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CARBON-BASED NANOSTRUCTURED COMPOSITE FILMS

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Scientific report

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1. Executive summary

Introduction

Carbon-based nanostructured composite (CBNC) films consisting of nanosize particles embedded in a carbon-containing host matrix (hydrogen-free or hydrogenated amorphous carbon, diamond-like carbon or polymer matrix) exhibit a variety of attractive properties in solid-state physics. These CBNC films can be produced by physical and chemical vapor deposition techniques, pulsed laser ablation, plasma-assisted techniques and other hybrid techniques as well as by solution chemistry methods such as sol-gel, electrodeposition and electroless deposition. Thick coatings can be prepared using thermal and plasma spraying of nanostructured powders. Depending on the size of embedded particles and interface effects, CBNC films may possess unique physical and/or chemical properties. These films may exhibit specific mechanical and tribological properties attractive for microelectromechanical systems (MEMS), electrical and dielectric properties for microelectronic devices, and optical properties as selective absorber films for flat plate solar collectors, as well as magnetic properties required for high-density magnetic recording data.

The primary objective of this workshop was to bring together an international group of physicists, chemists, researchers and engineers internationally recognized in the diverse fields of research mentioned above, to discuss about fundamental aspects and new experimental results emerging from research groups. The aim was to obtain a cross-fertilization between contiguous areas like for instance nano-electronics, optics, and complementary theoretical and experimental approaches in the field of CBNC films. Six broad topics were discussed in detail, particularly for the group discussions to identify the direction of future research programs and future collaborative research actions to be developed at the European level :

1. Synthesis and deposition techniques of films
2. Characterization methods
3. Mechanical and tribological properties
4. Electrical and dielectric properties
5. Optical properties
6. Magnetic properties of films

Scientific review

Carbon-based nanostructured composite films can be prepared by physical vapor deposition and plasma-assisted chemical vapor deposition techniques. The control of the size of metal or metal carbide clusters embedded in the carbon matrix together with the size effect on the properties of films remain challenging questions to be solved and understood for successful applications. MAX phase containing films exhibit a laminated structure promising for tribological applications. The growth mechanism leading to a self-organization of elements in CBNC films is not yet totally elucidated.

The structure of clusters embedded in the carbon matrix together with the shape and distribution in size of clusters can be determined by sophisticated methods such as X-ray absorption spectroscopy and electron transmission microscopy. These techniques sensitive to the difference in electron density are very attractive to investigate heavy metal particles incorporated in light element matrices.

Composite films containing transition metal dichalcogenide and carbon can be deposited by co-sputtering. The friction properties of these films are very promising for tribological applications at elevated temperatures (up to 400°C in room air). Metal (Ti,V, Zr, W)/carbon films containing up to 20 at.% of metal are attractive candidates to reduce the "chemical erosion" in fusion reactors. The growth of metal crystallites and formation of carbide phase can occur by annealing at a temperature in the range (700-1300) K. TiC/a-C and (Ti,Al)(N,C)/a-C composite films produced by magnetron

sputtering are also of interest for tribological applications. Future investigations are required for a better understanding of the growth mechanism and structure formation of films. Now, chromium containing composite films with improved oxidation resistance are under investigation.

The electrical resistivity of metal (Ag, Cu/carbon films was found to vary with the aging time. The compactness of films may play a key role on the stability of films. There is a demand in organic electronics for high capacitances produced from biocompatible materials such as carbon. For Ni/a-C:H films, the dielectric constant can reach 200 at a frequency of 10^5 Hz. However, additional investigations are needed to reduce the conductivity of films and understand the charge transfer phenomena.

Films based on a a-C:H-Si matrix containing TiSiC clusters can be of interest as solar absorber coatings. The thermal stability of CBNC films is a critical issue for this application. Organic light emissive diodes were produced from polymer films containing SiO_2 and TiO_2 particles. The major advantage of these particles is to modify the conductivity without affecting the optical properties of films.

The magnetic properties of CBNC films were also reviewed. Metal(CoPt)/carbon composite films can find applications for high density recording media. The increase in density can be obtained by a reduction of particle sizes and with very sharp interfaces.

Future directions of research

1. Better process analyses are required for a deeper understanding of major phenomena involved in **deposition processes**. A clear identification of the expertise of research groups in the field of process characterization is needed.
2. The interactions and communication between research groups expert in **characterization techniques** should be improved. The access to sophisticated characterization techniques should be facilitated. The creation of a network and specific research programs are very desirable for deeper cooperation at the European level.
3. There is a need for additional investigation of **mechanical properties** of CBNC films. The role of defects in the films should be elucidated. The **tribological properties** of films in hostile environment would be thoroughly investigated, in particular the friction phenomena at the microscale in the wear tracks should be identified using sophisticated characterization techniques.
4. The **electrical and dielectric properties** of films are very attractive for organic microelectronics. Future developments can be considered for biomedical applications. Additional investigations are needed to understand the transport and breakdown phenomena as well as ageing phenomena in dielectric CBNC films. Future collaborative actions could be of interest to link dielectric and optical properties of CBNC films.
5. The **optical properties** of CBNC films are promising to produce solar absorber coatings. The investigation of the optical properties of anisotropic films with self-organized layered structures has a basic scientific interest. The effect of cluster size distribution and percolation on the optical properties would be studied. The formation of a network can facilitate future collaborative actions and offer the opportunity to put together complementary techniques. A future European project would be focused on large-scale deposition technique of novel ternary nanocomposite films for advanced durable solar absorber coatings.
6. Further investigations on the **magnetic properties** of BCNC films are needed to prove unambiguously recent data published in the literature. The possibility of the existence of magnetism in special forms of carbon should be included in the research program.

