International Workshop on

Polymer/Metal Nanocomposites

September 22-23, 2003

Faculty of Engineering, Christian-Albrechts University Kiel, Germany

PROCEEDINGS
Program Overview

The workshop aims at bringing together physicists, chemists, and engineers from academics, and industry who are involved in the development of metal nanoparticles containing polymer composites for functional applications. Presentations range from advanced preparation techniques and new properties resulting from the nanostructure to devices. Theoretical work and computer simulations are also considered.

The technical program includes the following topics (list not comprehensive):

* PVD and CVD based preparation techniques,
* preparation by wet chemical methods,
* novel preparation approaches,
* optical properties and applications,
* magnetic properties,
* high-density data storage,
* magnetic devices for GHz range,
* catalytic properties and reactive membranes,
* electronic properties and devices,
* biological and medical applications.

List of Invited Speakers

H. Biederman, Charles Univ. Prague, Czech Republik

A. Biswas, Univ. of Kiel, Germany

W. Caseri, ETH Zurich, Switzerland

S. Deki, Kobe Univ. Japan

D. Fink, Hahn-Meitner-Institut, Berlin

D. Fritsch, GKSS Research Center, Geesthacht, Germany

A. Heilmann, IWM, Halle, Germany

A. D. Pomagailo, Russian Academy of Science, Russia

E. Quandt, CASAR, Bonn, Germany

W. Richtering, Univ. of Kiel, Germany

D. Salz, Fraunhofer Institute IFAM, Bremen

M. S. Silverstein, Technion, Haifa, Israel

L. Slusarski, Univ. of Lodz, Poland

T. Strunskus, Univ. of Bochum, Germany
Program committee

Program Chair: F. Faupel, Univ. of Kiel, Germany
H. Biederman, Charles Univ. Prague, Czech Republik
S. Deki, Kobe Univ., Japan
D. Fritsch, GKSS Research Center, Germany
V. Zaporojtchenko, Univ. of Kiel, Germany

Local Organizing Committee

F. Faupel, Univ. of Kiel, Germany
A. Biswas, Univ. of Kiel, Germany
U. Schürmann, Univ. of Kiel, Germany
B. Minten, Univ. of Kiel, Germany

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Sponsors

Technology Foundation Schleswig-Holstein (TSH)
Society for Support of the Faculty of Engineering (FTF)
German Science Foundation (DFG)
## Programm

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Preparation and properties of nanocomposites with non-uniform metal formations

Walter Caseri

Department of Materials, ETH Zürich, CH-8092 Zürich, Switzerland

Nanocomposites comprising non-uniform metal dispersions in an organic matrix were prepared in different ways. For instance, platinum colloids of diameter of 1-2 nm were prepared in situ in styrene which was subsequently polymerized. In presence of dialkyldithiophosphates, TEM images showed superstructures of typical diameters of 50-300 nm which phenomenologically resembled those of bilayer vesicles in aqueous solutions (Fig. 1). It is supposed that the formation of the superstructures in the nanocomposites is induced by crystallization of alkyl chains adsorbed at the surfaces of the platinum particles.

![Figure 1. TEM image of platinum colloids assembled in a superstructure induced by the presence of a dialkyldithiophosphate.](image)

As another example, silver and gold particles (average diameter 4.5 and 2.2 nm, respectively) with a surface layer of dodecanethiol were prepared according to modified methods described in the literature. These particles were dispersed in polyethylene solutions or melts, and subsequently films were prepared by casting or compression molding. After drawing at 120 °C, TEM images showed arrays of nanoparticles which were aligned in the drawing direction. The resulting nanocomposites showed highly anisotropic optical properties in polarized light, as evident from UV/vis absorption spectra in Fig. 2. The spectra of the drawn nanocomposites exhibited a strong dependence on the angle $\varphi$ between the polarization direction of the incident light and the drawing direction of the films. Accordingly, the color of the films depends strongly on the polarization direction of light; the silver films appeared red or yellow and the gold films blue and red for $\varphi = 0^\circ$ and $\varphi = 90^\circ$, respectively. The oriented nanocomposites are potentially useful in Liquid Crystal Display applications. A system comprised of a polarizer, a TN-cell and, finally, a film with a polarization-dependent color will transmit light in both the “on” and “off” state which allows for the preparation of a bicolored display.

![Figure 2. UV/vis absorption spectra of an oriented polyethylene-gold nanocomposite in linearly polarized light at various $\varphi$.](image)

More recently, we prepared quasi-one-dimensional arrays of metal atoms (in the oxidation state II, however) which were embedded in an organic matrix constituted by the respective ligands. The soluble, well-processible material which is stable towards air and water showed a typical semiconducting behavior and could be used, in collaboration with other groups, for the preparation of field effect transistors.
Membrane supported metal nano-particles for various applications

Detlev Fritsch

Institute of Chemistry, GKSS Research Centre, Max-Planck-Strasse 1,
D-21502 Geesthacht, Germany

Metallic clusters can be prepared by evaporation/condensation from metals or by thermal decomposition or reduction from metal salt precursors. However, they have a strong tendency to agglomerate to films (evaporation/condensation) or to particles of sizes above several 100 nm. In catalysis, on the other hand there is a demand for small sized metal nano-particles to use efficiently the surface of the precious material in heterogeneous catalytic reactions. The classical solution in catalysis is to support the catalytic metals on inorganic supports such as alumina, silica, titania or carbon. To provide high surface areas porous materials with surface area of up to several hundreds of m$^2$/g are applied. This works well in many cases, but also polymers may act as support for metal nano-particles. Here, some more possible applications are opening up.

An overview on preparation methods will be given and some aspects will be discussed in more detail. A simple, specially developed preparation method of metallic nano-particles will be presented and applied to preparation of membranes. These elastomeric membranes are loaded by Pd from 0-10 wt-% and tested in catalytic conversion of chlorophenol, chlorobenzene and acetophenone. Applied in a pervaporation process, enrichment of the organic component, reaction, and separation of the products are accomplished in one step.

Magnetic thin films and multilayers for high-frequency applications

Eckhard Quandt

Center of Advanced European Studies and Research (caesar)
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(e-mail: quandt@caesar.de)

The magnetic and high-frequency properties of special magnetoelastic thin films and multilayers are investigated with respect to applications in micro-inductors and as remote-interrogated sensors for mechanical quantities. Materials properties like saturation magnetization, anisotropy field, the resulting domain structure, electrical resistivity as well as the stress state of the films have to be carefully adjusted in order to meet certain requirements like high cut-off frequencies combined with low losses, and a high and controllable inverse magnetostrictive effect in the case of sensors. The magnetic high frequency properties of FeCoBSi thin films and FeCo/CoB multilayers, as well as the performance data of the devices will be discussed in view of typical device characteristics.
Nanocomposite films with plasma polymer matrix

H. Biederman and D. Slavinska
Charles University, Faculty of Mathematics and Physics, department of Macromolecular Physics, V Holesovickach 2, Prague, Czech Republic

Nanocomposite film materials such as metal inclusions within polymeric matrix have been investigated since 1970 ties. At first they were co-evaporated and later plasma polymerization process with metal co-sputtering or co-evaporation has been adopted. The main deposition systems are described and basic properties of these films discussed. Different metals incorporated into fluorocarbon and hydrocarbon plasma polymers including hard plasma polymers(C:H) and amorphous hydrogenated carbon (a-C:H) are considered. In conclusion more complex nanocomposite films such as SiOₓ/fluorocarbon plasma polymers are introduced. Possible applications are discussed.
Plasma Polymerized Fluoropolymer and Copper

Michael Silverstein
Department of Materials Engineering
Technion – Israel Institute of Technology
Haifa 32000, Israel

Plasma polymerization is a solvent-free, room temperature process that can be used to rapidly deposit thin polymer films on a wide variety of substrates. The deposition of fluoropolymers on copper, with its high thermal and electrical conductivities, is of interest for many applications. The interaction of the fluoropolymer with the copper is also of interest for the processes involved in polymer/metal nanocomposite formation, such as the co-deposition of copper and plasma polymer. This talk describes the deposition of plasma polymers from several fluorinated monomers (octofluorocyclobutane (OFCB), hexafluoropropylene (HFP) and trifluoroethylene (TrFE)), and evaluates their molecular structures. Films with relatively high F/C ratios were investigated in detail. The plasma fluoropolymers were transparent, yellow films that adhered strongly to the substrates and were deposited at constant deposition rates that ranged from 0.03 mm/min for plasma polymerized OFCB (PPOFCB) to 0.34 mm/min for PPHFP. The AFM-determined roughness of PPOFCB on copper is 0.46 nm, half the 0.97 nm roughness of the substrate. The significantly rougher PPTFe and PPHFP consist of spherical particles from predominantly gas phase polymerizations. The incorporation of fluorine in the polymer is greater and more efficient for PPOFCB and PPHFP than for PPTFe. For PPOFCB, F/C increases with decreasing W/F_m (where W is the plasma power and F_m is the mass flow rate) and, in a less sensitive manner, with increasing pressure. A typical PPOFCB has an F/C of approximately 1.5 and approximately 1.5% oxygen resulting from the reaction of long lived radicals in the plasma polymer with atmospheric oxygen. PPOFCB and PPHFP have similar molecular structures, consisting of random assemblies of fluorinated carbon groups. CF_2 groups are more prevalent in PPOFCB, reflecting the monomer structure and the low W/F_m. CF groups and unsaturation are more prevalent in PPHFP, reflecting the monomer structure and the high W/F_m.

