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Effect of Ar Annealing on Diffusion and Thermal Stability of Transition Metal Thin-Film Systems

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The processes of diffusion-induced structure and phase formation in nanoscale Ni/Cu/V thin films deposited by DC magnetron sputtering on a Si (100) substrate after annealing in the temperature range of 200–550°C in vacuum (10^{-3} Pa) and argon (200 Pa) atmospheres are studied. Thermal stability, diffusion mass transfer of components and changes of phase composition in vacuum and Ar atmospheres are analysed using synchrotron and copper radiation x-ray diffraction (XRD) and secondary ion mass spectrometry (SIMS). Due to the different diffusion mobility of Cu and Ni atoms with the temperatures increase in the studied interval, the two regions with different Ni and Cu concentrations are formed. Grain boundary and bulk mechanisms of Cu and Ni diffusion and the influence of the heat treatment atmosphere are discussed. As shown, annealing in vacuum atmosphere, compared to annealing in argon, results in an increase in the onset temperature of the Cu-based solid solution formation by 100°C and a decrease in the concentration of Ni in this solid solution. Thus, upon annealing in vacuum, the thin film maintains thermal stability over a larger temperature range compared with annealing in argon.

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Key words: nanosize films, solid solution, synchrotron radiation, heat treatment, diffusion, phase formation.

Досліджено процеси дифузійно-індукованого структуро- та фазоутворення в нанорозмірних тонких плівках Ni/Cu/V, одержаних методою магнетронного осадження на підкладинку Si (100), після відпалу в інтервалі температур 200–550°C у атмосферах вакууму (10^{-3} Па) та арґону (200 Па). Термічну стабільність, дифузійний масоперенос компонентів та зміну фазового складу в атмосферах вакууму та арґону проаналізовано за допомогою метод рентґеноструктурної фазової аналізи (XRD) із використанням синхротронного та мідного випромінювання та вторинно-йонної масспектрометрії (SIMS). Через різну дифузійну мобільність атомів Cu та Ni із зростанням температури у досліджуваному інтервалі формуються дві області з різною концентрацією Ni та Cu. Обговорюються зерноrраничний та об'ємний механізми дифузії Cu та Ni, а також вплив атмосфери термічного оброблення. Показано, що відпал у вакуумі порівняно з відпалом в арґоні приводить до підвищення температури початку утворення твердого розчину на основі Cu на 100°C та пониження концентрації Ni в цьому твердому розчині. Таким чином, за умов відпалу у вакуумі тонкоплівкова композиція зберігає термічну стабільність у більшому інтервалі температур порівняно з відпалом в арґоні.

Ключові слова: нанорозмірні плівки, твердий розчин, синхротронне випромінювання, термооброблення, дифузія, фазоутворення.

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1. INTRODUCTION

At present, Cu-based thin-film systems are of great importance and their research continues, since such systems have unique mechanical, electrical, and magnetic properties [1], which lead to new opportunities for their application in various fields of nanotechnology and solar energy. One of the important elements of solar cells (SC) is metal contacts, which greatly affect their functionality, stability, and cost. Currently, Ag paste is mainly utilized for metal contacts, usually fabricated using screen printing technology followed by high-temperature (700–900°C) annealing [2]. However, insufficient control over this process can unpredictably disrupt the p–n junction, leading to degradation of the passivation layers and possible shunting of the junction [3]. While the high conductivity of Ag and the established mass-production technology remain the main advantages, the great concern of these contacts is related to high market price of Ag which contributes to about 40% of the total cost of SC value. Therefore, alternative contact materials and technologies for their fabrication are also being considered, but at present their use has not yet reached the level of commercial product. Cu is one of the most promising materials for re-

placing Ag and viably reducing the SC cost up to ~100 times while maintaining high electrical conductivity. However, the high diffusion activity of Cu at the Si interface remains a major obstacle that prevents the use of Cu as a contact material for SC, since this can lead to the formation of intermetallic phases of Cu with Si that serve as recombination centres [4], as well as compromise the adhesion to substrate [5] due to a porous structure of the Cu/Si interface [6]. An effective solution of this problem may be the use of a diffusion barrier layer of different metals such as V, Cr, Ti, and others [7]. Additional challenging aspect is related to poor Cu oxidation resistance even at low temperatures. For this reason, the coating layer of Ni, Au, Mo can be used to prevent oxidation of the Cu film [8]. Therefore, multilayer metal structures with Cu as an internal and fully protected layer, providing long-term stable electrical properties of the device, are viable from scientific and applied points of view.

