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Optical Properties of Zigzag Nickel Nanostructures Obtained at Different Deposition Angles

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Abstract:
In this study, nickel (Ni) thin films were deposited at two different angles (65^o and 85^o) using Glancing Angle Deposition technique, to the thicknesses of 60 – 290 nm. Structural analysis of the deposited films was performed by scanning electron microscopy and X-ray diffraction, while spectroscopic ellipsometry was used for the investigation of optical properties. Electrical resitivity of the samples was determined by four-point probe method. Structural analysis showed that the Ni films grow in a shape of zigzag nanocolumns, where the deposition angle strongly affects their porosity. As the thickness of the films increase they absorb light strongly and become less dense. Besides, samples deposited at the angle of 85^o exhibit higher values of electrical resistivity as compared to the samples deposited at the angle of 65^o, which can be correlated with high porosity and the growth mechanism of the deposited nanostructures.
Keywords*: Nickel; GLAD; Nanostructures; Porosity; Optical properties.*

1. Introduction

Owing to its specific properties, nanostructured nickel (Ni) thin films obtained by Glancing Angle Deposition (GLAD) technique found a wide application in different technological fields. The design of nanostructured thin films is crucial for device improvements [1] and the fabrication of these films is of great interest. Since the type of nanostructure determines optical properties of the samples, combining the shape and the deposition angle make them useful for obtaining optical sensors, antireflection coatings [2, 3], solar cells [4, 5], battery components [6], light emitting diodes [7], for high catalytic activity [8], etc. Structural, optical and electrical properties of Ni thin films are strongly dependent on the deposition parameters, as well as on their thickness and porosity [1, 9-11]. GLAD technique enables the growth of Ni thin films that are extremely porous with a high specific surface area and excellent optical quality [12].

Spectroscopic ellipsometry, as surface-sensitive technique, is widely used for observation and control of optical properties of thin films [13, 14]. This non-destructive method measures change in polarization state of light after reflection from the sample surface [15]. Material properties such as thickness, surface roughness, composition, optical constants, etc., significantly affect the results obtained by ellipsometric measurements. Since the ellipsometric angles (Ψ and Δ) do not contain any readily useful information, the interpretation of the obtained data requires introduction of appropriate model. For nickel, two types of models could be used for the analysis of optical properties. For the frequencies up to

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plasma frequency Drude model is used, which describes light absorption by free electrons. On the other hand, Lorentz oscillator fits well in the UV range [16].

In this paper, we present the study of structural and optical properties of nanostructured Ni thin films consisting of zigzag nanocolumns. The aim was to analyze the influence of the deposition angle (65^o and 85^o) on the properties of different thickness of nickel films with a more complex structure. The obtained results indicate that the variation of optical and electrical properties could be related to the structural properties of the deposited thin films. In this way, the optical quality of the Ni samples might be controlled and modified only by managing thin film thickness and porosity.

2. Materials and Experimental Procedures

Nickel thin films were deposited onto glass substrates by using Glancing Angle Deposition technique. According to the angle between the surface normal and the direction of the evaporated Ni flux glass substrates were oriented in such way that the angles of deposition were 65^o and 85^o. Since the zigzag nanostructures are consisting of slanted columns, opposite to each other, the substrates were rotated for 180^o between each deposition of slanted columns. During the deposition process, the thicknesses of the Ni thin films were controlled using quartz crystal thickness monitor.

Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used for structural characterization of the deposited Ni thin films. SEM analysis was performed on a Mira XMU TESCAN electron microscope. The samples were analyzed in cross-sectional view using acceleration voltage of 20 kV. The phase analysis of nickel thin films was examined by Philips PW1050 X-ray diffractometer, with CuKα emission line (λ = 0.15418 nm). Optical properties of the films were observed by spectroscopic ellipsometry (SE) using HORIBA Jobin Yvon UVIS ellipsometer. The software used for data acquisition and fitting was DeltaPsi2. Finally, sheet resistance of the samples was measured by four-point probe method (JANDEL RM 3000).

