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Thermal stability of the Cu/Ni multilayer system in X-ray diffraction and scanning microscopy examinations

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The article presents the results of research into the effect of heating on the stability of a Cu/Ni multilayer applied onto a Si(100) substrate by the magnetron sputtering method. The multilayer was heated in a furnace atmosphere in a temperature range of 40–230 °C. The X-ray structural examination by the X-ray diffraction (XRD) and the grazing X-ray incidence diffraction (GIXRD) methods and microscopic observations of the multilayer surface were carried out. Structural changes were found to occur under the influence of heating due to the mutual diffusion of Cu and Ni, resulting in a loss of the multilayer nature of the structure. Early indications of a surface discontinuity of the multilayer, as noticed in microscopic observations and then confirmed by X-ray measurements, were found at a temperature of 220 °C. At higher temperatures, intensive delamination of the multilayer from the silicon substrate followed as a result of thermal stresses caused by a large difference in the thermal expansion coefficients between the multilayer and silicon.

Keywords: Cu/Ni multilayer, thermal stability, X-ray technique.

1. Introduction

Thin-layered metal systems (multilayers) constitute a group of materials that has been the subject of studies for more than 60 years. The development of new coating application technologies, including electrodeposition and vacuum techniques, and especially the most recent methods, such as chemical vapour deposition (CVD) and physical vapour deposition (PVD), has made it possible to obtain multilayer systems, not only metallic ones, with increasingly thin sublayers [1–5]. Multilayers with thicknesses in the order of several nanometres possess many interesting magnetic, optical, electrical and mechanical properties. From the application point of view, the gigantic magnetoresistance (GMR) phenomenon in ferromagnetic/diamagnetic material systems is regarded as the primary property. The thin-layered Cu/Ni structure is a classic example of a multilayer with such properties [2–8]. Thanks to the identical crystallographic structures (*fcc*) of copper and nickel and the very small lattice misfit (2.5%) of both elements, Cu/Ni multilayers are also characterized by good mutual adhesion of sublayers and the ease of making their arrangements [6, 7]. The properties of multi-layered coatings result from, and depend on the quality of interfaces. Both the high hardness and magnetic properties of multilayers at room temperature are reduced following the annealing of the multilayers at high temperatures. This is associated with the diffusing (widening) of the interfaces and vanishing of the nano-coating structure as a result of the mutual diffusion of atoms. An additional factor influencing the thermal stability of a multilayer is the expansion of the sublayers relative to each other and to the substrate.

The description of variations in material properties as a function of temperature for the purposes of operation applications, with respect to equipment operating at elevated temperatures, is commonly expressed using the term "temperature stability" [9–13]. The present article describes the examination of the temperature stability of a Cu/Ni coating, as annealed at temperatures in the range of 40–230 °C, using X-ray diffractometry and scanning electron microscopy (SEM) techniques.

2. Material and methods

The examination was carried out on a multilayer composed of 100 Cu/Ni bilayers. The multilayer was fabricated on a Si(100) nano-crystalline silicon substrate by the magnetron sputtering method. Prior to the deposition of coatings, the substrates were cleaned following the RCA-1 and RCA-2 wafer clean procedure. The magnetron process was conducted according to the face-to-face technology using 2 targets, each of approx. 2 kW. The sublayer thickness was controlled *in situ* using a quartz scales. The Cu sublayer thickness was 2.0 nm, while the thickness of Ni sublayers equalled 1.8 nm.

