>13</td>
</tr>
<tr>
<td><strong>Plant 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient</td>
<td>25</td>
<td>22</td>
<td>15</td>
<td>9</td>
<td>18</td>
<td>34</td>
<td>21</td>
<td>14</td>
<td>22</td>
<td>9</td>
</tr>
<tr>
<td>Bagging mixed</td>
<td>83</td>
<td>19</td>
<td>76</td>
<td>74</td>
<td>55</td>
<td>79</td>
<td>94</td>
<td>40</td>
<td>88</td>
<td>81</td>
</tr>
<tr>
<td>Bagging fluffy</td>
<td>75</td>
<td>22</td>
<td>67</td>
<td>53</td>
<td>42</td>
<td>82</td>
<td>60</td>
<td>24</td>
<td>75</td>
<td>51</td>
</tr>
<tr>
<td>Bagging night</td>
<td>27</td>
<td>13</td>
<td>51</td>
<td>47</td>
<td>12</td>
<td>77</td>
<td>73</td>
<td>14</td>
<td>77</td>
<td>47</td>
</tr>
<tr>
<td><strong>Plant 3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient*</td>
<td>15</td>
<td>11</td>
<td>30</td>
<td>16</td>
<td>14</td>
<td>28</td>
<td>21</td>
<td>12</td>
<td>23</td>
<td>11</td>
</tr>
<tr>
<td>Bag small bags</td>
<td>70</td>
<td>-4</td>
<td>107</td>
<td>92</td>
<td>48</td>
<td>99</td>
<td>104</td>
<td>49</td>
<td>96</td>
<td>71</td>
</tr>
<tr>
<td>Bag big bags</td>
<td>48</td>
<td>4</td>
<td>90</td>
<td>71</td>
<td>28</td>
<td>106</td>
<td>101</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: Only one filter series with concentrations above detection limit

**bold**: PM<sub>1</sub> sampler much closer to the source than the other two

±: absolute standard deviation
Table 7:  EC/TC ratios determined in the different working areas

<table>
<thead>
<tr>
<th>EC/TC ratio</th>
<th>Plant 1</th>
<th>Plant 2</th>
<th>Plant 3</th>
<th>Kerr(13)</th>
<th>Plant 1</th>
<th>Plant 2</th>
<th>Plant 3</th>
<th>Plant 1</th>
<th>Plant 2</th>
<th>Plant 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM10</td>
<td></td>
<td></td>
<td>PM2.5</td>
<td></td>
<td></td>
<td>PM1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient</td>
<td>31%</td>
<td>59%</td>
<td>53%</td>
<td>25%</td>
<td>60%</td>
<td>80%</td>
<td>42%</td>
<td>49%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bagging I</td>
<td><strong>85%</strong></td>
<td><strong>97%</strong></td>
<td><strong>86%</strong></td>
<td><strong>78%</strong></td>
<td><strong>76%</strong></td>
<td><strong>119%</strong></td>
<td><strong>105%</strong></td>
<td><strong>57%</strong></td>
<td><strong>92%</strong></td>
<td><strong>74%</strong></td>
</tr>
<tr>
<td>Bagging II</td>
<td><strong>78%</strong></td>
<td><strong>79%</strong></td>
<td><strong>72%</strong></td>
<td><strong>97%</strong></td>
<td><strong>68%</strong></td>
<td><strong>90%</strong></td>
<td><strong>22%</strong></td>
<td><strong>61%</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bagging night</td>
<td><strong>43%</strong></td>
<td><strong>93%</strong></td>
<td><strong>47%</strong></td>
<td><strong>95%</strong></td>
<td><strong>22%</strong></td>
<td><strong>61%</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in bold: Working areas with significant changes in particle mass or number concentration
Figures

Figure 1: Comparison of the two SMPS-systems, Plant 2

Figure 2: Time series of number concentrations and PM$_{10}$ during bagging in Plant 1

Figure 3: Number size distributions bagging N550 in Plant 1

Figure 4: Number size distribution for bagging E 570 (small bags) and non working period night time in Plant 2

Figure 5: Number size distribution for bagging fluffy carbon (E325) big bags in Plant 2

Figure 6: Number size distribution for a forklift in Plant 2

Figure 7: Number size distribution comparison for bagging N550 small bags, Plant 3

Figure 8: Number size distributions over the whole size range for bagging N339 big bags (break period shortly after bagging period)

Figure 9: Number size distribution for a forklift in Plant 3

Figure 10: Number size distribution during longer breaks in Plant 3
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5

APS by a factor of 100 lower than SMPS due to local wind field conditions.
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10
### 6. Equipment

**Aerosol generators**
- Palas Mage monodisperse aerosol generator
- TSI 3050 Bergland and Liu vibrating orifice aerosol generator
- Sinclair-La Mer generator
- Dräger VI mist generator
- Knauer HPN nebulizer
- Scheibel and Porstendörfer monodisperse aerosol generator
- Palas GFG 1000 graphite generator
- Environmental Research Corporation 7330 fluid aerosol generator
- TSI 3075 constant output atomizer
- TSI 3072 evaporation-condensation aerosol conditioner
- TSI 3433 small scale powder disperser
- TSI 3460 Tri-Jet aerosol generator
- TSI electrospray system