3. Results and Discussion

Cross-sectional SEM analysis was used for the inspection of the structure of deposited Ni films as well as measuring their thickness and diameter of the columns. According to the obtained results it was found that, for the samples deposited at the angle of 65^o, the thicknesses were 80, 150, 200 and 290 nm, while for the samples deposited at the angle of 85^o were 60, 90, 140 and 240 nm. Fig. 1 shows cross-sectional SEM images of the samples deposited at the angles of 65^o (Fig. 1a) and 85^o (Fig. 1b) thicknesses of 290 nm and 240 nm, respectively. The micrographs showed that the films grow as columns forming zigzag nanostructures. It is clear that the layers are porous especially for the samples deposited at the angle of 85^o. Also, it was found that the thickness of the columns was influenced by the thickness of the films as well as the deposition angle. The column diameter increases from 18 nm to 36 nm with the increase of layer thickness for the samples deposited at the lower angle. Similar trend was also observed for the samples deposited at the angle of 85^o, where the column thickness increases from from 21 nm to 43 nm. This behaviour is due to the greater shadowing effect during the deposition at higher angle, leading to large-sized grains and increased film porosity.

The crystal phases of nanostructured nickel thin films were analyzed by the XRD method. The diffractograms, recorded for a 290 nm and 240 nm thick Ni samples, deposited at the angles of 65^o and 85^o, respectively, are shown in the bottom right corner of Fig. 1a and Fig. 1b. The diffractograms in both cases confirm the presence of Ni phase by the appearance of line at approximately 2θ = 44.71° which corresponds to (111) reflection of face centered cubic Ni phase (JCPDS: 01-070-0989). It can be noticed that the (111) line is wide indicating the formation of fine-grained structure during the growth of thin films. The intensity of the line is lower for the sample deposited at the angle of 85° indicating the weaker crystallinity of the deposited layer at higher angle. Another observation is the presence of second line at the position of 52.10° only in the case of the sample deposited at the angle of 65° which is also attributed to nickel and corresponds to the reflection from (200) plane. By calculating the full width at half maximum of the (111) diffraction line and using Scherrer's formula [17], it was determined that the value of the mean crystallite size is 7 nm and 6 nm, for 290 nm (65°) and 240 nm (85°) thick Ni samples, respectively.

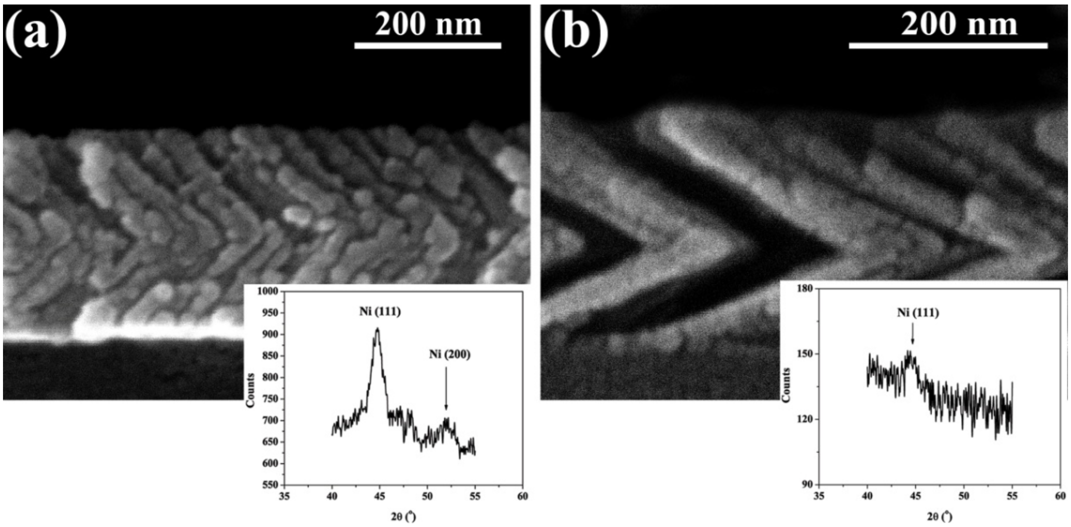

Fig. 1. Cross-sectional SEM images and corresponding diffractograms of Ni films thicknesses of: (a) 290 and (b) 240 nm, deposited at the angles of 65° and 85°, respectively.