The multilayer structure was subjected to X-ray measurements using two X-ray diffractometers: a powder Seifert 3003TT equipped with a heating device [14] and X'Pert MPD and the wavelength of radiation generated by a copper anode tube ($\lambda_{\mathrm{Cu}} = 0.154$ nm). The X-ray examination was made *in situ* while the multilayer was annealed in the temperature range of 23–230 °C. The duration of holding the multilayer at a given temperature corresponded to the time of making two (XRD and GIXRD) diffractions, and was approx. 60 min. The X-ray examinations included Bragg–Brentano symmetrical geometry (XRD) and grazing-incidence X-ray diffraction (GIXRD) measurements in the diffraction angle (2Θ) range of 35°–57° comprising reflections originating from the planes (111) and (200). In the powder diffractometer, in which the radiation was monochromatized through absorption with a Ni filter, Soller apertures on the incident and diffracted beams were used. The Cu/Ni multilayer being the subject of this study was previously examined using this configuration of the apparatus and it was found that a better visualization of the satellite reflections from this multilayer could be achieved when the X-radiation incident on its surface was within the angle range of 5°–10° [15]. This fact results most likely from the features of the multilayer structure (including texture), whose establishing depends on the design solutions of the magnetron apparatus chamber. Based on the authors' previous results reported in study [15], diffraction measurements were made in the present study, both in the symmetrical Bragg–Brentano geometry and with a constant radiation incidence angle of 9°.

After the temperature measurements, the coating was cooled down to room temperature. The state of the multilayer was examined by taking XRD and XRR measurements using an X'Pert MPD diffractometer and by microscopic observations.

The diffractometer used was adapted to the examination of thin layers – the filtering of radiation was done on a monocrystal, and the diffraction conditions corresponded to the parallel beam optics.

The microscopic observations were performed on the multilayer surface using a ZEISS Axiovert 25 optical microscope and a Jeol JSM 5400 scanning microscope to check for retaining the continuity.

3. Results

3.1. The X-ray measurements of the multilayer

The diffraction patterns from the multilayer, as recorded in XRD and GIXRD measurements, represent reflections originating from the planes (111) and (200). These

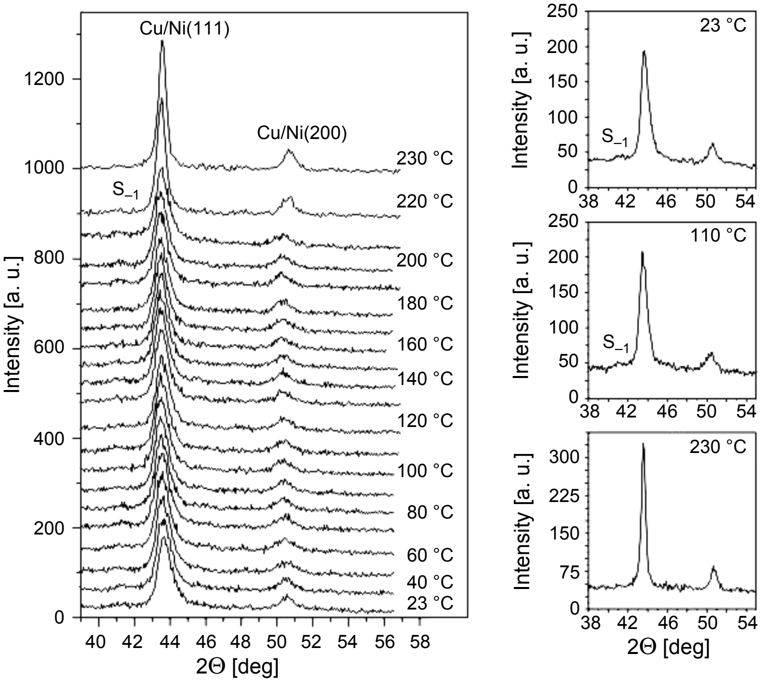

Fig. 1. Diffraction patterns from the temperature measurements of the Cu/Ni multilayer, as obtained by the XRD technique (Bragg–Brentano geometry).

