Oxidation and reduction processes in Ni/Cu/Cr/Si(100) thin films under low-energy ion irradiation

I O Kruhlov1,2, I A Vladymyrskyi1, O Dubikovskyi1, S I Sidorenko1, T Ebisu3, K Kato4, O Sakata5,6,7, T Ishikawa1, Y Iguchi1, G A Langer1, Z Erdélyi8 and S M Voloshko1

1 Metal Physics Department, National Technical University of Ukraine ‘Igor Sikorsky Kyiv Polytechnic Institute’, Prospect Peremogy 37, 03056 Kyiv, Ukraine
2 RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo-Cho, Sayo-Gun, Hyogo 679-5148, Japan
3 Department of Ion Beam Engineering, V. Ye. Lashkaryov Institute of Semiconductor Physics (ISP), NAS of Ukraine, Prospect Nauki 41, 03028 Kyiv, Ukraine
4 National Institute for Materials Science, 1-1-1 Kouto, Sayo-Cho, Sayo-Gun, Hyogo 679-5148, Japan
5 Department of Solid State Physics, Faculty of Sciences and Technology, University of Debrecen, P O Box 400, H-4002 Debrecen, Hungary
E-mail: kruhlov@kpm.kpi.ua
Keywords: ion bombardment, thin films, interface, surface, reduction processes

Abstract
Ni(25 nm)/Cu(25 nm)/Cr(25 nm) thin films were deposited by DC magnetron sputtering at room temperature onto Si(100) single-crystal substrates and irradiated by low-energy Ar+ ions in the energy range of 400–2000 eV with fluences of 1.4 × 1016–1.1 × 1017 ion cm−2. Influence of the ion bombardment on the structural properties, surface morphology and chemical composition was investigated using XRD, AFM, SEM, AES, XPS, SIMS and SNMS techniques. It was found that the low-energy ion bombardment does not lead to phase composition modifications, but causes reduction of Ni layer crystallites size. Optimal bombardment mode (energy 800 eV, fluence 5.6 × 1016 ion cm−2), providing reduction of impurities amount in all three layers of the stack without diffusion intermixing between main components, was determined. Calculated coefficients of internal layers passivation are in good agreement with found increase of Cr and Cu layers thicknesses due to the reduction processes. New model of reduction processes taking into account the long-range effect was proposed.

1. Introduction
Low-energy (<10 keV) irradiation of metals and alloys surfaces by ions of inert gases is widely used for coatings deposition with respect of physical and mechanical properties as well as adhesion enhancement [1–3]. Furthermore, such treatment could be used in different surface analysis techniques e.g. SIMS [4, 5] and TEM [6, 7] as well as for removing of some native oxides and different impurities from films surfaces [8, 9].

However, chemical activity of the surface could also be modified via low-energy sputtering by ions of inert gases. Initial studies of bulk materials showed that U, Fe, Al, and Cu surfaces could become passivated for oxidation under atmospheric conditions after low-energy bombardment by Ar+ or He+ ions with certain fluences [10–12]. The later more detailed studies of bombardment impact, using ions of inert gases with the energy of about 1 keV, on chemical activity of the surfaces were reported for Cu, Ni and Fe [13–18]. It was found that gas—surface interaction and surface chemical activity are controlled both by the optimal ratio between beam energy and density of primary ion current as well as by sputtering rate of native oxides and metals. Mechanisms of surfaces passivation were considered in details in [19, 20].

Low-energy interval of ion bombardment is highly attractive for modern thin films technologies as well. Higher energies could induce the ion implantation into the surface layers of metal films [1] or diffusion processes activation with corresponding modification of the properties [21, 22].

By varying the energy of ion beams in the low-energy interval, it becomes possible to control effectively different properties of deposited layers. Special attention is given to investigation of surface morphology of thin...
films under influence of low-energy ion irradiation, and a type of primary ions has a decisive role in this process [23]. Low-energy ion bombardment could lead to hindering of recrystallization processes, stabilization of nanocrystalline structure and lowering of oxidation during subsequent heat treatment [22]. Parida et al investigated impact of the low-energy (3 keV) bombardment with different durations on the surface state of Cu(20 nm)/Ni(40 nm) stacks [24]. It was found that 10 min of such irradiation is enough for complete reduction of Cu oxides from the surface. The similar effect of oxides reduction under low-energy ion bombardment up to clean metallic surfaces was discussed by Kubart et al [25]. Effect of O and C impurity atoms removal through the whole depth of Ni/Cu/ Cr layer stack after several modes of low-energy ion-plasma treatment was revealed in [21].

For our best knowledge, there are no systematic studies of low-energy ion irradiation effect on physical and chemical properties of Cu/Ni thin films despite the fact that these stacks are widely used in microactuators, nanomold for nanoprinting and magnetic devices [24].

Thus, in this paper we have studied structural properties, surface morphology, chemical and phase composition of Ni/Cu thin films with Cr adhesion layer under low-energy ion Ar+ irradiation in order to characterize oxidation and reduction processes in the energy range of 400–2000 eV and fluences of $1.4 \times 10^{16}$–$1.1 \times 10^{17}$ ion cm$^{-2}$.

### 2. Experimental

Ni(25 nm)/Cu(25 nm)/Cr(25 nm) layer stacks were deposited by DC magnetron sputtering at room temperature from high-purity Ni(99.995 at%), Cu(99.99 at%), and Cr(99.95 at%) targets onto Si(100) single-crystal substrates. The chamber was evacuated up to $2.0 \times 10^{-5}$ Pa before the sputtering. Dynamic Ar ($6.0 \times 10^{-1}$ Pa) was flowed during the deposition process. Layers thickness was evaluated by stylus profilometer and verified by secondary neutral mass spectrometry depth profiling. Thickness error was not higher than 5% for each layer.