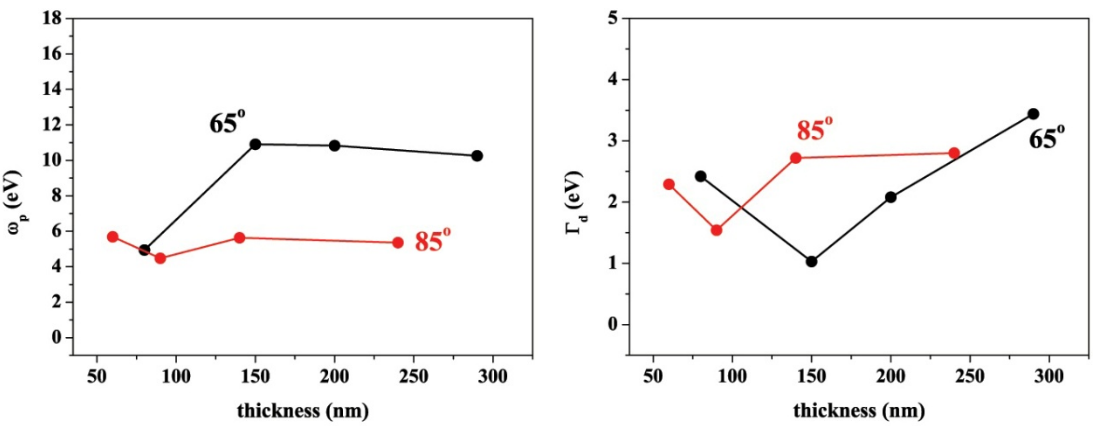

Fig. 2. Dependence of (a) ω_p and (b) Γ_d on thickness for the samples deposited at the angles of 65° and 85°.

As mentioned earlier, analysis of the obtained results by spectroscopic ellipsometry is performed using an appropriate model. The model applied in the interpolation is a corrected version of the model used in our previous work [18]. Namely, zigzag structures are viewed as a series of oblique columns that are directed in the opposite directions. Therefore, each layer of oblique columns is represented by a combination of Ni, NiO and voids. The layer at the top indicates roughness.

According to the modelling, two important parameters were obtained: plasma frequency (ω_p) and damping factor (Γ_d) and their dependence of the thickness of the films for both series of the samples is presented in Fig. 2. It can be seen that the values of plasma frequency (Fig. 2a) for the samples deposited at the angle of 85^o are quite lower compared to the values for the samples obtained at the angle of 65^o. This can be explained by the higher degree of porosity obtained for the samples deposited at the angle of 85^o. The observed increasing trend of damping factor (Fig. 2b) for both series of the samples, indicates that the thicker films have a higher concentration of defects.

