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Properties of Zig-Zag Nickel Nanostructures Obtained by GLAD Technique

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Abstract:

Zig-zag structure of the nickel thin film has been obtained using Glancing Angle Deposition (GLAD) technique. Glass substrate was positioned 75 degrees with respect to the substrate normal. The obtained nickel thin film was characterized by X-ray Photoelectron Spectroscopy, Scanning Electron Microscopy and Atomic Force Microscopy. Surface energy of the deposited thin film was determined by measuring the contact angle using the static sessile drop method.

Keywords: *Glancing Angle Deposition, XPS, AFM, Nickel thin film.*

1. Introduction

Glancing Angle Deposition (GLAD) is a technique for producing nanostructured thin films. In this method, the substrate can be rotated about two axes, as illustrated in Fig. 1 (left side). Rotation about one axis is changing the angle of the incident particle flux (tilt motor) while the rotating about the other one controls the structure of the deposited film (rotation motor) [3]. The motors that are connected to the computer control the movements about both axes. Controlled substrate motion allows producing predictable forms of nanostructures [4]. Obtained columnar nanostructures are inclined toward the direction of the incident particle flux. These structures may take form of slanted and vertical posts [5,6], helices [7] or zig-zag [8] columns.

Schematic illustration of the growth of columnar structures is given on the right side in Fig. 1. The formation of the nucleus from the arriving particle flux is a random process. Nuclei grow into columns giving rise to the development of the shadowing. Since the columns are not equal in size, as a result, some columns will screen their neighbors from the incoming particle flux. Because of this effect, shadowed columns will stop growing. For small angles of the incident particle flux, the roughness of the substrate and the shadowing effect are very important for the formation of columnar structures. The columns tilt angle (β) is smaller than the incident particle flux angle (α) and its value can be obtained using equation [9]:

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

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The size and density of obtained nanostructures will change as a function of incident particle flux angle (α) [10].

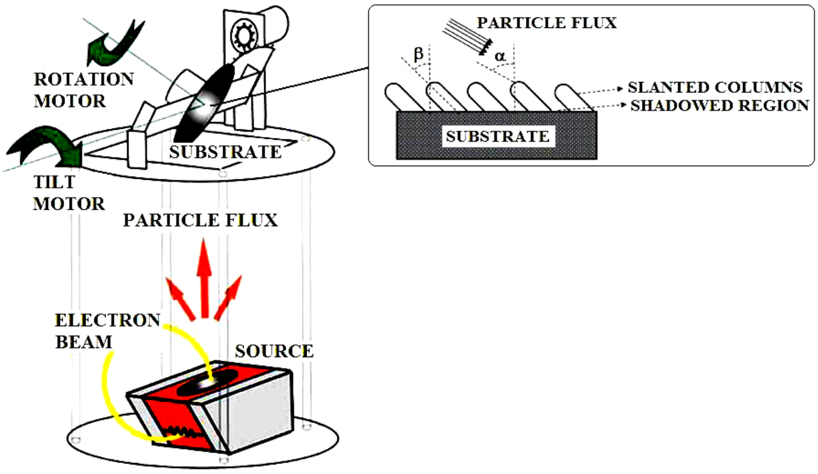

Fig. 1. Schematic view of GLAD apparatus and GLAD growth [1,2].

Since GLAD has been known for a couple of decades, many applications of this method have been developed. Depending on the type of nanostructures, the present method can be used in optically active coatings [11], nanoemitters [12], thin film wave plates [13], magnetic storage media [14], photonic crystals [15], humidity or pressure sensors [16], etc. The structure of thin films can be adjusted to suit the needs of the applications. For example, zig-zag structures are used for electrochemical capacitors [6], highly stretchable conductive electrodes [17], anti-Stokes emission testers [18], data storage with NiFe zig-zag structures [19], etc. Also, films with this structure are of interest for thermal protection applications. They reduce thermal conductivity and elastic modulus [20]. Further development of GLAD technique will lead to increase number of possible applications.

In this work, GLAD method designed and assembled in our laboratory was used for the deposition of nickel thin film with zig-zag structure.

2. Experimental procedure

Nickel thin film was deposited by evaporating nickel onto glass substrate. Prior to deposition, glass substrate was cleaned in ethanol solution in ultra–sonic bath and rinsed with 18.2 M Ω deionised water. After that, substrate was also cleaned by the ozone (NovaScan PSD-UVT) and then attached to substrate holder in the chamber. The base pressure of the system was 4×10^{-5} Pa. Emission current was constant and its value was 170 mA. The duration of the deposition was 3 hours. After 1 hour 30 minutes of deposition, the substrate rapidly rotates by 180 degrees and the deposition continues for another 1 hour 30 minutes. Repeating rotations and pauses will lead to the creation of the arms of zig-zag structures [21]. In our study, zig-zag structures were deposited with oblique angle of α = 75 degrees and -75 degrees with respect to the substrate normal.

