A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 57 2012 Issue 3
DOI: 10.2478/v10172-012-0072-x

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EVALUATION OF THE TEMPERATURE STABILITY OF A Cu/Ni MULTILAYER

OCENA TRWAŁOŚCI TEPERATUROWEJ WIELOWARSTWY Cu/Ni

The article presents investigation results for a Cu/Ni multilayer as annealed in the temperature range of 40÷300°C. The Cu/Ni multilayer with a Cu sublayer thickness of 2 nm and an Ni sublayer thickness of 6 nm was fabricated by the magnetron deposition technique. The X-ray structural analysis, XRD, was employed for examination. The characterization of the multilayer before and after the annealing process was done by the measurement of the texture for the Cu/Ni(111) plane, as well as by topography examination on an atomic force microscope (AFM). The state of the multilayer surface were observed using a scanning electron microscope.

The thermal stability tests showed that the multilayer had undergone delamination at temperature of 300°C. Up to this temperature, the multilayer retained clear phase boundaries, as confirmed by the presence of satellite peaks in the diffraction patterns. The annealing operation caused structural changes in the multilayer, such as grain growth and an increase in roughness and texture.

Keywords: Cu/Ni multilayers, thermal stability, X-ray diffraction, texture, atomic force microscopy

W artykule zaprezentowano wyniki badań wielowarstwy Cu/Ni wygrzewanej w zakresie temperatur 40÷300°C. Wielowarstwę Cu/Ni, o grubości podwarstwy Cu równej 2 nm i grubości podwarstwy Ni wynoszącej 6 nm, wytworzono techniką osadzania magnetronowego. Do badań zastosowano rentgenowską analizę strukturalną XRD. Charakterystyki wielowarstwy przed i po procesie wygrzewania dokonano poprzez pomiar tekstury dla płaszczyzny Cu/Ni(111) jak również badania topografii na mikroskopie sił atomowych Veeco. Stan powierzchni wielowarstwy badano przy użyciu elektronowego mikroskopu skaningowego Jeol.

Badania stabilności temperaturowej wykazały, że wielowarstwa uległa delaminacji w temperaturze 300°C. Do tej temperatury wielowarstwa zachowała wyraźne granice międzyfazowe, co potwierdzone zostało obecnością pików satelickich na obrazach dyfrakcyjnych. Wygrzewanie wywołało zmiany strukturalne w wielowarstwie, tj. rozrost ziaren, zwiększenie chropowatości i tekstury.

1. Introduction

Cu-Ni alloys exhibit an unlimited mutual solubility of components in solid state. Copper-nickel alloys have found a wide application in numerous branches of industry, e.g. as alloys for coinage and for manufacturing capacitor plates, springs and screws. Moreover, due to their high electric resistance, these alloys are used for production of resistors elements. Among Cu-Ni alloys, alloys called constantan and nickeline enjoy the greatest popularity. The former is used for the production of thermocouples, while the latter for cladding and manufacturing drawn and stamped products [1, 2].

In modern engineering, the elements Cu and Ni are used for producing thin multilayered systems that are characterized by gigantic magnetic resistance (GMR). Due to these specific properties, which result from the alternately arranged ferromagnetic and non-magnetic layers, they have been applied in electronics and in information recording and readouting devices [3-7]. The main criterion allowing such an application is the existence of distinct phase boundaries between individual sublayers of a multilayered system. Presently, X-ray diffractometry, including GXRD (grazing X-ray diffraction), is a non-destructive examination method which is most commonly used for the examination of the periodical nature of a multilayer.

Temperature stability is the basic term used for describing changes in the properties of material as a function of temperature, and it can be related both to the

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structure of the material and to its physical and mechanical properties [9, 10]. The ferromagnetic/paramagnetic material type systems, whose example is the Cu/Ni multilayer, do not operate at elevated temperatures; nevertheless, it is important to establish their maximum temperature at which the multilayers will retain the continuity and periodicity of the arrangements and will exhibit magnetic properties. Moreover, during the manufacturing process, e.g. during soldering, multilayers may be exposed to a temperature much higher than that of their operation.

