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The Effect of Thickness and Deposition Angle on Structural, Chemical and Magnetic Properties of Nickel Slanted Columns

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Abstract:
In this work, the influence of different deposition angles on the structural, chemical and magnetic properties of nickel (Ni) thin films was investigated. Nickel samples were deposited by glancing angle deposition technique at two different angles, 65^o and 85^o. Characterization of the thin films was carried out by scanning electron microscopy, X-ray photoelectron spectroscopy and magneto-optical Kerr effect microscopy. Structural analysis was found that the changes in the deposition angle have a great influence on the porosity of the film as well as on the amount of the present nickel oxide (NiO) in the samples. On the other hand, we have also found that different deposition angle changes the magnetic response of nickel film. The coercivity of the samples deposited at the angle of 85^o is significantly higher compared to the samples deposited at lower angle which could be correlated with the higher porosity and the amount of NiO in the thin films.
Keywords*: Nickel; Nanostructures; Porosity; Magnetic properties; Coercivity.*

1. Introduction

Nickel is a promising ferromagnetic transition metal which can be used in the form of thin films for the fabrication of solar absorbers [1] and microelectronic devices [2], in magnetic resonance imaging [3-5], ferrofluid technology, nanotechnology, by virtue of its characteristic properties such as high Curie temperature [6], good thermal conductivity [7], thermal stability [8] and corrosion resistance [9], low electrical resistivity [10], etc. Nickel thin films could be also used as the components of multilayer systems such as high-density recording media, magnetic sensors, biosystems and electromechanical systems, where the design of thin films is very important for device performance improvements [11]. Physical and chemical properties of Ni films are strongly dependent on the deposition technique, deposition parameters, as well as its thickness and porosity [12-14]. It is interesting to mention that the magnetization of the nickel thin films on insulator substrate is greatly influenced by the thickness variation [15], as well as by their morphology, structure and composition [16]. Also, Ni thin films deposited at oblique angle exhibit a magnetic anisotropy with an easy axis parallel to the incidence plane [17].

Ni films can be deposited by various methods such as chemical vapour deposition, atomic layer deposition, sputtering, thermal evaporation, pulsed laser deposition, electroplating, sol-gel method [18-25], etc. Among these techniques, physical vapour deposition, precisely glancing angle deposition (GLAD), still remains the most widely used process for obtaining nanostructured thin films. In this method the material is deposited at the certain angle, with respect to the substrate normal [26]. During the deposition process, the

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formed nuclei and islands grow preferentially at the substrate surface, leading to the appearance of the shadowing effect, which is the most important property of GLAD technique. As the deposition continues, the shadowing effect is enhanced and promotes the formation of columnar structures [11]. In this way, glancing angle deposition enables the formation of thin films that are extremely porous with high specific surface area [3].

In this work, we present the detailed experimental study of structural, chemical and magnetic properties of nanostructured nickel thin films consisting of slanted columns. Ni samples were deposited at the angles of 65° and 85° to the different thicknesses, so the influence of the deposition angle was analyzed as well. According to the obtained results it can be seen that the variations of magnetic properties could be directly correlated to the observed changes in structural and chemical parameters.

2. Materials and Experimental Procedures

Nanostructured Ni (Onyx-Met, 99.98 % purity) thin films were obtained using glancing angle deposition method onto glass substrates (Thermo Scientific, Menzel-Glaser). Prior to deposition the substrates were prepared by standard procedure, rinsed in ethanol, distilled and deionized water. The deposition was performed under different deposition angles to the different thicknesses. The films were growth under 65^o and 85^o deposition angles with deposition rate of 3.0 nm/min and 5.6 nm/min, respectively. During deposition the substrate position was fixed. In the case of the samples deposited at the angle of 65^o the thicknesses were 50 nm, 90 nm, 120 nm, 160 nm and 200nm, while for the angle of 85° the thicknesses were 60 nm, 80 nm, 120 nm, 160 nm and 200 nm.

Morphological studies of the deposited Ni samples were done in cross-sectional view using scanning electron microscope (SEM, Mira XMU TESCAN), at acceleration voltage of 20 kV. Chemical analysis of the samples was carried out using X-ray photoelectron spectroscopy (XPS, SPECS System with XP50M X-ray source and PHOIBOS 100/150 analyzer). The measurements were performed with a monochromatic Al Kα X-ray source, while e-flood gun was used to prevent sample charging. Surface impurities were removed by sputtering with 5 keV argon ions. Magneto-optical Kerr effect microscope (MOKE, Evico Magnetics GmbH) was employed for the investigation of the magnetic properties of deposited thin films, in the range of the magnetic field from -1500 Oe to 1500 Oe. The hysteresis loops were measured as a function of in-plane azimuthal angle (φ) from 0° to 360° with 20^o increment.

