ANNEX III. STUDY OF THE FORMATION OF FERRO-, PARA-, AND SUPERPARA-MAGNETIC NANOCLUSTERS BY ION IMPLANTATION INTO SUITABLE INSULATING MATRICES

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III-1. Summaries of projects presented at the meeting

1.1. Study of the formation of ferro-, para-, and super-paramagnetic nanoclusters by ion implantation into suitable insulators

1.2. Study of the ferromagnetic nanocrystalline thin films and nanowires on glass substrates prepared by ion beam erosion.

1.3 Study of Fe-implanted Zincoxide crystals and nanowires

III-2. Study of the formation of ferro-, para-, and super-paramagnetic nanoclusters by ion implantation into suitable insulators

During ion beam deposition of compound thin films, energetic ion impact enhances processes like sub-surface cluster formation, diffusion, surface segregation and sputtering. The interplay between these processes may result in the formation of self-organized layered nanocomposite thin films, such as metal-carbon nanocomposites. Triggering of self-organization mechanisms by adjusting ion energy, ion fluence and ion species is investigated for ion beam deposited metal-carbon nanocomposite thin films, grown by simultaneous co-deposition of metal and carbon ions in the energy regime 50-150 eV. The implication of self-organization effects for plasma-based film deposition techniques will be discussed.

The simultaneous deposition of energetic species of two different elements (co-deposition) usually leads to homogeneously mixed films due to diffusion and rearrangement processes in subsurface and surface regions. If the involved elements are immiscible, a phase separation with precipitates of one element within the other may occur. The size and distribution of such clusters is strongly dependent on the deposition parameters such as ion energy, provided stoichiometry, and temperature. A number of studies have shown that this phase separation process can also result in the formation of a self-assembled multilayer structure. This structure appears in particular under certain deposition conditions for the codeposition of carbon and certain metals, including the carbide forming metals Fe and Ni. These studies reveal that alternating nanoscale layers of carbon and metal were obtained after codeposition of the respective energetic species, but with two different methods: mass selected ion beam deposition (MSIBD) and dc-reactive magnetron sputter deposition, respectively.
Here, we report on the experimental results of the multilayer formation for the carbide-forming system a-C:Ni by means of MSIBD. The aim was to test the onset of multilayer formation and the predicted variation of the layer period with the ion energy and the fluence ratio from a simple model describing the multilayer formation. The results for Ni are compared with results for the carbide-forming system a-C:Fe.

Nickel is a weak carbide forming metal, forming only metastable carbides. The nickel containing amorphous carbon system therefore should be a demixing system, which possible could form a layered structure using the right deposition parameters.

The films were prepared by Mass-Selected Ion Beam deposition (MSIBD). The source of the energetic ions is a penning ion gun feed with CO₂ and equipped with a pure nickel target. The ions were extracted with 30 kV from the source and decelerated in front of the substrate to the desired energy of 100 eV. The beam is mass-separated using a 90° sector magnet therefore only carbon and nickel contribute to film growth. The ion current on the substrate is time integrated and measure by a computer. The computer controls the sector magnet and switches between both ions in interval of $0.5 - 1 \times 10^{15}$ ions split up according to the desired fluence ratio carbon and nickel ions. The fluence ratio was varied between $r_f = [C]/[Ni] = 93/7$ and $50/50$. The films were grown on p-type silicon in $<100>$ orientation which is cleaned by acetone and 1 keV $^{40}$Ar⁻ sputtering. Prior to the a-C:Ni deposition the substrate is coated with a pure carbon layer to prevent the development of a carbon-silicon-nickel mixing layer.