The study presents the results of investigation into the effect of temperature on the retention of its periodicity, grain size, texture and roughness by the Cu/Ni multilayer. The article presents the results of temperature examination of a Cu/Ni=2/6 nm multilayer.

2. Methodology and material

Tests were carried out on a Cu/Ni multilayer fabricated by the magnetron deposition technique. The deposition took place in argon atmosphere under pressure of $5 \cdot 10^{-5}$ Pa. Multilayers composed of 100 bilayers were deposited on a Si(100) monocrystalline silicon substrate (Fig. 1). The thickness of the Cu sub-layer was 2 nm, while the Ni sublayer thickness was three times greater, i.e. 6 nm. The thickness of individual layers was controlled by deposition time (the deposition rate was 0.126 nm/s).

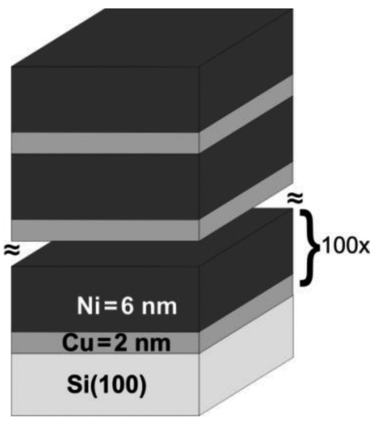

Fig. 1. Schematic representation of the examined multilayer

The multilayer was annealed in the temperature range of 40÷ 300°C in air. The multilayer structure was assessed by X-ray examinations carried out in the symmetric Bragg-Brentano geometry (XRD) within the diffraction angle range of 42÷65° including main reflections from the components of the Cu/Ni(111) and Cu/Ni(200) multilayers and associated satellite peaks. The X-ray examinations were conducted on a Seifert 3003TT diffractometer using the wavelength of radiation emitted from a cobalt anode tube (λ_{Co} =0.1789 nm). In the temperature range of 40÷ 220°C, the annealing was conducted during the X-ray measurement using a temperature adapter [11], while in the temperature range of 230÷300°C the annealing took place in a furnace, and the measurement was taken after the sample had been cooled down to room temperature. The duration of multilayer holding at a given temperature corresponded to the time of making X-ray diffractions, and was approx. 30 min.

Moreover, before and after annealing at 300°C and subsequently cooling down to room temperature, the multilayer was subjected to texture measurements and topography examination on an atomic force microscope (AFM). The texture measurement was taken for the planes Cu/Ni(111) and Cu/Ni(200) using radiation collimated to ∅2 mm. The AFM examination was performed on a Veeco microscope by the tapping method. The surface scanning area was 16 μm^2. Based on the measurements, the value of arithmetic mean roughness deviation, Ra, was determined using the Nanoscope software.

The continuity of the multilayer and its surface condition were checked using a JSM-6610LV Joel scanning electron microscope.

3. Results and discussion

The surface condition of the multilayer was checked through examination on a scanning microscope each time after being annealed. Cracks and multilayer delamination at the edge of the sample were only observed at temperature of 300°C (Fig. 2).

The coating delamination was due to the difference in thermal expansion coefficients between the multilayer components (for Cu $1.65 \cdot 10^{-5}$ K^{-1} and Ni $1.34 \cdot 10^{-5}$ K^{-1}) and the silicon substrate (0.2810^{-5} K^{-1}).

The results of diffraction measurements taken on the Cu/Ni multilayer at room temperature after annealing in the temperature range of 40÷300°C are illustrated in Figure 3. The main Cu/Ni(111) and Cu/Ni(200) reflections and the satellite peaks of the first order, S_{+1} and S_{-1}, integrated with the reflection Cu/Ni(111) were detected in the diffraction patterns. The occurrence of the satellite peaks is due to the diffraction of the X-ray beam at multilayer interfaces. This diffraction is the result of the difference in radiation absorption coefficients between individual layers. The satellite peaks detected in the diffraction patterns indicate well defined interfaces between individual sublayers, and thus the high quality of the multilayer structure. The X-ray measurements taken on the multilayer annealed in the temperature range of 40÷ 210°C showed changes in the shape of the diffraction reflections. Its were manifested themselves in a reduction of the maxima and narrowing of the half-widths of the main Cu/Ni(111) reflections and in increasing intensity of the S_{-1} satellite peak with increasing of temperature. Both S_{-1} and S_{+1} satellite peaks were separated form Cu/Ni(111) reflection for multilayer annealed at temperatures as from 220°C, but the further increase of its intensity was not observed. The presence of satellite peaks on all diffraction patterns obtained from the multilayers heated up to the temperature of 300°C indicates of the absence of mutual diffusion between individual sublayers and retention of distinct phase boundaries.