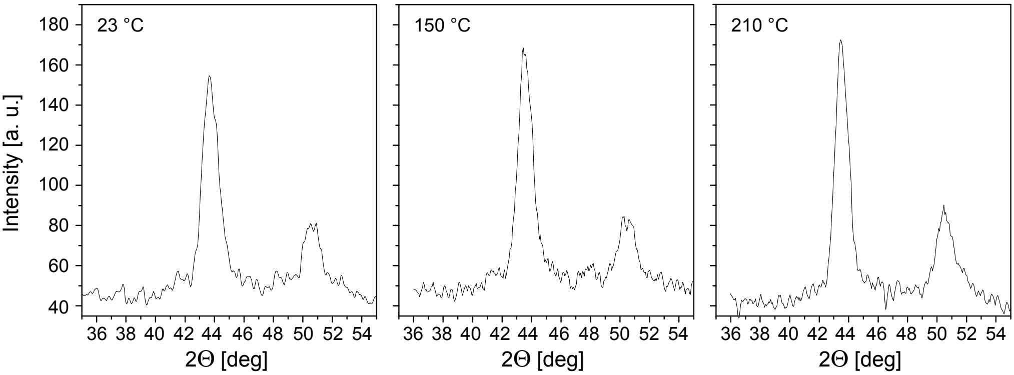

Fig. 2. Diffraction patterns from the temperature measurements of the Cu/Ni multilayer, as obtained by the GIXRD technique (the angle of radiation incidence on multilayer surface is 9°).

reflections are common for both multilayer components because of the similar values of interplanar distances for Cu and Ni (Figs. 1 and 2). Satellite peaks of the first order, S_{-1} and S_{+1}, occurred at the base of the main reflections, which originated from the diffraction of radiation on the boundaries of bilayers (periods) [16]. The presence of the satellite peaks was confirmed by the periodicity of the interfaces, which, at the same time, confirms the layered structure of the coating under examination.

As a result of annealing at temperatures up to 210 °C, the overall intensity of the main reflections and their half-widths β remained at a similar level, with a slight downward trend (Figs. 3 and 4). At temperatures of 220 and 230 °C, a distinct increase in the intensity of the main diffraction peaks occurred, with a simultaneous clear decrease in their width and a reduction of the satellite peaks (Fig. 2). The less clear-cut satellite peaks mean that the interfaces have widened. This widening might be a result of the mutual diffusion of Cu and Ni atoms, but the effect of more intensive vibrations

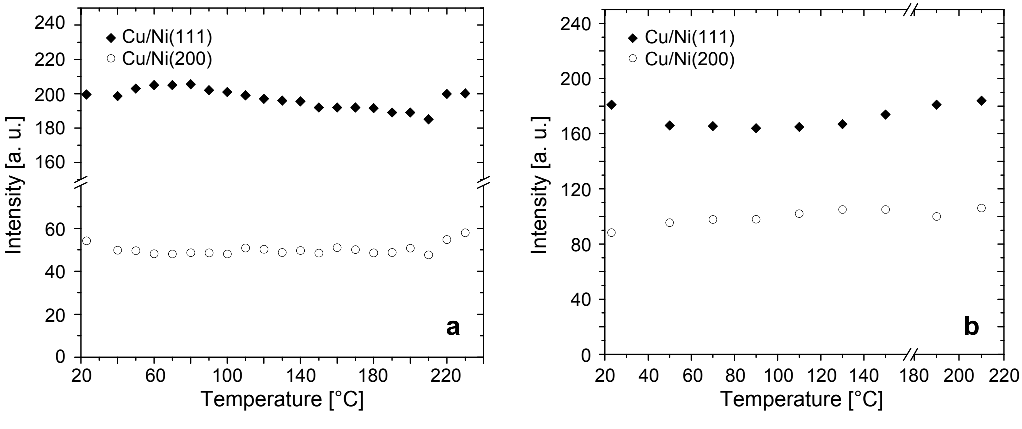

Fig. 3. The overall intensity of the main reflections and the satellite peaks as a function of temperature for XRD (**a**), and GIXRD (**b**) measurements.