Before deposition, the substrates were cleaned without removing of already existed native oxide layer. Removing of this layer by ion sputtering before Cr layer deposition is not reasonable due to potential beam-induced modification of Si substrate crystalline structure [26] and its roughening [27]. Whereas we aimed to study surface modifications, having no influence on initial phase composition of the stack. Moreover, oxide sublayer at the Cr/Si interface enhances the Cr adhesion and prevents formation of the chromium silicide. It should be noted that Cr reveals high affinity to O (enthalpy of Cr$_2$O$_3$ formation is $–1120$ kJ mol$^{-1}$). Cr 25 nm-thick adhesion layer was deposited prior to Cu in order to enhance the Cu/Si interface which had exhibited a poor adhesion [28].

Low-energy Ar+ ion bombardment of films surfaces was performed using OMI-0010 source with energies in the range from 400 to 2000 eV, durations from 5 to 40 min, and a constant ion current of 8.5 μA. Ion fluences were calibrated using standard Faraday cup and varied in the range of $1.4 \times 10^{16}$–$1.1 \times 10^{17}$ ion cm$^{-2}$.

Parameters of ion bombardment are summarized in table 1. For clarity numbering corresponds to the increase of energy.

The thickness of non-sputtered Ni layer was evaluated by surface profilometry technique using SurfCorder ET 4000 LS (Kosaka Laboratory Ltd) device, applying a force of 10 μN. This data is also given in table 1.

Ranges of both ions energy and treatment duration were chosen using previous theoretical calculations of Ni sputtering yields based on Sigmund’s theory [29]. Ni sputtering yield S(E) in case of bombardment by monokinetic ions with energy <1 keV, assuming spring collisions with target atoms, was calculated using the following equation:

### Table 1. Parameters of the low-energy ion bombardment modes and thickness of non-sputtered Ni layer.

| Mode | Beam energy [eV] | Duration [minutes] | Fluence ($\times 10^{15}$) [ion cm$^{-2}$] | Residual Ni thickness [nm] |
|------|------------------|--------------------|------------------------------------------|--------------------------|
| 1st  | 400              | 40                 | 11                                       | 16                       |
| 2nd  | 600              | 5 × 6 times        | 8.4                                      | 17.3                     |
| 3rd  | 600              | 30                 | 8.4                                      | 20.5                     |
| 4th  | 800              | 5 × 4 times        | 5.6                                      | 23                       |
| 5th  | 800              | 20                 | 5.6                                      | 16.8                     |
| 6th  | 1400             | 10                 | 2.8                                      | 20.5                     |
| 7th  | 2000             | 5                  | 1.4                                      | 19                       |
where $M_1$ and $M_2$ are atomic weights of Ar and Ni; $E_{\text{sub}}$ is a sublimation energy of Ni; $E_i$ is the energy of Ar primary ions; and $\alpha$ is a coefficient, which characterizes efficiency of energy transfer and can be determined from $M_1$ to $M_2$ ratio. For ion energies above 1 keV, the dependence of the sputtering yield on nuclear and electron stopping was also taken into account.

Our quantitative estimation of Ni sputtering yield with the following check using SRIM2010 software [30] suggest its almost linear dependence on ion energy within the chosen range.

Restrictions on the Ni sputtered thickness were imposed based on the features of the x-ray diffraction analysis technique. We aimed to determine structural characteristics of Ni under in situ sputtering. We used low-energy ion action can be both continuous and pulse-periodic. Often there is a need to take spectra at regular time intervals or alternate ion sputtering with other technological operations. For pulsed irradiation during 5 min with $x$-times ($x = 6$ and 4, respectively) repetition, we used selective energies of 600 eV and 800 eV, which are commonly used for depth profiling [32] and were reported to promote the passivation of the bulk materials surfaces [20].

Structural properties of the stacks after deposition and ion bombardment were analyzed by x-ray diffraction (XRD), using synchrotron radiation and grazing-incidence wide-angle x-ray scattering method at RIKEN SPRing-8 Materials Science BL44B2 Beamline. The Debye-Scherrer camera of 286.5° with an image plate detector (400 × 200 mm). The grazing angle between the beam and sample surface was 0.5°, while the x-ray wavelength was adjusted to 1.08 Å. Vertical and horizontal beam sizes were 0.01 mm and 3.0 mm, respectively.

Averaged crystallite sizes (or coherence lengths) $L$ of film layers were evaluated from XRD data using Scherrer equation by measuring full width at half maximum (FWHM) of the peaks [33]:

$$L = \frac{K\lambda}{\beta \cos \theta}$$

where $L$ is the crystallite size, $\lambda$ is a wavelength of x-ray, $\theta$ is a diffraction angle, $K$ is a constant related to a crystallite’s shape ($K = 0.94$, assuming the spherical particle’s shape), and $\beta$ is the physical broadening of the peak. $\beta$ was calculated as $\sqrt{B^2 - b^2}$, where $B$ is the broadening obtained from film and $b$ is the instrumental broadening, obtained using SRM 1976b reference material.

All measurements were carried out for all samples in one cycle, applying the identical conditions and parameters of the experiment. Previous to experimental studies of the irradiation-induced modifications, all samples were examined by spectral depth analysis and the layers thickness in the initial state was controlled.

The composition-depth profiles of the as-deposited and ion irradiated samples were extracted by an INAA type secondary neutral mass spectrometer (SNMS, SPECS GmbH Berlin). The direct bombardment mode with inductively coupled low-pressure radiofrequency Ar plasma was used and served as a source of bombarding ions as well as a post-ionization medium. The sputtering area was 3 mm in diameter. In order to get both high depth resolution ($<2$ nm) and intensity for concentration determination, a bias voltage of 350 V was applied to the sample. X-ray photoelectron spectroscopy (XPS) of the samples was carried out at the same device without breaking the vacuum.