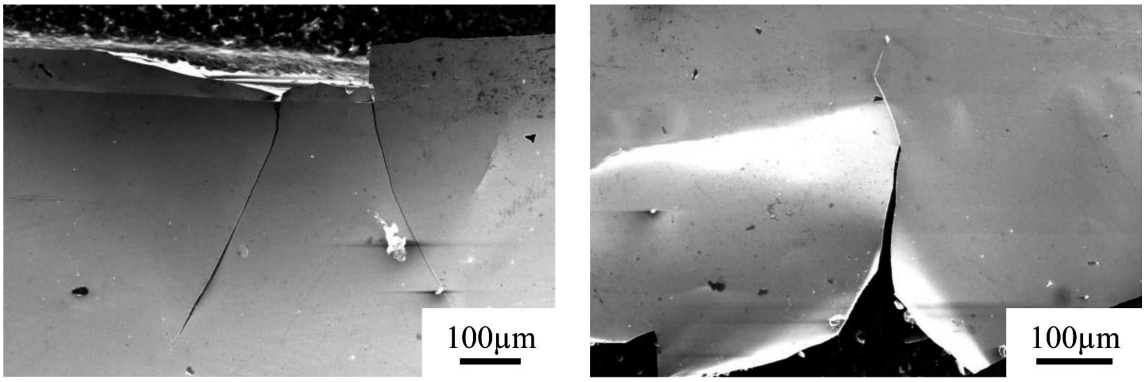

Fig. 2. Degradation of Cu/Ni multilayer after annealing at 300°C

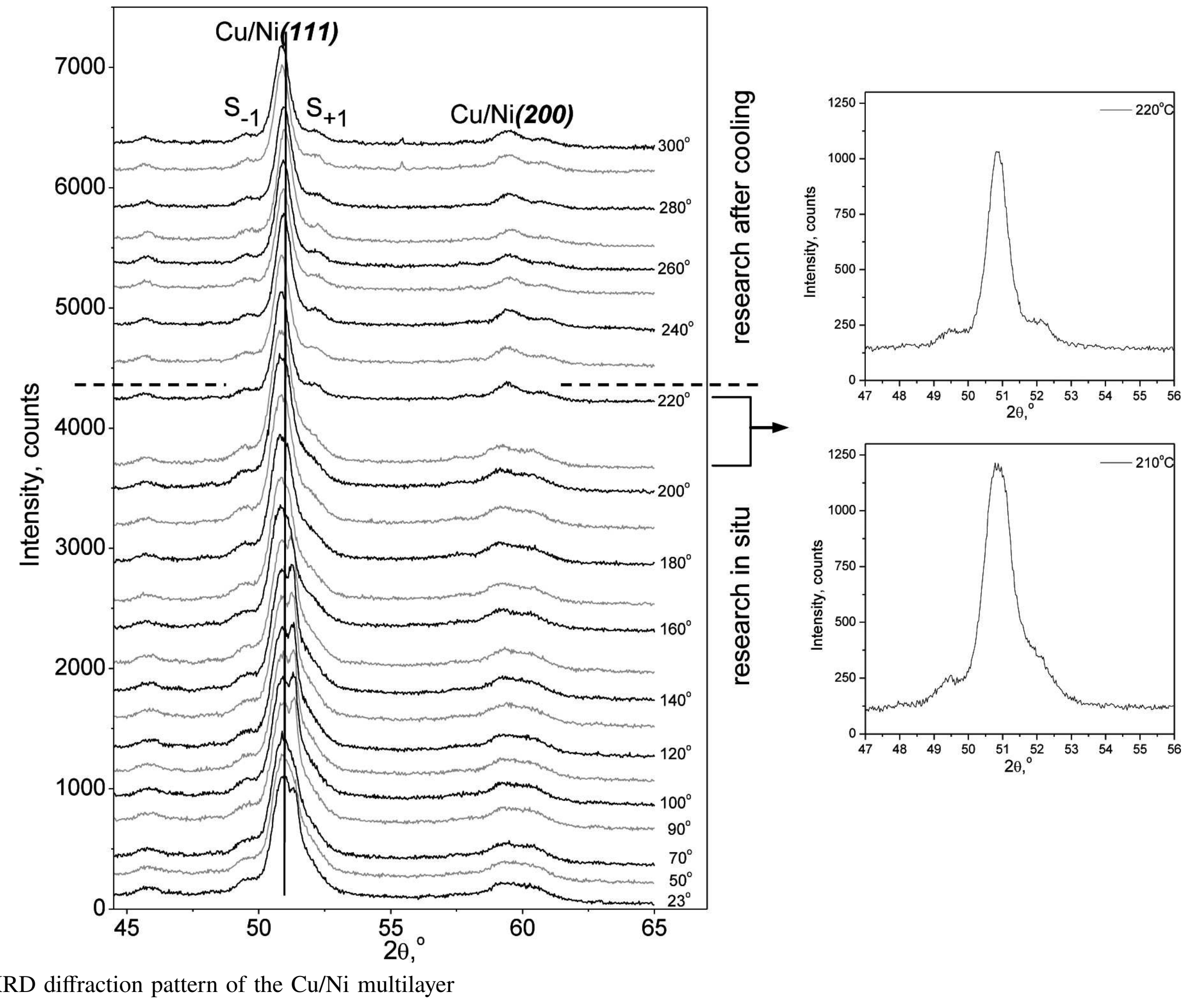