Thermal stability of electric contacts for SC is an important component of their functionality. When multilayer structures are considered as contacts, this becomes vital because various environmental conditions are inevitable during the operation of the SC, such as low and high temperatures, different atmospheric composition, exposure time, heating and cooling rate, humidity, *etc*. In addition, the thermal stability of multilayer components is essential for their successful fabrication [9]. Understanding of thermal stability of a multilayer metal device is impossible without studying the diffusion processes inside these structures. The most commonly corresponding diffusion distance is in the range of nanometres and the study of diffusion length allows to characterize the degree of film degradation and can be used as a measure of its thermal stability. In addition, in nanoscale structures with an increased number of components and interfaces, diffusion intermixing and phase formation should be specifically addressed because they greatly affect the physical and functional properties of the material. Interfacial reactions between components can lead not only to inhomogeneity of phase composition and formation of new phases, sometimes atypical to the corresponding equilibrium phase diagrams of bulk materials, but also to degradation of the functional properties of the elements. Furthermore, the chemical composition of the fabrication and exploitation environment may affect the structural characteristics and diffusion kinetics in nanostructured materials at elevated temperatures [10]. Therefore, the implementation of Cu-based thin-film elements in advanced devices for microelectronics and photovoltaics is greatly restricted by the lack of ample understanding and good control of their diffusion kinetics and thermal stability under aggressive thermal conditions in various environments.

Thermal treatment of thin films in Ar atmosphere is widespread. [11–14]. By varying the processing environment, the control over the

phase transformations kinetics and temperature intervals, structural properties, surface roughness and thermal stability have been achieved. However, the annealing environment can affect the diffusion kinetics and thus thermal stability of the structure [15]. It is therefore necessary to give due consideration to studying the thermal stability of particular transition metal contacts when exposed to Ar.

This study examined the effect of Ar-annealing on the structure, phase composition, diffusion behaviour and thermal stability of functional transition metal nanosize film system Ni (25 nm)/Cu (25 nm)/V (25 nm). The system was deposited by DC magnetron sputtering on a single crystal Si (100) substrate. In order to simulate in laboratory conditions, the extremely aggressive thermal effect on functional elements annealing was carried out under Ar flow (200 Pa) and a wide temperature range of 200–550°C. A further comparison was made for the same structures annealed in vacuum (10^{-3} Pa). Such conditions are much more extreme than the actual fabrication and operational ones, although they provided the important information on the stability of studied system in a broad temperature range. The feasibility of suggested multifilm arrangement with Cu layer in the middle and Ni in the upper part as oxidation barrier and V in the lower part as diffusion barrier with substrate is discussed.

2. METHODS

Ni (25 nm)/Cu (25 nm)/V (25 nm) thin films were deposited by the DC magnetron sputtering on single crystal Si (100) substrates at room temperature from high-purity targets of Ni (99.995 at.%), Cu (99.99 at.%) and V (99.95 at.%). Deposition rates were 0.5 nm/s, 0.27 nm/s and 0.065 nm/s for Cu, Ni and V, respectively. The vacuum level was $2.0\cdot 10^{-5}$ Pa before deposition, while the argon flow during the deposition process was $6.0\cdot 10^{-1}$ Pa. The thicknesses of the film layers were calculated from known sputtering rates and further verified by depth profiling. The layer-by-layer chemical analysis was performed by secondary ion mass spectrometry using Ion Time-of-Flight IV system with a primary beam of 1 keV O^+ positive ions. Heat treatment was carried out in the temperature range of 200–550°C for 15 minutes in a vacuum of $2\cdot 10^{-3}$ Pa and in an argon atmosphere (200 Pa). Structural and phase analysis was performed using x-ray diffraction (XRD) using the grazing incidence geometry in copper radiation (1.5405 Å) on the Rigaku Ultima IV device. For a more detailed study of the thermally-induced formation of structure and phase composition, synchrotron radiation with a wavelength of 1.08 Å and the grazing incidence wide-angle x-ray scattering geometry (GIWAXS) on the materials science beamline BL44B2 (RIKEN SPring-8 synchrotron radiation facility, Japan) were used. Debye–Scherrer camera with a radius of 286.48 mm and an 'im-

age plate' detector with dimensions of 400×200 mm was applied for XRD analysis [16]. The angle between the beam and the surface of the sample was 0.5°. The vertical and horizontal dimensions of the beam were 0.01 mm and 3.0 mm, respectively.