Interdisciplinary research programs at the European level **and collaboration of research groups** with complementary expertise are vital for the successful development of this new field of scientific research.

2. Scientific content of the workshop

Wednesday, August 30, 2006
The workshop was attended for 3 working days by 29 scientists coming from 15 different countries. Each topical session (of half-day) was opened by a keynote speaker followed by 3 or 4 contributed speakers and was closed after a group discussion of 1h30. The content of group discussions is reported in section 3 (assessment of the results and contribution to the future direction of the field) of the scientific report. The program of the workshop started with a presentation of the European Science Foundation (ESF) organization and activities given by Dr. M. Tkatchenko, ESF Representative (CEA Saclay, France).

The first session on the **synthesis and deposition techniques of films** was opened by a keynote of 40 min on "Preparation of CBNC films by physical vapour deposition (PVD) and plasma-assisted chemical vapour deposition (PACVD) techniques" given by K. Bewilogua (Fraunhofer Institute, Braunschweig, Germany). The first part of the presentation was a survey of various types of amorphous carbon from tetrahedral carbon (ta-C) to hydrogenated amorphous carbon (a-C:H) with a sp^3 content ranging from 70 to 20 % and methods of preparation of ta-C films by vacuum arc deposition (laser-Arco® technology) and PACVD from various gas precursors. The second part was focused on the preparation of composite films by reactive magnetron sputtering and applications of these films and multilayered coatings such as a-C/Cr/CrN/Cr/substrate structures in automotive industry. The control of the size of metal or metal carbide clusters embedded in the carbon matrix together with the size effect on the properties of films still remain challenging questions to be solved and understood for successful applications.

The keynote was followed by 3 contributed presentations of 20 minutes.
The deposition of Ti-Si-C composite films by DC and RF reactive magnetron sputtering was discussed by W. Gulbinski (Technical University of Koszalin, Poland). Titanium and silicon targets are sputtered in acetylene or methane discharges. The films with the stoichiometry, Ti_3SiC_2 (MAX phase where M is a transition metal, A is Al, Si, Ge or Sn and X can be C or N) exhibit a laminated structure promising for tribological application (low friction coefficient).
The growth mechanisms leading to a self-organization of elements in carbon-based nanocomposite films were discussed by H. Hofsäss (University of Göttingen, Germany). The self-organized multilayer formation was observed for metal (Cu, Ag, Au, Ni or Fe)/carbon composite films produced by ion beam deposition (ion energy ranging from 50 to 150 eV) and magnetron sputtering. Using carbon ions (C^+) of 100 eV, the sp^3 carbon content in these films was as high as 80 %.
Noble-metal (Ag)/DLC nanocomposite and nanolaminate films prepared by dual cathode sputtering and by pulsed laser deposition (using a Ag-graphite composite target) were investigated by P. Patsalas (University of Ioannina, Greece). The properties of Ag/a-C composite films were found to be dependent on the DC bias voltage applied between the target and substrates. The sp^3 carbon content decreased with increasing Ag content. Silver incorporated in the films can act as a killer of bacteria for biomedical applications (dentistry, orthopaedics).

Session 2 was dedicated to the **characterization methods of films**, i.e., advanced techniques for the determination of the chemical composition, electronic structure of atoms and microstructure of the deposited material. The keynote presented by D. Babonneau (University of Poitiers, France) was focused on the "structural characterization of metallic nanoclusters (Ni, Ag) in carbon- and BN-based films". The structure of clusters was investigated by sophisticated methods based on transmission electron microscopy and X-ray elastic scattering, which are still under development. Grazing incidence small angle X-ray scattering (GISAXS) has been used to determine the distribution in size and the shape of silver particles embedded in the carbon matrix. This technique

sensitive to the difference in electron density is very attractive to investigate heavy metal particles incorporated in light element (C, BN) matrices.

3 contributed talks have been given in this session.
The presentation of N. Laidani (ITC-IRST, Povo, Italy) dealt with the composition, structure and growth mechanism of Ni/carbon and ZrO_2/carbon composite films. One of major objectives of the research program in her "Plasma and Advanced Materials Group" is the investigation and modelling of synthesis or deposition processes from plasma phase.
The microstructural characterization of metal (Au, Pt, W, Fe)-containing DLC films, which consists to determine the metal particle sizes and distance between particles was performed by K.I. Schiffmann (Fraunhofer Institute, Braunschweig, Germany). A large variety of methods based on transmission electron microscopy (TEM), scanning tunnelling microscopy (STM), X-ray absorption spectroscopy have been used and combined to get a deeper insight on the microstructure of films.
The nanolaminated structure of MAX-phase films, particularly the electronic structure and bonding-type was characterized by U. Jansson (Uppsala University, Sweden). The interest of these films is to combine the properties of ceramic materials (stable at high temperature) and metallic materials (low electrical resistivities). Bulk MAX phase materials (Maxthal®) are commercially available from Kanthal AB Company. The major difficulty is to produce MAX-phase thin films at relatively low temperatures compatible with the thermal stability of various substrates.