Fig. 3. XRD diffraction pattern of the Cu/Ni multilayer

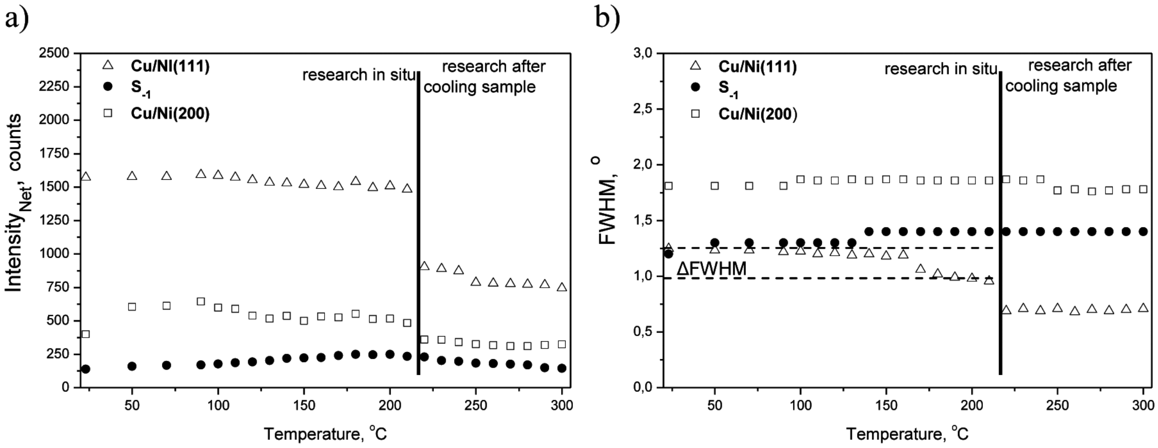

Fig. 4. Overall intensity (a) and half-width of reflections (b) as a function of temperature

