**Thin Films**

**Growth modes of undoped ZnO thin films by reactive pulsed magnetron sputtering**

The growth modes of ZnO thin films on amorphous SiO$_2$/Si and single crystalline Al$_2$O$_3$(0001) substrates are investigated. The films are characterized by XRD, AFM, and spectroscopic ellipsometry (SE). On amorphous substrates at $T_S > 500^\circ$C, films with high (0001) texture are formed, with AFM scaling analysis suggesting competitive unstable 3D growth with shadowing effects. As confirmed by XRD $\varphi$-scans, deposition on chemically cleaned Al$_2$O$_3$ (0001) substrates results in the formation of epitaxial ZnO layers in a wide range of deposition parameters, with two types of domains, one of them being rotated by 30° relative to the dominating orientation. An additional oxygen plasma cleaning of the substrate allows to form single-domain epitaxial films. Under optimized conditions, these films remain epitaxial for a wide range of oxygen partial pressures ($1.4 \times 10^{-4}$-$3.4 \times 10^{-3}$ mbar) at a substrate temperature of 550°C. The largest grain size of approximately 100 nm and the best (0001) texture of ZnO are formed at oxygen partial pressure of $1 \times 10^{-3}$ mbar with a minimum FWHM of the XRD rocking curve of 0.366°. In this case, AFM shows surface morphology patterns characteristic for 2D growth. SE indicates the absence of grading of the optical constants across the film, and a significantly lower optical absorption compared to films grown without oxygen plasma pretreatment.

**Collaboration:** ¹Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Madrid, Spain

**Indium tin oxide thin film annealing by electric current**

As a new method of indium tin oxide (ITO) annealing in vacuum, direct electric current (DC) flow through the film is explored. ITO films of about 170 nm thickness were produced by reactive pulsed magnetron sputtering. During annealing at constant electric power, the film resistance, free electron density, and structure evolution were monitored *in-situ*. Compared to conventional isothermal annealing, the current annealing is more efficient with a noticeable reduction of the thermal budget and a decrease of the kinetic exponent of crystallization. Electrical inhomogeneities of the film, which produce locally overheated regions, are discussed as potential reason for the acceleration of the crystallization process. However, the DC annealing requires electrical contacts to the film. An advanced contactless method of annealing by microwave induced current has been developed which provides a fast amorphous-to-crystalline transformation of ITO films with a significant decrease of their resistivity.

**Nitrogen incorporation in carbon nitride films produced by direct and dual ion-beam sputtering**

Carbon and carbon nitride (CN$_x$) films were grown on Si(100) substrates by direct ion-beam sputtering (IBS) of a carbon target at different substrate temperatures (RT – 450°C) and Ar/N$_2$ sputtering gas mixtures. Additionally, the effect of concurrent nitrogen (N) ion assistance during the growth of CN$_x$ films by IBS was investigated. The samples were analyzed by ERDA and XANES. The ERDA results showed that significant nitrogen amount (up to 20 at.%) was incorporated in the films, without any other nitrogen source but the N$_2$-containing sputtering gas. The N atomic fraction in the films is proportional to the N$_2$ content in the sputtering beam and no saturation limit is reached under the present working conditions. The film areal density decreases at increasing growth temperature, with a correlation between the C
and N losses. The XANES results indicate that N atoms are efficiently incorporated into the carbon network and can be found in different bonding environments, such as pyridine-like, nitrile-like, graphite-like, and embedded N2 molecules. The contribution of molecular and pyridine-like nitrogen decreases when the temperature increases while the contribution of N in the nitrile-like configurations increases. The N ion assistance results in the significant increase of the N content in the film but it induces a further reduction of the deposited material. Additionally, the assisting ions inhibited the formation of the nitrile-like configurations while promoting N environments in graphite-like positions. The N incorporation and release mechanisms and dominance of a certain N chemical environment is influenced by the type of N precursors and the hyperthermal particle induced atomic displacements and bond breaking on the surface of the growing film.