Thursday, August 31, 2006
The third session entitled **mechanical and tribological properties of films** started by the keynote on "High temperature tribological behavior of nanocomposite carbon-containing transition metal dichalcogenide (C-TMD) self-lubricating films" presented by A. Cavaleiro (University of Coimbra, Portugal). The temperature effect on the friction coefficient and oxidation resistance of pure a-C:H films was reviewed. For these films, the friction coefficient increases at tribological test temperatures as low as 250°C whereas the oxidation of films is detected at temperatures higher than 500°C. The hardness of these films of approximately 20 GPa decreases after annealing at 400°C. The role of hydrogen and variation of the hydrogen content in tribological tests at moderate temperatures in air are not yet elucidated. Composite films containing TMD and carbon have been deposited by co-sputtering techniques under experimental conditions similar to those used for deposition of a-C:H films. Depending on the deposition conditions, laminated and nanocomposite films can be produced by co-sputtering. Friction coefficients as low as 0.05 and wear rates in the range 10^{-7} mm^3/N m for W-S-C films are comparable to those obtained from a-C:H films. For these W-S-containing films, the friction coefficient was found to be lower in vacuum or dry atmosphere than in humid air. In addition, the friction coefficient was dependent on the contact load. Promising results are obtained at test temperatures ranging from 100°C to 400°C, i.e., the friction coefficient can be as low as 0.04 above 100°C and these films are thermally stable up to 400°C. The friction properties of composite films containing less than 70 at.% of carbon are superior to those of a-C:H films. For tribological applications at moderate temperatures in air, these W-S-C films appear to be much more promising than Mo-Se-C films, which decompose above 200°C.

The program of this session continued with 4 contributed presentations.
The hardness of transition metal doped carbon films and the thermally-induced effect on the microstructure of films were studied by M. Balden (Max-Planck-Institut für Plasmaphysik, Garching, Germany). Various difficulties arise from the erosion of graphite induced by plasma-surface interactions in various applications (fusion reactors). The graphite erosion and hydrogen retention result from hydrogen impacts on the surface. One possible approach to reduce this "chemical erosion" is to use metal (Ti, V, Zr, W)/carbon films containing up to 20 at.% of metal. The growth of metal crystallites and formation of carbide phase by thermal annealing of films between 700 and 1300 K were investigated by X-ray absorption spectroscopy (XAS) and extended

X-ray absorption fine structure (EXAFS). Carbide phases were detected after annealing at 1100 K. The variation of hardness and graphitization of films remain to be thoroughly investigated and understood.
The presentation of R. Groenen (NV Bakaert SA, Zwevegem, Belgium) was related to the analyses of the microstructure of DLC and SiO_x containing-DLC films. Films with silicon oxide (SiO_x) particles embedded in DLC matrices, named as DLN films are commercially available (Dylyn®) and can be used for various applications (automobile, textile machinery, optical disk mould parts). For successful industrial applications, the effect of particles (coming from the atmosphere) on the surface morphology of films is a crucial point to control.
The results discussed by I. Efeoglu (Atäturk University, Erzurum, Turkey) are related to the deposition and characterization of metal (Ti)/diamond-like carbon (Me/DLC) films. Titanium-containing films have been deposited by closed-field unbalanced magnetron co-sputtering. Improved adhesion on various substrates determined by scratch tests was obtained from functionally gradient multilayers. The compacity of films was dependent on the sputtering mode (pulsed DC plasma was compared to biased DC substrates). The magnitude and evolution of residual stresses in these films remains to be determined.
The microstructural evolution and properties of magnetron-sputtered titanium carbide/amorphous carbon (TiC/a-C) and (Ti,Al)(N,C)/a-C nanocomposite films were reviewed by M. Stüber (Forschungszentrum Karlsruhe, Germany). These composite films have been produced using a magnetron sputtering equipment commercially available (Hauzer). On the basis of these results, various directions for future investigations can be identified, in particular for a better understanding of the growth mechanism and structure formation of composite films, development of oxidation-resistant new films (Cr-Al-N-C films), modeling of mechanical and tribological properties at the nano and microscale, and scale-up the deposition processes and equipments.

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The fourth session was focused on the **electrical and dielectric properties of films**. The keynote entitled "Electrical properties of composite films with plasma polymer matrix" was given by H. Biederman (Charles University, Prague, Czech Republic). Metal (Ag, Cu) clusters sputtered from a metal target were embedded in polymer matrix deposited by plasma polymerization. Aging phenomena occur in these films. The electrical resistivity of composite films was found to vary with the aging time. The compacity of films may play a key role on the aging behavior of films.