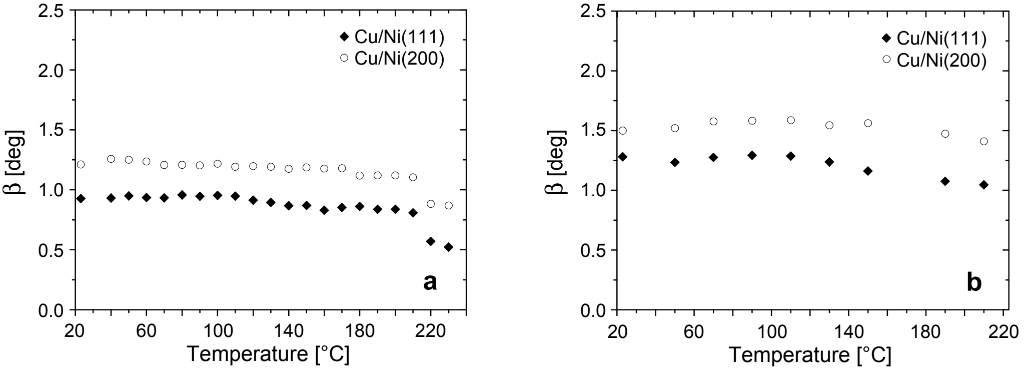

Fig. 4. The half-width of the main reflections for XRD (**a**), and GIXRD (**b**) measurements.

at elevated temperature cannot be excluded either. The parameters of the diffraction reflections, as recorded by the GIXRD technique, do not change in a linear manner with temperature. At a temperature of about 110 °C, their intensity reaches a minimum, whereas the half-widths attain a maximum. This effect can be attributed to the increase in stresses as a result of the thermal expansion of the multilayer on the monocrystalline substrate that is characterized by much lower expansion compared to that of Cu and Ni. At higher temperatures, these stresses undergo partial relaxation as a result of the initiation of atom diffusion processes and the increase in the size of crystallites. The distinct stress relaxation occurred at the moment of the multilayer breaking, which manifested itself by a dramatic decrease in the half-width of the reflections recorded at temperatures of 220 °C and 230 °C by the XRD technique (Fig. 4**a**).

The change in both diffraction reflection parameters might result both from the increase of crystallite size and from the relaxation of stresses in the multilayer. The half-width is, ultimately, always a combined result of both of these phenomena:

$$\beta = \beta_z + \beta_k \tag{1}$$

The narrowing of the reflection, resulting from the relaxation of stress β_z, can be determined from the Taylor relationship [17]:

$$\beta_z = 4e\tan(\Theta) \tag{2}$$

where: e – lattice deformation, Θ – Bragg angle, rad.

The half-width of the reflection, expressed as a function of crystallite diameter, is described by the Scherrer equation [18]:

$$\beta_k = \frac{K\lambda}{D_{hkl}\cos(\Theta)} \tag{3}$$

where: β_k – reflection width, depending on crystallite size, rad; K – constant that equals unity; λ – radiation wavelength, Å; D_{hkl} – crystallite size in the direction perpendicular to (hkl), Å; Θ – Bragg angle, rad.

In addition to the change in the profile of the reflections, also their shifting took place. Starting from a temperature of approx. 100 °C up to a temperature of 200 °C, the reflections shifted towards larger angles; the shift was the greatest at the temperature of 200 °C. At 210 °C, the reflection shift decreased, and at 220 °C the reflection returned to its position before the annealing (Fig. 5).

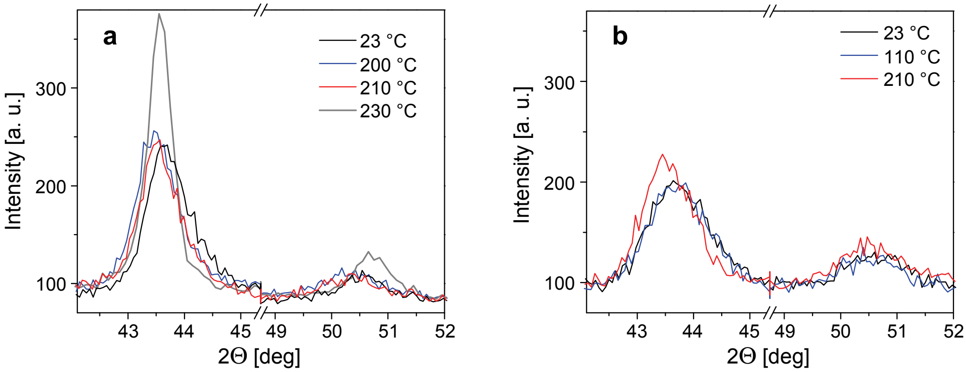

Fig. 5. Change in the position of the main reflections under the influence of annealing, XRD (**a**), and GIXRD (**b**) diffractions.

