Thin films for neutron optics

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ABSTRACT

Thin film multilayers play a crucial role for the efficient transport of neutrons from the source to the experiments at the Swiss Neutron Spallation source SINQ. In order to develop and optimise the neutron optical components a magnetron sputtering facility has been installed at PSI aimed at the deposition of thin films covering large substrate areas. Initial uniformity tests are very encouraging showing thickness variations of only 1% for 5 nm layers over an area of 500x400 mm².

A detailed study of the structure and stability of Ni/Ti multilayers in relation to the deposition conditions is underway and results from analysis using TEM, neutron and X-ray diffraction and reflection are presented. The results point towards the use of alloyed materials and reactive sputtering to sharpen and stabilize the interface between Ni and Ti.

1. INTRODUCTION

Artificial multilayers play an ever increasing role¹ in optical components for neutron beam research, where elements such as monochromators, neutron guides, filters and polarizers are in common use. The optical elements are based on bilayer structures with high scattering contrast between individual layers. Increasing demands on the performance of these optical elements lead to stringent requirements on the film and multilayer structure. Essentially very thin uniform films with minimal interfacial roughness and inter-diffusion over a large number of periods are required and accurate film characterisation and precise control of the deposition process are essential for the fabrication of well defined structures².

For non-polarizing applications, bilayers comprising Ni, which has a high positive scattering length density and Ti, which has a negative scattering length density have been commonly used due to their large scattering contrast. However, these two materials in their pure form do not constitute an ideal pair with respect to the stringent requirements on the film structure^{3,4}. Both materials form large-grained crystalline films leading to large interfacial roughness and poor neutron reflectivity. Furthermore the inter-diffusion of Ni and Ti is significant. Improved reflectivity was obtained when Ti was deposited as an amorphous layer³ and when the grain size of Ni was reduced, leading to the proposition that an optimised neutron multilayer would be composed of amorphous layers, since ideally epitaxial layers are ruled out

by size requirements.

During the course of progressing towards the conception of an optimised neutron multilayer, preliminary experiments demonstrate that the admixture of certain impurities to both the Ni and the Ti layers leads to better performances. By choosing substances whose neutron scattering length have the same sign as the layer material and are preferably large, it is possible to achieve higher scattering length densities. Carbon has a high positive scattering length and turns out to be a good candidate for the amorphization and the enhancement of the neutron scattering length density in Ni⁵. Similarly, since hydrogen has a negative scattering length for neutrons and is readily taken up by Ti⁶, the scattering length density of the Ti layers can be made more negative by appropriate loading with hydrogen. Furthermore, the admixture of impurities into the layer materials can reduce the interfacial diffusion.

In this paper we present experimental results obtained from NiC_x/TiH_y films produced by DC magnetron sputtering. In particular the structure of Ni layers with increasing C content and of Ti layers with increasing hydrogen content have been systematically studied by X-ray diffraction (XRD), neutron reflection (NR) and transmission electron microscopy (TEM).

2. EXPERIMENTAL

Film deposition was carried out using an in-line, DC magnetron sputtering facility recently installed at the Paul Scherrer Institute (PSI). Substrates, with maximum dimensions of 500x400 mm², were placed on a carrier, which is transported below three large cathodes with maximum target dimensions of 488x87 mm². The base pressure of the system was 2×10^{-7} mbar. A mass spectrometer allowed to analyze gaseous impurities in the sputtering gas down to levels of 1 ppb. Special attention was paid to the design and installation of the facility to achieve good uniformity of film thickness over the whole substrate area, which leads to thickness variations of better than $\pm 1\%$.