X-ray Photoelectron Spectroscopy (SPECS Systems, PHOIBOS 100/150) was used to determine the chemical composition of the deposited thin film. A monochromatic Al Kα X-ray source was used for sample analysis. To control charging of the sample, the charge neutralizer filament was used. Concentrations of elements present in the film were obtained using CASAXPS software. To remove the surface impurities, as well as in order to perform depth analysis, the sample was sputtered for 80 sec with 5 keV argon ions.

Field Emission Scanning Electron Microscope, Mira XMU (TESCAN, Czech Republic) at 20 kV was used for morphology studies. Cross sectional SEM image of the sample was used to determine the thickness of the film. Prior to the FESEM analysis, the sample was sputter coated with Au-Pd alloy.

The obtained nickel thin film was also characterized using Multimode Quadrex SPM with Nanoscope IIIe controller (Veeco Instruments, Inc.). In this work, Atomic Force Microscope (AFM) was operated in the tapping mode, using a commercial Veeco FESP probe with a cantilever length of 225 μm. Surface topography and diameter of the columns were observed.

Surface free energy of the deposited thin film was determined by measuring the contact angle using the static sessile drop method. Apparatus for the measurement is made in our laboratory. The contact angle was determined by using ImageJ1.46r [22] program. The behavior of 2 μl droplets of deionized water and ethylene glycol on a nickel thin film were observed. Based on the values of the contact angles, surface free energy of the thin film was calculated.

3. Results and Discussion

XPS analysis was performed after 80 sec of sputtering with argon ions (Fig. 2). Nickel LMM and XPS spectra peaks of nickel, oxygen and carbon were recorded for the deposited thin film. It was found that the thin film consists of 7.6 at.% of carbon, 2.9 at.% of oxygen and 89.5 at.% of nickel. Since the deposited thin film has a porous structure, the presence of carbon is probably due to the absorption from the ambient atmosphere.

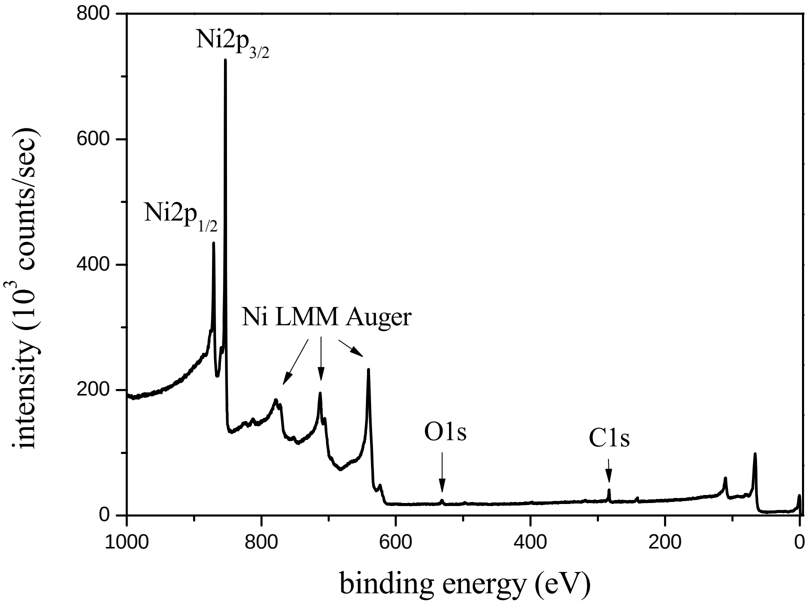

Fig. 2. XPS spectra of the nickel thin film.

For determination of the film thickness, sample is analyzed by SEM. Specimen was prepared cross sectional, which is shown in Fig. 3. It can be seen that the thin film has zig-zag structure. According to SEM image analysis it was found that the thickness of the nickel thin film is (440 ± 30) nm. In addition, it is seen that some of the columns stop growing. As deposition continues, the surviving columns become larger. It can be noticed the presence of small particles over the whole sample surface. These particles originate from the Au-Pd alloy coating.

Surface of the sample was analyzed by AFM technique (Fig. 4). It can be seen that the grains of almost the same size exist on the sample surface. Also, it can be noticed that the grains posses different separations. Based on the topographic image the diameter of the columns found to be (22 ± 2) nm [23] and the surface roughness value equal to (1.60 ± 0.08) nm.