Based on the shift of the reflection (111), the narrowing of its corresponding half-width β_z, was calculated from Eq. (2) – Fig. 6. For the temperature of 200 °C, the calculated reflection narrowing, β_z, was 0.09°, while the total half-width change was 0.05°. This indicates that during heating up to the temperature of 200 °C, a crystallite growth also took place, which was associated with a reflection width reduction by 0.04°. The crystallite size growth corresponding to this narrowing, as calculated from Eq. (3), was approx. 0.6 nm, which constitutes approx. 30% of the single layer thickness. Assuming that the multilayer cooled down from the temperature of 230 °C

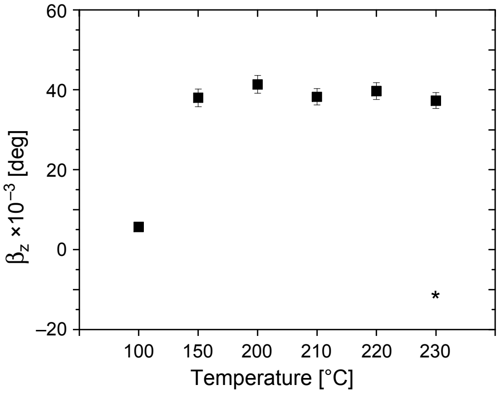

Fig. 6. Change in the half-width of the reflection (111) resulting from stress relaxation, * – the level stresses in the multilayer heated at 230° and then cooled down to room temperature.

is almost completely free from stresses ($\beta = \beta_k$), the crystallite size, as calculated from Eq. (3), is 17.1 nm.

Cooling down the multilayer from the temperature of 230 °C to ambient temperature caused both main reflections Cu/Ni(111) and Cu/Ni(200) to have shifted towards smaller angles (Fig. 7). This means that stresses were present in the multilayer after its deposition and before the soaking. It should be emphasized that in spite of soaking the multilayer, the S_{-1} and S_{+1} satellite peaks were still visible in the diffraction pattern made after cooling the multilayer to room temperature (Fig. 7), though their intensity decreased, which indicates that the soaking did not result in the disappearance of the multilayer structure, but only in a widening of the interfaces.

The XRR examinations confirmed the conclusions drawn from the measurements by the XRD and GIXRD techniques. In its as-deposited state before soaking, the Cu/Ni multilayer had a periodic structure, as evidenced by the presence of Bragg peaks in

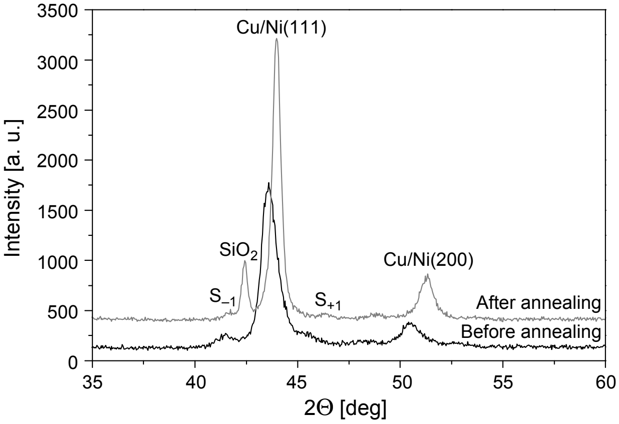

Fig. 7. Diffraction patterns of a Cu/Ni = 2/1.8 nm multilayer recorded at ambient temperature (prior to and after soaking).