For the present study various samples consisting of Ni/Ti, NiC_x/Ti and Ni/TiH_y multilayers, including different NiC_x/TiH_y neutron supermirrors, as well as NiC_x and TiH_y monolayers were deposited on float-glass and on crystalline Si substrates. The coatings on Si substrates were used for XRD and TEM investigations, whereas glass substrates were used for neutron reflectivity measurements, since these are the substrates used for most of the neutron optical applications. The monolayer thicknesses were 5 nm or 100 nm and the multilayers consisted of 20 bilayers with bilayer thickness $d = d_{\text{Ti}} + d_{\text{Ni}}$ varying between 4 and 12 nm, which allows the study under conditions of typical neutron optical applications. Sputtering target powers were varied up to 12 W/cm² with sputter gas pressures between 2×10^{-3} mbar and 5×10^{-3} mbar of argon. No substrate heating or cooling was used in either case, since preliminary measurements indicated that heating of the substrates does not exceed a critical value during the deposition.

Various carbon concentrations were obtained by gluing carbon disks with a diameter of 5 mm and a thickness of 1 mm onto a pure Ni target. Awaiting analysis of the final film composition by appropriate techniques the concentration of C in Ni has been estimated from the fraction of the erosion area covered

by C and from the angle of total reflection of neutrons. Accordingly, 1 carbon disk corresponds approximately to a carbon concentration of 0.32 %. Hydrogen was introduced into the argon sputtering gas to produce the TiH_x films.

The films were characterized mainly by XRD and NR. The diffraction pattern near grazing incidence is sensitive to the properties of the interfaces and on the multilayer superstructure while at high angles information on the crystalline structure of individual layers is obtained. The two sets of information are complementary. The X-ray measurements were made in a $\theta/2\theta$ mode using $\text{CuK}\alpha$ radiation (0.15418 nm) on a Siemens D500 diffractometer. Similarly the neutron measurements were made using a conventional double axis diffractometer at the reactor Saphir at PSI and a well collimated ($\delta\theta=0.007^\circ$) beam with a wavelength of 0.2328 nm.

NR was used mainly to study supermirror reflectivity profiles and the transmission functions of micro-guides. Such micro-guides are essentially miniaturised neutron guides composed of two (coated) glass plates separated by a small distance in the range 0.1 to 0.5 mm. With this set up it is possible to simulate a real neutron guide with a length in the range from 20 m to 90 m. Due to the small separation between the plates, neutrons incident below the critical angle of the coating will undergo several reflections in the micro-guide thus allowing the reflectivity to be measured more precisely than by a single reflection.

Additionally, we have investigated some selected multilayers using TEM which were carried out at EPF Lausanne using a Philips EM 430 electron microscope with a maximum resolution of 0.2 nm in the high resolution mode. Samples were prepared by conventional cross-section techniques. Final thinning was done by Ar ion milling at 5 kV at an angle of incidence of 18 degrees with respect to the specimen surface. The specimen was rotated about the surface normal with a variable velocity to ensure uniform thinning. Furthermore, specimens were cooled by liquid N_2 during milling to avoid possible structural damage.

3. RESULTS

The high-angle diffraction patterns from monolayers of pure materials show strong Ni (111) and Ti (002) reflections confirming the crystallinity and preferred orientation found previously³. There is evidence from electron diffraction that the Ni layers remain crystalline but lose the preferred orientation for film thicknesses

Figure 1 XRD pattern of multilayers consisting of 20 bilayers of NiC_x/Ti with $d=10$ nm.

greater than ~ 10 nm. Under conditions where significant inter-diffusion of the layers is observed (mostly TEM measurements) the Ni and Ti Bragg peaks are shifted presumably due to extended mixing.

In Fig. 1 we present high angle X-ray data showing the change in structure of Ni layers with $d_{\text{Ni}}=5$ nm in a multilayer having $d=10$ nm as the C content is increased. At low C contents the diffraction pattern is dominated by the Ni (111) peak as in the pure layers. The peak between the Ni (111) and the Ti (002) peaks may be due to an interference effect between superlattice and Bragg peaks or due to Ti_2Ni (511, 333) peaks from Ni and Ti intermixing at the interfaces. As the C content is increased the intensity of the Ni (111) peak is reduced. The intensity reduction of the Ni peak may be due to an amorphization process, since no intensity gain for other reflections was observed.