3. EXPERIMENT

Figure 1 shows the results of XRD studies of Ni/Cu/V thin films after deposition and heat treatment in vacuum (*a*) and argon atmosphere (*b*). The increased value of the lattice constant of the f.c.c. Cu film in the initial state (Cu thin film lattice constant = 0.3596 nm) compared to the bulk (Cu bulk lattice constant = 0.3615 nm [17] is likely due to the formation of tensile stresses in vacuum condensates, which relax during further annealing [18]. As the temperature increases upon annealing in vacuum (Fig. 1, *a*), a gradual shift of the Cu (111) peak towards high diffraction angles and a corresponding decrease in the Cu lattice parameter are observed. At the same time, the position of Ni diffraction peaks remains unchanged throughout the whole temperature range. This diffraction pattern is typical for the Cu-based Ni–Cu solid solution formation processes and has been previously observed for submicron films [19–21].

Diffraction data of the Ni (25 nm)/Cu (25 nm)/V (25 nm) thin films after deposition and annealing in Ar atmosphere in the 350–550°C temperature range are shown in Fig. 1, *b*. Similarly, to the vacuum annealing, the Cu peak shift towards high angles is observed, but this effect is noticeably recorded at a lower temperature (400°C instead of 500°C). The diffraction peak position of Ni (111) is unchanged through

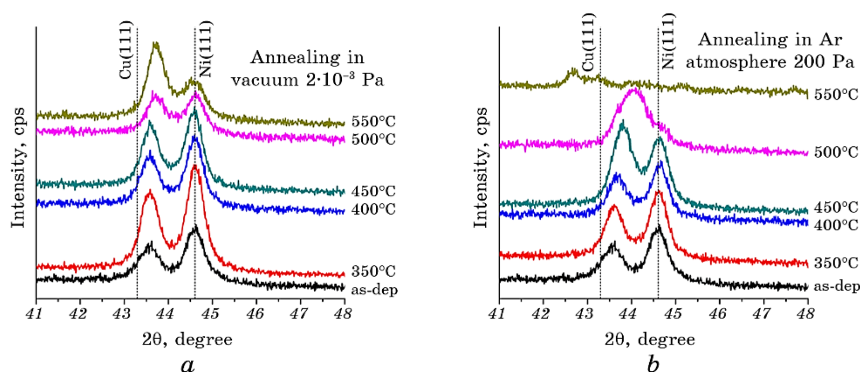

Fig. 1. X-ray pattern of the Ni/Cu/V thin film in the initial state and after annealing in vacuum (*a*) and in an argon atmosphere (*b*) at temperatures of 350°C, 400°C, 450°C, 500°C, and 550°C (wavelength of 1.54 Å, dotted line corresponds to the peak position of Cu [17] and Ni [22] bulk materials).

the whole temperature range similar to vacuum annealing. The disappearance of peaks of both Cu and Ni after annealing in Ar at 550°C makes it drastically different from the result of vacuum annealing.

It should be noted that diffraction peaks from Cu oxide phase are not observed in both annealing atmospheres, which confirms the effectiveness of using Ni top layer to protect Cu film from oxidation.

At elevated temperatures there is also an obvious change in the intensity ratio of the Cu and Ni peaks and this change starts sooner (at lower temperature) in the Ar atmosphere. Initially (as deposited), the stronger peak of Ni becomes less intense than the peak of Cu at 450°C in Ar (Fig. 1, *b*), while in vacuum this result becomes apparent only at 550°C (Fig. 1, *a*). According to the atomic scattering factor, the intensity of the Cu (111) diffraction peak should be higher than that of the Ni (111) at temperature up to 400°C [23]. However, when applying Ni as a top layer, it leads to the decrease of the Cu diffraction peak intensity in initial state, *i.e.*, $I_{Ni} > I_{Cu}$ for all reflection orders. As the annealing temperature increases, the diffraction peaks intensity ratio changes: the Cu (111) peak intensity becomes higher, and Ni (111) becomes proportionally smaller. This is most likely result of the Cu-based Ni–Cu solid solution formation, since the changes are observed only in the Cu crystal lattice period, but not vice versa. The observed intensities redistribution may be associated with different diffusion mechanisms of Ni and Cu atoms.