X-ray photoelectron spectroscopy (XPS) of copper surfaces exposed to an OFCB plasma, for times as short as 1 s and as long as 30 min, was used to characterize the copper, the PPOFCB and the interface between them. During a 1 s OFCB plasma exposure, copper fluorination occurs, producing CuF (with a F ion peak appearing in the F_1s spectrum) as well as the deposition of fluorocarbon species (with a CF_n peak in the F_1s spectrum). During the next few seconds of OFCB plasma exposure, the amount of fluorocarbon deposited begins to dominate the surface, although oxidized copper and oxidized hydrocarbon contaminant from exposure to the atmosphere are still observed. The copper substrate beneath a 15 nm PPOFCB film is not detectable via XPS. The F/C ratio for PPOFCB can be as high as 1.68 after brief deposition times (30 s), reaching a plateau value of 1.5 after several more minutes of plasma exposure; this reduction in F/C can be associated with ion bombardment and vacuum UV defluorination.
Electrical, magnetic and optical properties of metal/PTFE nanocomposite films prepared by RF magnetron sputtering.

U. Schürmann¹, H. Takele¹, V. Zaporojchenko¹, M. Es-Souni², F. Faupel¹

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²Institute for Materials & Surface Technology, University of Applied Science, Grenzstr. 3, 24149 Kiel, Germany

The physical properties of small metal particles embedded in polymer matrix has been of continuing interest for last decade due to the fundamental and technological importance. Preparation of such nanocomposites on basis of dielectric fluoropolymer films by means of RF sputtering of polytetrafluoroethylene as well as other fluoropolymers has been investigated in last two decades. Here, we present a study of physical-chemical properties of thin PTFE films with embedded ferromagnetic metals as well as silver and other noble metals which were deposited by RF magnetron sputtering from a composite (PTFE/metal) target. The deposition rate were monitored by a quartz crystal microbalance, which was calibrated by measuring film thickness after deposition with a profilometer. To study optical, electrical and magnetic properties, nanocomposites with thickness of some hundred nanometers were deposited on microscope slides or silicon wafers. Thin, electron-transparent films for the nanostructure investigation with TEM were deposited on carbon-coated copper grids. Based on TEM micrographs, the influence of the RF parameters and Ar pressure on the particle size, shape, and density was analyzed. The metal volume fraction and uniformity of the nanocomposites was monitored by SEM/EDX using a metal/polymer standard, which was calibrated gravimetrically. X-ray photoelectron spectroscopy and FTIR-spectroscopy were also applied to characterize the chemical composition and chemical stability of the composites. Variation of the resistivity and dielectric constant measurements as a function of metal volume fraction were carried out on a impedance measurement device. The variation of electrical properties of Ag/PTFE nanocomposites close to the percolation threshold will be discussed. The difference in the UV/VIS-spectra depending on metal concentration and particle size and density is also observed. Preliminary results on PTFE-magnetic metal composites and an outlook are presented.

Fig. 1: UV/Vis-spectrum of a silver/PTFE composite material

Fig. 2: TEM micrograph of sputtered PTFE containing silver cluster

Lit.:
WITH HELP OF AEROSOLS TO FUNCTIONAL NANOCOATINGS.

Dr. Georg Bolte*

At the production of nanocoating, methods of the plasma coating, galvanization and others like that are used mainly. These methods are often indicated by difficult method technical basic conditions. So, the production of a vacuum, often prevents or makes the material throughput more expensive. In the context of the lecture a method as a technical alternative is represented under atmospheric conditions. Adequately great material throughputs can be obtained. To this various liquid aerosols are used in various gasses.

**AEROSOLS: An opportunity for nanotechnology**

**Definitions:**
1. Liquid drops << 1μm
2. Ca. 20% reactive chemicals
3. Evaporation of solvents/water

\[ \Phi = 0.5\mu m \quad \text{Spread to 1/10 of the diameter} \quad \text{Evaporation: 90%} \quad \Rightarrow \text{ca. 5nm thickness} \]

By the variation of gasses, solvents and liquids or solids, corresponding surface effects can be obtained in the nanometer area. Stand of the art is the technology e.g. for both side foil treatments with work breadths of > 2,000 mm and run speeds of 70-80 m/min. In this case the aim is better adhesion of inks on the foil.

Numerous effects like bonding improvement, catalyst orders, Antistatik, scratching strength ... . be reached by the method.

As example the production of gliding ability of a PE foil is represented by Eruca acid amide in detail.

Diffusion processes in nanoparticle-containing polymer films

A. Heilmann
Fraunhofer Institute for Mechanics of Materials, Heideallee 19, 06120 Halle, Germany

Generally, metal nanoparticles embedded in a polymer matrix show an adequate long-term stability, but diffusion processes of metal atoms take place at temperatures far below the melting point of the embedded metals. These diffusion processes result in changes in the size and shape distributions of the embedded particles, which includes changes of the inner or outer interfaces. The simplest way to effect of nanostructural changes is thermal treatment of the films, but also Laser irradiation or electron beam irradiation cause nanostructural changes. The nanostructural changes result in substantial changes of the optical and electrical properties of the films. The spectral position, the half width and the relative intensity of the optical plasma resonance absorption of the nanoparticles is changed.

Various types of material transport in thin films are distinguished. These mechanism of the nanostructural changes are caused by: atomic diffusion through the matrix (Ostwald-ripening), atomic diffusion along the particle surface (recrystallisation and coalescence) and particle migration (Fig.). All these processes are considered with the assumption of a closed system, in other words no material is lost or supplied during the nanostructural changes.

The proportion of the surface energy is much increased for small particles, compared to the total binding energy, due to the high proportion of surface atoms. Thermal activation e.g. by annealing leads to an increased atomic mobility. Because of the different surface energies, atomic diffusion from the smaller to the larger particles occurs through the matrix after an extensive thermal treatment. This process of the changes of size and shape of the embedded particle is defined as Ostwald-ripening.

A second process is based on the minimization of the surface energy of non-spherical (recrystallisation) or two contacting particles (coalescence). Both leads to the formation of more spherical particles by the diffusion of metal atoms along the grain boundaries and along the particle surface.

The term recrystallisation is used if one nonspherical particle change to a more spherical particle. Coalescence is used if two or more particle coalesce to one particle. The further process considers particle mobility in the matrix, which can take place if the matrix material is heated close to the melting point, or if a polymer is above the glass transition temperature after a thermal annealing. If two particles collide because of their movement in the matrix, it leads to coalescence.

By using of annealing experiments in situ the electron microscope, examples for Ostwald ripening, coalescence and reshaping and their effects to the optical properties are demonstrated for silver or gold nanoparticle-containing plasma polymer thin films.
Polymer thin films containing nano-sized metal or semi-conductive nano-particles are of great interest because of unique characteristics of nanoparticles owing to the quantum sizes effect, greatly different from those of the corresponding bulk metal. We have reported novel fabrication process to prepare polymer thin films containing metal or semiconductor nano-particles, in which the process relies on a consecutive deposition of polymer and metal, followed by heat treatment. In this procedure, the heat-treatment induces the dispersion of metal nanoparticles into polymer layer due to the structural relaxation of polymer matrix. By using this process, we had previously developed and reported the preparing process of nylon 11 thin films containing noble metal or semiconductor nanoparticles, and poly-acrylonitrile (PAN) thin films containing metal nanoparticles. Recently, we have succeeded in preparing polymer thin films containing alloy nanoparticles, by using of slightly modified RAD process. In this procedure, we used two independent evaporation sources for each metal to obtain alloy nanoparticles, and the composition of alloy nanoparticles were easily controlled by tuning the evaporation rates of each metal. Interestingly, we found two different alloying behaviors depending on the component. For Au/Pd or Au/Cu systems, which are the typical continuous solid solution systems in bulk phase diagram, the as-deposited alloy nanoparticles are consisted of both components and the lattice parameter was found to follow Vegard’s law, indicating the obtained nano-particles are thermodynamically stable in the as-deposited state. On the other hand, for Au/Co system, which is the typical phase-separation system, thermodynamically meta-stable Au/Co alloy nanoparticles were first obtained by simultaneous evaporation of gold and cobalt, and post-heating above 673 K was required to release the internal stress and transform into thermodynamically stable solid solution. Au/Fe system also showed Au/Co-type alloying behavior. The lattice parameter of the Au/Fe alloy nanoparticles changed gradually upon heat-treatment (Figure 1). As-deposited Au$_{0.5}$/Fe$_{0.5}$ nanoparticles have a lattice parameter of 0.4023 nm (from electron diffraction analysis), which is relatively close to that of bulk Au (0.4078 nm) in comparison with fcc-Fe (0.3612 nm). Upon heat-treatment under nitrogen flow, the lattice parameter decreased to 0.3939nm (at 673 K) and 0.3887 nm (at 873 K), which is close to the lattice parameter of thermodynamically stable solid solution of Au$_{0.5}$/Fe$_{0.5}$ (0.3845 nm, from Vegard’s law). For the sample after the heat-treatment at 873K, diffraction peaks assigned to graphite were also observed. The graphite component was thought to be derived from the decomposition of polyacrylonitrile (PAN), used for the matrix.

Figure 1. Variation of SAED patterns for Au$_{0.5}$/Fe$_{0.5}$ nanoparticles before and after heat-treatment.

References
Carbon and carbon/metal core–shell nanostructures

Xin Jiang
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In recent years, carbon nanotubes and nanofibers have attracted much attention in both academic and industrial research. Various nano- or micrometer-scaled fascinating structures and morphologies have been reported. They have many potential applications such as micro-to-nano-scale needles for biomedical science and mechanical robust and thermal stable tips for scanning probe microscopy, chiral catalyst, generator of magnetic beams, electromagnetic wave absorbers or filters, and the building blocks of the nanodevices, etc. Here we report the synthesis of new carbon nanostructures, tubular graphite cones [1] and self-assembly of carbon nanohelices and carbon/Ni core–shell nanowire heterostructures (Fig. 1) using microwave plasma chemical vapour deposition (MWCVD) and electro-chemical deposition (ECD) [2]. Their microstructures and morphologies were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED) and Raman spectroscopy (RS). Primary electrical and mechanical properties were also investigated.