For larger Ni layer thicknesses, $d_{\text{Ni}} \approx 100$ nm, the Ni(111) intensity reduction is most likely due to a reorientation of the grains as evidenced by XRD from 100 nm monolayers shown in Fig. 2. The decrease in the Ni (111) peak intensity with concomitant broadening is accompanied by an increase in the Ni (200) peak intensity. Furthermore, the peak positions are shifted to lower scattering angles with increasing carbon concentration, which is an indication for a lattice dilatation. The observed broadening of the peaks gives evidence for a reduction of the grain size. Even at a high C content crystalline structure is still observed but clearly the preferred orientation has been altered.

Figure 2 XRD pattern of NiC_x monolayers with a thickness of 100 nm.

Figure 3 XRD pattern of multilayers consisting of 20 bilayers of NiC_x/Ti with $d_{\text{Ti}}=2.5$ nm and $d_{\text{Ni}} \leq 2.5$ nm.

The change in texture can be explained as follows: The deposition of pure Ni results in a closed packed arrangement of the Ni atoms in surface-parallel planes, giving rise to a (111) orientation along the growth direction of the Ni layers. With the addition of carbon to Ni a face centred arrangement of the Ni atoms in surface-parallel planes is preferred in order to facilitate the inclusion of carbon in the gaps formed by the Ni atoms. Presumably for larger layer thicknesses, this leads to a preferred orientation along the (200) axis for the carbonized Ni layers.

In Fig. 3 we present XRD results from NiC_x/Ti multilayers with a nominal period of 5 nm as a function of the carbon content of the Ni layer. Apart from the increasing number of C disks on the Ni target, the sputtering conditions were identical for all the samples shown in Fig. 3, thus due to the lower sputtering efficiency of C compared to Ni, the resulting NiC_x layer thicknesses decrease systematically with increasing C content as indicated. The observed modulations in the diffraction profiles do not seem to correspond exactly to known alloy structures that may arise from intermixing at the interfaces. On the other hand it is plausible that such modulations may arise from coherence effects between thin highly crystalline films. Nevertheless it is clear from Fig. 3 that the crystallinity of the Ni layers is drastically reduced as the C content is increased to such an extent that no diffraction peaks can be observed for $x=c_4$.

In Fig. 4 we compare X-ray diffraction patterns of Ni/TiH_y multilayers (20 bilayers) with $d=10$ nm for various H contents. $y=c_4$ correspond to a content of 50% H_2 in the Ar sputtering gas. Without H_2 the pattern is as usual dominated by the Ni (111) and the Ti (002) peak, as already described. With the

Figure 4 XRD pattern of multilayers consisting of 20 bilayers of Ni/TiH_y with $d=10$ nm.

Figure 5 Low-angle XRD pattern of multilayers consisting of 20 bilayers of Ni/TiH_y with $d_{\text{Ni}}=5$ nm and $d_{\text{Ti}} \leq 5$ nm.

admixture of hydrogen in the Ti layer, pure Ti is progressively replaced by TiH_2 , as evidenced by the absence of all Ti peaks accompanied by the observation of various intense TiH_2 reflections e.g. (111) in Fig. 4. Furthermore, we observed for the present multilayer period a reduction of the Ni (111) peak with increasing hydrogen content. Presumably, the texture of the Ni layers is reduced by the presence of TiH_2 , since the (111) d spacing of TiH_2 is much larger than that of Ti (002) or Ni (111).

Fig. 5 shows the same section of the diffraction pattern as Fig. 4, but now with Ni/TiH_y multilayers with $d_{\text{Ni}}=5$ nm and a variable TiH_y thickness in the range from 5 nm for $y=0$ to 1.8 nm for $y=c_4$ (50% H_2 in the Ar sputtering gas). For thinner TiH_y layers (and increasing hydrogen content) regular modulations in the diffraction pattern appear concomitant with a decrease in the TiH_2 (111) peak intensity and an increase (and splitting) of the Ni (111) peak intensity. Such observations may be explained by coherence effects between individual crystalline layers which become apparent as the TiH_2 layer become very thin with discrete layer thickness. Simulations of the XRD patterns from the measured thicknesses for $y=c_4$ do indeed confirm the absence of the bulk TiH_2 peak and the observed splitting of the Ni (111) peak.

