**Thin Films**

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**Evolution of sp² networks with substrate temperature in amorphous carbon films: experiment and theory**

The evolution of sp² hybrids in amorphous carbon (a-C) films deposited at different substrate temperatures was studied experimentally and theoretically. The bonding structure of a-C prepared by filtered cathodic vacuum arc was assessed by the combination of visible Raman spectroscopy, x-ray absorption spectroscopy and spectroscopic ellipsometry. The experimental results show a transition from tetrahedral a-C (ta-C) to sp²-rich structures at ~250°C. The sp² hybrids are mainly arranged in small olefinic (chain-like) clusters and graphitic structures are only promoted for sp² fractions above 80%. Molecular-dynamics simulations of the growth process with a modified version of the Brenner potential reproduce the preferred pairing of sp² sites in ta-C as well as the pronounced formation of rings for sp² fractions > 80%. However, the theoretical results do not predict the dominance of sixfold rings in sp²-rich samples.

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**Relaxation kinetics in amorphous carbon films: an insight from atomic scale simulation**

Using molecular-dynamics techniques and a hydrocarbon potential of Brenner with an increased carbon-carbon interaction range, the kinetics of relaxation processes in tetrahedral amorphous carbon films (ta-C) with high sp³ fractions was studied. Annealing at a temperature of 1000 K reduces both film stress and energy exponentially with annealing time, satisfying a simple rate equation. The exponential dependency can be interpreted in terms of structural transformations in the amorphous carbon networks. The relaxation times for the energy and stress do not coincide, indicating that some atomic rearrangements in the networks may reduce their energy without changing the stress. The relaxation constant for energy was found to be in the range of 0.5 – 0.7 ns, which considerably exceeds an estimate of 10 ps for the thermalization stage of the subplantation model for ta-C film formation by energetic C ions.

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**Formation and evolution of sp² clusters in amorphous carbon networks as predicted by molecular dynamics annealing simulations**

A theoretical comparative study of clustering of sp²-bonded atoms in as-deposited and annealed tetrahedral amorphous carbon (ta-C) networks was performed. The “as-deposited ta-C films” were annealed in the temperature range of 600 – 1200 K, using molecular-dynamics. Size and type of the sp² clusters in the films were analyzed as a function of the annealing temperature as well as the model parameters for stress and temperature control. An essential finding of the study is that at a density less than 3.0 g/cm³ the structure of ta-C can become unstable with respect to formation of large sp² clusters.

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**On the synthesis of fullerene-like CNₓ by IBAD: role of film-forming species, ion bombardment and film growth rate**

Carbon nitride CNₓ (0 ≤ x ≤ 0.28) thin films, deposited by ion assisted sputtering (IAS) with various sputtering beam compositions at different temperatures and by electron beam evaporation of graphite with simultaneous low-energy nitrogen ion assistance (LE-IBAD), have been studied by the means of
infrared, Raman and X-ray near edge absorption spectroscopies, spectroscopic ellipsometry, ERDA and TEM. Nitrogen concentration in the films increases with the nitrogen content in the sputtering beam and decreases with temperature. The IAS film density variation with the composition presents two regimes: up to 150°C the density decreases with nitrogen content in the sputtering beam, while at temperatures above 150°C the density increases with nitrogen content. The promotion of the formation of pyridine-like and nitrile configurations are observed in the films prepared by IAS while nitrile groups are prevailing in the films prepared by LE-IBAD. Films grown at high growth rates (0.1 – 0.2 nm/s) by LE-IBAD are completely amorphous while the films grown at low growth rates (0.01 nm/s) by IAS can be characterized by small (∼ 1-2 nm) ordered straight and curved domains embedded in the amorphous matrix. The microstructure of the films is a consequence of several concurrent processes such as temperature induced ordering and growth of graphene sheets, the nitrogen induced defect formation at the edges of graphite clusters due to pyridine-like configurations, and the film growth rate. The results suggest that one of the principal roles of the assisting low energy ion bombardment is the promotion of the growth of graphene sheets provided that the film growth rate is not too large.

**Collaboration:** 1Department of Physics, Kyiv National Taras Shevchenko University, Kyiv Ukraine

**Ion-implantation induced phase transformation in carbon and boron nitride thin films**

The mechanisms behind energetic ion-impact induced stress reduction in ta-C and BN thin films have been investigated by real-time in-situ spectroscopic ellipsometry and ex-situ electron microscopy. Highly stressed carbon and boron nitride films were grown by filtered cathodic vacuum arc and RF magnetron sputtering, respectively, and subsequently implanted by 5 – 10 keV Ar ions. In both cases the films were observed to expand due to a reduction in the density of the ion modified layer. Electron microscopy of the carbon films showed that this reduction in density is associated with a conversion of diamond-like bonding to graphite-like bonding. In-situ stress measurements performed on the boron nitride films revealed a simultaneous reduction in stress with expansion of the material.