In this session, the keynote was followed by 4 contributed presentations.
The dielectric properties of Ni/a-C:H composite films prepared by plasma-assisted deposition techniques were discussed by A. Sylvestre (CNRS-Grenoble, France). There is a demand in organic electronics for high capacitances produced from biocompatible materials such as carbon. The permittivity of a-C:H films approximately equal to 3 is too low to produce these type of devices. High-k dielectric films based on carbon are very attractive for biomedical applications. The effect of the frequency and temperature (up to 400°C in nitrogen ambient) on the dielectric constant of Ni/a-C:H films was thoroughly investigated. For films containing 20 at.% of nickel, the dielectric constant was as high as 200 at a frequency of 10^5 Hz. The dissipation factor of 0.2 at 10^5 Hz was relatively high compared with that of 0.01 for a-C:H films. The electrical conductivity of Ni/a-C:H films is 6 orders of magnitude higher than that of a-C:H films. Additional investigations are needed to reduce the conductivity of metal/carbon composite films and understand the charge transfer phenomena.
The next talk given by Z. Kutnjak (J. Stephan Institute, Ljubljana, Slovenia) was related to the dielectric properties of vinylidene fluoride-trifluorothylene-based composite films. Polymer films such as poly-vinylidene fluoride (PVDF) films, poly-vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) films as well as polymer films containing lanthanum-doped lead zirconate titanate [PLZT, $(Pb,La)(Zr,Ti)O_3$] particles were thoroughly investigated by differential scanning calorimetry and impedance analyses.

The electrical properties and morphology of nanocomposite films studied by computer simulation were discussed by S. Novak (J.E. Purkyne University, Usti nad Labem, Czech Republic). The simulation is based on the spatial distribution of objects, distribution of nearest neighbors and size distribution of objects. The transport properties of films by tunnel effect and ohmic transport related to the percolation threshold can be predicted. A collaborative research program would be of interest to collect experimental data and demonstrate the validity of predictions provided by the computer simulation.
The correlation between electrotransport and structure of nanocomposite films was established by P. Lobotka (Institute of Electrical Engineering SAS, Bratislava, Slovakia). Films exhiting various structures and compositions such as Fe-Ta-O nanocomposite films, Fe/AlN multilayered films, Ni/a-C films have been deposited by co-sputtering and sequential sputtering. Anisotropic magnetoresistivity was observed for Ni/a-C films deposited at 800°C.

Friday, September 1, 2006
Session 5 was dedicated to **optical properties of films**. The keynote entitled "Optical properties of metal-doped carbon based nanocomposite thin films : comparing experiment to effective medium theories" was presented by A. Schüler (EPFL, Lausanne, Switzerland). The presentation started with a comparative review on various theories (Maxwell-Garnett, Bruggeman, Ping-sheng and Drude) proposed in the field of optical properties of films. The experimental methods such as spectrometry, ellipsometry, in situ laser reflectometry and in situ photoelectron spectroscopy (operated under vacuum) were described. The major results discussed in the keynote are related to the refraction index, n, and extinction coefficient, k, of metal (Au, W, Ti)/a-C:H composite films Metal (Cr)/a-C:H multilayered coatings are of interest as solar absorber coatings. A critical issue for this application is the thermal stability of coatings for ageing tests carried out at various temperatures. Films based on a-C:H-Si matrix containing TiSiC clusters can be of interest for this type of application.

4 contributed talks have been given in this session.
Results on the optical investigations of poly(phenylene vinylene) (PPV) and derivatives based composites were presented by T.-P. Nguyen (University of Nantes, France). Organic semiconductor such as PPV could emit green yellow light (wavelength, λ = 550 nm). However, this material is not soluble. Organic light emissive diodes (OLED) were produced from PPV containing SiO_2 and TiO_2 particles. The major advantages to use composite films arise from the possibility to increase the electrical conductivity with TiO_2 particles and decrease the conductivity using SiO_2 particles whereas the optical properties remain unchanged. These composite films are promising candidates to produce organic photovoltaic cells.
The contribution of G. Dennler (Johannes Kepler University, Linz, Austria) dealt with conjugated polymer : fullerene based organic solar cells and related devices. Organic LEDs are commercially available for screens of mobile phones. The world market increases by 40 % per year. The absorption of photons leads to the formation of excitons (electron-hole pairs), which need to be separated at the interface donor-acceptor semiconductor. Composite films are of interest to produce graded interfaces.
The direct ion beam deposition of doped diamond-like carbon (DLC) films was performed by S. Tamulevicius (Kaunas University of Technology, Lithuania). These films were investigated by X-ray photoelectron spectroscopy, atomic force microscopy and scratch tests. The magnitude of stresses in these films was determined as a function of the temperature. Composite films such as SiO_x/a-C:H films can be used as anti-adhesive layers in nano-imprint lithography (NIL).
The influence of the deposition conditions on the optical properties and thermomechanical stability of nanostructured SiO_2-containing DLC films was studied by V. Bursikova (Masaryk University, Brno, Czech Republic). Her research group is involved in plasma source development and plasma diagnostics by optical emission spectroscopy, and electrical measurements (Langmuir probes).

These characterization techniques were used for PACVD of carbon nanotubes and SiO_x/DLC films produced from various gas precursors such as hexa-methyl-disiloxane (HMDSO), methane and acetylene. The magnitude of residual stress in a-C:H films ranging from – 0.8 to – 1.7 GPa was investigated as a function of the substrate bias voltage. The thermal stability, hydrogen content and graphitization of films were determined after annealing up to 410°C.