Figure 1: Self-assembly of carbon nanohelices and carbon/Ni core–shell nanowires
Plastic metallization via surface modification by atmospheric pressure plasma

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Introduction:
Metallized plastics have become very important. Small weight and low production costs are only two advantages. As they are insulators plastics need a special pre-treatment before they can be galvanised. A DBD treatment is an environmentally friendly alternative to the usual wet chemical pre-treatments.

Dielectric barrier discharge (DBD)
Plasma processes enable a great variety of surface modifications. Unfortunately most of these processes require vacuum which results in high costs. That’s why the Fraunhofer Institute for Surface Engineering and Thin Films (IST) is working on the development of atmospheric pressure plasma processes, too. These processes are used for surface activation/ functionalisation, coatings and also for cleaning of surfaces.

![Figure 1: principle DBD](image)

Figure 1 shows the principle of an atmospheric pressure DBD, which was used in the present case.

Method:
1. plasma pre-treatment (amino functionalisation)
2. Pd chemisorption on amino groups
3. electroless metallization

Plasma treatment:
In the context of a student research project different substrates (foils of PP, PET, BOPP, PE) were treated with different gases (forming gas N₂/H₂, air, N₂). The main point of interest was to find out the parameters (gas, treatment time, …) that results in a good and homogeneous metallization of about 1 μm in thickness. The experiments aim at finding a set of parameters that result in a preferably high surface energy and a high amount of aminogroups applied to the substrate’s surface.

The more aminogroups are present the higher is the probability that PdCl₂ is chemisorbed more homogeneously. (Because of the differences in size not every NH₂-group is able to take up a PdCl₂ complex.)

The experiments showed, that the number of aminogroups is dependent on the gas used in the DBD process. Aminogroups were detected by fluorescence labelling. A PET substrate treated in N₂/H₂ carries twice to thrice as many aminogroups as a PET substrate treated in air under same conditions.

The surface energy was measured by test ink. Here a higher treatment times results in a higher surface energy.

Plasma printing:

![Figure 4: Increased adhesion by plasma printing](image)

Figure 4: Increased adhesion by plasma printing
Patterned metallization (dots: 300 μm diameter)

![Figure 3: Patterned amino functionalisation](image)

Figure 3: Patterned amino functionalisation visualized by fluorescence labeling

Another forward-looking technology Fraunhofer IST focuses on at the moment is plasma printing. Here a patterned dielectric is used to receive a patterned amino functionalisation and accordingly a patterned metallization. A possible application will be printing conductor paths on a plastic substrate:
Vapor Phase Deposition of Polymers and Metal/Polymer Composites

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Vapor phase deposition of polymers can be used as a technique for certain polymers to prepare polymer thin films. It is a alternative method to plasma deposition or casting from solution. On selected examples the vapor deposition technique will be introduced and the properties of the prepared films will be compared to the properties obtained by other techniques.

In the second part the use of vapor phase deposition to prepare polymer films containing metal nanoclusters films will be demonstrated. One way is to deposit the organic precursor molecules and the metal at the same time. In this case the formation of metal clusters requires an additional heating step. The growth of the clusters is then controlled by the heating process. Some results will be shown relating optical properties to the morphology of such composite films.

Another way is to deposit alternatively the organic precursors and the metal. In this case cluster formation on the surface can be controlled by several means, i.e., the number of defects on the surface, the deposition rate and also by subsequent heating steps.
Polymer-Metal Nanocomposites for Softmagnetic Ultrahigh Frequency and Multi-wavelength Optical Functional Applications

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A major goal of nanotechnology is to develop new nanomaterials for functional applications. Polymer-metal nanocomposites are promising candidates particularly for interesting magnetic and optical technological applications besides other not yet fully explored properties. Nanocomposites of magnetic nanoparticles distributed in polymer matrix are promising materials and could play important roles particularly as low loss miniaturized inductive components in future GHz frequency driven mobile communication handsets and portable information tools or even data storage applications. Principle requirements for such soft magnetic applications are high saturation magnetization (M_s) alongwith a finite but low anisotropic field (H_u) and highest possible resistive material. Appropriately volume filled isolated magnetic nanoparticles dispersed three dimensionally in a polymer matrix possess good potential to produce high M_s, alongwith significantly minimised eddy current losses due to the surrounding highly insulating zones, thus fulfilling the technological needs for soft magnetic applications in the region of 1 GHz frequency and above. Apart from this, optically functional nanoparticles embedded in polymer matrices offer interesting possibilities to generate ultra thin color filters as a result of characteristic particle plasmon resonance selective absorption at a particular wavelength. Further, generating multiple particle plasmon wavelength response from one system is highly desirable from potential optical data storage to multi color filters applications. However, generating appropriately narrow size distribution along with retaining perfect metallic nature of the nanoparticles, a major requirement for most of the applications, is a technological challenge from the preparation point of view. In this invited talk, a simple and one step vapor phase co-deposition at elevated target temperature is introduced to produce polymer-metal nanocomposites for the above functional applications. Nanocomposites of Teflon AF containing Fe-Ni-Co, Ag, Au and Cu nanoparticles are fabricated and characterized for magnetic and optical applications. Extremely narrow particle size distribution is also demonstrated. Nanocomposites of Teflon AF containing Fe-Ni-Co nanoparticles of thicknesses 100 nm – 300 nm are produced showing quite high saturation magnetization of nearly 2 Tesla and capable to function in the GHz frequency range. Further, double and triple characteristic plasmon wavelengths response from a single system consisting of a combination of different nanocomposite structures generating sharp interfaces are also shown among other results.
Microstructure of polymer-metal composite thin films grown by pulsed laser deposition

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Polymer-metal composites were prepared at room temperature using pulsed laser deposition (PLD). A KrF excimer laser with wavelength of 248nm and 30ns pulse duration was focused on bulk targets. Laser fluences of 60 mJ/cm² in the case of polymer deposition and 5 J/cm² in the case of metals were needed. For the polymer matrix BPA-polycarbonate (PC) was used, as metals Ag, Au, Cu and Pd.

The samples were characterized by x-ray reflectometry (SAXS) and transmission electron microscopy (TEM). For the TEM measurements, the PC-metal composite alloys and multilayers were investigated in top-view and after cutting using an ultramicrotorn in cross-section.

As shown in the top-view of Fig. 1, spherical Ag grains are randomly oriented and homogeneously embedded in the PC matrix.

The size and density of the Ag grains can be controlled by the pulse number of Ag during deposition.

In the case of PC-Cu and PC-Pd, a higher number of much smaller Cu and Pd grains, respectively, is observed.

For polymer/metal multilayers, deposited for the first time by a thin film technique, the interface roughness strongly depends on the used metal. For Ag, the average island size increases up to more than 10 nm, before coalescence takes place (see cross-section of a multilayer with increasing Ag pulse number and layer thickness in Fig. 2).

Differences between the polymer-metal systems are discussed with respect to the different diffusion coefficients, reactivities and growth mechanisms of Ag, Cu and Pd on polymer surfaces.

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THE PECULIARITIES OF CATALYSIS
BY POLYMER-METAL NANOCOMPOSITES

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Catalysts of this type are of prime theoretical interest since they allow modelling of the size
effects on the catalytic activity. They may be used to exemplify many concepts of basic
theories of the catalysis: multiple theory, theory of active ensembles, and theory of
skeletal catalysis. The application of polymer-immobilised cluster and nanoscale particles
provides an additional possibility to shed light on the relationship between homogeneous,
heterogeneous, and enzymic catalysis [1-3].

According to some features, these particles are close to homogenous catalysts: they are
obtained from ordinary, soluble metal compounds by increase in their nuclearity, the
polymer often performs the functions of macroligand and stereochemical environment,
they can function under mild conditions, e.g.,
at temperatures below 100 °C. At the same
time, these contacts also inherit major
properties of heterogeneous systems: reactions
occur at the interface, the activation of the
substrate results from adsorption on the
surface, the catalyst is easily separated from
the reaction products and may be regenerated.
The peculiarities of enzymic catalysis
(substrate enrichment, structural
correspondence, favourable orientation of
reacting molecules, additional activation of the
substrate by the multicentre catalytic system,

etc.) are also easily simulated using polymer-
imobilised clusters and nanoparticles. Of particular interest are catalysts based on
organic-inorganic hybrid materials in which
catalytically active metals incorporated into an
oxide network are dispersed.

In many cases, the polymer-immobilised
nanoparticles manifest high activity and
selectivity. This may be exemplified by the
processes of ionic-coordinational
polymerisation, hydrogenation, and oxidative
transformations.

The activity of these catalysts essentially
depends on the nature of the polymer and the
size of nanoparticles. These particles have
highly active surfaces and developed internal
structures. A polymeric matrix hinders
smoothing of numerous defects upon catalyst
ageing. Of prime importance in the catalysis is
a knowledge of the surface composition and
S_spec and the possibility to control these
parameters. The inherent size of nanosized
particles is comparable with the molecular
sizes of the compound subjected to catalytic
conversion. This fact is responsible for the
characteristic features of the kinetics and the
mechanism of the reactions with the
participation of nanosized particles. In
particular, the high efficiency of colloidal-
metallic catalysts in multiple-electron
processes results from the fact that these
catalysts are 'reservoirs,' which can readily
incorporate electrons.

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Complexes and Metals in Macromolecules,
Hybrids of Metal Nanoparticles and Hyperbranched Macromolecules as Separable Soluble Catalysts: A Neutron Scattering Study

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Homogeneous transition metal catalysts based on soluble metal complexes are highly active and selective under mild conditions. A notorious drawback is the tedious separation from the reaction products, a problem not encountered with typical heterogeneous catalysts. Colloidal solutions containing metal nanoparticles can potentially bridge this gap for a number of important catalytic transformations.