Secondary ion mass spectrometry (SIMS) measurements were carried out with primary beam of positive O$^+$ (1 keV) and negative Cs$^-$ (2 keV) ions, using Ion ToF IV device. In addition, a 3D-visualization of the secondary ions distribution was performed from $1 \times 1$ μm$^2$ area in the center of ion etching crater to prevent the crater wall effect influence. Positive Ar$^+$ ions were applied as well for registration of main components and fragmentary $^{77}$NiO$^{-}$ and $^{60}$CrO$^+$ ions, using MC-7201M spectrometer. Discharge current of ion gun was 0.4 mA with primary beam current of 10 μA (current density of 2 μA mm$^{-2}$), and base pressure of 5.5 × 10$^{-9}$ Pa.

The use of different primary ions was employed due to the limited sensitivity of some ions to certain elements (Cu in Ar$^+$, Cr in Cs$^-$, C and fragmentary oxides in O$^+$ ions). Therefore, a comprehensive approach was applied, allowing to get a maximum information about the chemical composition of the studied stacks.
Auger electron spectroscopy (AES) measurements were accomplished using Jamp-9500F (Jeol) device. AES depth profiling was carried out by etching the surface of the film with 1 keV Ar\(^{+}\) ions at 30° incidence to the sample surface. Spectra were recorded at the primary electron beam energy of 10 keV and a current of 30 nA with a 0.6% resolution. Ion sputtering craters were also investigated by scanning electron microscopy (SEM) using both secondary and Auger electrons at sample tilt angle of 45°.

Modification of surfaces morphology under ion sputtering was studied by atomic force microscopy (AFM), using Bruker Dimension Icon device.

3. Experimental results

SNMS depth profiles (figure 1) illustrate decrease of Ni layer thickness after different modes of ion bombardment and sputtering, being in a good agreement with the profilometry data. Residual thickness of Ni layer is in the range of 16–23 nm (please see table 1), depending on the mode, but is not less than 2/3 of the initial value (which was a required condition). The lowest residual Ni thickness (16 nm) is observed for the highest ion fluence (1st mode), while the highest one is found for pulsed 4th mode with an intermediate energy value of 800 eV.

Ni sputtering rate \(v_p\) which depends on the \(S(E_i)\) sputtering yield (equation (1)), for different modes of ion bombardment, in case of a bulk defect-free polycrystal can be calculated by known relation [34]:

\[
v_p = 1.04 \times 10^{-4} \frac{j_i M_i S(E_i)}{\rho}
\]

where \(j_i\) is ion current density and \(\rho\) is the density of Ni.

Calculated theoretical dependence of \(v_p\) on the energy is given in figure 2, where the experimental values evaluated on the data from figure 1 are also shown. It can be seen that 1st, 2nd, 5th and 7th modes are close to the theoretical line, while values for 4th and 6th modes are much lower compared to the theory. Intermediate sputtering rate is observed in case of 3rd mode.

The deviations between experimental data and theoretical calculations found for some modes are attributed to the fact that thin layered films are significantly influenced by a number of factors, such as perfection of crystalline structure, grain size, chemical composition of layers and interfaces, atomic mixing, surface roughness [35]. These features are not considered by Sigmund’s theory.

XRD analysis using synchrotron radiation of the as-deposited film reveal diffraction peaks with \(d\)-spacing corresponding to fcc-Ni, fcc-Cu and bcc-Cr (figure 3) phases. Calculated lattice constants of these phases are

\[a_{\text{Ni}} = 3.526\ \text{Å}, \quad a_{\text{Cu}} = 3.621\ \text{Å}, \quad a_{\text{Cr}} = 2.888\ \text{Å},\]

being in good agreement with the literature data [36]. It is worth noting that the following ion bombardment does not lead to any modification of the initial phase composition and no peaks from oxides or other compounds in both as-deposited and ion irradiated films were detected. Only bombardment with the highest energy of ion beam (2000 eV) leads to a slight decrease of Ni lattice constant from 3.526 Å to 3.514 Å, while \(a_{\text{Cu}}\) and \(a_{\text{Cr}}\) remain constant.

It is clear that the reduction in the amount of material due to the sputtering process should accordingly lower the integral intensity of Ni peaks at diffraction scans. However, the overlapping of some peaks from Ni and Cr (IOP Publishing Mater. Res. Express 6 (2019) 126431 I O Kruhlov et al.
i.e. Ni\((111)\) and Cr\((110)\) as well as Ni and Cu (i.e. Ni\((200)\) and Cu\((200)\)) should be considered, complicating the interpretation of experimental data. In order to unambiguously associate the experimentally observed decrease in the integral intensity of the Ni peaks to its sputtering and to exclude influence of other factors, theoretical XRD patterns were simulated using GNU Octave software. Simulation was performed for the Ni/Cu/Cr stack with a layers thickness of 25 nm (figure 4(a)), as well as for stacks with a gradual thinning of the upper Ni layer. The calculations were based on the assumption that no diffusion intermixing between the film layers had occurred.

Figures 3(a)–(c) shows simulated XRD patterns in case of initial Ni layer thickness decrease for 0 nm, 5 nm and 10 nm, respectively. These results allowed to distinguish the contribution from Ni\((111)\) and Cr\((110)\) diffraction peaks to the integral intensity. Theoretical and experimental values of intensity ratio between Cu\((111)\) peak and Ni\((111)\) + Cr\((110)\) integrated peak are summarized in figure 4(d). Reasonable agreement between the theoretical and experimental data was obtained for all modes, except of 1st mode with the highest fluence of the ion irradiation.
This effect can be attributed to the high roughness of the irradiated surface, leading to the formation of Cu islands \[24\], as well as to the radiation-induced diffusion processes activation \[21\]. However, intensities of Cu peaks and \(I_{\text{Cu}(111)}/I_{\text{Ni}(111)+\text{Cr}(110)}\) ratio should be increased in case of Cu diffusion through the Ni layer with the following Cu accumulation at the Ni surface. XPS data confirmed that only in the case of 1st mode about 10 at\% of Cu is registered at the outer surface. This factor was not considered in our theoretical calculations, while the concentration gradient of components through the film depth should be taken into account to eliminate the error. Finally, for 2nd – 7th modes the decrease in Ni peaks integral intensity is attributed to its ion sputtering, and in case of 1st mode additionally to the diffusion of Cu towards the outer surface.