In Fig. 6 and Fig. 7 we compare the results of low angle X-ray measurements of the $\text{NiC}_x/\text{TiH}_y$ multilayers (20 bilayers, $d=10$ nm) for various concentrations of H (Fig. 6) and C (Fig. 7) to the Ni and the Ti layers. The diffraction patterns show superlattice peaks indicating a well defined composition modulation in the growing direction of the multilayers. The diffraction pattern of a perfect superlattice

Figure 6 Low-angle XRD pattern of multilayers consisting of 20 bilayers of Ni/TiH_y with $d_{\text{Ni}}=5$ nm and $d_{\text{Ti}} \leq 5$ nm.

Figure 7 Low-angle XRD pattern of multilayers consisting of 20 bilayers of NiC_x/Ti with $d_{\text{Ti}}=5$ nm and $d_{\text{Ni}} \leq 5$ nm.

with a precise composition-modulation wavelength may have superlattice peaks in the growth direction at scattering vectors Q that are a multiple of $2\pi/d$. Due to the lower sputtering rate for increasing C as well as increasing H content the thickness of the layers decreases, which leads to a shift of the observed superlattice peaks towards higher scattering angles. From Fig. 6 it is obvious, that at a H content $y=c_2$, which corresponds to a concentration of 14 % hydrogen in the Ar sputtering gas, superlattice peaks up to the 11th order are observed. At higher H content superlattice peaks are visible up to a scattering angle

of 11 degrees. The optimal H content seems to be in this upper range of concentrations, since a maximum number of superlattice peaks up to a maximum scattering angle is observed in these cases. The quality of the multilayer is therefore improved by addition of H , most likely due to reduced inter-diffusion. The influence of C in the Ni layer on the quality of the composition modulation is also clearly shown in Fig. 7. As we previously demonstrated, the addition of C in the Ni layer causes amorphization processes and less texture, which results in a reduction of the interface roughness. The observation of superlattice peaks up to the 10th order in Fig. 7, is in agreement with this assumption. At a C content $x=c_4$ corresponding to 32 carbon disks on the Ni target, we observe better defined superlattice peaks but only up to the 7th order, indicating a lower C content to be optimal.

Figure 8 Bright field TEM micrograph of a multilayer consisting of 20 bilayers of Ni/TiH_y with $d=5$ nm.

Simulation of the data is in progress to quantify these results and to determine optimal concentrations of H and C.

In order to complement the XRD and NR experiments, TEM was used to study the morphology and microstructure of selected multilayers. We present here the TEM results for a multilayer consisting of 20 Ni/TiH_y bilayers with $d=5$ nm, deposited using 7% hydrogen in the Ar sputtering gas on a crystalline [111] oriented Si substrate. Fig. 8 shows a bright field TEM image of the above sample in transverse section with a electron beam incidence along the [110] direction of the Si substrate. The Ni layers appear in a dark contrast and the Ti layers in a bright contrast. The image reveals that the individual layers are planar over the whole multilayer stack. A high resolution electron microscopy (HREM) micrograph of the same multilayer is shown in Fig. 9. The crystallinity

Figure 9 Bright field HREM micrograph of a multilayer consisting of 20 bilayers of Ni/TiH_y with $d=5$ nm.

as well as the [111] texture of the Ni layer is clearly observed. The contrast variation in the Ni layers is due to different small angular tilts (of the order of 1 degree) of the Ni [111] crystallites away from the substrate surface normal. The Ti layers show an amorphous structure with some crystalline regions. Furthermore, the interfaces are only in certain regions well defined. Inter-diffusion between the Ni and the Ti layers as well as roughness on the scale of 2 to 3 nm is observed. Because the specimen is thinner

Figure 10 Electron diffraction pattern of a multilayer consisting of 20 bilayers of Ni/TiH_y with a repeat distance of 5 nm.

beam are superlattice peaks. TEM measurements on carbonized Ni layers and for larger H concentrations in the Ti layers are in progress.