**Collaboration:** 1Centro de Micro-Análisis de Materiales, Universidad Autónoma de Madrid, Spain, 2Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas, Madrid, Spain

**Growth of carbon and carbon nitride thin films by low-energy N2/Ar ion assisted evaporation of C60**

The growth of C and CNx films by evaporation of C60 fullerene and simultaneous low-energy (~150 eV) N/Ar ion bombardment has been investigated. The films have been grown at different ion to molecule arrival ratios \( \frac{I_{\text{ion}}}{I_{\text{Mol}}} \) (4 – 10) and substrate temperatures (RT – 300°C). The film areal density and composition has been obtained from ERDA, their thickness from spectroscopic ellipsometry, and their chemical bonding structure from Raman spectroscopy. Raman spectra of the films grown without ion assistance show similar features as the Raman spectrum of the C60 precursor powder. N or Ar ion assistance in the present energy range results in decomposition of C60 in the films independent of \( \frac{I_{\text{ion}}}{I_{\text{Mol}}} \). The N and Ar atomic ratios in the films (16 – 27 at.% for N and 2 – 4 at.% for Ar) are proportional to \( \frac{I_{\text{ion}}}{I_{\text{Mol}}} \) and no saturation limit has been obtained for the used experimental conditions. The amount of deposited material decreases with increasing \( \frac{I_{\text{ion}}}{I_{\text{Mol}}} \) for a given substrate temperature for both type of ions. Ion assistance also results in a densification of the films.

**Collaboration:** NanoMaterials Ltd., Israel

**Effect of a TiN buffer layer on the growth of NiTi sputtered thin films**

Shape Memory Alloy (SMA) NiTi thin films have attracted much interest as functional materials. However, there are still important issues unresolved like texture development and its control. Near-equiatomic NiTi films of ~ 800 nm were fabricated on SiO2/Si(100) substrates by co-sputtering from Ni/Ti and Ti targets in a process chamber installed in the HUBER goniometer at ROBL. In-situ XRD analysis during the growth of these films was applied to investigate the influence of a TiN buffer layer grown prior to the deposition of the NiTi films. TiN acts not only as a diffusion barrier, but may also induce different crystallographic orientations of the NiTi film on top. A (111) textured TiN layer of about 200 nm thickness induces the preferential growth of (110) planes of the NiTi B2 phase already from the beginning of the deposition. Using a thin non-textured TiN buffer layer \( (d < 80 \text{ nm}) \), the diffraction peak B2(110) also appears from the beginning but much less intense. In this case, the B2(211) was additionally detected with comparable intensity to the B2(110). These results confirm the possibility to launch a certain crystallographic orientation of NiTi thin films by a TiN buffer layer, which has a strong influence on the extent of the strain recovery.

**Collaboration:** 1CENIMAT, Campus da FCT/UNL, Monte de Caparica, Portugal
Surface structure and properties of ion implanted NiTi alloy

Shape memory and superelastic NiTi alloy is a promising material for biomedical applications, provided the release Ni ions into the biological environments can be sufficiently reduced. Oxygen plasma immersion ion implantation at an ion energy of 20 keV, an ion fluence of $10^{17} - 10^{18}$ cm$^{-2}$, and substrate temperatures below 250°C results in the formation of a transparent rutile TiO$_2$ surface layer with a Ni content down to below 1 at.%. Concurrently, the underlying alloy is enriched with Ni. Phases of Ni$_4$Ti$_3$ and Ni$_3$Ti are also found in addition to NiTi. The oxide layer thickness as well as the surface roughness are controlled by the balance of reactive ion-induced diffusion and ion sputtering. The nickel depleted TiO$_2$ layer serves as a barrier to corrosion and out-diffusion of Ni ions. Biocompatibility tests show a largely superior in vitro blood compatibility of the oxygen ion implanted NiTi surfaces compared to untreated materials.

Effect of ion energy on structure and composition of cathodic arc deposited alumina (Al$_2$O$_3$) thin films

The effect of energy supplied to the growing alumina film on the composition and structure has been investigated by varying substrate temperature and substrate bias potential. The constitution and composition were studied by XRD and ERDA, respectively. Increasing the substrate bias potential from $-50$ to $-100$ V caused the amorphous or weakly crystalline films to evolve into stoichiometric, crystalline films with a mixture of the $\alpha$- and $\gamma$-phase above 700°C, and $\gamma$-phase dominated films at temperatures as low as 200°C. All films had a grain size of < 10 nm. In order to correlate phase formation with synthesis conditions, the plasma chemistry and ion energy distributions were measured at synthesis conditions. These results indicate that for a substrate bias potential of $-50$ V ion energies in excess of 100 eV are attained, both from a high energy tail and the accelerated ions with a charge state > 1. These results are of importance for an increased understanding of the evolution of film composition and microstructure, also providing a pathway to $\gamma$-alumina growth at temperatures as low as 200°C.