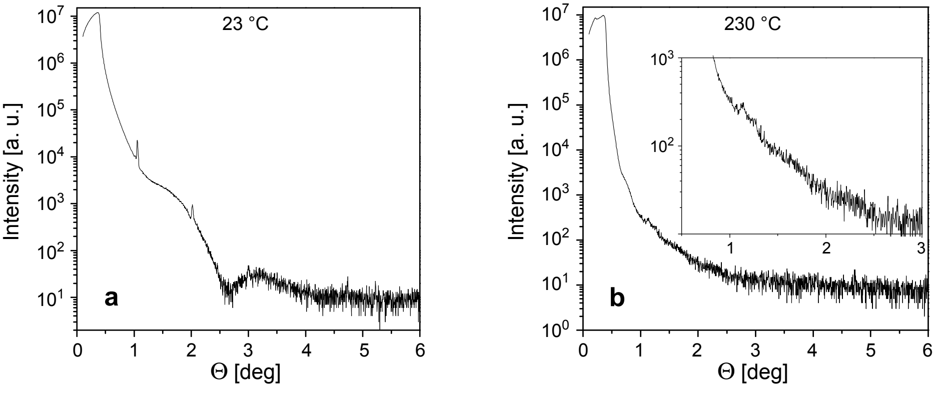

Fig. 8. XRR curves of the multilayer obtained at room temperature: in as-deposited state (**a**), after annealing at 230 °C (**b**).

Fig. 8. After the multilayer has been soaked at 230 °C and then cooled down, the Bragg peaks have very low intensity, which is indicative of the interface widening effect and the mutual diffusion between Cu and Ni sublayers. Based on atom probe tomography (APT) examination, the study by Balogh *et al.* [16] demonstrated that soaking resulted in the diffusion of Cu to the interfaces at the cost of a reduction in the width of the Ni sublayer. The term "interface widening" means that an increasingly wide solid solution zone forms within the interface, and the geometrical conditions for obtaining satellite reflections from the multilayer cease existing. As demonstrated by study [16], a short-lasting soaking, even at higher temperatures 500 °C/2 min), may cause a better sharpness of Cu/Ni interfaces. In the present study, despite using a relatively low soaking temperature, the total soaking time was longer by several times.

3.2. Thermal expansibility of the multilayer

The linear coefficient of expansion of the multilayer was calculated from the following equation:

$$\alpha_{hkl} = \frac{d^T_{hkl} - d_o}{d_o \Delta T} \tag{4}$$

where: α_{hkl} – coefficient of linear expansion, K^{-1}; d^T_{hkl} – interplanar distance, as determined at temperature T, nm; d_o – interplanar distance, as determined at ambient temperature, nm; ΔT – difference between the examination temperature and ambient temperature, K.

The calculation was made assuming different temperature ranges, with the starting temperature corresponding to ambient temperature being equal to 23 °C (Fig. 9). Within the whole temperature range used, the Cu/Ni multilayer had a thermal expansion coefficient value considerably higher than that of the monocrystalline Si(100) silicon substrate. A certain increase in the coefficient of thermal expansion of the multilayer

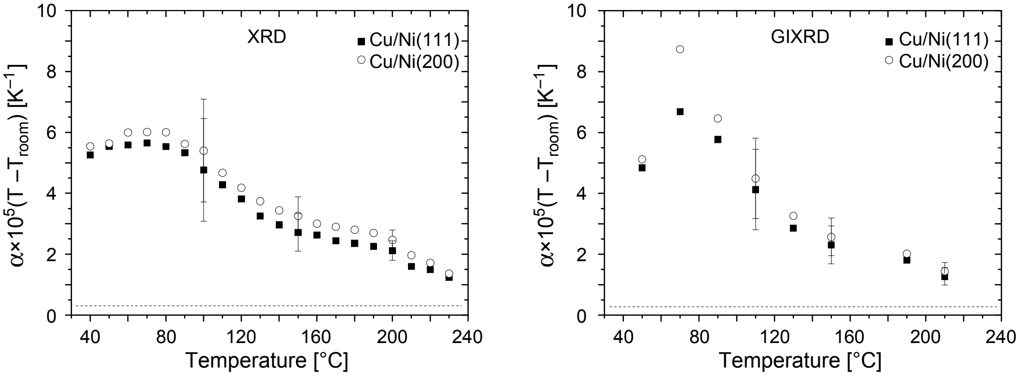

Fig. 9. The coefficient of thermal expansion of the Cu/Ni multilayer as a function of temperature for the main reflections (111) and (200).

was found in temperature ranges of up to 70 °C, following by its progressive decrease down to a value close to the thermal expansibility of Cu and Ni within the largest temperature range of 23–230 °C.