The averaged values of crystallites size of each layer were calculated for most clearly separated diffraction peaks (Ni(220), Cu(220) and Cr(211)) and are summarized in figure 5. As can be seen, ion bombardment does not lead to the considerable changes in crystallites size of Cu and Cr layers compared to the as-deposited state. The calculated values are ~10–11 nm and ~6–7 nm for Cu and Cr, respectively. At the same time, decrease of the Ni crystallites size from ~13 nm (as-deposited state) to ~8 nm was established after 5th and 7th modes, while not so pronounced changes (~10 nm) were established for other modes.

Comparison of the 2nd pulsed and 3rd continuous modes, subjected to the same ion energy of 600 eV and identical fluences, showed different effect on the thickness of sputtered Ni—it was higher after pulsed bombardment. However, almost no difference in crystallites size was detected. The comparison of 4th (pulsed) and 5th (continuous) modes with higher energy of 800 eV and equal fluences gives slightly different results. The thickness of the sputtered layer is much higher, and the crystallites size of Ni is smaller in case of continuous bombardment. The crystallites size of Ni in case of pulsed irradiation is found to be almost the same as for the as-deposited state.

It can be concluded, that according to the XRD results, ion bombardment with energies < 2000 eV does not lead to modification of the initial phase and structural composition of the film. Activation of bulk diffusion processes was not detected as well. At energy of 2000 eV, slight structural modifications—the decrease of both lattice constant and crystallites size—were found out in the upper Ni layer only, while no changes in the deeper ones were detected. Since there is no clear correlation between the experimental sputtering rate (figure 2) and

![Figure 4. Simulated (a)–(c) XRD patterns of the as-deposited film (thickness of Ni layer is 25 nm) and after Ni thinning down to 20 and 15 nm. Figure (d) represents Cu(111) to Ni(111) + Cr(110) intensity ratio evaluated from the experimental and simulated XRD data.](image-url)
residual thickness (table 1) of Ni layer with the crystallites size after ion bombardment, it was expedient to study in detail the chemical composition of the films.

It is noteworthy that XRD analysis revealed no oxide phases in the films. Nevertheless, it is known that magnetron sputtering under low-vacuum plasma conditions is often accompanied with the incorporation of impurities, and especially O, in a growing film [37]. As a result, formation of ultrathin oxide sublayers with various chemical composition and structure may occur at the film/substrate interface [38] as well as at the internal interfaces. As reported by Cen et al. [39, 40] existence of such oxide sublayers were detected even at the interface between Ni and noble metals, e.g. Au. In addition to O, an increased content of C can be observed at the interfaces as well [41].

SIMS approach is known for its ultrahigh sensitivity, allowing to determine not only very low elemental concentration (1 per 10⁶ particles), but also presence of chemical compounds [42, 43]. In our case SIMS technique was applied in order to check presence of O and C in the films, since even very limited O amount could negatively affect the functional properties of thin films. Application of chemically inert Ar⁺ ions in combination with dynamic SIMS mode provide quantitative characteristics of O amount through the depth of Ni/Cu/Cr stack in the as-deposited and irradiated samples. However, there is a limitation of direct observation of the upper layer surface due to the relatively high rate of its sputtering.

Figure 6 shows SIMS distribution of fragmentary secondary +74(NiO)²⁺ and +68(CrO)²⁺ ions obtained with primary Ar⁺ ions. Left side of the figure 6 represents results for Ni layer from the outer surface to the Cu interface, while the right side shows results for Cr layer from the Cu interface to the highest value of I⁺CrO intensity. Such profiles were not obtained for Cu due to its high sputtering yield and, respectively, low coefficient of secondary ions emission (although the data for CuO are shown in the central part in figure 6. These data were obtained with Cs⁻ primary ions and will be discussed below). Oxides presence was detected in all films, while ion irradiated samples demonstrated lower intensities of the fragmentary +74(NiO)²⁺ and +68(CrO)²⁺ ions, reaching the minimum values in case of 5th mode.

Notably, that in case of 6th mode I⁺NiO signal is even higher than for as-deposited film, which can be attributed to the sputtering-induced modification of the surface relief. It is well known that reactivity of metal surfaces depends not only on its chemical activity but on the structural properties as well, including surface roughness [13]. AFM scanning measurements of the surface showed that most significant increase of the root-mean-square (RMS) roughness was achieved after 6th mode (figure 7). For 6th mode a non-uniform surface topography of the ion-irradiated sample with an average roughness of ~2.46 nm was explored, while in the as-deposited state a uniform and smooth surface with an average roughness of ~0.4 nm was observed. Other modes are characterized by intermediate RMS within this interval, whereas the 5th mode revealed the lowest value ~0.72 nm among the irradiated samples.

Coefficients of surface passivation were calculated using the data presented in figure 6, in the same way as it was performed in [17, 18]. Passivation coefficient γ of Ni was calculated as:

\[
\gamma_{Ni} = \frac{I_{NiO}/I_{NiO_{dep}} - I_{NiO}/I_{NiO_{ib}}}{I_{NiO}/I_{NiO_{dep}}} \times 100\%
\]
where $[I_{\text{NiO}}/I_{\text{Ni}}]_{\text{dep}}$ and $[I_{\text{NiO}}/I_{\text{Ni}}]_{\text{irr}}$ are the intensity ratios of NiO and Ni secondary ions received for the as-deposited and ion irradiated films, respectively. The passivation coefficient $\gamma$ for Cr was determined similarly.