Collaboration: 1Materials Chemistry, RWTH Aachen, Germany

Phase control of Al$_2$O$_3$ thin films grown at low temperatures

Alumina (Al$_2$O$_3$) thin films are widely used as wear-resistant or diffusion barrier coatings. Usually the hard and thermally stable $\alpha$-phase is required. Low-temperature growth (500°C) of $\alpha$-Al$_2$O$_3$ thin films by reactive magnetron sputtering was achieved for the first time. The films were grown onto Cr$_2$O$_3$ nucleation layers and the effects of the total and O$_2$ partial pressures were investigated. At 0.33 Pa total pressure and $\geq 16$ mPa O$_2$ partial pressure $\alpha$-Al$_2$O$_3$ films formed, while at lower O$_2$ pressure or higher total pressure (0.67 Pa) values only the $\alpha$-phase was detected in the films. Heavy-ion ERDA measurements reveal that all films were stoichiometric. These results showed that the phase content of the films could be controlled by controlling the energy of the depositing species. The effect of residual water vapour ($\sim 10^{-4}$ Pa) on the films was also studied, showing no change in phase content and no incorporated H (< 0.1 at.%). Overall, these results are of fundamental importance for the further development of low-temperature grown Al$_2$O$_3$ films.

Collaboration: 1Linköping University, Linköping, Sweden

Studies of compositional and structural changes in ZrO$_x$N$_y$ films depending on growth conditions

The presence of oxygen in transition metal nitrides allows the tailoring of film properties between those of metallic nitrides and the correspondent ionic
oxides. Changing the oxide/nitride ratio gives the possibility to tune the bandgap, bandwidth, crystallographic order and hence the properties of the films. The work focuses on the analysis of ZrO\textsubscript{x}N\textsubscript{y} thin films, the composition evolution with changing growth conditions and its relation to the structural and morphological properties of the films. The films were prepared by rf reactive magnetron sputtering, using different reactive gas flows. Composition and structure were measured combining IBA and XRD techniques. The depth profiles of nitrogen and oxygen have been obtained by ERDA. Results showed that the oxygen fraction in the films increases with gas flow, reaching a value of x ~ 0.33 for a reactive gas flow mixture of 6.25 sccm. During growth mixed zirconium nitride and oxide phases form. Furthermore, the deposition rate correlates with the oxygen content variations, showing a continuous decrease with reactive gas flow.

Collaboration: \textsuperscript{1}Nuclear and Technological Institute, Sacavem, Portugal; \textsuperscript{2}University of Minho, Guimaraes, Portugal

Efficient oxidation protection of $\gamma$-TiAl alloys by ion implantation of halogens

For the development of a commercially viable process for enhancing the high-temperature ($>700^\circ$C) oxidation resistance of $\gamma$-TiAl alloys, exploratory beamline co-implantation studies have been performed using F\textsuperscript{+} + B\textsuperscript{+}, F\textsuperscript{+} + C\textsuperscript{+}, F\textsuperscript{+} + N\textsuperscript{+}, F\textsuperscript{+} + Y\textsuperscript{+}, (SiF)\textsuperscript{+}, and Cl\textsuperscript{+} + Y\textsuperscript{+} ions with overlapping implantation profiles at a mean depth of 100 nm. Oxidation tests at 900$^\circ$C in synthetic air demonstrated a lowest mass gain after 100 h for (SiF)\textsuperscript{+} implant followed by F\textsuperscript{+} + B\textsuperscript{+}, F\textsuperscript{+} + C\textsuperscript{+} and F\textsuperscript{+} + N\textsuperscript{+} implants. Initial efforts using PIII of CI from an 80 \% Ar / 20 \% Cl plasma have focused on the optimization of the process. Highest oxidation resistance has been achieved with 106 pulses at a bias voltage of 30 kV, a frequency of 250 Hz, and an RF power of 350 W. Increasing the power to 1000 W leads to appreciable deterioration of the oxidation behavior. The optimized PIII of CI produces largely improved oxidation resistance similar to that achieved by beamline implantation of Cl. In order to ease practical handling, dichlormethane (CH\textsubscript{2}Cl\textsubscript{2}) has been used as an alternative precursor gas, with an even slightly increased oxidation resistance compared to the Ar/Cl processing. This may be explained by the combined effect of Cl and C as a microalloying element. The oxidation time for the CH\textsubscript{2}Cl\textsubscript{2}- treated samples has been extended to 1000 h, and excellent oxidation resistance has been retained throughout the test.