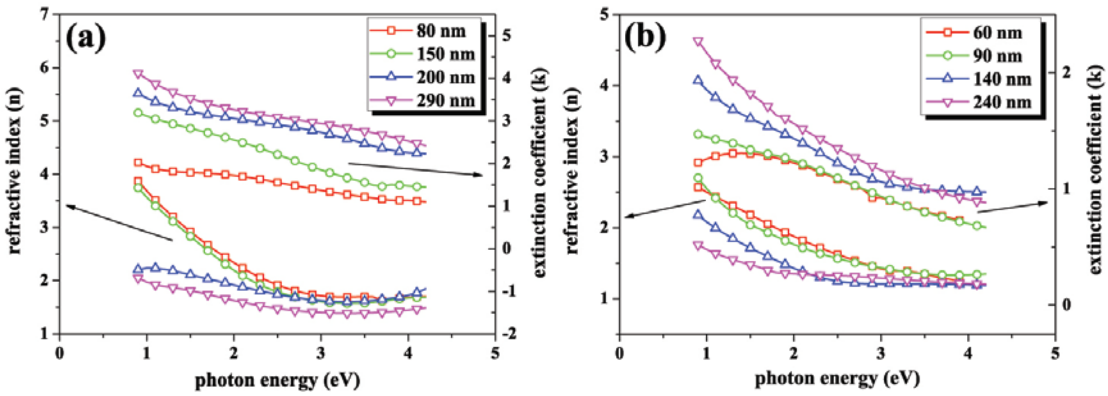

Fig. 3. Variations of the refractive index and extinction coefficient of Ni films deposited at the angles of: a) 65^o and b) 85^o.

Other parameters obtained by modelling are the refractive index (n) and extinction coefficient (k) which are presented in Fig. 3 for all Ni samples. It is observed that the refractive index curves, for samples with a thickness of 80 nm and 150 nm, deposited at the angle of 65^o, have a similar shape and slope. However, with a further increase in thickness, the values of the refractive index start to change becoming lower, especially in the low-energy region meaning that these samples have a reduced optical density in comparison to thinner samples. Since the refractive index is directly related to the degree of porosity, it can be concluded that thicker samples possess higher porosity, compared to thinner ones. Similar results were obtained for the samples deposited at the angle of 85^o. On the other hand, there is a clear trend of increasing extinction coefficient with increasing thickness of the samples, for both series of the samples, indicating higher light absorption of thicker samples. This means that the light cannot easily pass through the thicker samples.

The refractive index was used to calculate the porosity of the samples using equation: $P = (1 - (n^2-1)/(n_d^2-1)) \times 100(\%)$. By knowing the values of the refractive index for the Ni sample (n) and for the bulk nickel (n_d) at $\lambda = 633$ nm (1.96 eV) [19], the porosity of the thin films was calculated. It was observed that the porosity increases with thickness and reaches a value of 47% for a 290 nm nickel sample deposited at the angle of 65^o. On the other hand, for the samples deposited at the higher angle of 85^o the porosity drastically increases reaching the value of ≈73% for 240 nm thick Ni sample.

By using the parameters ω_p and Γ_d, the optical resistivity of the deposited samples is determined. The calculated data, together with the electrical resistivity measurements obtained by the four-point probe method, for both series of the samples, are shown in Fig. 4, as a function of the film thickness. For the samples deposited at the angle of 65^o (Fig. 4a), it can be seen that optical and electrical resistivities show similar trend as a function of thickness. It is clear that the electrical resistivity decreases from 14.84×10^2 μΩ cm to

7.84×10^2 μΩ cm with an increase of the thickness from 80 nm to 150 nm. With further increase of the thickness electrical resistivity starts to increase reaching the value of 10.46×10^2 μΩ cm for the 290 nm thick Ni sample. It can be assumed that there are more defects in the thicker layers, which probably originate from the more complex structure of the samples consisting of zigzag nanostructures, as well as from the growth mechanism.