Passivation coefficients of Ni and Cr were found to be the highest after 2nd and 5th modes of ion bombardment (figure 8), reaching ~70%. These modes are also considered as optimal in respect to the Ni crystallites size (8–10 nm, figure 5), sputtering rate (figure 2), and $I_{\text{Cu(111)}}/I_{\text{Ni(111)}+\text{Cr(110)}}$ intensity ratio, which are close to the theoretical values (figure 4).

The lowest passivation is observed after 3rd and 6th modes of the treatment. Moreover, in case of 3rd mode the $\gamma_{\text{Cr}}$ reveals a negative value, indicating the development of oxidation processes.

Further investigation of chemical composition of the as-deposited and irradiated films was performed using SIMS with primary negative Cs$^-$ ions (figure 9). Advisability of Cs$^-$ ions application for thin films analysis [44] is associated with the fact that Cs has the lowest ionization potential (3.9 eV) among the all elements and could reduce the work function of the matrix electrons. Thus, a neutral atom leaved from the surface could capture an...
electron from the matrix and become to a negative ion state with a higher probability. Consequently, lower energy consumption is needed for excitation and work function of electrons in case of primary Cs ions application, while the probability of matrix atoms ionization will be increased.

In addition, since Cs is a chemically active metal and interacts extensively with O, significant enhancement of the sensitivity to O and confirmation of O presence in the film could be achieved by using of primary Cs ions. Thus, in addition to the main elements (Ni, Cu, Cr), the depth distribution of O, C and fragmentary NiO, CuO, CrO ions were also investigated.

For the both as-deposited state (figure 9(a)) and after all bombardment modes (figures 9(b)–(h)), the intensity from O increases significantly at Ni outer surface as well as at the internal Cu/Cr and Cr/Si interfaces compared to the film volume. However, after irradiation, the O intensity decreases by about an order of magnitude, indicating the lowering of O content in the film. Notedly, that a similar effect is observed for C. The lowest amount of both O and C impurities is observed in case of 5th mode (figure 9(f)). The highest degree of surface roughness is found for 6th mode (figure 9(g)), which is most likely attributed to the highest surface roughness (figure 7). The biggest amount of residual C is observed for 3rd mode (figure 9(d)), both in film depth and at the film/substrate interface.

Comparing the pulsed and continuous modes, the ion energy of 600 eV for 2nd mode (figure 9(c)) revealed larger amount of O and lower amount of C as compared to the 3rd mode (figure 9(d)). For a higher beam energy of 800 eV the difference was mainly focused on Ni layer, when the pulsed 2nd mode (figure 9(c)) showed more intense oxidation and C saturation compared to 5th mode (figure 9(f)). It should be emphasized, that the total amount of impurities in Ni and Cu was reduced with energy rise from 600 eV to 800 eV. Interestingly, that further increase of energy up to 2000 eV (figure 9(h)) reversed this effect and the contaminants amount was enlarged.

Application of primary negative Cs ions allowed to increase the sensitivity of the analysis to Cu and to determine \( \gamma_{Cu} \) from equation (4). \( \gamma_{Cu} \) values were summarized in figure 8, varying in the range of 55%–70% for different modes. A good agreement between passivation coefficients obtained in Ar\(^+\) (Ni, Cr) and Cs\(^−\) (Cu) primary ions was found.

According to figure 2, the obtained Ni sputtering rate was much smaller compared to the theoretical one for the 4th and 6th modes, and this result now can be interpreted. High intensity of fragmentary secondary NiO ions at the surface in case of these modes (figures 12(e), (g)) indicated a higher content of O in the near-surface layer. Since it is known that \( \nu_p \) strongly depends on the chemical composition of material being sputtered, the usually higher binding energy of formed oxide as compared to pure metal determines \( \nu_p \) decrease. The intermediate Ni \( \nu_p \) values for the 3rd mode could be explained in terms of complex effects of oxidation and grain size reduction.

In addition, SIMS data confirmed that only in case of the 1st mode (figure 9(b)) Cu is registered at the surface. Therefore, in this case a deviation of the \( \text{Cu(111)}/\text{Ni(111)+Cr(110)} \) ratio from the theory (figure 4(d)) is caused by Cu concentration gradient through the film depth.

SIMS profiling with application of primary O\(^+\) ions (figure 10) allowed to increase the intensity of Cr signal by three orders of magnitude as compared to the primary Cs\(^−\) ones. The raise of Ni signal intensity at the surface is related to the irradiation-induced oxidation processes, and the evaluated thickness of the oxide layer is in good agreement with the surface roughness values (figure 7). These processes developed most intensively after 3rd
Figure 9. SIMS depth profiles of the as-deposited film (a) and films after ion irradiation with different modes (b)–(h) obtained using Cs$^+$ primary ions (colour online).
and least more pronounced after 5th modes (figure 10(f)). That is, under certain modes of ion bombardment oxides reduction may occur, whereas in some cases oxidation processes may intensify. Similar complex non-monotonic effect was previously reported for the bulk metals [17, 18].

The elevated Cr emission intensity at the Cr/Si interface confirms the presence of thin oxide sublayer. This intensity raise does not lower for irradiated samples, however, being shifted towards the substrate for different distances, depending on the mode.

**Figure 10.** SIMS depth profiles of the as-deposited film (a) and films after ion irradiation with different modes (b)–(h) obtained using O\(^+\) primary ions (colour online).
The key outcome found from the SIMS measurements using different primary ions is the non-monotonic thickening of the Cu and Cr layers under different irradiation modes (Figure 11). Since the intensity of both O and complex NiO, CuO, CrO oxides ions decreases for almost all bombardment modes, it seems reasonable to associate this effect of thickness modification with the reduction processes.