The **magnetic properties of films** were discussed for last session of the workshop.
The keynote given by M. Farle (University of Duisburg-Essen, Germany) was dedicated to "magnetic interactions, magnetic anisotropy and intrinsic particle properties in nano-assembled magnetic films". The motivation is to start from atoms to build size-controlled nanoparticles, which can serve as single building blocks and produce composite films from these building blocks. The synthesis of nano-particles such as $Fe_xPt_{(1-x)}$ of 3 to 100 nm in size was carried out from colloidal suspensions. An uniform distribution of particles can be obtained using the spin-coating technique. The magnetization of films was investigated as a function of the magnetic field.

This keynote was followed by two contributed talks.
Metal (CoPt)/carbon nanocomposite films for high density recording media were proposed by I. Panagiotopoulos (University of Ioannina, Greece). The increase in density can be obtained by a reduction of particle sizes and with very sharp interfaces. Annealing treatments of films can lead to an increase in grain size and dispersion of particles in the carbon matrix.
The talk given by M. Bystrzejewski (Warsaw University, Poland) was related to the carbon encapsulation of magnetic materials, in particular to the synthesis, characterization and applications. The films synthesized by RF plasma technique can be used for biomedical applications.

3. Assessment of the results and contribution to the future direction of the field

The critical assessment of existing knowledge on CBNC films and determination of directions of future research programs were accomplished for the group discussions of 1h30 held at the end of each session. In addition, future collaborative research actions involving participants of the workshop were also identified.

The **group discussion on "Synthesis and deposition techniques of CBNC films"** was moderated by K. Bewilogua (Fraunhofer Institute, Braunschweig, Germany).
In the field of the synthesis and deposition of films, it becomes important to consider combinations of different processes to produce films exhibiting optimum properties; For instance, films produced by electrodeposition can be combined with films prepared by physical vapor deposition (PVD) techniques. Such combinations lead to corrosion AND wear-resistant coatings. Other combinations, which were actually discussed, are related to plasma diffusion (plasma or ion nitridation) and PVD or PACVD for top layers. The adhesion of all types of films, not only those produced by a combination of deposition techniques, is extremely important for applications.

The effect of the substrate bias voltage on the properties of films produced by pulsed laser deposition (PLD) and other techniques is still not clear. Intensive research efforts are necessary to investigate the effect of pulsed substrate bias voltages. Complete processes including all steps of deposition (sputter cleaning, interlayers) should be investigated.

Better process analyses are required for a deeper understanding of major phenomena involved in deposition processes. Today, the measurements of various parameters at different positions in large chambers used for industrial deposition equipments become more and more necessary. The exchange of analytical results and cooperation between partners is needed to improve the situation.
To find practically applicable solutions, the basic and applied researchers should know in more details the existing problems of industrial applications and their demands for efficient solutions. Then they can try to solve the problems directly.

Deposition processes leading to a self-organization of elements such as in carbon-based nanocomposite films discussed by H. Hofsäss (University of Göttingen, Germany) are scientifically very interesting. Furthermore, MAX phase films are very promising for a variety of applications. However, today one of major difficulties encountered in deposition of these films is the very high substrate temperature needed to obtain the lamellar structure. Of course, the challenge is to lower the deposition temperature of MAX phase films.

A clear identification of the expertise of research groups in the field of process characterization is needed. The participants, in particular those involved in the investigation of deposition processes should inform on their capabilities and facilities of measurements of process characteristics. It was resolved upon preparing a short report giving an overview on the measurement techniques of major characteristics of deposition processes as well as on the technical possibilities to use these techniques available in various research groups.

Possible European projects could be in the field of preparation of solar absorber coatings. In this field, both improvement of coating properties and more effective (faster, more reliable, more cost efficient) deposition techniques are desirable. The content of projects would be prepared in the next weeks by participants of the workshop.

In the second **group discussion on "Characterization methods of CBNC films"** moderated by D. Babonneau (University of Poitiers, France), the need for a careful structural characterization at different scales was clearly identified to get a deeper understanding on both physical properties and growth mechanisms of films.

The combination of various characterization techniques is of paramount importance. The objective is to take advantage of the complementarities of advanced laboratory techniques (X-ray diffraction, atomic force microscopy, ellipsometry, X-ray photoelectron spectroscopy, Raman spectroscopy, etc.), synchrotron radiation X-ray based methods (grazing incidence small angle X-ray scattering, X-ray absorption spectroscopy, etc.), and ultramicroscopic techniques (conventional, high resolution, and scanning transmission electron microscopy, conventional and valence electron energy loss spectroscopy, etc.).

Accordingly, it was proposed to improve the interactions and communication between participants of the workshop highly qualified in characterization techniques. The access to sophisticated characterization techniques should be facilitated. To fulfill this challenging task, a deeper cooperation at the European level is very desirable. The creation of a network or specific research program supported by a European agency such as ESF would be welcome. The network can help and facilitate the contacts between groups specialized in characterization of films with permanent staff members and groups investigating the properties of films.