The first sample was deposited with 100 eV ion energy and with a fluence ration of $r_f = 90/10 = 9$. The total metal sputtering coefficient calculated by $S_M = r_f \cdot S_{C\rightarrow M} + S_{M\rightarrow M}$ using SRIM yields $S_M = 3.4 > 1$. For this case, the qualitative film growth model predicts the formation of homogenously distribution of small clusters in an amorphous carbon matrix. This is exactly what is found by cross-section Transmission Electron Microscopy (X-TEM) and Energy Dispersive X-ray Spectroscopy (EDX). We find small (<3 nm) nickel clusters homogeneously distributed in a matrix consisting of amorphous carbon. Using Rutherford Backscattering Spectroscopy (RBS), we found – knowing the total amount of deposited nickel – that only a fraction of $f_{\text{surface}} = 0.66$ of the nickel ion-implanted into the films segregates to the films surface and is subject to sputtering. Due to the high total metal sputtering coefficient this nickel will not form stable cluster but will be sputtered off. With this results the model predicts the evolution of a layered structure for the a-C:Ni system with deposition energy of 100 eV at fluence ratios of $r_f < 2$. A film deposited with a fluence ratio of $r_f = 60/40 = 1.5 < 2$ ($S_M = 0.84$) shows a layered structure clearly visible in X-TEM and EDX with a layer periodicity of around 33(2) nm. The metal rich layers consist of nickel cluster while the metal deficient layers consist of very small nickel clusters in an amorphous carbon matrix. Another film deposited with a fluence ratio of $r_f = 70/30 = 2.3$ ($S_M = 1.12$) shows a weak layer structure with a periodicity of 18 – 24 nm. Assuming a little lower mean deposition energy due to the energy straggling of the ion source of 90 eV ($S_M = 0.99$) the layer growth is possible within the limits of the model. The model enables us in the case of a-C:Ni to predicted the structure of the growing film, i.e., either layered structure or homogeneously distributed clusters.

In another experiment, a-C:Ni films were grown by dc-magnetron sputtering using an argon:methane ratio of 3:2 and 5:2 and a substrate target distance of 5 cm without any bias or heating of the substrate. TEM analysis shows a pronounced layered structure, with a layer period of about 10 nm. A film grown with an argon:methane ratio of 1:2, i.e., a carbon rich plasma does not show any layered structure. Qualitatively this observation can also be interpreted with the model applied for MSIBDS grown films, however, the deposition
conditions in DC magnetron sputtering are difficult to quantify regarding fluxes and particle energies.

**III-3. Study of textured ferromagnetic nano-crystalline thin films and nanowires on glass substrates prepared by ion beam erosion**

Ripple patterns created by sputter erosion of iron thin films induce a correlated magnetic texture of the surface near region. We investigated the magnetic anisotropy of films deposited on glass substrates as a function of the residual film thickness and determined the thickness of the magnetically anisotropic layer as well as the magnitude of the magnetic anisotropy using MOKE and RBS measurements. Polycrystalline 140 nm thick Fe films were deposited at the room temperature glass substrates of $7 \times 10$ mm$^2$ using electron beam evaporation. X-ray diffraction of the as-deposited and sputter eroded films gave a width of FWHM = 0.8(1)$^\circ$ for the Fe(110) diffraction peak, corresponding to an average grain size of about 12-15 nm. Ripple patterns were created by sputter erosion with 5 keV Xe ions under grazing incidence of $80^\circ$ with respect to the surface normal. Since MOKE is a surface sensitive measurement with a sensitive depth of about 15 nm, MOKE analysis from the top side and bottom side of the films provides unambiguous information of the size of the textured layer and the magnitude of the anisotropy.

The as deposited samples exhibit an isotropic surface topography and an isotropic magnetic behaviour. After erosion with ion-fluences above $1 \times 10^{16}$ cm$^{-2}$ the formation of ripples with wavelengths between 30 nm and 80 nm oriented parallel to the ion beam direction is observed. A clear uniaxial anisotropy with magnitude of about 10-20% and easy axis along the ripple direction is seen for films with about $d = 50-70$ nm residual thickness. For $d < 60$ nm the magnetic anisotropy increases and approaches 60 -100% for small residual thickness, depending on the roughness of the substrate used. The measured MOKE anisotropies can be explained in the framework of a two-layer model by an about 12 nm thick surface layer with uniaxial magnetic anisotropy on top of the magnetically isotropy bulk. This layer thickness is comparable to the average grain size as determined by XRD. As long as the residual film thickness is less than $\approx 30$ nm, the magnetic anisotropy of the whole film is dominated by the anisotropy induced by the surface ripples. For increasing film thickness, the underlying isotropic film partially suppresses the anisotropy of the top layer down to a fraction of 25%. The Fe films on glass exhibit a weaker anisotropy, only 65% compared to Fe on Si, which is assumed to be due to the higher roughness of the glass substrate. Our results indicate that the magnitude of the magnetic anisotropy depends only weakly on the values of the ripple wavelength and amplitude, however, the variation in wavelength and ripple amplitude in our studies was limited to about 30 – 120 nm and less than about 5 nm, respectively. All sputter experiments were done at room temperature. It is well known that ripple patterns depend on the substrate temperature via surface diffusion processes. Higher temperatures give rise to larger ripple wavelengths and eventually smoother surfaces. Thus, the substrate temperature may have an influence on the magnetic anisotropy of ferromagnetic films. Further systematic studies regarding these aspects may be done in the future.