It can be seen that thickness of Cu and Cr layers gradually increases with the rise of the irradiation energy up to 800 eV (5th mode), but then tends to decrease. The only exception was registered for 3rd mode when no thickening of Cr layer occured. Simultaneously, the highest amount of C was observed in Ni layer and at the Cr/Si interface for this mode (Figure 9). It should be noted that the polymerization of carbohydrate compounds at the surface in the process of plasma ion action was reported [45, 46]. In our case the probable formation of a such polymerized sublayer at the outer surface could lower the effect of ion-induced modifications of the deeper layers, and the increased amount of C at the Cr/Si interface could restrain the expansion of the Cr layer towards the substrate.

Observed Cu layer thickening is lowest under 2nd and largest after 5th modes, being well-agreed with the data obtained for γ_Cu passivation coefficient (Figure 8) and confirming the hypothesized association of thickening with oxides reduction. The reduction processes in Cu layer, which are characterized by γ_Cu (Figure 8) and are accompanied by Cu thickening (Figure 11), correlate well with C distribution (Figure 9). As discovered, the thickening of the Cu layer is inhibited in case of modes where the increased amount of C is fixed at the interfaces with Ni and Cr layers.

To verify the effects of oxides reduction accompanied by Cu and Cr thickening additional AES measurements were performed. As an example, the AES depth profiles of the as-deposited film as well as ion irradiated films with 2nd and 5th modes are demonstrated in figure 12. The 2nd mode exclusively showed no thickening of the Cu layer, and the 5th mode was characterized by the highest passivation coefficients of all layers. The data are presented in the way that allows to demonstrate clearly the radiation-induced modifications of each layer thicknesses during the ion bombardment—the profiles were aligned by the center of Cu peak, since this layer was not directly subjected to the ion beam.

It can be seen that 5th mode showed higher atomic concentration of both Cu and Cr which could be attributed to the film purification from O and C impurities, whereas in case of 2nd mode only Cr content was increased. The most significant changes were observed at the Cr/Si interface, which characterized in the thickening of the Cr layer by about 2.7 nm and 4 nm for 2nd and 5th modes, respectively. Considering a different sensitivity of the techniques, AES results are well-agreed with the SIMS data (Figure 11).

Figure 13 shows the elemental distribution maps through the films’ depth, obtained in Auger electrons from tilted AES sputtering crater without breaking the vacuum. These maps allow to visualize the increase of Cu and Cr layers thicknesses caused by the irradiation-induced reduction processes in these layers, which are also shown in SEM images in secondary electrons.

Comparison of the Cu and Cr passivation coefficients with evaluated thickening indicates their satisfactory agreement for all modes except of 6th and 7th. We assume that when the ion beam energy exceeds of 1 keV, the modification of the layers thickness is determined not only by the reduction activity, but by the generation of defects as well. For instance, the effect of radiation-induced swelling voids formation is known for bulk materials [47]. Perhaps observed thickening together with a low passivation for high energies is attributed to such kind of radiation effect.
4. Discussion

As has been already mentioned, during the magnetron sputtering a thin oxide sublayers are formed at the internal interfaces due to the presence of residual O in the deposition chamber. Figures 14(a)–(d) demonstrate the 3D distribution of the fragmentary ions of the main components oxides and O through the film depth after deposition. The most pronounced oxidation occurred at the interface with the substrate (figure 14(e)) due to the presence of a native oxide layer at the Si single crystal.

According to the SIMS profiling data (figures 9, 10), a residual incorporated C was also detected in the film, most pronounced locating at the interfaces.

Ion flux with beam energy < 2000 eV did not induce the lattice constant modifications, changes of grain preferred orientation as well as phase transformations (figure 3) or diffusion intermixing between the layers (figures 12, 13). Although the sputtering of Ni layer (figure 1) and some decrease of its crystallite sizes (figure 5)
was found. The effect of grains size reduction under ion irradiation is not of particular new [48, 49] and is usually associated with implantation effects, defects generation in near surface area and evolution of internal stresses.

It was also explored that the oxides reduction processes develops in the layers not subjected directly to ion beam (figure 8), which cause thickening of the Cu and Cr layers (figure 11). Perhaps the released from oxide O can interact with C to form CO or CO₂ compounds followed with its disposal from the film. Finally, ion bombardment of the film helps to remove residual impurities—the amount of both O and C is reduced. Most pronounced reduction processes occurs at the Cu/Cr and Cr/Si interfaces. Elemental depth distribution maps obtained by AES and SIMS measurements (figure 15) clearly demonstrate layers thickening in irradiated with 2nd and 5th modes samples. The shift of the Cr/Si interface towards the substrate is a consequence of a thickening effect and found to be depended on the ion beam energy and fluence.

The proposed model of the influence of low energy Ar⁺ ion irradiation on reduction processes in thin Ni/Cu/Cr/Si film is shown in figure 16. Our estimated calculations using the SRIM software indicate that the mean projected ion range for all used modes does not exceed 1.8 nm. Therefore, the processes described above can be a manifestation of the so-called long-range ion effect.

By the long-range phenomena is meant the effect when the depth of the modified layer is much larger than the magnitude of the incident ion path in the target [50, 51]. Such effect can be realized in the layers disposed far

![Figure 15. Elements distribution maps of as-deposited and ion irradiated (with 2nd and 5th modes) thin films obtained by AES (a) and SIMS (c) techniques (colour online).](image1)

![Figure 16. Schematic model of the reduction processes in Ni/Cu/Cr thin films under the ion irradiation (colour online).](image2)
from the area of direct ion impact in solids with not equilibrium states at relatively low energies, not promoting the temperature rise [32].