The **group discussion on "Mechanical and tribological properties of CBNC films**" was moderated by A. Cavaleiro (University of Coimbra, Portugal). There is a need for additional investigation of mechanical properties. The difficulties arise from the large variety of values of

mechanical properties, such as hardness, toughness, elastic modulus, etc. This variety may originate from the effect of defects difficult to control.
The thermal stability and oxidation resistance of films should be investigated at increased temperatures in connection with the mechanical properties and mechanical behavior of films. The improvement of film adhesion to various substrates is crucial to increase the lifetime of mechanical components. For this purpose, the use of sub- or inter-layers and gradient layers associated with the modification of the substrate surface by ion implantation for metals or plasma treatment for polymers is a promising approach. A better understanding of the origin of residual stresses and mechanisms involved in the reduction or elimination of stresses can contribute to control more strictly the adhesion of films In addition, the investigation of the distribution of stresses through the films and determination of stresses at the nanoparticle-matrix interfaces are also of interest. The determination of residual stresses in amorphous films would be performed either by Raman spectroscopy or by measurements of the effect of residual stresses on the structure of substrates.

The tribological behavior of films in hostile environment (corrosive atmosphere, elevated temperatures, …) should be investigated in more details. The load bearing capacity should be improved by using interlayers of hard materials. The analyses of sliding contacts at the nanoscale and additional characterization of transfer layers are needed to get a deeper insight of friction mechanisms. Powerful and sophisticated techniques such as high resolution transmission electron microscopy (HRTEM), Raman spectroscopy, and extended X-ray absorption fine structure (EXAFS) would be used to identify the surface layers formed in the wear tracks. Nanotribilogical tests using atomic force microscopy (AFM) would be of interest to understand the macroscopic tribological behavior of films. Furthermore, for a better understanding and control of friction properties, the tribological performance of composite films with a monolithic structure would be compared with that of composite films with a nanolayered structure.

In the field of mechanical and tribological properties of CBNC films, two future possible collaborative research programs between participants of the workshop could be identified. The first project is related to the investigation of the thermal stability and oxidation resistance of films at increased temperatures. Six research teams would participate in this project : A. Cavaleiro (University of Coimbra, Portufgal), M. Stüber (Forschungszentrum Karlsruhe, Germany), U. Jansson (Uppsala University, Sweden), P. Patsalas (University of Ioannina, Greece), W. Gulbinski (Technical University of Koszalin) and R. Groenen (NV Bakaert SA, Zwevegem, Belgium). The objective of the second project is to investigate the tribological behavior of films under extremely high loading conditions. Four partners would cooperate in this research program : A. Cavaleiro (University of Coimbra, Portugal), K. Bewilogua (Fraunhofer Institute, Brauschweig, Germany), I. Efeoglu (Atäturk University, Erzurum, Turkey) and R. Groenen (NV Bakaert SA, Zwevegem, Belgium).

The **group discussion on "Electrical and dielectric properties of CBNC films"** was moderated by H. Biederman (Charles University, Prague, Czech Republic). Dielectric films exhibiting either low or high permittivity are developed for microelectronic applications. There is a need for organic electronics to produce transistors with low threshold voltage from materials compatible with biological applications. The target capacitance is 40 mF/cm^2 at a frequency of 1 kHz. Carbon-based dielectric films are very attractive candidates for these applications.

Basic research works are needed to investigate thoroughly and understand the transport and breakdown phenomena as well as ageing phenomena in dielectric composite films. DC electrical properties and electrical breakdown of films containing various metal particles embedded in a-C and a-C:H matrices should be investigated. Electromigration phenomena and structural changes of films promoted by high DC electrical fields remain to be studied. The identification of conduction

mechanisms and photoconduction measurements are also of interest. Measurements using dielectric spectroscopy to investigate the permittivity of films as a function of the frequency at various temperatures should be performed. The exchange of experimental data is required for a correct evaluation of models related to transport properties of composite films.

A collaborative research program would involve S. Novak (J.E. Purkyne University, Usti nad Labem, Czech Republic) in charge of computer modeling of experimental electrical data versus tructure of films, A. Sylvestre and Y. Pauleau (CNRS-Grenoble, France) performing AC measurements with high-K dielectric films, G. Dennler (Johannes Kepler University, Linz, Austria) for photoconduction measurements and H. Biederman for the investigation of basic electrical characteristics and depolarization current measurements. The development of future collaborative actions could be of interest to link dielectric and optical properties of composite films.

The **group discussion on "Optical properties of CBNC films"** was moderated by A. Schüler (EPFL, Lausanne, Switzerland). Challenging aspects in optics are to investigate the applicability range and precision of Maxwell-Garnett, Bruggeman and Ping Sheng effective medium theories. The finite size effects on the electronic structure of complex alloy clusters, the refractive index and extinction coefficient data for these complex clusters, cluster-matrix and cluster-cluster interactions should be investigated. Numerical simulations of optical properties for known structures should be compared with experimental data. There is a basic scientific interest in the investigation of the optical properties of anisotropic films with self-organized layered structures.

The influence of cluster size distribution and percolation on the optical properties of films would be studied. On the basis of these data, the growth of clusters during annealing could be monitored by optical measurements. Correlations between optical and dielectric properties would be established. Composite films can find applications as selective absorber coatings for solar collectors, organic light emitting diodes, transparent coatings on moulds for embossing microstructures.

The formation of a network can facilitate future collaborative actions. The optical experiments can be performed ex-situ. A number of research groups may collaborate and put together complementary techniques. A future European project would be focused on large-scale deposition technique of novel ternary nanocomposite films for advanced durable solar absorber coatings.