A numerical analysis of the diffraction patterns was performed by approximating the overall intensity and half-width of reflections with the Pseudo Voigt curve. The results of the analysis are illustrated in Figure 4. With the increase in the annealing temperature of the Cu/Ni multilayer, a reduction in the overall intensity, J_{Net}, of the main Cu/Ni(111) and Cu/Ni(200) reflections and a slight increase in the intensity of the satellite peak S_{-1} integrated with the main reflection Cu/Ni(111) occurred (Fig. 4a), which was also deduced from the direct comparison of the diffraction patterns in Figure 3. With increasing testing temperature, the half-width of the reflections decreased, which is clearly seen for the reflection Cu/Ni(111). The fitting results for the reflection Cu/Ni(200) are burdened with a larger error, resulting from its smaller intensity and large broadening. The half-widths of the satellite peak S_{-1} increased with increasing temperature (Fig. 4b). The reduction of the half-widths of the peaks deriving from the multilayer components is associated with the increase in the size of crystallites, as well as the stress relaxation within the multilayer.

From the Taylor relationship, the stress level in the multilayer was determined based on the angular position of the reflection Cu/Ni(111) [12]:

$$\beta_z = 4etg\theta \tag{1}$$

where:

θ – Bragg angle [°],

e – lattice deformation $e = \frac{\Delta d_T}{d_{o(23°C)}}$ and d – interplanar distance of reflection Cu/Ni(111) [nm].

The increase in annealing temperature has caused stress relaxation in the multilayer (Fig. 5).

Comparison of the multilayer surface condition before and after annealing at 300°C was performed by the AFM microscopic examination.

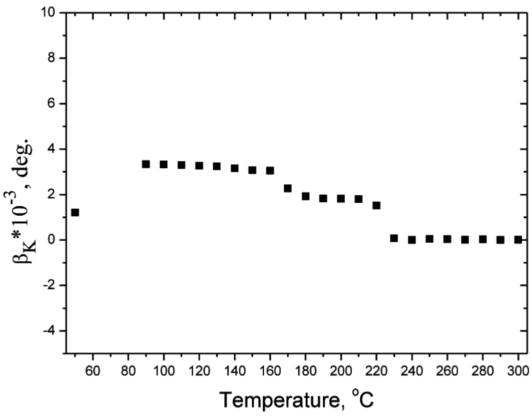

Fig. 5. Multilayer stress level determined from the Taylor formula

The surface of the multilayer prior to annealing was characterized by a conical topography, typical for the magnetron deposition technique, whereas after annealing and cooling down to room temperature it showed a globular type of surface (Fig. 6). Based on the AFM images, grain sizes were measured using the Nanoscope software. The AFM images show that an increase in the grain size and roughness of the multilayer occurred due to the increase in annealing temperature (Fig. 7). The grain size was determined based on the size of globules. Annealing of the multilayer at 300°C resulted in a fourfold increase in grain size and a twofold increase in roughness.

The size of crystallites was determined by X-ray examination from Scherrer's formula [13]:

$$D_{hkl} = \frac{k \cdot \lambda}{\beta \cdot \cos \Theta} \tag{2}$$

where:

D – x-ray average size of crystallites in the *hkl* direction [mm],

k – Scherrer's constant (=1),

λ – radiation wavelength [nm],

β – reflection half-width [rad],

θ – Bragg angle [°].