**Aerosol measurement systems**

*Sampling and collecting systems:*
- sampling systems (filters, TSI 3110 isokinetic dust sampler, TSI 3100 electrostatic aerosol sampler)
- impactor (Anderson stack sampler, Sartorius HV100 high volume sampler)
- small-scale cyclones
- mass measurement systems (TSI PMM 3200 particle mass monitor, TEOM)
- electrostatic precipitator
- High Volume Sampler DHA 80, Digitel, PM 10 and PM 2.5 inlets
- 2 Low Volume Sampler 3, Derenda, PM 10 and PM 2.5 inlets
- Cascade Impactor for TXRF Measurements, PM 10, PM 2.5, PM 1
- 2 β-Gauges, Kugelfischer

*Optical particle counters:*
- TSI 3755/3751 laser particle counter
- Met One 205
- Climet CI-7400 / CI208
- Polytex HC15
- PMS HS-LAS 32
- PALAS PCS 2000

*Condensation nucleus counters*
- TSI 3022/3022/3025/3760
- General Electric CNC-2
- Kanomax UPC 3861
- Expansion-type CNC Scholz
**electrical mobility analyzers:**
- TSI 3071 dynamical mobility analyzers and prototypes of different lengths
- Hauke EMK100
- TSI 3030/3070 electrical aerosol detector
- radial-type DMA

**others:**
- TSI 3300 aerodynamical particle sizer
- TSI 3077 neutralizer
- TSI 3040 diffusion battery
- PALAS VKL10 dilution system

**Particle measurement systems**
- Lightmicroscopes and image analysis system (SIS)
- Confocal Laser Scanning Microscope (CLSM)
- Atomic Force Microscope (AFM)
- On-line surface scanner (OSCAR)

**Gas measurement systems**
- Environment One Corporation diffusion denuder
- URAS 3G/7N/36 gasanalysator
- TSI 9100 Laser Doppler System
- Technolab helium flow visualizing system

**Liquid measurement systems**
- Lauda TD1 tensiometer
- Conductivity meters

**Diagnostic systems**
- Laser beam diagnostic system

**Clean room technology**
- clean rooms class 100, 10 and 1
- clean working benches class 10 and 1

**Others**
- Weather Station (Ambient rh, Temp, Pressure, Wind Speed and Direction, Solar Irradiance)
- 2 Climate Chambers for Ambient Aerosol Monitoring Systems
- Aethalometer, Measurement of aerosol Black Carbon
- Edwards Auto 306 Vacuum Coater
- Polytec Nd-YAG Laser SL 800
7. **Other activities**

7.1 **Cooperations**

**Institute of Energy and Environmental Technology e. V. (IUTA, Duisburg)**
Prof. Dr. K.-G. Schmidt, Dr. Kuhlbusch

**University of Minnesota**
Prof. Dr. D. Pui

**Center for Technological Education Holon aff. Tel-Aviv University**
Prof. Dr. A. Peled

**University of Lund**
Dr. K. Deppert

**University of Duisburg**
Solid-State Electronics Department, Prof. Tegude

**University of Duisburg**
Dept. of Physics, Prof. Wassermann, Prof. Lorke

**Department of Physics, Indian Institute of Technology Delhi, India**
Prof. Dr. Bodh Mehta
7.2 Committee activities

Gesellschaft für Verfahrenstechnik und Chemie (GVC)
Fissan – Board GVC-Program „Nanoparticle Technology”
Fissan – Head of Working Group in GVC “Sustainable Development of Nanoparticle Technology”
Fissan - Member of GVC-Working Group on “Particle Measurement Technology”

Kommission Reinhaltung der Luft (KRDL)
Fissan - Beirat IV
Kuhlbusch – Arbeitskreis „Messen von Ruß“
Trampe – Arbeitskreis „Partikelanzahlkonzentrationsmesser“

Gesellschaft für Technische Gebäudeausrüstung (TGA)
Trampe - Fachausschuss Reinraumtechnik
Trampe Richtlinienausschuss VDI 2083

European Aerosol Assembly (EAA)
Kruis - Chairman of the Working Group on Nanoparticles
Kuhlbusch – Co-chair of the Working Group Chemistry
Kuhlbusch – Co-chair of the Working Group PM10/PM2.5

Forum für Umweltforschung der GMU
Fissan - Mitglied (Sprecher)

European Committee for Standardization (CEN)
Kuhlbusch - Member of the CEN/TC 264/WG 15 “PM 2.5 sampling methods“

WMO Global Atmospheric Watch Programme (WMO-GAW)
Kuhlbusch – Committee Member of the Aerosol Component of GAW

American Geophysical Union (AGU)
Kuhlbusch – Committee Member of Biogeochemical Cycles

Sonderforschungsbereich 445
Fissan – Board Member

American Association for Aerosol Research
Fissan – Award Committee Member

NanoSTAG of COST (EU)
Fissan – Member