The **group discussion on "Magnetic properties of CBNC films"** was moderated by M. Farle (University of Duisburg-Essen, Germany). Carbon-based magnetic nanostructures comprise a wide field of materials and potential applications. Various important questions in basic research should be discussed. Recent data in the literature indicate that various forms of pure carbon exhibit ferromagnetic long-range order. Further developments and investigations are needed to prove unambiguously these findings, which may lead to ultralight magnets. The technology moves into the nanoscale world by producing sensors and storage devices based on magnetic materials with atomic dimensions. Research efforts in terms of development of single particle or nanoscale magnetic detection techniques should be accomplished. Magnetic materials can be "constructed" by using nanosize particles as building blocks. These building blocks could be different materials, which will be assembled in a controlled way into new materials. Such materials could be spray coated or deposited by ion beam on any surface thereby providing magnetic coatings with embedded coding.

The ultimate goal is to obtain magnetic coatings exhibiting various properties, which can be controlled and tuned such as hardness, wear resistance, low friction, thermal stability, corrosion resistance, electrical resistivity. A viable road is the exploitation of embedded patterned magnetic

structures consisting of self-assembled well defined nanosize entities in a dia-, para-, ferro- or antiferromagnetic matrix. The possibility of the existence of magnetism in special forms of carbon (ultralight ferromagnet for motors, switches, sensors,…) should be included in the research program.

Centers for magnetic characterization of films should be funded. For industrial production, techniques for online characterization need to be developed. Analytical techniques like synchrotron based techniques must be made available. The scalability of nanoscale techniques or materials produced in laboratories to the industrial scale needs to be demonstrated. In basic research, various issues need to be investigated : the composition homogeneity (surface, interface, bulk) of nanoscale materials, the formation of clusters versus dispersed atoms in the films, the locally resolved strains (local, lattice distortions < 2 %) in nanostructures, the magnetic interactions (collective behavior, single cluster magnetism).

The **group discussion on "Near Future Activities"** was moderated by Y. Pauleau (National Polytechnic Institute of Grenoble, France). During the group discussions, the need for permanent contacts between participants of the workshop was evoked. A **questionnaire** will be proposed to participants to collect their comments about the interest for a future European research network on CBNC films.

The preparation and publication of a **book** entitled "Carbon-Based Nanostructured Composite Films" would be of interest to contribute to the critical assessment of existing knowledge on CBNC films as well as to identify directions for future research programs. The contents of this book would be prepared and a book proposal would submitted to publish a book in the frame of the Elsevier/E-MRS Publishing Agreement related to a monograph series of books titled the "E-MRS Monograph Work".

A proposal for the organisation of a **symposium** on CBNC films prepared by A. Schüler (EPFL, Lausanne, Switzerland), D. Babonneau (University of Poitiers, France) and M. Balden (Max-Planck-Institut für Plasmaphysik, Garching, Germany) was submitted to the E-MRS. This symposium would be held for the E-MRS Spring Meeting in Strasbourg in May 2008. This meeting would be an opportunity for the interchange of information between researchers and scientists from Europe and other countries on the science, technology and applications of CBNC films.

4. Final program

Wednesday, August 30, 2006 - Morning
Opening remarks
Chair : Yves Pauleau
08:20-08:30 : Welcome
08:30-08:50 : Dr. Malgorzata Tkatchenko, (ESF Standing Committee for Physical and Engineering Sciences), CEA Saclay, Gif sur Yvette, France
"Presentation of the European Science Foundation (ESF)"
Session 1. Synthesis and deposition techniques of films
Chair : Yves Pauleau
08:50-09:30 : Keynote speaker – K. Bewilogua, Fraunhofer Institute, Braunschweig, Germany
"Preparation of carbon-based coatings by PVD and PACVD techniques"
09:30-09:50 : W. Gulbinski, The Technical University of Koszalin, Poland
"Ti-Si-C system - the deposition of thin films"
09:50-10:10 : H. Hofsäss, University of Göttingen, Germany
"Self-organization mechanisms in carbon-based nanocomposite thin film growth"
10:10-10:30 : P. Patsalas, University of Ioannina, Greece
"Noble-metal/DLC nanocomposites and nanolaminates: PLD vs. sputter growth"
10:30-11:00 : Coffee break
11:00-12-30 : Group Discussion – Moderator : K. Bewilogua
12-30-14:30 : Lunch

Wednesday, August 30, 2006 - Afternoon
Session 2. Characterization methods of films
Chair : Witold Gulbinski
14:30-15:10 : Keynote speaker – D. Babonneau, University of Poitiers, France
"Structural characterization of metallic nanoclusters in carbon-based nanocomposite films"
15:10-15:30 : N. Laidani,ITC-IRST, Povo (Trento), Italy
"Characterisation of carbon-based composite films structure and growth by electron spectroscopies and mechanical measurements"
15:30-15:50 : K.I. Schiffmann, Fraunhofer Institute, Braunschweig, Germany
"Microstructural and microtribological characterization of metal containing DLC coatings"
15:50-16:10 : U. Jansson, Uppsala University, Sweden
"Characterization of nanolaminated MAX-phase films"
16:10-16:40 : Coffee break
16:40-18-10 : Group Discussion – Moderator : D. Babonneau