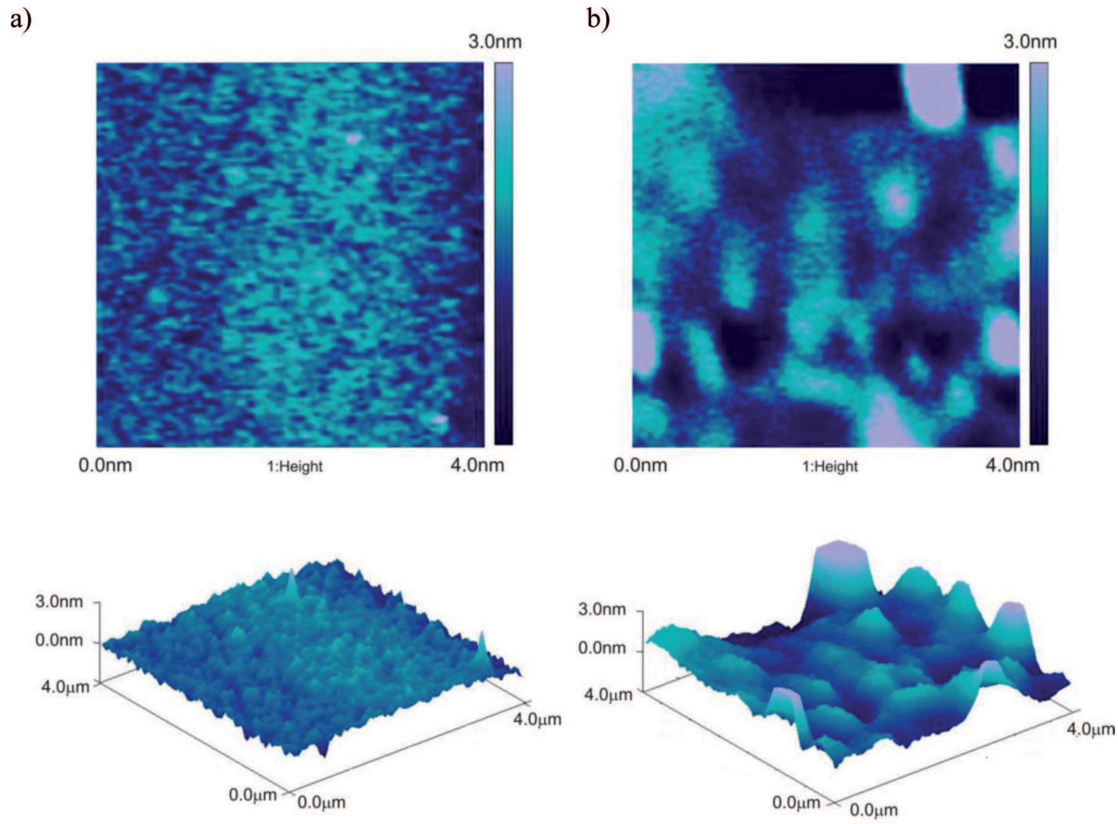

Fig. 6. AFM images of the multilayer surface: a) before annealing, b) after annealing at 300°C

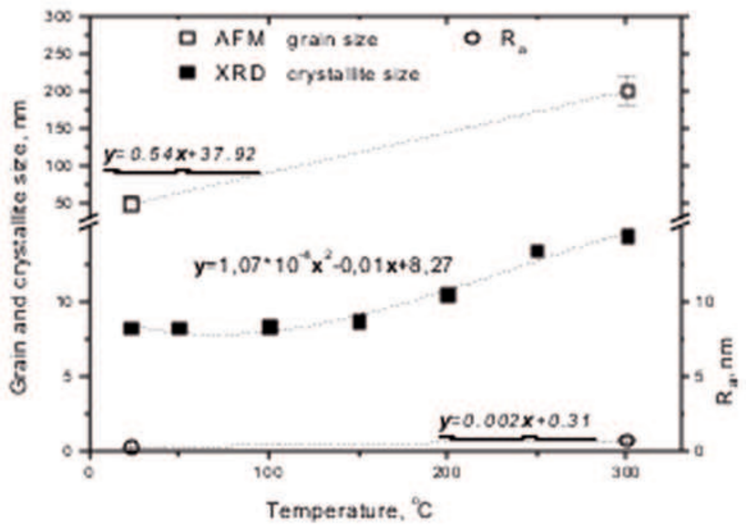

Fig. 7. The grain size and roughness of the Cu/Ni multilayer as a function of temperature

The crystallite size, as determined using the X-ray technique (size of crystallites in direction [111] perpendicular to surface), is eight times smaller than the grain size in the AFM measurements (size of the globules on the surface, approx. "diameter" of columnar crystallites in multilayer); however, it also shows an increasing trend with the increase in temperature (Fig. 7). It has been calculated that the crystallite size in the multilayer annealed at 300°C and then cooled down to room temperature is 0.75 times larger than in the non-annealed multilayer.

By comparing the obtained results with the half-widths of the reflection Cu/Ni(111) and the stress level in the multilayer it can be stated that the narrowing of the diffraction line following the increase in multilayer annealing temperature has occurred as a result of stress relaxation and crystallite size increase.