Solubilization of metal salts by well-defined hyperbranched polymers and subsequent reduction yields stable solutions of metal colloid/polymer hybrids. Recently, a one-step synthesis allowing for a convenient access to hyperbranched polyglycerols of controlled, narrow molecular weight distributions was reported. Partial esterification of the OH-groups with long chain fatty acids yields amphiphilic molecules which can function as nanocapsules. Such metal nanoparticle / hyperbranched polymer hybrid materials display remarkable catalytic activity and stability.

Hyperbranched polyglycerols and polyethyleneimines with different molecular weights of the polymer core and different degree of derivatization were characterized by means of small angle neutron scattering in different solvents and at different concentrations. The radius of gyration was obtained via the Guinier approximation. Amphiphilic hyperbranched polyglycerols with different degree of esterification (25 - 100%) with palmitoic acid did not reveal a size change. Contrast variation experiments that have been performed with colloid/polymer hybrids will be discussed.
Characterization of Pd and Pt species in the polymers matrices. The effect of reducing properties of electroactive polymers

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Number of recently published papers have been focused on applying noble metals (Pt, Pd, Ag, Cu) dispersed in polymers matrices as heterogeneous catalysts in various hydrogenation reactions. Specific properties of polymers and among them the ability of swelling, hydrophobic/hydrophilic character and steric effects make these materials very promising from catalytic point of view. Thus, experimental variables affecting the state and thereby reactivity of metallic centres is of primary importance. Such examinations have been undertaken in the present work using systems composed of Pd and Pt and several electroactive polymers namely polyaniline (PANI), poly(α-methoxyaniline) (POM), poly(pyrrrole) (PPy) and electro-inactive poly(4-vinylpyridine) (PVP). Owing to the presence of N groups all the polymers exhibit alkaline properties and can be easily protonated. Lone pairs of electrons in N atoms as well as delocalised π-electrons are also a potential centres of metal coordination. All the conducting polymers PANI, POM and PPy can also be involved in redox reactions. Incorporation of Pd or Pt was performed by reacting at room temperature the powdered polymers with appropriate precursor solutions, PdCl₂ or H₂PdCl₄ up to the complete sorption of Pd or Pt ions. Since activity in hydrogenation reactions offered only the catalysts prepared in the solutions of very low HCl content, such conditions of preparation were used in the present studies. Aqueachlorocomplexes like [PdCl₂(H₂O)₂]\(^{+}\) (and Pt\(^{4+}\)) dominating in these solutions (confirmed by UV-VIS) seem to very convenient species also in view of metal ions coordination via ligand exchange mechanism involving structural units of the polymers. Several techniques have been used to characterize Pd, Pt species in the obtained samples and to examine the changes in polymers structure occurring on metal insertion. Redox mechanism resulting in partial reduction of Pd\(^{2+}\) to Pd\(^{0}\) (60-80 % in the whole introduced Pd) predominated on Pd insertion into powder of all the electroactive polymers. Similar Pd species were identified in Pd/PPy, Pd/POM and Pd/PANI by Pd 3d XPS core level spectra showing metallic Pd and Pd\(^{2+}\) mostly as Pd-Cl with very low contribution of Pd\(^{2+}\) coordinated to polymer chain. More information about local structure around Pd atoms and in particular the type of atoms - nearest neighbour of Pd provided extended X-ray absorption fine structure spectroscopy (EXAFS).

Three type of atoms Pd, Cl and O/N were also established by this technique in the nearest surrounding of palladium in the POM and PPY matrices. Because of very similar Pd-N and Pd-O distances, exact discrimination between N and O atoms was difficult. Oxygen atoms can be interpreted in the Pd/POM as related to OCH₃, whereas in the Pd/PPY they can be associated with carbonyl defects like C=O, C-OH usually present in the PPY chain as result of polymer hydrolysis occurring on its preparation in aqueous media. In the EXAFS spectra of both Pd/POM and Pd/PPY the peak characteristic of Pd-Pd distances identical as the ones registered in the Pd-foil standard evidently predominated. This finding revealed that Pd/PANI, Pd/POM and Pd/PPY represented in fact systems composed of metallic palladium particles dispersed in polymers matrices. It was detected either at low (2 wt %) and at high (8 wt %) Pd loading in the samples. In agreement with the EXAFS findings, large crystalline Pd particles occasionally distributed over the agglomerates of all electroactive polymers were detected by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The size (0.2-1 μm) and the contribution of Pd crystallites were identical independently of the total Pd loading in the Pd/POM. Coordination of Pd to the POM structure was found only at high loading of Pd. Thus, reducing properties of electroactive polymers were mainly involved in the reaction with aquachlorocomplexes of Pd. Formation of nonuniformly distributed relatively large metallic crystallites showed as a very probable mechanism, nucleation of metallic particles on structural defects, followed by a growth of Pd crystals, facilitated by electrons delocalized through the polymer chain [1]. On the other hand, coordination and protonation reactions were established by FTIR and Raman techniques on reacting the same Pt, Pd precursor solutions with electro-inactive polymer PVP. Reduction of the latter metal species (with formaldehyde or hydrogen) resulted in finely dispersed metallic particles, homogeneously distributed over the surface of PVP agglomerates [2] [1]. A. Drelinkiewicz, M. Hasik, M. Kloc, Synth. Met. 102 (1999) 1307
POLYMER-IMMOBILIZED RHODIUM CLUSTERS: SYNTHESIS AND CATALYTIC PROPERTIES

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Cluster-containing polymers are of great interest as catalysts for different reactions, combining the advantages both of homogeneous catalysts and heterogeneous ones [1]. They may be obtained in two ways: by immobilization of cluster compounds on macroligands, or by polymerization reactions of some hypothetic monomers [2-3]. Heterogenization of metal clusters allows to isolate the intermediate products and to study the mechanism of catalytic reactions.

Polymer-immobilized clusters were obtained via polymer-analogous reactions between Rh₆-clusters and macromolecular compounds. The copolymers of styrene and 4-vinylpyridine (Mₘ = 150,000-200,000) or allyldiphenylphosphine (Mₘ = 9,000-80,000) were used as initial macroligands. The macrocomplexes containing 1.8 to 4.1 wt.% of Rh were obtained by the interaction of Rh₆(CO)₁₅CH₃CN and copolymer of styrene with allyldiphenylphosphine in benzene. By analogous procedures the macrocomplexes on the base of copolymers of styrene with 4-vinylpyrididine were obtained. The contents of Rh were in the range of 3.1 to 12.7 wt.%.

The polymer immobilized clusters is catalytically fairly active. Although during the first cycle of hydrogenation of cyclohexene its speed was not high (0.015 mole/(g-atom Rh s)), with a larger number of cycles, the reaction speed increased and reached 2 moles /(g-atom Rh s). The kinetic curves of hydrogen absorption during the cyclohexene hydrogenation in the presence of the immobilized copolymer demonstrated the presence of an induction period in the first cycle and the increase of catalyst activity when used in the following cycles (Fig. 1).

![Graph showing the consumption of H₂ in the hydrogenation of cyclohexene in the presence of Rh₆(CO)₁₅CH₃CN polymer-immobilized catalyst (T = 40°C, isopropyl alcohol, the curve numbers indicate the cycle numbers, [cyclohexene] 1.2 – 4, 5 mmole, 3, 4, 5 – 6, 5 mmole)](image)

It is supposed, that during the hydrogenation reaction the cluster fragmentation occurs with the formation of active species that include cluster structures of lower nucleation, and mononuclear complexes stabilized with the polymer matrix.

Structural, magnetic and electrical studies of Fe-implanted polyimides

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Synthesis and characterisation of metal nanoparticles in various polymers are the subjects of intensive research. Nanostructured metal-polymer materials exhibit unique physical properties and show practical significance for various applications. Ion implantation is one of the wide-used methods to synthesise desirable nanocomposites. Ion implantation causes a breaking of molecular bonds, cross-linking and carbonisation of polymer. The radiation-modified polymer layer is similar to amorphous carbon or graphite-like structure. In the case of implantation by metal ions to high fluences (ion synthesis regime), the implanted atoms may coagulate to form nanoscale metal particles in the carbonised region. In the report we present results on the ion synthesis of ultra-dispersed metal phase in polyimide (PI) by implantation of iron ions. Influence of the implantation parameters and subsequent thermal annealing on the microstructure, magnetic and electrical properties of iron nanoparticles synthesised in the irradiated PI are investigated.

Metal-polymer nanocomposites were formed in PI foils by implantation of 40 keV Fe ions with the fluences of 0.25-1.25×10¹⁴ ions/cm² at the ion current density of 4 μA/cm². The implanted samples were annealed at T = 600 K for 2 h in vacuum of 10⁻³ Torr. Structural and compositional alteration of the implanted layers was studied using atomic force microscopy (AFM), transmission electron microscopy (TEM) and Rutherford back-scattering (RBS) spectroscopy. Magnetic and electrical properties of both the as-implanted and subsequently annealed samples were investigated by ferromagnetic resonance (FMR) at X-band (9.5 GHz) and DC sheet resistance measurements in the temperature range of 10-300 K.

The RBS analysis of the implanted PI shows carbonisation of about 100 nm thick surface layer followed by the oxygen and nitrogen depletion. The precipitation of crystalline Fe nanoparticles in the carbonised region is found by the TEM observations. Mean lateral size of the iron nanoparticles varies in the range of 60-115 nm depending on the implantation fluence. Areal density of the metal nanoparticles also rises with the fluence. It is found that the annealing provides both the coalescence of the nanoparticles and increase of their lateral sizes. Cross-sectional TEM and AFM studies show that the metal nanoparticles are located under the surface at the depth ranging from 30 to 100 nm, and they originate the semispherical bumps on the surface.