19:30-20:30 : Dinner

Thursday, August 31, 2006 - Morning
Session 3. Mechanical and tribological properties of films
Chair : Yves Pauleau
08:30-09:10 : Keynote speaker – A. Cavaleiro, University of Coimbra, Portugal
"High temperature tribological behaviour of nanocomposite carbon containing transition metal dichalcogenide (C-TMD) self-lubricating coatings"
09:10-09:30 : M. Balden, Max-Planck-Institut für Plasmaphysik, Garching bei München, Germany
"Hardness of transition metal doped carbon films and the effect of thermally induced nano structuring"

09:30-09:50 : R. Groenen, NV Bakaert SA, Zwevegem, Belgium
"Microstructure analysis of diamond like carbon (DLC) and DLC nanocomposite (DLN) films"
09:50-10:10 : I. Efeoglu, Atäturk University, Erzurum, Turkey
"Deposition and characterization of metal/diamond-like carbon (Me/DLC) thin films prepared by closed-field unbalanced magnetron sputtering"
10:10-10:30 : M. Stüber, Forschungszentrum Karlsruhe, Germany
"Microstructural evolution and properties of magnetron-sputtered titanium carbide/amorphous carbon (TiC/a-C) and (Ti,Al)(N,C)/a-C nanocomposite coatings - a review"
10:30-11:00 : Coffee break
11:00-12-30 : Group Discussion – Moderator : A. Cavaleiro
12-30-14:30 : Lunch

Thursday, August 31, 2006 - Afternoon
Session 4. Electrical and dielectric properties of films
Chair : Witold Gulbinski
14:30-15:10 : Keynote speaker – H. Biederman, Charles University, Prague, Czech Republic
"Electrical Properties of Composite Films with Plasma Polymer Matrix"
15:10-15:30 : A. Sylvestre, Joseph Fourier University, CNRS, Grenoble, France
"Dielectric properties of nickel/hydrogenated amorphous carbon composite films"
15:30-15:50 : Z. Kutnjak, J. Stefan Institute, Ljubljana, Slovenia
"Dielectric and calorimetric properties of vinylidene fluoride-trifluoroethylene-based composite films"
15:50-16:10 : S. Novak, J.E. Purkyne University, Usti nad Labem, Czech Republic
"Electrical properties and morphology of nanocomposite films"
16:10-16-30 : P. Lobotka, Institute of Electrical Engineering SAS, Bratislava, Slovakia
"Correlation between electrotransport and structure of a nanocomposite"
16:30-17:00 : Coffee break
17:00-18-30 : Group Discussion – Moderator : H. Biederman

19:30-20:30 : Dinner

Friday, September 1, 2006 - Morning
Session 5. Optical properties of films
Chair : Yves Pauleau
08:30-09:10 : Keynote speaker – A. Schüler, EPFL, Lausanne, Switzerland
"Optical properties of metal-doped carbon based nanocomposite thin films: comparing experiment to effective medium theories"
09:10-09:30 : T.-P. Nguyen, Institut des Matériaux Jean Rouxel, Nantes, France
"Optical investigations of poly(phenylene vinylene) and derivatives based composites"
09:30-09:50 : G. Dennler, Johannes Kepler University, Linz, Austria
"Conjugated polymer : fullerene based organic solar cells and related devices"
09:50-10:10 : S. Tamulevicius, Kaunas University of Technology, Lithuania
"Direct ion beam deposition of doped diamond like carbon films"
10:10-10:30 : V. Bursikova, Masaryk University, Brno, Czech Republic
"Influence of the deposition conditions on the optical properties and thermomechanical stability of nanostructured silicon oxide containing DLC films"
10:30-11:00 : Coffee break
11:00-12-30 : Group Discussion – Moderator : A. Schüler
12-30-14:30 : Lunch

Friday, September 1, 2006 - Afternoon
Session 6. Magnetic properties of films
Chair : Witold Gulbinski

14:30-15:10 : Keynote speaker – M. Farle, Universität Duisburg-Essen, Germany
"Magnetic interactions, magnetic anisotropy and intrinsic particle properties in nanoassembled magnetic films"

15:10-15:30 : I. Panagiotopoulos, University of Ioannina, Greece
"CoPt/C nanocomposite films for high density recording media"

15:30-15:50 : M. Bystrzejewski, Warsaw University, Poland
"Carbon encapsulation of magnetic nanomaterials: synthesis, characterization and applications"

15:50-16:20 : Coffee break

16:20-17-50 : Group Discussion – Moderator : M. Farle

17:50:18:30 : Group Discussion on "Near Future Activities" – Moderator : Y. Pauleau

19:30-20:30 : Dinner

5. Statistical information on participants

Countries of origin of 29 participants

Country	Austria	Belgium	Czech Republic	France	Germany
Number of participants	1	1	3	5	6

Country	Greece	Italy	Lithuania	Poland	Portugal
Number of participants	2	1	1	3	1

Country	Slovakia	Slovenia	Sweden	Switzerland	Turkey
Number of participants	1	1	1	1	1

Age structure

Age range	21-30	31-40	41-50	51-60	> 60
Number of participants	1	7	13	7	1

Young researchers : 8 participants less than 40 years old

6. Final list of participants

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