Finally, we present in Fig. 11 a neutron transmission profile of a neutron micro guide made with a supermirror coating, consisting of 35 NiC_x/TiH_y bilayers and a covering layer of 200 nm pure Ni. The multilayer was deposited with 32 C disks on the Ni target and with 7% H₂ in the Ar sputtering gas. The

at the top, the otherwise darker Ni layer has become more transparent to electrons.

More evidence for the crystallinity of the Ni layers and the TiH_y layers of the same multilayer is shown in the electron diffraction pattern of Fig. 10. 7% H₂ in the sputtering gas is not sufficient for a complete formation of TiH₂, as this is observed for higher H content, we expect to have a mixture of pure Ti and various Ti hydrides. In this diffraction pattern, the Ni (111) and the Si (111) peaks are clearly shown. The Ti and TiH_y cannot be resolved separately, however they are shown between the Ni (111) and the Si (111) peaks, corresponding to typical d-spacings in the range of 0.22 nm to 0.26 nm. Various Ni_xTi_y may also be observed close to the Ni (111) reflections. The small strips located at the upper and at the lower border of the transmitted

Figure 11 Transmission profile for a microguide with a supermirror coating consisting of 35 $\text{NiC}_x/\text{TiH}_y$ bilayers and a 200 nm pure Ni cover layer.

density. Thus the reflectivity profile would be expected to show a dip just at the critical angle corresponding to bulk Ni as observed in Fig. 11. The reduced density is also confirmed by the observed lattice dilatation of approximately 3% in HREM and XRD measurements. The results of the refinement of the measured transmission profile of the neutron microguide are summarized in table 1. The apparent slope of the reflectivity profile in the region of total reflection of the pure Ni layer as well as other asymmetries result from geometrical asymmetries of the microguide set up. The study of supermirrors with different hydrogen and carbon contents is in progress.

layer thickness sequence for the supermirror was calculated with an algorithm developed by J. Hayter and H. Mook⁷. The transmission profile shows essentially two different regions. One region were the neutrons are nearly totally reflected by the pure Ni covering layer and the region for supermirror reflections. Since the transmitted neutron intensity is proportional to R^n where R is the reflectivity and n the number of reflections in the micro guide, the microguide set-up represents an ideal method for the precise determination of the reflectivities. The supermirror sequence was designed to diffract neutrons with grazing incidence between one and two times the critical angle of pure bulk nickel. In fact our observations on pure Ni layers shows that the film density of Ni is some 10% lower than the bulk

Table 1. Supermirror Specification

Number of Bilayers	35
Covering Layer	pure Ni 200 nm
Substrate	float glass
Reflectivity (Ni)	99.0(2) %
Reflectivity (SM)	90.0(2) %
m	2.06(5)

Critical cutoff: m times the critical angle of bulk Ni

4. CONCLUSIONS

Addition of carbon to the Ni layers leads to both, a reorientation of the crystal grains and a reduction of the grain size. This leads to a reduction of the interface roughness as already observed². Inter-diffusion can be suppressed by both, carbonization of the Ni layers as well as hydrogenation of the Ti layers. However, hydrogenation is more effective. The morphology of the layers depends also on the layer thickness. Coherence effects were observed for layer thicknesses below 4 nm, resulting in the appearance of superlattice diffraction peaks in high angle XRD patterns. For other multilayer systems showing these effects see for example Ref. 8. Coherent interfaces between the NiC_x and TiH_y layers and reduced structural size mismatch, due to strains between the layers, presumably causes this effect, when at least one of the layer thicknesses does not exceed 4 nm. The amelioration of the individual layer structure

enables the production of multilayers with improved neutron optical performance.

5. ACKNOWLEDGMENT

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6. REFERENCES

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