Iron nanoparticles embedded in the carbonised PI reveal the magnetic resonance response. Intensity of the resonance rises with increase of the iron concentration. The strong out-of-plane angular dependences of the resonance signal are observed for the samples implanted with high fluences. This effect is typical for FMR of granular metal magnetic films. The magnetisation value of the synthesised nanocomposites was extracted from the angular dependencies of the FMR spectra. As a result, plots of the magnetisation versus the implantation fluence were obtained for both the as-implanted and subsequently annealed samples. It is shown that the metal-polymer nanocomposites formed by highest fluence of 1.25×10¹⁷ ions/cm² reveal characteristics of a continuous magnetic film: the remanence and the coercivity.

DC sheet resistance of the PI decreases by several orders of magnitude with the increase of the iron fluence, i.e. with the carbonisation and rise of metal filling factor in the implanted polymer. Temperature dependences of the resistance are well described by Mott equation: R₂ vs. exp(T²/T'M), where m ranges from 1/4 to 1/2 depending on the fluence and annealing. For the sample implanted with highest fluence of 1.25×10¹⁷ ions/cm², the change of the electron transport mechanism from variable range hopping to semi-metal one is observed. The percolation transition with the fluence increase is in agreement with the above-mentioned FMR data.

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Modification of Polymers with Metal Salts of Organic Acids
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Modification of polymers with metals or metal derivatives attract more and more attention. It is interesting and promising because in such a way properties of polymer matrices e.g. their structure, mechanical and thermal properties could be changed as well as materials with special magnetic, electrical, optical, biological, catalytic and other properties could be obtained. A lot of work has been done on introduction of metals to polymers, their dispersion and interfacing interactions with a matrix. In the lecture some particular case is discussed and namely an activity of metal and organic acids salts in chemical reactions occurring during processing of polymer materials. In the case of general purpose, hydrocarbon polymers, their adhesion to polar materials is rather low. This concerns also tensile properties if the polymers are crosslinked with organic peroxides or radiation. Their structure could be modified during polymerization. Usually commoners containing carboxyl groups, e.g. acrylic acid for that purpose are used. Presence of carboxyl or other polar groups influences positively cohesive and adhesional properties of the polymers. Reactive polar groups could be also used to form ionic crosslinks, e.g. in reaction with metals or metal oxides. However diffusional mobility of the functional groups bonded with macromolecules is restricted. So e.g. since years ZnO is used as an activator of rubbers crosslinking with sulphur or sulphur donors. However higher aliphatic acid, e.g. stearic acid should be also added. Catalytic activity of zinc ions does not manifest itself in the presence of the carboxyl groups only, bounded with macromolecules. In the lecture another route of polymers modification is presented. It consists in application of modifiers in form of metal salts of organic acids. They could be formed "in situ", i.e. during processing of polymer materials, containing dispersed metal or, rather metal oxide particles and an appropriate organic acid. The modifiers could be also prepared separately and introduced to a polymer, during its processing. It is important to apply organic acids with solubility parameter values close to the polymer matrix and reactive to free radicals. Owing that it is easier to graft a polymer onto molecules or particles of a modifier, what exerts positive effect on the properties of the system. In the lecture effect of salts of maleic and tetrahydrophthalic monoesters of different metals, with saturated or unsaturated organic rests on structure and properties of rubbers and plastics is discussed. Changes in surface energy, structure of crystalline phase and chemical structure of a network formed were observed and commented.

The results obtained have been published in the following papers:
Silver Polymer-Nanocomposites
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In this contribution some non-conventional methods are presented for the synthesis of silver-/polymer nanocomposites. Major applications of such systems are aiming at high electrical conductivity and/or bacteriocidic effects.

Silver/polymer nanocomposites are typically prepared in a 2-step-process: Nanoparticle synthesis followed by a dispersion or compounding step. Two different powder morphologies have been synthesized: a) nanoporous powders via condensation of a supersaturated silver vapor in the presence of an inert gas, and b) nanoparticles that are isolated from each other and that show only little agglomeration in the subsequent compounding step. This is achieved by coating of silica-clusters via chemical reduction of a silver salt. Both above types of silver-based filler have some distinct advantages:

Nanoporous silver powder is a prospective filler material for polymer matrix composites that must combine good mechanical properties with high electrical conductivity. The underlying concept is similar to using carbon soot. E.g., dispersion of such highly porous silver-powders in cured epoxy show a specific resistance of less than 0.01 Ωcm, at a Ag fraction in the composite of just 14 vol% (=60 wt%). At the same time, due to the small contents and the porous morphology of the filler these nanocomposites behave more “polymer-like”, i.e., less embrittlement and less fatigue effects are observed, esp. at thermal cycling, as compared to commercially available composites with higher content of silver filler and a flaky filler morphology.

Polymer matrix composites with a volume fraction of 55% isolated and silver-coated SiO2-nanoparticles showed a specific resistance of ≈0.1Ωcm thus combining the properties of silver- and silica-clusters, namely high electrical conductivity and sedimentation restraining effects, respectively.

Finally, in-situ synthesis/processing for metal/polymer nanocomposites has many distinct advantages. As an example a method is presented to prepare silver containing polymer films via inert gas silver evaporation followed directly by a plasma polymerization treatment. Here silver clusters are deposited on a suitable substrate and immediately covered with a ≈40 nm thick silica-like plasma polymer film. It is assumed that the observed bacteriocidic effect is induced by Ag+-ions that are diffusing across the thin film polymer coating.
Functional Nanofibers by electrospinning

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Electrospinning is a versatile technology for the preparation of nanofibers with well defined structures. A polymer solution is pumped through the tip of a syringe. Between the tip and a counter electrode a strong electric field is applied. This leads to the formation of polymer fibers with diameters down to ten nanometers; typical diameters are in the range of several hundred nanometers. Electrospun fibers have possible applications in areas like filtration, tissue engineering, nanoscaled reinforcement or as template for the production of nanotubes.

Polylactide fibers with palladium acetate can be used as templates for metal-containing nanotubes. The template fiber with a typical diameter of several hundred nanometers is coated with another material like Poly-p-xylene and subsequently removed by pyrolysis. The precursor is reduced to palladium and tubes with metal particles on the inside are formed.

Phase separation processes or modifications in the process parameters can be used to obtain fibers with different surface morphologies. Smooth or structured fibers with and without beads are accessible.

A variation of the technique allows the encapsulation of other materials into nanofibers. The resulting fibers can either have a structure with droplets incorporated into the fiber or a core-shell morphology with one polymer compound coated with the other one.

SEM micrograph of a structured polylactide fiber

TEM micrograph of polyamide nanofibers
Polymer/Metal Nanocomposites and Ion Tracks

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The linearly extended zones of highly concentrated radiation damage -so-called „ion tracks“ - that emerge after swift heavy ion impact into insulators such as polymers exhibit two interesting properties. One is the possibility to trap diffusing matter such as metallic nanoclusters so that they may rearrange similarly as pearls of a string to form nanowires [1].

The other peculiarity is the possibility to dissolve readily the highly damaged matter along the tracks, so that pores – the so-called „etched tracks“ emerge. Metal nano-crystals can be deposited chemically on the inner walls of such etched tracks so that conducting nanotubules emerge. By adjusting the nanocrystal density and size, the electronic properties of the nanotubes can be tailored. Hitherto, current / voltage and current / temperature examinations of such conducting nanotubes have revealed at least two charge transport mechanisms: Schottky emission and Ohmic conduction processes, which are valid for insulated nanoclusters and inter-connected clusters, respectively [2].

Such conducting nanotubes play an important role in a newly discovered family of electronic structures denoted as "TEPOS" (= Tunable Electronic Material with Pores in Oxide on Silicon) [3]. These structures derive their electronic function essentially from the high resistivity of the tracks due to the embedded metal nanoclusters. TEMPOS structures are temperature dependent and photosensitive; in certain working modes they also are capable to emit sparkling multi-color light. TEMPOS elements show simultaneously both resistive and capacitive coupling, the latter property being favorite for sensing applications. TEMPOS properties can also be influenced by layers of polymer / metal nanocomposites deposited onto the dielectric layer of these structures.


Nanostructuring by energetic ion beams

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Development of nano phase materials have become of wide interest due to their exotic properties and interesting physics aspects. Energetic ions play crucial role in the the development of nano materials. Ions of different energy regime have different roles in growth of nano phase. Low energy ions (typically up to a keV or so) in plasma, have been in use for growth of nano particle thin films. Low energy ions (typically a few hundred keV) from ion implanter are used for growth of nanoparticles in a matrix. High energy heavy ions (swift heavy ions) have been in use in recent years for growth of nanostructure and also for modifying nanostructure. Highly charged slow moving ions too have potential for creating nanostructures. Out of these several possible roles of energetic ions, there have been developments at NSC Delhi in growth of nano structures by RF plasma, low energy ions and swift heavy ions.
Nucleation and Growth of Metallic Films on Polymer

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Metallic films on polymers have wide range of applications in the field of MEMS, sensors and especially in the field of optical devices such as diffractive optical elements [1]. Formation of such elements is connected with the optimization of optical and mechanical properties of microstructures. From this point of view metallization of the polymer can be considered as three step process involving, interface formation and continuous films production. The first two steps can be considered as a way to produce two-dimensional polymer based nanocomposites.

Nanostructured metal (Al)-polymer (PET) (used in the current experiment) composites reveal synergism of properties of initial components, which gives rise to specific electrical, mechanical, optical and chemical properties related to an ordered distribution of nanoparticles over the matrix volume.

Nanostructured metal (Al)-polymer (PET) (used in the current experiment) composites reveal synergism of properties of initial components, which gives rise to specific electrical, mechanical, optical and chemical properties related to an ordered distribution of nanoparticles over the matrix volume.

This paper reports on the experimental analysis of the production of nanocomposites by vacuum electronic evaporation of the metal (Al) on polymer (PET) substrate and formation of continuous metallic film. The morphology, optical and mechanical properties were studied as a function of deposition time. Kinetics of the Al film growth on PET was compared with the one for the silica glass substrate.