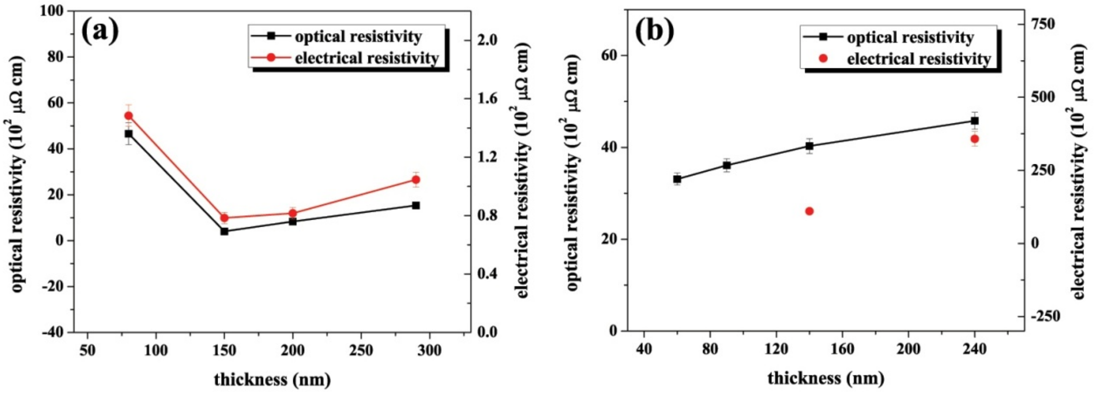

Fig. 4. Optical and electrical resistivity of the Ni thin films deposited at the angles of: a) 65° and b) 85°.

Therefore, with the increase in the density of defects, the electrical resistivity will also increase. On the other hand, for the samples deposited at the angle of 85° (Fig. 4b), the optical resistivity increases as the layer thickness increases. Similar trend was found for the electrical resistivity for the samples thickness of 140 nm and 240 nm (it was not possible to measure the electrical resistivity for thinner samples). It was found that the electrical resistivity increased more than three times from 110×10^2 μΩ cm to 358×10^2 μΩ cm with increase the thickness of the films. This can be related with the more porous structure observed in thicker samples enabling the increase of oxygen on the grain boundaries. Therefore, the highest value of resistivity, obtained for the sample with a thickness of 240 nm, could be related to the high value of porosity (≈73 %).

4. Conclusion

In this work we have investigated structural, optical and electrical properties of nickel zigzag nanostructures, deposited at two angles (65° and 85°), by GLAD technique. The thickness of the samples was in the range from 80 nm to 290 nm and from 60 nm to 240 nm, depending on the deposition angle. According to SEM analysis, it was found that the diameter of the columns increases with film thickness, as well as that the samples possess more porous structure. XRD analysis indicates growth along (111) plane for both series of the samples. As reported by spectroscopic ellipsometry, the increasing trend of Γ_d with thickness, for the samples deposited at both angles, indicates that the thicker samples have a higher concentration of defects. According to the obtained n and k parameters, it can be concluded that with increasing film thickness Ni films become more porous, i.e. they have a lower density. The highest value of porosity was calculated for 240 nm thick Ni sample, deposited at the angle of 85° (73 %). On the other hand, increasing in the k values indicates higher absorption of the light. Samples deposited at the angle of 85° are characterized by higher values of electrical resistivity, compared to the samples deposited at lower angle. This could be related to the growth mechanism, as well as the film porosity.

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Сажетак: *У овом раду, танки слојеви никла (Ni) су депоновани под два различита угла (65^o и 85^o) користећи методу депоновања при малим угловима, до дебљина које су се налазиле у опсегу од 60 – 290 nm. Структурна анализа депонованих слојева је урађена помо ћу скенирајуће електронске микроскопије и рендгенске дифракције, док је спектроскопска елипсометрија коришћена за анализу оптичких својстава. Електрична отпорност узорака је одређена помоћу методе четири тачке. Структурна анализа је показала да се Ni филмови састоје из цик-цак наноструктура, а да угао депоновања има велики утицај на њихову порозност. Како се дебљина узорака повећава, они боље апсорбују светлост и поседују мању густину. Такође, узорци депоновани под углом од 85^o имају веће вредности електричне отпорности, у поређењу са узорцима који су депоновани под углом од 65^o, што се може повезати са већом порозношћу и механизмом раста депонованих наноструктура.*

Кључне речи*: никл, метода депоновања при малим угловима, наноструктуре, порозност, оптичка својства.*