Collaboration: \textsuperscript{1}Karl-Winnacker-Institute of the DECHEMA e.V., Frankfurt/Main, Germany

Enhanced biocompatibility of human endothelial cells on ion-beam-treated polyurethane surfaces

To improve the biocompatibility of polyurethane (PUR) in blood-contacted devices, PUR surfaces were modified by ion irradiation using C, O, N, or Ar ions with energies of 0.3 – 50 keV and doses of $10^{13}$ – $10^{15}$ ions/cm\textsuperscript{2}. Adhesion, proliferation and cytotoxicity of human umbilical vein endothelial cells (HUVEC) were compared to unmodified control surfaces (uPUR). Ion irradiation strongly influences surface topography and free energy as demonstrated by AFM and contact angle measurement, respectively. The surface roughness is lowest at medium ion energies and increases at elevated ion dose. The largest contact angles result from medium ion energies. A triple immunostaining for actin cytoskeleton, vinculin (as a marker of focal contacts) and nuclei (DAPI), was employed for adhesion studies. The apoptosis rates were calculated by counting fragmented nuclei. WST-1 assay was used for analysis of cell proliferation. A strong improvement in endothelial cell adhesion and proliferation on ion implanted surfaces was
observed. Intensive cell spreading and most focal contacts were found on O- and N-implanted surfaces, followed by Ar-implanted, or N- and O-plasma treated implants. In contrast, C-implanted surfaces display low adhesion and a higher apoptosis rate. Ion energy has a stronger effect on cell numbers (24 h) and cell proliferation (5 d) than ion dose. 

Collaboration: 1 Institute of Anatomy, TU Dresden, Germany, 2 Techno-Coat Oberflächentechnik GmbH, Zittau, Germany

**Surface passivation of silicon solar cells by a-Si/Si₃N₄ dual layers**

Surface passivation of silicon by a dual structure consisting of a hydrogenated amorphous silicon (a-Si) thin film capped by a Si₃N₄ anti-reflection layer, both layers deposited by plasma enhanced chemical vapour deposition, was investigated. The results show that a synergetic effect on the surface passivation properties is obtained from such a dual structure. Moreover, the surface passivation can be significantly enhanced after a short anneal for temperatures up to about 500°C, whereas anneals at higher temperatures result in degradation of the passivation properties. From NRA of the as-deposited and annealed structures, the enhanced surface passivation experienced after annealing is indicated to be due to hydrogen release from the structure towards the Si substrate, possibly followed by a redistribution of hydrogen and subsequent passivation of Si dangling bonds in the sub-interface region.

Collaboration: 1 Renewable Energy Corp. AS, Høvik, Norway, 2 Center for Material Science and Nanotechnology, University of Oslo, Norway, 3 Section for Renewable Energy, Institute for Energy Technology, Kjeller, Norway

**Ohmic contacts on Si(001) by selenium modification of metal/semiconductor-interface**

The deposition of about one monolayer (ML) of Se onto Si(001) leads to the restoration of surface geometry and consequently to an electronic and chemical surface passivation. In particular, it is possible to realise metal-contacts with negative Schottky barriers on Se-passivated n-type Si(001). We studied the deposition of Se on n-type Si(001) after various surface preparation steps to find conditions for self-limited growth of only 1 ML. The depositions were performed in a MBE system in ultrahigh vacuum (UHV). Selenium was evaporated by using two different source materials: SnSe₂ and WSe₂. The surface retention of Se atoms, that means the remaining Se areal density and as well as that of contaminations were measured ex-situ by RBS with He ions. It could be shown that Se only sticks to “clean”, silicon terminated Si(001) surfaces, achieved by growing a Si buffer layer of 80 nm or by etching-off the native SiO₂ in UHV a chemical reaction of impinging Si at 700°C which reduces SiO₂ to volatile SiO. Due to the low binding energy of Se at Si the Se desorption during the exposition to atmosphere and later during the RBS measurement cannot be avoided and therefore samples had to be enhanced with a metallic cap layer that disables the Se loss. Using the compound SnSe₂ as source material a contamination of the Se coverage with Sn at the level of about 1 at.% was unavoidable. In the case of WSe₂ the W contamination in the passivation layer is below the RBS detection limit of <10¹¹ atoms/cm².

Collaboration: 1 TU Chemnitz, Germany 2 Forschungszentrum Jülich, Germany