![Fig.1 The AFM 3D image of Al (thickness 100nm) on silica substrate](image1)

The influence of metal coverage on interface composition, structure, morphology, and particle size of Al/PET nanocomposites has been studied employing atomic force microscopy (AFM) and X-ray diffraction, and X-ray photoelectron spectroscopy. Identified nanoparticles of aluminum size were in the range of 20-300 nm.

![Fig.2 The AFM 3D image of Al (thickness 100nm) on polymer (PET) substrate](image2)

The electronic speckle pattern interferometer combined with the microtensile equipment was used to measure in-plane displacement of different points of sample gauge surface under tensile testing conditions [2]. The tensile tests on Al/PET nanocomposites and continuous Al film on PET have been performed.

The gauge length of the specimens was 6 mm with a gauge width of 3mm. Typical stress-strain curves obtained by tensile testing were presented. Young’s modulus of those structures was evaluated. It is shown that mechanical properties of such structures correlate with the kinetics of growth of thin films illustrating transition between nanostructured metal polymer component to continuous film.


References


Self organized metal Micro- and Nanostructures on van der Waals bound layered crystals.

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Like in polymers, a main binding force found in layered crystals are van der Waals forces. Materials, in which van der Waals forces dominate, tend to be chemically inert systems in terms of saturated bonds. Also on the surfaces of transition metal dichalcogenide (TMDC) layered crystals, no dangling bonds from unsaturated atoms can be found. As this is coupled with the a low density of defects due to step edges or point inhomogeneities, long diffusion length due to a low nucleation probability can be observed. Metal evaporation leads not only to a simple cluster formation, but also, depending on the preparation conditions, to nanowires, down to 8 nm thin, covering in a network with mesh diameters of 200-400 nm crystals on the millimeter scale [1], see fig. 1. Moreover, other structures like cluster arrays in the form of triangles or parallelograms can be found as well as large tunnel network structures or large branched structures with kinetically limited growth, see fig. 2. The nanowires and other structures occur because, on the one hand, long diffusion length enable a long range organization. On the other hand, the weak substrate adsorbate interaction enables more complex phenomena to determine the structuring. In contrast to simple diffusion rules like “if position is reached, then stay” which will be found on surfaces with pronounced adsorption energy differences, here more complex “second order” phenomena such as strain, charge transfer and differences in diffusion length dictate the structures. Besides the details of the formation mechanisms, the influence of preparation conditions and the physical properties of the nanowire networks and the other structures will be discussed.

Fig. 1: Different parts of nanowire networks obtained after copper evaporation on VSe2. a) Vacuum STM b) SEM image, c) Air-AFM image in non contact mode. d) SEM overview image shows the entangled nature of the networks.

Fig. 2: Dendrite shaped copper, SEM overview.

Dispersion of Noble Metal Nanoclusters in Bisphenol-(A)-polycarbonate by Acetone Vapor Sorption and Crystallization

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If noble metal (e.g. copper or gold) is evaporated onto amorphous bisphenol-(A)-polycarbonate, the polymer surface will be covered by nanoclusters and not by a continuous metal layer. These clusters can be dispersed into the bulk by acetone vapor induced crystallization of the polymer. Samples have been produced by solution casting onto silicon wafers, metallization was performed in a UHV evaporation chamber. Films were exposed to a controlled acetone atmosphere after evacuation of the glass equipment. The crystallization, embedding and dispersion of gold was analyzed with depth profiling X-ray photoelectron spectroscopy, transmission electron microscopy, thermal analysis and atomic force microscopy. The time scale for sorption and crystallization was determined by mass-uptake and absorption measurements. We will show the influence of the crystallization process parameters on the metal cluster dispersion and surface morphology development. We will present a tentative model of the dispersion process. The penetrating organic vapor provides the long-range mobility to the polymer chains, which can rearrange into the energetically preferred crystalline state. Initially the clusters are embedded by the lowering of the surface Gibbs free energy, later the crystallization appears to provide the driving force for the dispersion process. We are suggesting that the penetrating crystallization front, coming along with an energetic difference of metal cluster incorporation, is responsible for the cluster embedding. This model has been extended to explain the dispersion stop in a certain embedding depth.

\textbf{Figure 1}: XPS intensity profile of gold embedded by vapor induced crystallization, simultaneously recorded intensity of Al marker layer applied after crystallization.

\textbf{Figure 2}: Influence of the gold on the surface morphology: large and smooth spherulites without gold (left), flat but rough structure with gold (right), suggesting strong influence of the clusters on the crystallization mechanism.
Surface Chemical Modification-Based Approach For Controlled Formation and Growth of Metal Nanoparticles in Thin Polyimide Layers

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Polyimide films containing metal nanoparticles are one potential class of materials for future applications in electronics and optical devices, because of size quantization effects of dispersed nanoparticles and excellent properties of polyimide matrix as a low dielectric insulator with good thermal, mechanical, and chemical stability. The development of a fabrication process, with which the microstructure including particle size, volume fraction, and film thickness could be highly tunable, is challenging.

Fully cured polyimide is known to be inert to most chemicals but has been shown to be modified by alkali-induced hydrolysis. Our previous research has shown that polyimide layers modified by the alkali treatment are capable for insertion of metallic ions through ion exchange reaction to form precursors of metallized polyimides. The heat treatment in hydrogen atmosphere applied for the ion-doped precursor layers results in formation of monodispersed metal nanoparticles, accompanied by re-imidization of the modified layers. The present study centers on a controlled synthesis and detailed characterization of thin layers of PMDA-ODA type polyimide nanocomposites containing metal nanoparticles (e.g., Cu and Ni). The present technique involves a aqueous KOH treatment-induced hydrolysis of the polyimide film to form metal salts of poly (amic acid) and subsequent ion exchange reaction using aqueous CuSO4 and NiCl2, followed by hydrogen-induced reduction of the doped metallic ions. Various characterization data obtained from ICP, XPS, TEM, and FT-IR spectroscopy is used for investigating the fabrication process of thin metal/polyimide nanocomposite layers.

During heat treatment, doped metallic ions are reduced to metals and modified polyimide layers are converted into polyimides through condensation reaction between carboxylic acid groups and amide bonds to form heterocyclic imide rings, thus generating metal/polyimide nanocomposite thin layers. These process for Cu/polyimide system can be seen in Fig. 1. The absorbance ratio, A1780cm⁻¹/A1500cm⁻¹ in FT-IR spectra, was used to monitor the degree of imidization. The reduction of the doped metallic ions is found to be closely related to conversion of the poly (amic acid) into polyimides. The temperature at which reduction and re-imidization occur was different for Ni/polyimide system. The formation mechanism of the nanoparticles will be discussed.

**Figure 1** Variations of remaining Cu ions in the modified layers and degree of re-imidization as a function of heat treatment temperature.

**References**
Combined Polymer-Metal Nanocomposite Structures for Ultrathin Multi-Color Filters Application

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Nanocomposites of optically functional nanoparticles embedded in polymer matrices offer interesting possibilities to generate ultra thin color filters as a result of characteristic particle plasmon resonance selective absorption at a particular wavelength. Capability to generate or control multiple particle plasmon wavelength response from one system is highly desirable for potential optical data storage and multi color filters applications. We have used a simple method of vapor phase co-deposition coupled with selective masking at elevated target temperature to produce a combination of different nanocomposite structures with sharp interfaces. This essentially generates a system with regions of different particle plasmon resonance wavelength response. Distinct double and triple plasmon wavelength absorptions could be generated from such a single system consisting of interface forming multilayers of either two nanocomposites or three nanocomposite structures, respectively. Production technique and the characterization results are presented and discussed.

![Image](image_url)

**Fig 1**: (a) Photograph of the combined nanocomposite structure consists of an interface of Teflon AF/Au and Teflon AF/Ag nanocomposites. (b) UV-Vis spectra of such interface showing double wavelength response.
Nanoparticle self organization in carbonaceous matrix upon swift heavy ion irradiation of polymer-metal nanocomposites

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Distinct nanoparticle self organization in the nanocomposites (~ 100 nm) of Teflon AF containing different metallic clusters is reported upon swift heavy ion irradiation of 120 MeV Au beams at different ion fluences ranging from 1 x 10¹¹ ions/cm² to 3 x 10¹² ions/cm². Two dimensionally distributed Au clusters are found to be transformed into long cluster chains of seemingly helical pattern in the organic matrix like pearls on a string. Whereas, comparatively diluted three dimensionally arranged Ag nanoparticles are observed to be concentrated in the formed apparent mesh of carbon-enriched nanoregions upon irradiation. The nanoparticle self organization in such carbonaceous nanowires (diameter ~ 25 nm) finally leads to a quasi one dimensional distribution at the highest fluence with several particles apparently being aligned in one direction. It appears most probable that a high Au cluster concentration in the polymer matrix leads to direct ion-cluster interaction. This probably initiates irradiation-enhanced and thermally assisted diffusion of the clusters coupled with intermixing in the polymer layers. Moving clusters are assumed to be trapped in the ion beam induced additional free volume leading to a long-string of helical-type nanoscale configuration. On the other hand, with diluted clusters arrangement, irradiation induced electronically excited inter-cluster organic regions are interpreted to act as trapping centres for the nanoparticles that self organize along the ion damaged zones. Transmission electron microscopic investigations have been applied to analyse the irradiated and pristine nanocomposites.

(a) (b) (c) (d) (e) (f)

TEM images of the 120 MeV Au ion beam irradiation induced nanostructures in Teflon AF/Au ((a), (b), (c)) and Teflon AF/Ag ((d), (e), (f)) nanocomposites at different ion fluences.
Pd deposited on polyaniline - coated silica gel. Physicochemical and catalytic properties.