The decrease of the thermal expansion coefficient could have been influenced by the strong adhesion of the layer to the substrate that prevented the free dilatation of the layer, which, as a consequence, caused a build-up of thermal stresses within the multilayer [16]. After exceeding the critical stress value, delamination of the multilayer followed as a result of stress relaxation.

3.3. Microscopic observations of the multilayer surface

Early signs of the multilayer losing its continuity were observed after annealing at 220 °C (Fig. 10). Numerous fine discontinuities elliptical in shape and arranged in

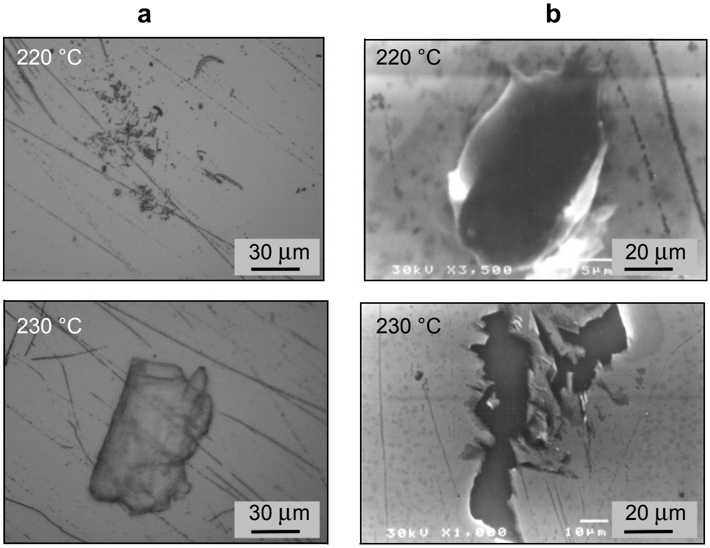

Fig. 10. Discontinuities in the Cu/Ni multilayer caused by annealing at temperatures of 220 and 230 °C, respectively: optical microscope (**a**), SEM (**b**).

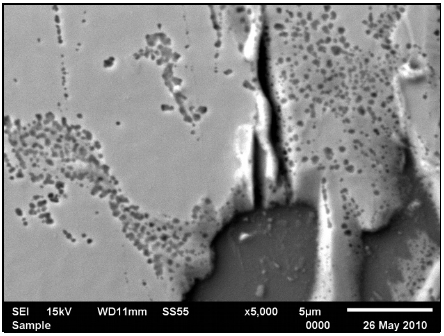

Fig. 11. The character of losses in the Cu/Ni multilayer after annealing at 230 °C.

chains, and a few larger ones, occurred on the surface. Fine discontinuities did not embrace the whole thickness of the coating, but only its outermost layers, whereas larger discontinuities exposed the substrate. The discontinuities were preferentially located in surface scratches, but a chain-like arrangement of discontinuities also formed, where no scratches were observed. The observations made before the annealing tests found that the presence of scratches did not break the continuity of the coating. Annealing at 230 °C resulted in considerable losses in the coating, which were caused by the detachment of the coating from the silicon substrate (Fig. 11). The discontinuities developed, which were irregular in shape and had straight edges. Observations made at a magnification of 5000× indicated that the delamination of the entire multilayer after being annealed at 230 °C was not associated with the elliptical surface losses, but was due to the different coefficient of thermal expansion from that of the substrate. The complete breaking of the multilayered system cohesion