3. Results and Discussion

The structure of nickel thin films deposited at the angles of 65^o and 85^o was analyzed using SEM. Fig. 1 shows the micrographs in the cross-sectional view for the samples deposited at the angles of 65^o (Fig. 1a) and 85^o (Fig. 1b) with the thickness of 200 nm. The micrographs show that the nickel films have a slanted columnar structure with clearly visible uniformly arranged columns which extend from the substrate to the surface. Another important observation is high porosity of the films which is expected due to shadowing effect mechanism during GLAD deposition. It has been noticed that Ni films deposited at the angle of 85^o are more porous, compared to the samples deposited at the lower angle, which is expected due to the more noticeable shadowing effect at higher deposition angles [11,27].

Using SEM micrographs the diameter of the columns was measured and it was found that its value increases with thickness from 18 nm to 31 nm, for the samples deposited at the angle of 65^o. Similar trend, with slightly higher values, was observed for the samples deposited at higher angle, where the diameter of the columns increases from 23 nm to 45 nm.

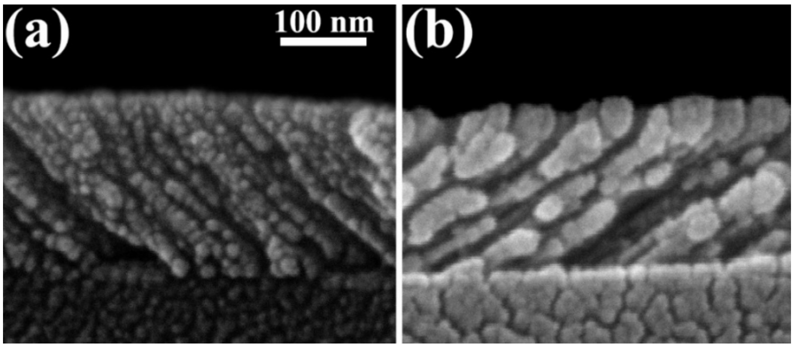

Fig. 1. SEM cross-sectional micrographs of Ni slanted columns thicknesses of 200 nm, deposited at the angles of: (a) 65^o and (b) 85^o.

Additionally, from the SEM images, the inclination angle of the columns was measured and compared with theoretically predicted values. According to the literature, the inclination angle is estimated using equation [11]:

$$\beta = \alpha - \arcsin\left(\frac{1-\cos\alpha}{2}\right) \qquad (1)$$

where α represents the deposition angle. For the samples deposited at the angle of 65^o, the measured inclination angle is in the range from 47^o to 48^o and these values are in good agreement with the calculated one of 48^o. Similarly, the angles of the slanted columns were measured for the samples deposited at the angle of 85^o and it was found that the values are between 57^o and 58^o, which are very close to the calculated value of 58^o.

XPS measurements were accomplished for determining elemental composition of the samples, as well as for the identification of the chemical bonds. The analysis reveals that the Ni films consist mainly of Ni, and small amounts of oxygen and carbon impurities. For both series of the deposited samples the nickel content is in the range of 90.0 at.% to 93.1 at.%, while the proportions of oxygen and carbon are from 4.2 at.% to 7.0 at.% and 2.6 at.% to 3.0 at.%, respectively. Detailed XPS spectra, taken in the FAT20 mode, together with the fitting results, of Ni2p3/2 and O1s lines for 200 nm nickel samples, are presented in Fig. 2.

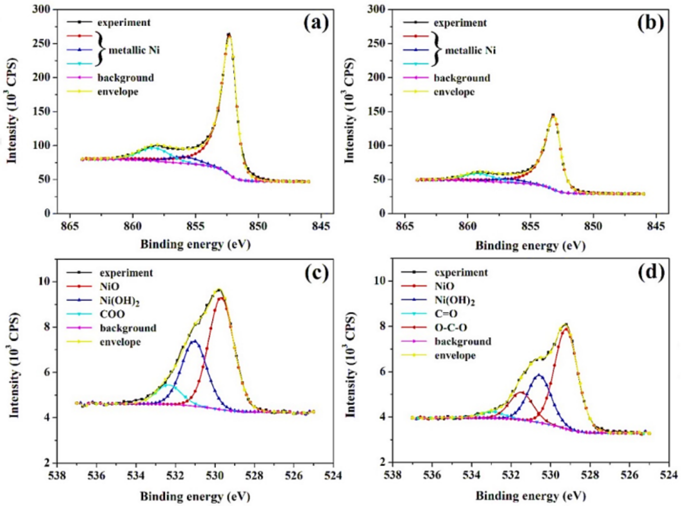

Fig. 2. Fitted high-resolution XPS spectra of Ni2p3/2 and O1s lines obtained for the 200 nm thick Ni samples deposited at the angles of 65^o (Fig.2a,c) and 85^o (Fig. 2b,d).