Various manifestations and mechanisms for describing the long-range effect induced by ion irradiation of the surface of materials are known. The long-range influence of ion bombardment was observed in terms of modification of mechanical properties [32–54], dislocations density distribution [31, 55], increased atomic mobility and phase transformations [50, 56, 57]. Observed phenomena are usually attributed to irradiation-induced stress evolution and non-linear lattice oscillations.

However, it should be noted that in all cases the manifestation of the long-range effect is difficult to interpret in terms of classical solid state physics and radiation damage theory. The non-monotonic nature of the observed modifications and the absence of clear regularities also impede unequivocal interpretation of this effect.

An important feature of the ion bombardment of the surface of thin films is a change in their internal stress state. Generally, the deposition of polycrystalline thin metal films by PVD methods causes its tensile residual stresses [58, 59]. It was shown in a numerous studies [58–61], that ion irradiation of the surface of thin films promotes the relaxation of tensile stresses and propagation of compressive stresses, the magnitude of which tends to rise with increasing radiation fluence. The authors associate the evolution of internal stresses to the processes of ion implantation and to the formation of cluster defects.

We assume that the nature of the long-range effect described in present study is also associated with the evolution of stresses field during the Ar\(^+\) ion bombardment, which contributes to the development of reduction processes throughout the film depth. It is important to note, that unified theory giving explanation of all received experimental data has not been developed yet. Thus, mechanisms of long-range effect have to be specified, requiring the following more detailed investigation.

5. Conclusions

Influence of Ar\(^+\) ion irradiation with energy of 400–2000 eV and fluences of \(1.4 \times 10^{16} – 1.1 \times 10^{17}\) ion cm\(^{-2}\) on the structural properties, surface morphology and chemical composition of Ni(25 nm)/Cu(25 nm)/Cr (25 nm)/Si(100) thin films was investigated. Chosen modes lead to the sputtering of the Ni layer with a corresponding thinning from 25 nm to 16 nm depending on the energy and fluence of irradiation, but are not accompanied by components diffusion intermixing and changes of the initial phase composition. In case of 800 eV energy and a duration of continuous ion exposure of 20 min, a decrease in the crystallites size in the Ni layer from ~13 nm (as-deposited state) to ~8 nm was observed. This mode also demonstrated the highest values of the passivation coefficients of Ni, Cu and Cr according to SIMS analysis. The application of primary Cs\(^+\) and O\(^+\) ions in SIMS studies has confirmed that ion irradiation with this mode leads to a decrease in the amount of residual O and C, remaining in the film after magnetron deposition. Thus, this mode can be considered as an optimal in terms of film purification from impurities.

The development of oxides reduction processes at the internal interfaces and, foremost, at the Cr/Si interface is accompanied by a thickening of Cu and Cr layers according to the AES and SIMS maps of the elements distribution. The results obtained are interpreted in terms of long-range effect of ion bombardment, when the modified layers are away from the irradiated zone.

Acknowledgments

This study was carried out in frames of joint project between RIKEN SPring-8 Center and National Technical University of Ukraine ‘Igor Sikorsky Kyiv Polytechnic Institute’ on the base of Memorandum of Understanding to collaborate on the subject of synchrotron and free-electron laser technologies since August 15th 2016.

The synchrotron radiation experiments were performed at Materials Science BL44B2 beamline in SPring-8 with the approval of RIKEN (Proposals No. 20170039 and 20170040). We would like to thank Mr K Ishino and Mr K Shigeta for their support with synchrotron experiments, as well as to Mr T Miura for AFM measurements assistance.

This work was partially supported by the Ministry of Education and Science of Ukraine (Project 0118U000221). This work was also supported by the GINOP-2.3.2-15-2016-00041 project co-financed by the European Union and the European Regional Development Fund.
ORCID iDs

I O Kruhlov @ https://orcid.org/0000-0003-2078-4159
I A Vladymyrskyi @ https://orcid.org/0000-0002-2106-9176