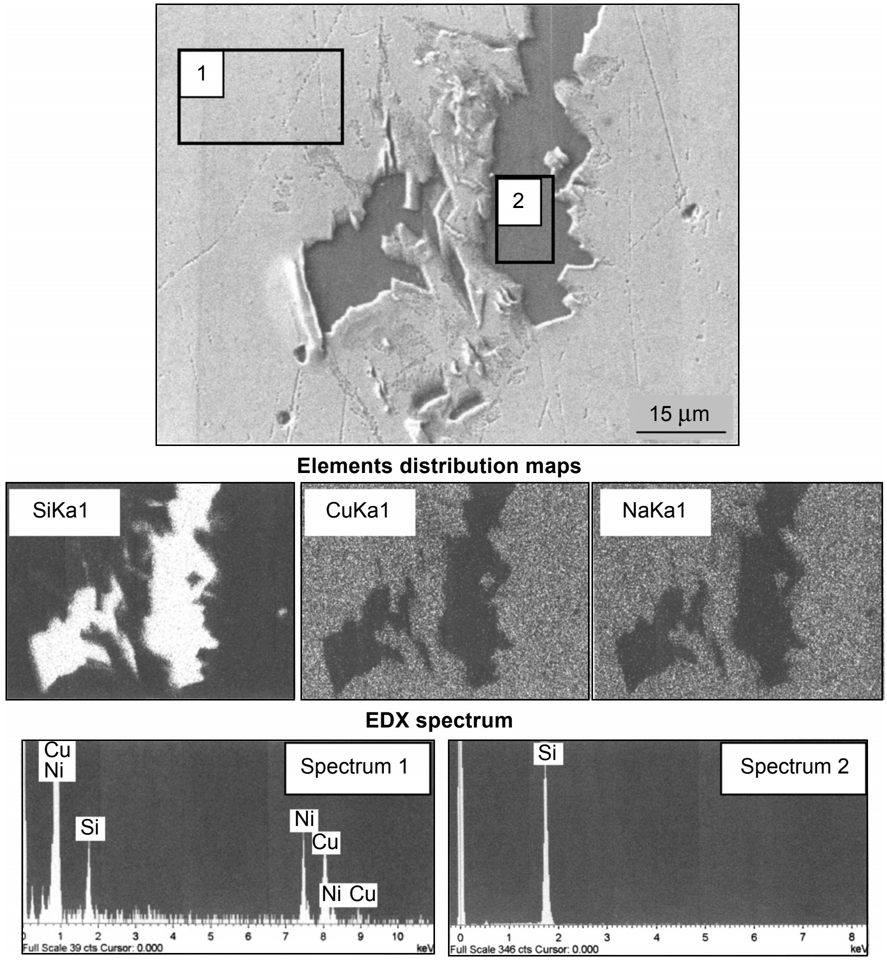

Fig. 12. The area of Cu/Ni multilayer degradation after the process of annealing at 230 °C.

and the delamination of the coating were confirmed by the EDX examination and by the elements distribution map (Fig. 12).

The X-ray diffraction examination showed a reduction in the intensity of the first--order satellite peaks, S_{+1} and S_{-1}, above the temperature of 220 °C. In the GIXRD measurements, diffraction patterns with no satellite peaks present on the layers annealed at a temperature of 210 °C were already obtained, but in the XRD measurements, some small satellite reflections were also recorded after annealing at 230 °C. This means that the applied annealing operation did not cause the total damage of the layered structure of the coating in the process of mutual diffusion of sublayer components, *i.e.*, Cu and Ni, and the delamination is the result of the difference in expansibility between the multilayer and the substrate.

4. Conclusions

The investigation has demonstrated that the Cu(2 nm)/Ni(1.8 nm) multilayer, as fabricated by the magnetron sputtering method, undergoes mechanical damage at a temperature of 220 °C as a result of the loss of continuity and detachment from the silicon substrate. Minor, elliptical surface discontinuities make up the first stage of damage and provide the indication that the thermal stresses within the multilayer have reached a critical level. The thermal stresses result from the great difference in thermal expansion coefficients between the multilayer and the Si(100) substrate and good adhesion to the silicon substrate, which prevents the free dilatation of the layer. The thermal expansion coefficient of the multilayer in the initial temperature ranges is by more than 10 times greater than that of the substrate. The thermal stability of the multilayer is related with fine technological scratches present on the surface, in which initial elliptical surface discontinuities preferentially lie down.

Progressive damage of the subtle multilayer structure takes place in the annealing process, which is accompanied by the disappearance of satellite peaks on the diffraction patterns. In the applied ranges of temperatures and testing times, the loss of adhesion preceded the disappearance of the layered character of the structure due to diffusion.

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