**Collaboration:** 1University of Sydney, School of Physics, Australia; 2RMIT University, School of Applied Sciences, Australia

**Investigations towards high-rate deposition of hard diamond-like carbon films**

Amorphous, hydrogenated carbon films (a-C:H) were prepared by PECVD (13.56 MHz rf-plasma) from the source gases methane and acetylene with the aim to enable high growth rates while keeping films with high hardness (25 ± 3 GPa). The films were characterized in terms of deposition rate, micro-hardness, hydrogen content and surface roughness. The NRA analysis of the films deposited at 200°C substrate temperature revealed an homogenous hydrogen content across the whole film thickness. The hydrogen concentration of films deposited at pressures from 2 Pa to 15 Pa was determined to 29 at.% for films deposited with the source gas methane and between 22 ÷ 32 at.% using acetylene plasma. The investigations confirm that the film hardness and the hydrogen content of the films are determined by the ratio between the flux of energetic CxHy ions and the flux of film forming neutrals.

**Collaboration:** 1Institut für Physik, Technische Universität Chemnitz
Hydrogen bonding and structural order in hydrogenated amorphous silicon prepared with hydrogen-diluted silane

The compositional and structural evolution of hydrogenated amorphous silicon (a-Si:H) films during PECVD with hydrogen-diluted silane has been studied. The total hydrogen concentration and its silicon-bonded fraction have been characterized by means of NRA and infrared (IR) spectroscopy, respectively. The content of molecular hydrogen is below the detection limits of the measurements. Hydrogen is uniformly distributed throughout the film thickness, and the IR absorption modes at 2000 cm⁻¹ (monohydrides) and 2100 cm⁻¹ (polyhydrides or clustered monohydrides) remain unaltered. For films deposited at a low substrate temperature of 150°C, Raman spectroscopy reveals an improved ordering of the amorphous network on the short and medium range scale at increasing film thickness. At an enhanced substrate temperature of 270°C, the tendency of structural improvement is seen only on the medium range scale.

Collaboration: ¹Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria; ²Physics Department, National Technical University, Athens, Greece

Limitations on ultra-thin multilayers: pulsed cathodic arc and computer simulation

Nanoscale metallic multilayers were deposited by pulsed double-cathodic arc deposition and examined by XTEM. The individual layer thickness was varied from a few to tens of angstroms. TRIDYN computer simulations were performed for a better understanding of the nanoscale deposition process. For higher ion fluences (> 10¹⁶ cm⁻²) and larger bilayer thicknesses (> 2 nm), the periodicity of the multilayers is satisfactory. However, the results of the simulations for lower ion fluences and smaller bilayer thicknesses reveal that the individual layers are intermixed and diffused. The experimental results are in good agreement with the simulations. In the present case the lower limit of the bilayer period is approx. 2 nm.

Collaboration: ¹Department of Advanced Materials Science and Engineering, Mokpo National University, Jeonnam, South Korea; ²National Institute of Advanced Industrial Science & Technology, Osaka, Japan

Texture development during growth of Ti₁₋ₓAlₓN thin films studied by in-situ x-ray diffraction

To improve the understanding of the relationship between deposition parameters, microstructure, and performance of Ti₁₋ₓAlₓN thin films in-situ XRD studies during the film growth were performed using the deposition chamber installed at ROBL. All films were deposited by reactive co-sputtering from Ti and Al targets; one series at constant x = 0.06 varying substrate temperature, bias voltage, and nitrogen partial pressure and thus growth rate. In another series, x was systematically varied from 0 to 0.73 while keeping all other parameters constant. Values of x < 0.15 and high deposition rates lead to a typical cross-over behavior between initial (002) and final (111) preferred orientation. Reducing the deposition rate leads to (002) preferred orientation practically independent of film thickness and substrate temperature. Yet, suppressing collisionally-induced atomic N on the sample surface by applying a positive bias voltage, recovers a (111) preferred orientation. Keeping the deposition rates low, (111) preferred orientation can also be induced by increasing x above 0.15, which in the presence of atomic N can be explained by its higher adatom mobility. Increasing x towards the AlN segregation threshold at x = 0.60 leads to extremely hard nanocomposite TiAlN/AlN, and pushing x further to 0.73 leads to highly stressed AlN with an a-axis off-plane texture.

Supported by DFG
Influence of aluminium on the growth of nickel disilicide on Si(001)

For an improved lattice matching between Si and nickel silicide the influence of aluminum incorporation on the growth of nickel disilicide layers was investigated. Thin films of 10 to 20 nm thickness with different atomic ratios of Ni and Al were co-deposited by magnetron sputtering and then annealed at temperatures between 500 and 900°C using RTA in nitrogen atmosphere. RBS/channeling, SEM, TEM, XRD, AES and sheet resistance measurements were performed to characterize the deposited films. The forming temperature of thin epitaxial nickel disilicide layers decreases from 750°C without Al to lower than 500°C at an atomic ratio of Ni : Al = 9 : 1. The interface roughness also decreases rapidly with a higher amount of Al. Annealing of pure Ni layers creates pyramidal shaped nickel disilicide islands, whereas at an atomic ratio of Ni : Al = 4 : 1 nearly smooth epitaxial nickel disilicide layers are grown, featuring a low level of misfit dislocations as indicated by the low $\chi_{\text{min}}$ value of 0.04 in the channeling spectra.