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Polyaniline (PANI) is a π-conjugated, electroactive polymer frequently used to investigate incorporation of metallic particles under electrochemically as well as chemically performed doping of polymer chain. Owing to the presence of –NH- and –N= groups PANI exhibits alkaline and redox properties. It can be easily protonated by acids while in the oxidation reaction –NH- can be transformed to –N= . Nitrogen groups are also potential centres of metal ions coordination. All of these reactions have been identified on reacting powder of PANI base with PdCl2 solutions of various HCl content [1]. Protonation of PANI predominated in the PdCl2 solution of high acidity and resulted in PdCl2− as couterions in the obtained Pd–PANI powder. Redox mechanism involved in the PdCl2 solution of low acidity produced metallic Pd in the form of relatively large crystallites. In the present work Pd was incorporated into PANI film in the form of coating (5-25 wt %) onto the surface of silica gel particles (~15-60 μm in size) PANI(SiO2). Polymer was introduced under polymerization of aniline carried out in the presence of silica gel [2]. Several methods: infrared (FTIR) UV-VIS and X-ray photoelectron (XPS) spectroscopy, scanning and transmission electron microscopy (SEM, TEM) have been used to characterize Pd species in the Pd/PANI(SiO2) catalysts prepared in PdCl2 solutions of various acidity. In contrast to the PANI powder – PdCl2 system, doping of polymer film in the present PANI(SiO2) proceeded identically, independently of acidity of PdCl2 solution as well as the extent of PANI protonation in the starting sample. Doping by Pd manifested in conformational changes in the polymer chain occurring due to coordination of Pd2+ anionic complexes to the PANI. Participation of N groups and electrons delocalized through the PANI chain in coordination of Pd2+ has been revealed by N 1s, Pd 3d and Cl 2p XPS core level spectra. Catalytic properties of Pd/PANI(SiO2) were tested in two types of hydrogenation reactions carried out in batch reactor at atmospheric pressure of H2 and temperature 20-60°C. The course of reaction was followed by measuring volume of hydrogen consumed, products analysis was performed with GCMS and HPLC. In the first, the hydrogenation of 2-ethylanthraquinone (EAQ) (Scheme 1) the key step in anthraquinone process of H2O2 production, Pd/PANI(SiO2) exhibited much higher activity than Pd/PANI powdered catalysts. High selectivity towards the hydrogenation of aromatic rings in EAQ offered by Pd/PANI(SiO2) is an interesting and profitable properties of these catalysts, especially for technology of anthraquinone process. Such a tendency of Pd/PANI(SiO2) can be attributed to the modification of silica surface by PANI. Owing to alkaline properties of PANI the course of C=O hydrogenolysis in EAQ, catalysed by acids and observed on commonly applied silica and alumina supported Pd was strongly restricted. Steric effects of the polymer as affecting access of reactants molecules to the Pd centres localized inside the PANI matrix can also be taken into consideration. PANI film onto SiO2 also affected the activity, but especially selectivity of C=C hydrogenation in carbonyl type compounds 2-methyl-3-butyne-2-ol [CH3-C (CH3) (OH) - C=CH] and 2-butyne-1,4-diol (Scheme 2), the latter - an important reaction in the production of endosulfan (insecticide) and Vitamins A and Bc. Catalytic properties of Pd/PANI(SiO2) in both reactions depended on the procedure of Pd insertion, and the best systems giving almost selective C=C to C=C hydrogenation are the ones obtained in PdCl2 solutions of very low acidity. Selective hydrogenation of C=C was also observed on Pd/PANI powdered catalysts, however their activities were distinctly lower than those with PANI film onto the surface of silica gel.

Physicochemical and catalytic properties of polypyrrole and poly(4-vinylpyridine) supported palladium catalysts. The effect of polymer matrix

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Pt and Pd doped electroactive, π - conjugated polymers namely polyaniline and polypyrrole (PPY) have been successfully used in electrocatalytic oxidation of various organic compounds. Recently, their use as heterogeneous catalysts in the hydrogenation of nitrobenzene and C≡C bonds in hexyne has also been published. One can expect that the properties of metallic centres and therefore their catalytic reactivity are to some extent affected by the presence of electroactive matrix, but in none the publication this problem has been discussed. From this reason the present work was undertaken. Two polymers of similar physicochemical properties (specif surface area, basicity) but differing in electrical properties, an electroactive – polypyrrole (PPY) and electro-inactive poly(4-vinylpyridine) (PVP) were used as the matrices for dispersing palladium. PPY was prepared by oxidative polymerization of pyrrole carried out at O°C in the presence of (NH₄)₂S₂O₈ and HCl, PVP was the commercial (Aldrich) reagent. By reacting powder of polymers with aqueous solution of Na₂PdCl₄ (pH 3 - 4) the catalyst with 1-5 % Pd were prepared. Their catalytic properties were tested in the hydrogenation of acetophenone (ACT) and compared to that of commonly used Pd/Al₂O₃. Substantial difference between PPY and PVP with respect to the reaction with Pd²⁺ occurring on incorporation of palladium, and consequently different Pd species in the final catalysts were established by X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM) and temperature programmed desorption of hydrogen (TPD). Under treatment of PPY with Na₂PdCl₄ very quick uptake of Pd occurred resulting in the partial reduction of Pd²⁺ to metallic palladium. XRD showed formation of crystalline particles of Pd. Further reduction of Pd²⁺ occurred under treatment the as-prepared samples with H₂ (30 min at 60°C) inside the catalytic reactor. In the final samples both Pd⁰ and Pd³⁺, the latter bounded with Cl and coordinated to pyrrole rings were identified by Pd 3d XPS core level spectra. SEM and TEM images show the occasionally distributed Pd particles of size within wide range 5 nm – 1,5 µm. The preferential location of metallic Pd inside the agglomerates of PPY was revealed by very low surface concentration of Pd (1.8 at %) and temperature programmed desorption of hydrogen. Thus low stabilising properties of PPy matrix to the metallic Pd have been postulated. On treatment electro-inactive PVP with precursor solution, very slow hydrolysis of Na₂PdCl₄ occurred resulting in the precipitation of palladium hydroxide onto the very external surface of the polymer agglomerates [1, 2]. After activation with H₂ (conditions identical as those of Pd/PPY) very homogeneously distributed Pd – clusters 3-40 nm in size were identified by XPS and TEM. TPD profiles showed the presence of only very weakly chemisorbed hydrogen, easily desorbed at relatively low temperature (~60°C). Very high surface concentration of Pd (22.2 at %) resulted in high activity of Pd/PVP in the ACT hydrogenation, comparable to that of Pd/Al₂O₃ but much higher that of Pd/PPY. Hydrogenation experiment was carried out at batch-type reactor at atmospheric pressure of H₂ and temperature 20-60°C. The course of reaction was followed by measuring the amount of hydrogen consumed as a function of reaction time. Product analysis was performed with GCMS method. Catalytic experiments have been performed over a wide range of operating conditions. The effects of solvents, Pd content, concentration of ACT and the additives of reaction products 1-phenylethanol (ACP) and ethylbenzene (ETB) have been studied. ACT reduces to ETB via 1-phenylethanol (ACP) as intermediate on all catalysts. The difference between Pd/PVP and Pd/PPY with respect to this consecutive process occurred. C≡O in ACT reduces at high selectivity (~100 %) to C-OH on Pd/PVP and Pd/Al₂O₃. The additives of reaction products ACP and ETB did not affect the rate of ACT reduction thus showing Pd centres selectively acting in the adsorption of ACT. On the other hand, the additives of ACP and ETB exhibited inhibitory effect on the rate of C≡O reduction on Pd/PPY. The competition of the products with ACT to Pd centres in Pd/PPY as well as their difficult access for the reactants resulted in low utilization of Pd centres in the catalytic reaction and in low selectivity of C≡O reduction. Formation of ETB on Pd/PPY occurred from the very beginning of reaction, together with C≡O reduction.
PREPARATION OF POLYMER-METAL NANOCOMPOSITES VIA THERMOLYSIS OF UNSATURATED METAL CARBOXYLATES AND THEIR CHARACTERIZATION

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The thermal transformation of unsaturated metal carboxylates is a promising method for synthesis and stabilization of metal nanoparticles in polymer matrix [1,2]. Such an approach allows to combine and regulate the simultaneous formation of polymer matrix and metal nanoparticles in situ. We studied transition metal acrylates, maleates, acetylenedicarboxylates and their cocrysatllites as starting metal-containing monomers. Their thermolysis involve three main macrostages: dehydration (< 393 K), solid phase polymerization (453-473 K), and decarboxylation (> 573 K). The yield products are metal (or its oxide) nanoparticles with a narrow size distribution incorporated homogeneously into polymer matrix (Fig. 1).

![Figure 1. TEM microstructure and diffraction pattern for the product of Fe(III)-Co(II) acrylate cocrysatllite (annealed at 643 K, weight loss Δm=42%)](image)

According to the data of TEM investigations microstructure of materials consisted of both agglomerated and individual crystallites, which were homogeneously distributed in the polymer matrix. Mean crystalline size of 7-14 nm.

As follows from the X-ray diffraction data, the product of Ni(II) acrylates thermolysis is a mixture of three phases Ni-NiO-Ni2C with the ratio of Ni:NiO:Ni2C ≈ 0.51:0.81:1.0. Crystalline phases, which were found in the fully processed products of thermal decomposition of Fe-Co cocrysatllates at 643 K were ferrimagnetic Fe3O4, CoFe2O4 and antiferromagnetic CoO (Fig. 2).

![X-ray diffraction pattern for the product of Fe-Co-acrylate decomposition](image)

All the composite materials exhibit soft magnetic properties at room temperature. The magnetic properties depend on the intrinsic magnetic properties of the constituents and agglomeration of the particles. The temperature dependencies of the magnetisation M(T), measured in a field of 1 T, show typical ferromagnetic behaviour.