We have also shown that films with very thin residual thickness separate into individual nanowires or nano-rods due to the ripple structure. Thus, ion beam erosion with gracing incident ion beams allow to fabricate ferromagnetic nano-rods and nano-wires with pronounced uniaxial magnetic anisotropy.
Room temperature ferromagnetism has been proposed for Transitions metal (TM) doped ZnO, and therefore ZnO:TM is of high potential for spintronic applications. Additionally, TM-doped semiconductors show optical active and sharp intra-3d-transition with long life-times. Such intra-shell transitions are usually forbidden, but due to the incorporation into a suitable matrix the crystal field splitting leads to long-life partly allowed transitions.

ZnO nanowires were grown by vapor liquid solid (VLS) growth mechanism, where silicon substrates covered with a 4 nm thick Au film and pure ZnO powder were placed in a horizontal tube furnace and heated up to 1350°C. An argon gas flux of 50 sccm transports the evaporated ZnO to the substrates, which were placed in a temperature zone of about 1100°C. The pressure was adjusted to about 100 mbar during the whole growth process. The as-deposited nanowires are typically up to 100 µm long and between 40 and 500 nm in diameter, as determined by scanning electron microscopy (SEM).

Fe ions were implanted into VLS-grown ZnO nanowires and ZnO single crystals (CrysTec GmbH, Berlin) with a box like profile and different fluences to obtain transition metal concentrations of 1, 2 and 4 at.%. The implanted ZnO samples were annealed at 700°C for 30min in air. During the ion implantation of Fe and annealing no secondary phases or out diffusion of Fe was observed in the ZnO nanowires or crystals, which was confirmed with transmission electron microscope. Due to the sputtering during the ion implantation process the surface roughness of the nanowires increases and is visible in TEM images. The successful implantation of Fe was confirmed with energy dispersive X-ray and energy electron loss spectroscopy which show the corresponding Fe singles. RAMAN measurements show an increasing intensity of the disordering band around the A₁(LO) phonon vibration with increasing Fe concentration. In comparison to Mn implanted ZnO no additional elemental specific local vibration mode was found by RAMAN spectroscopy. Cathodoluminescence and photoluminescence studies show a sharp and intense intra-3D luminescence of Fe³⁺ in ZnO in the red/near-infra-red luminescence region between 1,70 and 1,78 eV. The intensity of the intra-3D luminescence of the Fe implanted ZnO is a half magnitude lower than the maximum peak intensity of the entire luminescence, which is located in the green luminescence band. Especially the structured form of the green luminescence band is consequence of the ion implantation process and is also visible after ion implantation of other transition metals into ZnO. Intra-3D luminescence decreases with increasing Fe concentration in the ZnO single crystals compared to the ultra violet luminescence. The magnetism of the Fe implanted ZnO single crystals was characterised with MOKE and shows a weak paramagnetic or ferromagnetic signal at room temperature for the
2 at.% and 4 at.% doped samples, whereby the 1 at.% Fe doped ZnO single crystal reveal only diamagnetic properties. Mössbauer measurements before annealing reveal the appearance of Fe in the $3^+$ and $2^+$ charge state which should reordered during the annealing and principally the Fe$^{3+}$ charge state should remain in the crystal.