Collaboration: 1Institut für Physik, Technische Universität Chemnitz

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

For the development of an efficient, commercially viable process for enhancing the high-temperature (> 700°C) oxidation resistance of $\gamma$-TiAl alloys, the plasma immersion ion implantation (PIII) route has been further developed. The ion fluence per pulse has been determined for Cl implantation. Metal contamination, which was found to be associated with the long low voltage tail of the pulse, was efficiently suppressed by pulse shaping using a specially designed ferrite coil. Experiments to explore the sensitivity of $\gamma$-TiAl to various implantation temperatures (RT to 800°C) have been conducted using standard beam line implantation ($F^+$, 60 keV, $1\times10^{17}$ cm$^{-2}$). Optimized F implants produce markedly improved oxidation resistance even under harsh conditions of thermocyclic oxidation in a wet ambient. For implantation temperatures in the range of RT to 600°C, the degree of protection is sufficiently high and practically independent of temperature, but decreases dramatically at 800°C.

Collaboration: Karl-Winnacker Institut der DECHEMA e.V.

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Structure and properties of boron implanted Ti-4Al-1.5Mn

The influence of beam-line high dose boron implantation on the mechanical properties and corrosion behavior of near-alpha titanium alloy Ti-4Al-1.5Mn was investigated. Boron was implanted into Ti-alloy at 60 keV with fluences ranging from $1\times10^{17}$ cm$^{-2}$ to $5\times10^{18}$ cm$^{-2}$. The implantation results in the Gaussian boron distributions with maximum concentrations ranging from $\sim 10$ to $\sim 85$ at.%. XRD shows that for B fluences $\leq 5\times10^{17}$ cm$^{-2}$ (maximal B concentration $\sim 50$ at.%) only the TiB phase is formed, while by increasing the B fluence above $5\times10^{17}$ cm$^{-2}$ the formation of TiB$_2$ is observed. The hardness of the implanted layer increases with increasing fluence. For the highest fluence the hardness is $\sim 4.5$ times higher than that of unimplanted Ti-4Al-1.5Mn. Corrosion potential at room temperature of the implanted surfaces in aerated 1% NaCl solution is closer to the noble values in comparison to the unimplanted Ti-4Al-1.5Mn. In the passive corrosion region the B implanted surfaces are also more corrosion resistant. The improvement of the corrosion behavior is attributed to the implantation-induced formation of titanium borides.

Supported by DAAD

Collaboration: 1Lipets State Technical University, Lipetsk, Russia
Structural in-situ studies of Shape Memory Alloy (SMA) Ni-Ti thin films

In-situ XRD experiments allow to improve the knowledge of the structural development (time dependent crystal reorientation, metastable phase formation, strain evolution) during Ni-Ti SMA thin film growth by magnetron co-sputtering (Ni-Ti + Ti) and its correlation with the deposition parameters. Films were deposited on naturally oxidized Si(100) substrates at a temperature of approx. 470°C. During film growth the B2 phase started by stacking onto (200) planes. The (110) stacking started after a stress relaxation of the B2(200). There is a significant decrease of the peak intensity ratio of B2(110)/B2(200) when a substrate bias (- 45 V) is applied. Depending on the desired properties for functional devices, either B2 phase or additional Ni rich or Ti rich phases (precipitates) could be fabricated by varying the power of co-sputtering (Ni-Ti + Ti) for otherwise fixed deposition parameters.

Collaboration: ²CENIMAT, Campus da FCT/UNL, Monte de Caparica, Portugal

Structural evolution on thermal cycling in Ti-rich NiTi shape memory alloys (SMA)

Annealing of a Ti-rich Ni-Ti SMA has been followed by in-situ high temperature XRD at ROBL in order to register the texture as well as the microstrain/microstress evolution. The knowledge of the preferential orientation is an important information, as the anisotropic response of the material contributes to the success of the envisaged SMA application. Using high-temperature pole figures measurement, we obtain a relation between the change of preferential orientation and the structural evolution taking place during annealing. The most significant change of the microstrain and the coherency domain length of the sample takes place above 350°C where recrystallization occurs. Annealing at temperatures higher than 600°C gives rise to a significant decrease of the FWHM of the B2(110) peak (at 700°C its FWHM reaches a value smaller than 0.05°). This grain growth step of the structural evolution is accompanied by a significant increase of the Ti2Ni(511) peak, showing that a precipitation phenomenon has been induced. Two main components of austenite texture, \{110\}<110> and \{111\}<110>, i.e. \(\alpha\) fiber II texture, were found during annealing up to 400°C. At 500°C \{111\}<110> became the dominant texture component.

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