Metal particle containing PTFE films deposited by sputtering from a composite target

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\textbf{Abstract}

Nano composite films join the properties of the respective partners. In many cases it is desired to change for instance the electrical or optical behavior while retaining the excellent property of a basic material, such as hydrophobicity. Here, we present a technological realization to produce such nano composite thin films. The thin polymer films with embedded silver or gold nanoparticles were deposited by r.f. magnetron sputtering from a composite target (PTFE/Metal). The nanostructure of the resulting film, which is characterized by the content of metal in the polymer matrix and by the particle size and shape distribution, depends on the target composition as well on the r.f. power density. The thickness of the investigated films was usually in the range between 100 nm and 1.5 µm.

Beside technological aspects we report about the physical and chemical film properties. For the chemical analysis Fourier transform infrared (FTIR)-spectroscopy and X-ray photoelectron spectroscopy (XPS) were applied. It was observed, that the chemical structures of the deposited polymer differentiate significantly from the target PTFE. The fine structure of the C1s peak in the XPS-spectrum was analyzed. The determination of the surface energy done by contact angle measurements has shown that the sputtered films possess nearly the same values as the target PTFE. By sputtering the films on specific nanoporous substrates, a contact angle for water of almost 180° could be reached.

Transmission electron microscopy (TEM) was used in order to receive information about the nanostructure of the films in lateral and vertical direction. The lateral nanostructure was investigated on samples deposited on carbon-coated copper grids. For determination of the vertical nanostructure, cross-sectional preparation was carried out using Focused Ion Beam technology (FIB). Based on these micrographs, the lateral and vertical particle size and shape distribution was analyzed with optical image processing, and its dependency on the target composition and on the r.f. power was investigated. The difference in the optical properties at varying metal content is shown in the optical UV/VIS-spectra. Moreover, the sputtered films were investigated regarding their mechanical properties (hardness, density).

\textbf{TEM-micrographs of gold nanoparticle-containing PTFE films (deposited at a power of 50 W (left) and 150 W (right).}
Molecular Dynamic Simulations of the Formation of Metal Nano-
Particles

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The properties of particles are related to their structure. The structure is the result of
the particle formation process which includes nucleation, growth by coagulation or
coalescence and sintering. The understanding of the kinetic processes and their
dependence on the state conditions makes it possible to steer the process and
influence on the resulting properties.

In this work we investigate the formation of iron particles from the supersaturated
vapor phase by molecular dynamics (MD) simulation. The metal vapor atoms are
embedded in an inert gas atmosphere, which is responsible for the heat exchange of
the system. In case of simple fluids such as the inert gas argon with van der Waals
interactions an effective pair potential is employed. In case of metals many-body
interactions are accounted for.

The formation of iron particles from the gas phase is investigated at different state
conditions. One can recognize differences in the structure as well as in the roughness
or the difference in the surface fraction. In currently ongoing work we investigate the
heterogeneous nucleation of metal vapor at polymer surfaces. The aim is to
understand the kinetics of the metal condensation and the role of the polymer template
in the growth process.
Atomic Layer Deposition of Cu diffusion barrier layers on low-k dielectrics

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The thickness of Ta based diffusion barriers in present generations of integrated circuits is about 10nm. Future generations require even thinner barrier layers of about 3-5nm. The shrinking dimensions and complex topographies of single and dual damascene structures present major challenges for the deposition techniques used for barrier layer deposition. Not only good adhesion to both Cu and dielectric is of great importance, but conformality, step coverage and microstructure of the liners are also important. PVD techniques, most commonly used in industry today, are expected to be incapable of achieving the formation of ultra-thin, conformal and pin-hole free diffusion barriers on structures with high aspect ratios.

Atomic Layer Deposition is a promising technique for the deposition of ultra-thin barrier layers. Its self-limiting nature allows precise control over conformation and growth of conformal films one monolayer at a time. Fig. 1 shows an illustration of a basic ALD process.

Controlling the interface formation and understanding the interfacial chemistry are essential in interface engineering and formation of good diffusion barriers. This study examined and compared the interfacial chemistry of Ta and TaN barrier layers deposited by Plasma Enhanced Atomic Layer Deposition (PEALD) and PVD using In-situ XPS.

In-situ XPS allows to study the interfacial chemistry directly in between deposition steps without breaking the vacuum. The peak development and peak shifts provide information about the interactions between Ta and the substrate. Fig. 2 shows the evolution of the C1s peak during Ta-PVD on SiLK™. The changes in the C1s spectrum suggest the formation of charge transfer complexes between carbon and tantalum.

Pre-treatments also play an important role in the ALD process. A proper pre-treatment can considerably increase the number of reactive sites on the surface to which precursor atoms can adhere and increase the initial growth rate. But not only do they change the initial deposition conditions but they can also seal the surface of porous low-k dielectrics against precursor penetration. The influence of atomic hydrogen and nitrogen plasma on the ALD process was examined in this study.

Figure 1 Illustration of a basic ALD process: 1. Exposure to precursor, adsorption to surface, 2. Purging, 3. Exposure to reactive gas, 4. Purging

Figure 2 C1s evolution during Ta-PVD on SiLK™
SYNTHESIS OF SILVER NANOPARTICLES IN PMMA BY ION IMPLANTATION

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The formation of nanoparticles (NP) in organic matrices was realized only at the beginning of 80th by Koon et al. in their experiments on implantation of the Fe ions into polymers [1]. Variety of metal ions was used for implantation into polymers. Present work focuses on the polymer based optical materials containing the metallic nanoparticles (Ag, Au etc.) characterised by the strong optical plasmon resonance. Only recently such materials were fabricated by Ag implantation into epoxy resins [2] and PMMA [3]. The unusual week plasmon resonance absorption was detected in the case of the Ag-PMMA composition despite on the high concentration of the synthesised Ag nanoparticles [3]. One of the suggestions about the reason of the week absorption was the carbon network formation in PMMA due to radiation effects that typically taking place in organic matrix.

To exam this suggestion the optical extinction of the Ag-PMMA composite was evaluated here using the Mie scattering theory and taking into account carbonisation effect in polymer.

PMMA substrates were implanted by 30 keV Ag ions with doses in the range from 3.1x10^{15} to 7.5x10^{16} ion/cm^2 at constant ion current density of 4 μA/cm^2. In a control experiment the Xe-ion implantation into PMMA at the same conditions was performed. Spectra of optical density were measured from 300 to 900 nm. Simulated optical spectra in present work are shown as spectral dependencies of σ_{ext} ~ Optical Density using the well known Mie equations [4].

The ion synthesis of NP initiated by implantation is not a simple process (Fig.1). It is depends on ion dose, current density, temperature of substrate etc. At present study the dose influence on formation NP is studied.

As it was detected by electron microscopy for samples prepared with similar doses that within the implanted layer of PMMA the Ag particles of a spherical shape and sizes smaller than 15 nm were synthesised at the irradiation doses higher than 3x10^{16} ion/cm^2. Diffraction patterns corresponded to face-centred cubic metallic Ag.

Absorption of the Ag-PMMA composites looks similar to the Xe-PMMA ones for the doses lower than 3x10^{15} ion/cm^2. The absorption monotonically increases with ion dose, especially near ultraviolet, that may be explained in terms of the degradation of polymer under ion beam, particularly by radiation defects and carbonisation. On the other hand, the increase of the Ag dose and the formation of the Ag NP shifts of the absorption maximum of plasmon resonance from 420 nm to a longer wavelengths of ~ 570-600 nm. With rise of ion implantation dose the carbonisation level is supposed to be also increasing. The growth of the metal particles simultaneously with carbonaceous phase evolution in the implanted polymer layer at high doses could be simulated using the model where the Ag core is covered with a thin carbon shell (Fig. 2) using “recursion formalism” [4].

Fig. 2 Mie-modelling of Ag-C particles in PMMA.

The presented modeling of extinction spectra of the Ag-PMMA composite synthesized by ion implantation gives reasonably good agreement with features of the experimental optical spectra and emphasizes the effect of the carbonization.

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Line pattern induced by ultrashort, linearly polarized laser pulses in plasma polymer films with embedded gold nanoparticles

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Abstract

We report on a new and simple method to generate parallel grid-like arranged line structures in thin organic films with embedded gold nanoparticles. The films, with a thickness of about 100 nm, deposited by alternating plasma polymerization of hexamethyldisilazane and metal evaporation, are characterized by a multilayer structure, i.e. all particles are arranged in one plane within the plasma polymer matrix. Irradiating these samples with linearly polarized, ultrashort (130 fs) laser pulses in far field arrangement, clearly visible color changes occur in the film. The change in the optical properties is the result of nanostructural changes.

As typical periodic length, values in the range of 170 nm to 600 nm could be determined, respectively. This means that the generated structure widths are smaller than the laser wavelength used. The direction of the particle lines correlates to the linear polarization of the laser pulses. This structural dependence on the laser polarization is mirrored in corresponding anisotropic optical and electrical film properties. Line arrays with areas up to hundreds of microns could be generated. Further factors, which influence the periodic changes in the nanostructure, are both the proportion of embedded metal and the intensity distribution of the laser.

As we find out from transmission and scanning electron microscopic (TEM, SEM) investigations, periodically arranged line-like structures are formed after the irradiation. Three different laser wavelength (300 nm, 400 nm, 266 nm) we have used so far, and it seems that the period length \( \Lambda \) of the line structures is a linear function of the wavelength of the incident laser light \( \lambda_{\text{laser}} \):

\[
\Lambda = f \left( \lambda_{\text{laser}} \right)
\]

Optical extinction spectra of a plasma polymer film with gold nanoparticles measured with linearly polarized light: solid line: original spectrum; dashed lines: after laser irradiation (averaged over the whole irradiated area)