References

[1] Zucco S, Napolitani E, Tessaro E, Zuppella P, Corso A J, Gerlin F, Nardello M and Pelizzo M G 2015 Opt. Mater. Express 5 176
[2] Li X, Lin K W, Liing H T, Hsu H F, Galkin N G, Wroczynskyj Y, Van Lierop J and Pong P W T 2015 Nucl. Instrum. Methods Phys. Res., Sect. B 365 196
[3] Repetto L, Lo Savio R, Setina Batic B, Firpo G, Angeli E and Valbusa U 2015 Nucl. Instrum. Methods Phys. Res., Sect. B 354 28
[4] Niinomiya S, Ichiki K, Yamada H, Nakata Y, Seki T, Aoki T and Matsuwo J 2011 Surf. Interface Anal. 43 95
[5] Fujiwara Y and Saito N 2015 Appl. Phys. Express 8 076601
[6] Sugiyama M and Sitesato G 2004 J. Electron Microscopy 53 527
[7] Bakhsh T A, Sadr A and Tagami J 2015 J. Adhes. Sci. Technol. 29 232
[8] Metzler D, Li C, Lai C S, Hudson E A and Ohrelin G S 2017 J. Phys. D: Appl. Phys. 50 254006
[9] Saghiri M, Walker M, McConville C F and Balakrishnan G 2016 Appl. Phys. Lett. 108 061602
[10] Cheripin V T, Vasilev M A and Ivaschenko Y N 1973 Doklady AN SSSR 210 821 (in Russian)
[11] Hindiyi Y M and Solodovnikov A P 1974 Doklady AN SSSR 214 82 (in Russian)
[12] Ashworth V, Grant W A, Procter R P and Mawinston T C 1976 Corros. Sci. 16 393
[13] Cheripin V T, Kosyachkov A A and Vasilev M A 1976 Surf. Sci. 58 609
[14] Miranda R, Rojo J M and Salmeron M 1980 Solid State Comm. 35 83
[15] Gonzalez L, Miranda R and Ferrer S 1982 Solid State Comm. 44 1461
[16] Miranda R and Rojo J M 1984 Vacuum 34 1069
[17] Chenakin S P 1986 Vacuum 36 655
[18] Chenakin S P 1995 Appl. Surf. Sci. 84 91
[19] Do T and McIntyre N S 2001 Surf. Interface Anal. 31 1068
[20] Vaslyev M O, Sidorenko S I, Voloshko S M and Ishikawa T 2016 Usp. Fiz. Met. 17 209
[21] Orlow A K, Kruhlov I O, Kolenko I E, Sidorenko S I and Voloshko S M 2017 Metallofiz. Noveishie Tekhnol. 39 349 (in Ukrainian)
[22] Kruhlov I O, Kolenko I E, Gryshchenko V O, Sidorenko S I and Voloshko S M 2019 Metallofiz. Noveishie Tekhnol. 41 1 (in Russian)
[23] van den Boogaard A R, Zoethout E, Makhotkin I A, Louis E and Bijkerk F 2012 J. Appl. Phys. 112 123502
[24] Parida S K, Medicherla V R R, Mishra D K, Chaudhary S, Solanki V and Varma S 2014 Bull. Mater. Sci. 37 1569
[25] Kubart T, Nyberg T and Berg S 2010 J. Phys. D: Appl. Phys. 43 1
[26] Gago R and Vazquez L 2001 Appl. Phys. Lett. 78 3316
[27] Pahlovy S A, Mahmud S F, Yanagimoto K, Aikawa N and Miyamoto I 2012 Nucl. Instrum. Methods Phys. Res., Sect. B 272 206
[28] Russell S W, Rafalski S A, Spreitzer R L, Li J, Moinpour M, Moghadam F and Alford T L 1995 Thin Solid Films 262 154
[29] Sigmund P 1969 Phys. Rev. 184 383
[30] Zieger F, Zieger M D and Biersack J P 2010 Nucl. Instrum. Methods Phys. Res., Sect. B 268 1818
[31] Taglauer E 1990 Appl. Phys. A 51 238
[32] Pidum M, Lesch N, Richter S, Karduck P, Bock W, Koparnski M and Willic P 2000 Microchim. Acta. 132 429
[33] Scherrer P 1918 Z. Phys. Chem. B 98
[34] Cheripin V T 1987 Secondary Ion Mass Spectroscopy of Solid Surfaces (Utrecht: VNU Science Press BV)
[35] Zinner E 1983 J. Electrochem. Soc. 130 1995
[36] Harter T P, Dijaziri S, Raghavan R and Dehm G 2015 Acta Mater. 83 318
[37] Pokorny P, Musil J, Fid J, Novotny M, Lancock J and Buril J 2014 Plasma Process. Polym. 12 416
[38] Hu M, Noda S and Komiyama H 2003 J. Appl. Phys. 93 9336
[39] Cen X, Thron A M, Zhang X and van Benthem K 2017 Ultramicroscopy 178 131
[40] Cen X, Thron A M and van Benthem K 2017 Acta Mater. 140 149
[41] Grezczynski G, Mralez S, Hultman L and Schneider J M 2016 Appl. Surf. Sci. 385 356
[42] Benninghoven A 1975 Surf. Sci. 53 596
[43] Benninghoven A, Rudenauer F G and Werner H W 1987 Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications, and Trends (New York: Wiley)
[44] Singh C K, Ilango S, Dash S and Tyagi A K 2016 Mater. Chem. Phys. 173 475
[45] Yasuda H 1981 J. Polymer. Sci. Macromol. Rev. 16 199
[46] Akhavan B, Wise S G and Bilek M M 2016 Langmuir 32 10835
[47] Lu K Y, Liu Y, Sun C, Wang H, Shao L, Fu E G and Zhang X 2012 J. Nucl. Mater. 425 140
[48] Huang T C, Lim G, Parmigiani F and Kay E 1985 J. Vac. Sci. Technol. A 3 2161
[49] Krishna R, Baranwal V, Kathariya Y S, Kabiraj D, Tripathi A, Singh F, Khan S A, Pandey A C and Kanjilal D 2006 Nucl. Instrum. Methods Phys. Res., Sect. B 244 78
[50] Zhang L, Tang G and Ma X 2010 Phys. Lett. A 374 2137
[51] Tereshko I V, Khodyrev V I, Liptsy E A, Goncharenya A V and Tereshko A M 1997 Nucl. Instrum. Methods Phys. Res., Sect. B 127 861
[52] Tetelbaum D I, Azov A Y, Kurilchik E V, Bayankin V Y, Gilmutdinov F Z and Mendeleeva Y A 2003 Vacuum 70 169
[53] Tetelbaum D I, Kurilchik E V and Latisheva N D 1997 Nucl. Instrum. Methods Phys. Res., Sect. B 127–128 153
[54] Levshunova V I, Pokhil G P, Tetelbaum D I and Chernykh F N 2010 J. Surf. Invest. 4 350
[55] Tereshko I V, Gushchenko V V and Tereshko A M 2002 Comput. Mater. Sci. 24 139
[56] Goloborodskiy B Y, Ovchinnikov V V and Semionkin V A 2001 Fusion Technol. 39 1217
[57] Krenidel Y E and Ovchinnikov V V 1991 Vacuum 42 1
[58] Misra A, Fayeulle S, Kung H, Mitchell T E and Nastasi M 1999 Nucl. Instrum. Methods Phys. Res., Sect. B 148 211
[59] Misra A and Nastasi M 1999 J. Mater. Res. 14 4466
[60] Misra A, Fayeulle S, Kung H, Mitchell T E and Nastasi M 1998 Appl. Phys. Lett. 73 891
[61] Laugier M 1981 Thin Solid Films 81 61