The first observation seen from Ni2p3/2 photoelectron lines, for both deposition angles, (Fig. 2a,b), is their asymmetric shape, which is characteristic for metallic samples. The lines were interpolated according to the model used by M.C. Biesinger for metal Ni [28]. These lines were fitted to the superposition of three peaks, positioned at binding energies of 852.6, 856.2 and 858.6 eV. The dominant line has asymmetric Lorentzian shape convoluted by Gaussian [29], whilst the other two lines have GL (30) pseudo-Voight profiles. The high resolution XPS spectra of the O1s lines, taken in the range from 537 to 525 eV, are shown in Fig. 2c,d. Similar to Ni2p3/2, it can be stated that the O1s peaks are broad and asymmetric, which implies the presence of several contributions. Indeed, for a 200 nm thick Ni sample, deposited at the angle of 65^o (Fig. 2c), the line is successfully resolved in 3 distinct components. The two dominant contributions at 530.0 eV and 531.1 eV are attributed to NiO and $Ni(OH)_2$ [28], while smaller peak at 533.3 eV can be associated to the COO group [30]. For the Ni thin film deposited at the angle of 85^o, the O1s line was interpolated using four components. Contributions at 529.9 eV and 531.3 eV correspond to NiO and $Ni(OH)_2$ [28], as in the case of the sample deposited at a lower angle. Smaller contributions at the positions of 532.2 eV and 533.7 eV correspond to organic impurities, namely C=O and O-C-O [30], respectively.

Interpolation of the O1s lines made it possible to determine the amounts of NiO in the observed samples. For the Ni thin films, deposited at the angle of 65^o, the quantity of nickel oxide was in the range from 4.0 at.% to 6.0 at.%, while for the samples deposited at the angle of 85^o, the proportion of NiO was found to vary with film thickness from 5.0 at.% to 8.5 at.%. By comparing the obtained values for both series of the samples, it can be noticed that the amount of NiO has a higher value for the Ni films deposited at the angle of 85^o, which is probably due to the more porous structure of these samples.

In order to correlate the structure and chemical composition with magnetic properties of Ni thin films, MOKE analysis was carried out. Measurements were performed at room temperature, with an in-plane magnetic field of 1500 Oe. From the measured hysteresis loops the coercivity (Hc) was deduced and, for the illustration, the azimuthal dependence of the coercivity for 200 nm thick Ni samples, deposited at both angles, is presented in Fig. 3. It should be mentioned that zero azimuthal angle was defined when the coercivity has a maximum value. Based on the obtained results, it can be regarded that deposited Ni thin films possess uniaxial magnetic anisotropy [31], which means that the magnetic properties of the analyzed samples are different depending on the observed direction.

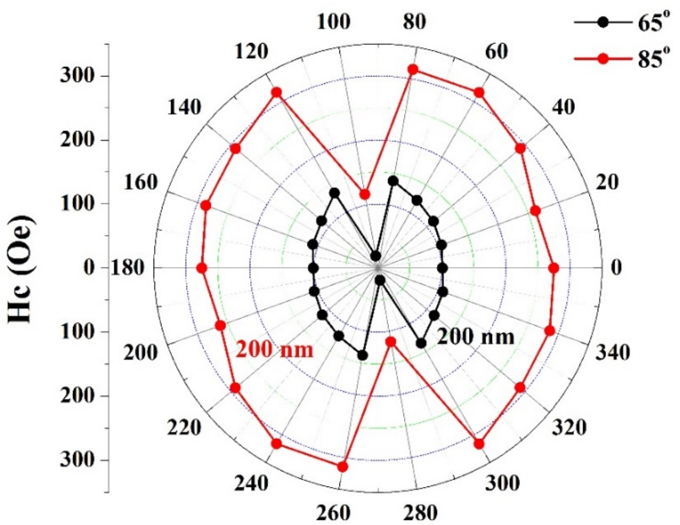

Fig. 3. MOKE coercivity in the function of the angle of applied magnetic field for the 200 nm thick nickel samples deposited at the angles of 65^o and 85^o.