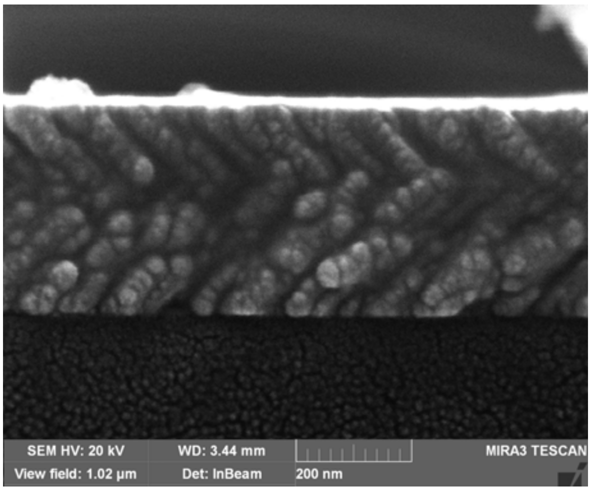

Fig. 3. SEM cross section image of the nickel thin film.

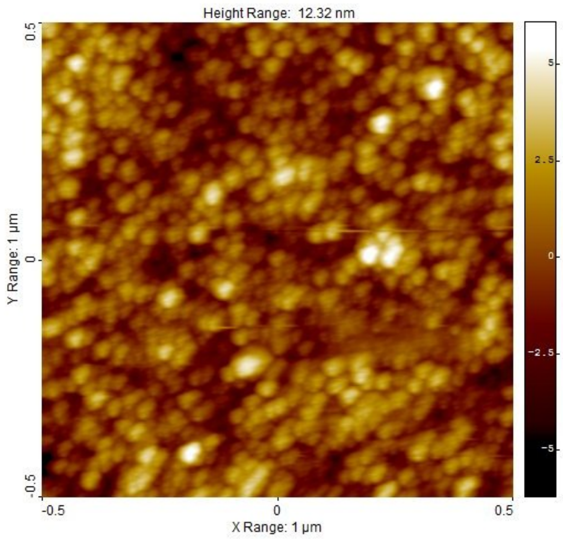

Fig. 4. Topographic AFM image of the nickel thin film.

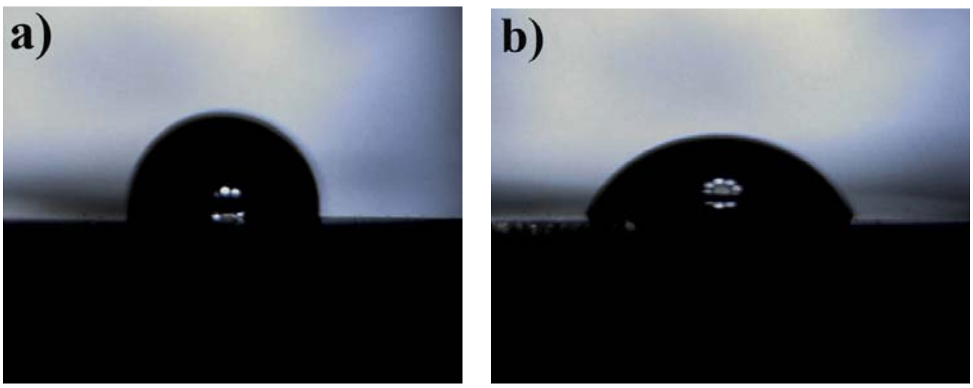

Fig. 5. Droplets of a) water and b) ethylene glycol on the nickel thin film.

According to static sessile drop method (Fig. 5) it was found that the contact angles for water and ethylene glycol were (88 ± 5) degrees and (61 ± 3) degrees respectively. The value of the contact angle for water indicates that the deposited thin film represents hydrophilic material. Based on the values of the contact angles, obtained surface energy of the nickel thin film was $\gamma_s = (29 \pm 2)$ mJ/m^2. In this case, a deposited thin film has lower value for the surface free energy as compared to the bulk [24].

4. Conclusions

In this paper, we have demonstrated that the deposition of nickel thin film with zig-zag structure can be achieved using GLAD technique. As confirmed by XPS analysis, it was found that the thin film consists of 89.5 at.% of nickel. Thickness of the deposited thin film was 440 nm. According to AFM analysis it was found that the diameter of the columns is 22 nm and the surface roughness value is 1.60 nm. Static sessile drop method enabled us to determine the surface free energy of the nickel thin film, which was 29 mJ/m^2.

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Садржај: *У овом раду, користећи методу депоновања при малим угловима, су добијене цик-цак структуре танког слоја никла. Никл је депонован на подлогу од стакла која је постављена, у односу на нормалу на површину, под углом од 75 степени. Добијени танки слој никла је карактерисан помоћу рендгенске фотоелектронске спектроскопије, микроскопа у пољу атомских сила и скенирајућег електронског микроскопа. Површинска слободна енергија депонованог танког слоја је одређена методом капљице и то мјерењем контактног угла.*

Кључне ријечи: *депоновање при малим угловима, рендгенска фотоелектронска спектроскопија, микроскоп у пољу атомских сила, метода капљице, никл*