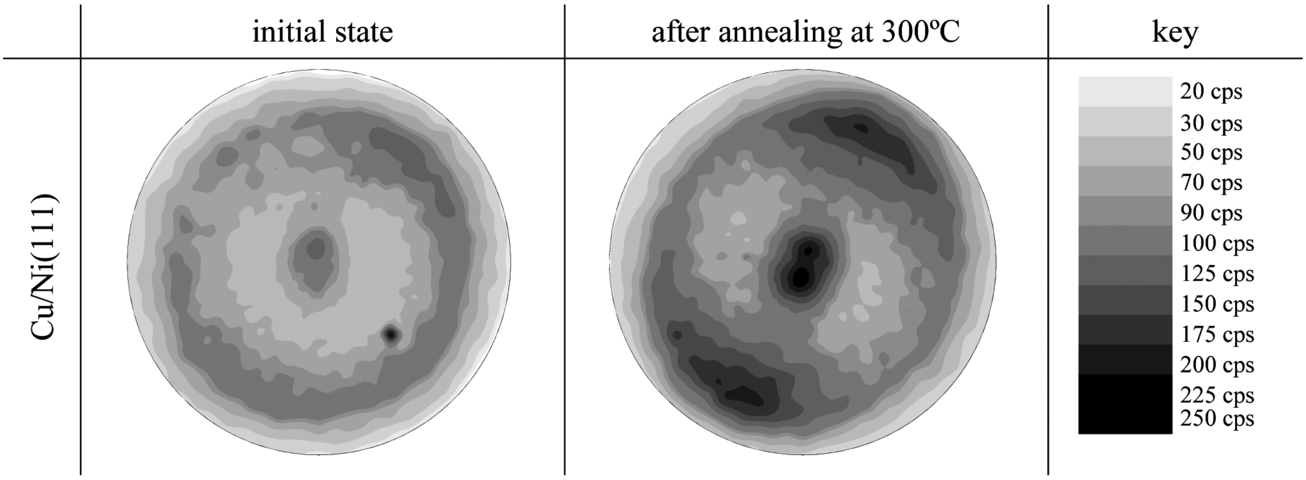

Fig. 8. Pole figures of the main reflection Cu/Ni(111) before and after multilayer annealing at 300°C

Similarly, like the AFM examination, also texture measurements too were made on the multilayer in the initial state and after annealing at 300°C (Fig. 8). The pole figures indicate a texturing of the planes (111) in the direction perpendicular to the surface (fibrous texture) with a misorientation of 7° in two directions. Both Cu and Ni has a face-centred cubic structure (fcc), in which the closest packing of atoms occurs in the growth plane {111}. The lower intensity of the pole figures originating from the planes (200) indicates a weaker texturing of layers in this direction. The texturing of the multilayer increases with increasing annealing temperature. Very strong maxima occur in some places in the pole figures, indicating a texture in a specific direction, different from perpendicular to the surface.

4. Summary and conclusions

The thermal stability investigations showed that the PVD Cu/Ni=2/6 nm multilayer became completely destroyed at a temperature of 300°C (similarly as electrodeposited Cu/Ni multilayers presented in paper [15]). Cracks and a multilayer delamination were observed at the edge of the sample, due to the large difference in thermal expansion coefficients between the multilayer components (Cu and Ni) and the silicon substrate.

The X-ray examination confirmed the presence of satellite peaks around main reflections Cu/Ni(111) and Cu/Ni(200) for multilayer annealing even at 300°C, what indicates a distinct phase boundary in multilayer. It attest to the destruction of multilayer structure integrity occurred prior to the mutual diffusion of the multilayer components.

The annealing resulted in grain growth and an increase in roughness and texture, as confirmed by the AFM and X-ray examinations of the pole figures.

The degradation of Cu/Ni=2/6 nm multilayer took place at higher temperature than the degradation of Cu/Ni=2/1.8 nm multilayer, which was degraded at 230°C [15]. It can, therefore, be concluded that the thicker the Ni sublayer the higher the resistance of the multilayer to higher temperatures.

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Received: 20 February 2012.