According to the acquired values, for both series of the samples and for the azimuthal angle of 0^o, the thickness dependence of the coercivity was calculated and presented in Fig. 4. For the samples deposited at the angle of 65^o it is noticed that the coercivity increases with increasing film thickness to 90 nm, reaching the maximum value of 274 Oe, and then starts to decrease to 101 Oe for 200 nm thick Ni film. Similar trend was observed for the samples deposited at the angle of 85^o where coercivity first increases to the value of 398 Oe, for 160 nm thin film, and then begins to decrease to 275 Oe, as calculated for 200 nm Ni sample. It can be also noticed that the obtained coercivities are significantly higher, compared to the samples deposited at the angle of 65^o. This can be described by the development of more porous structures at higher deposition angle, which influences the coercivity. Similar behavior was found by F. Tang et al. who investigated magnetic properties of the Co columns deposited on the SiO_2 substrate [32]. On the other hand, XPS analysis reveal that samples deposited at the angle of 85^o have higher amount of NiO which probably influence the increase in coercivity of these films [33].

The decrease in coercivity with thickness can be related to the structure of the columns themselves. As mentioned earlier, stochastic nature of the nucleation on the substrate surface leads to the formation of columns with varying dimensions and structural non-uniformity [11]. Since each column consists of a large number of grains, as the film thickness increases, the quantity of the formed grains also increases. Furthermore, the mobility of the domain walls between the grain boundaries [34] increases as well, which could lead to the easier rotation of the magnetization vector [35]. If it is assumed that each grain has at least one magnetic domain, nickel vertical posts could be considered as complex multidomain structures [36]. Rotation of the magnetization vector in only a few grains will affect other to align the same, causing a decrease in the demagnetizing filed [37]. Thus, the coercivity will be lowered.

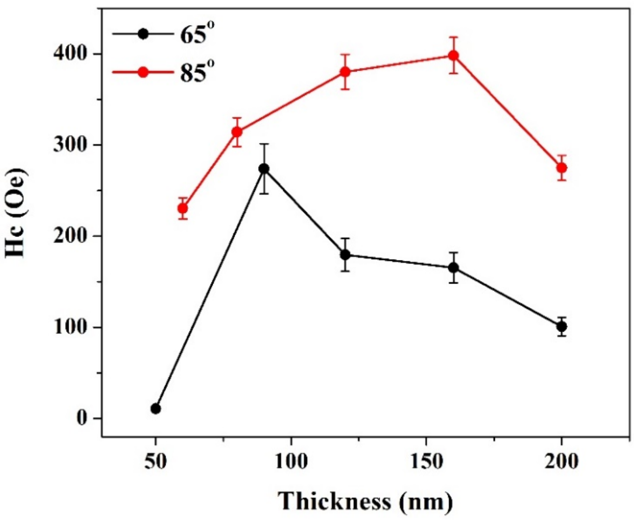

Fig. 4. Coercivity (Hc) of nanostructured Ni thin films as a function of film thickness for the samples deposited at the angles of 65^o and 85^o.

4. Conclusion

Structural, chemical and magnetic properties of the nanostructured nickel thin films, deposited at the angles of 65^o and 85^o, were investigated. From the SEM analysis it was observed that the thicknesses of the samples, for both deposition angles, are in the range from 50 nm to 200 nm, while the diameter of the columns increases with thickness. According to

SEM measurements it was found that Ni samples deposited at the angle of 85° have a higher porosity compared to the samples deposited at the smaller angle. It is assumed that the higher porosity also affected the amount of nickel oxide in the observed samples. These changes are correlated with the magnetic properties through the magnetization study where it is shown that the decrease of Hc values reflects the changes in the diameter of the columns. Since every column could be deemed as a multidomain structure, the inversion of just a few unusual grains will affect the others to align the same, which leads to decrease in coercivity. It is noted that for the samples deposited at the angle of 85°, the coercivity values are significantly higher than in the samples obtained by deposition at the angle of 65°, which can be explained by the higher porosity and the amount of NiO.

Acknowledgments

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Сажетак: *У овом раду је испитиван утицај дебљине и угла депоновања на структурна, хемијска и магнетна својства танких слојева никла (Ni), који су добијени методом депоновања при малим угловима. Депоновање је вршено при два угла и то: 65^o и 85^o. Анализа танких слојева је урађена помоћу скенирајућег електронског микроскопа, рендгенске фотоелектронске спектроскопије и микроскопа заснованог на магнето-оптичком Керовом ефекту. Структурном анализом је нађено да промене у углу депоновања утичу на порозност и удео никл оксида (NiO) у депонованим узорцима, које се могу повезати са варијацијама магнетних својстава. За узорке депоноване при углу од 85^o вредности коерцитивности су значајно веће у поређењу са узорцима добијеним при мањем углу. Овакво понашање се може приписати њиховој већој порозности, као и већем уделу NiO.*

Кључне речи*: никл; наноструктуре; порозност; магнетна својства; коерцитивност.*