The XRD data in the Fig. 2 show the temperature dependence of the lattice parameters of Ni and Cu in different annealing atmosphere. There is no significant change in the lattice parameter of Ni and Cu at temperatures up to 350°C. The change in the Cu lattice period (Fig. 1, *a*) from 0.3596 nm in the initial state to 0.3585 nm within the temper-

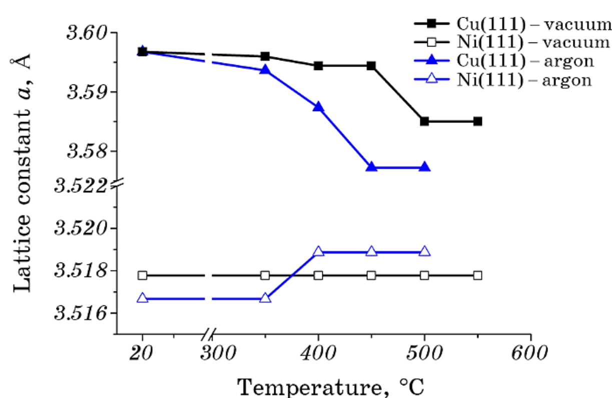

Fig. 2. Ni and Cu lattice parameters of the Ni/Cu/V system as a function of temperature based on XRD data after annealing in vacuum and argon for 15 minutes.

ature range of 350–450°C are defined. The Ni lattice parameter stays unchanged in vacuum in the entire temperature interval. However, a significant change in the lattice parameter of Cu is observed in vacuum at 400°C and at 450°C: in argon atmosphere $a = 0.3577$ nm, and in vacuum $a = 0.3594$ nm. Therefore, a higher concentration of Ni in the formed solid solution is observed when the films annealed in argon compared to vacuum.

It is apparent, that annealing thin film structures in Ar tends to be more vigorous in modifying the initial structures compared to vacuum annealing. Similar structural changes in thin films occurred in Ar at lower temperatures than they started in vacuum. For this reason, further experiments were performed for thin films annealed in argon to reveal the underlying mechanisms of such behaviour.

More detailed structural phase analysis was performed using synchrotron radiation. The advantages of synchrotron radiation for the study of nanosize multilayer films are discussed elsewhere [24]. Fig. 3 (left panel) shows *2D* diffraction patterns of the Ni (25 nm)/Cu (25 nm)/V (25 nm) system after heat treatment in an argon atmosphere (200 Pa) in the temperature range of 200–500°C for 15 minutes, obtained using image-plate detector and radiation wavelength of 1.08 Å.

These results were supplemented by traditional XRD data. The analysis of Debye diffraction rings allowed to exclude the potentially possible formation of the grains' predominant orientation, which is evidenced by the uniform distribution of the intensity of all diffraction rings. To specify the structural parameters, the dependence of the diffraction peaks' intensity on the 2θ angle shown in Fig. 3 was used.

While the traditional XRD analysis allowed to detect only the highest intensity (111) peaks of Ni and Cu phases in studied thin films, the use of synchrotron radiation enabled to determine the diffraction of the 2nd and 3rd orders and, thus, more accurately calculate the lattice parameters using diffraction peaks at high angles. In the initial state, only the fcc Ni and f.c.c. Cu peaks are present. The b.c.c. V peaks are not observed, which indicates on its amorphous or fine-grained structure, most likely attributed to the particularly slow deposition rate of the growing film on cold substrate. The onset temperature of diffusion-induced solid solutions formation between Ni and Cu according to these data is 400°C. The composition is gradually homogenized with the formation of Ni_xCu_y solid solution upon further increase of the annealing temperature up to 500°C, which is evidenced by the merging of the diffraction peaks from two f.c.c. phases. However, it is still possible to distinguish the signals from residual Cu and Ni f.c.c. phases.

The crystallites size of Cu and Ni phases was evaluated based on the synchrotron radiation XRD data using the Scherrer equation [25]. In the initial state, the Cu lattice parameter is 0.361 nm, and for Ni—0.352 nm. The Ni–Cu solid solution formation is accompanied by a de-

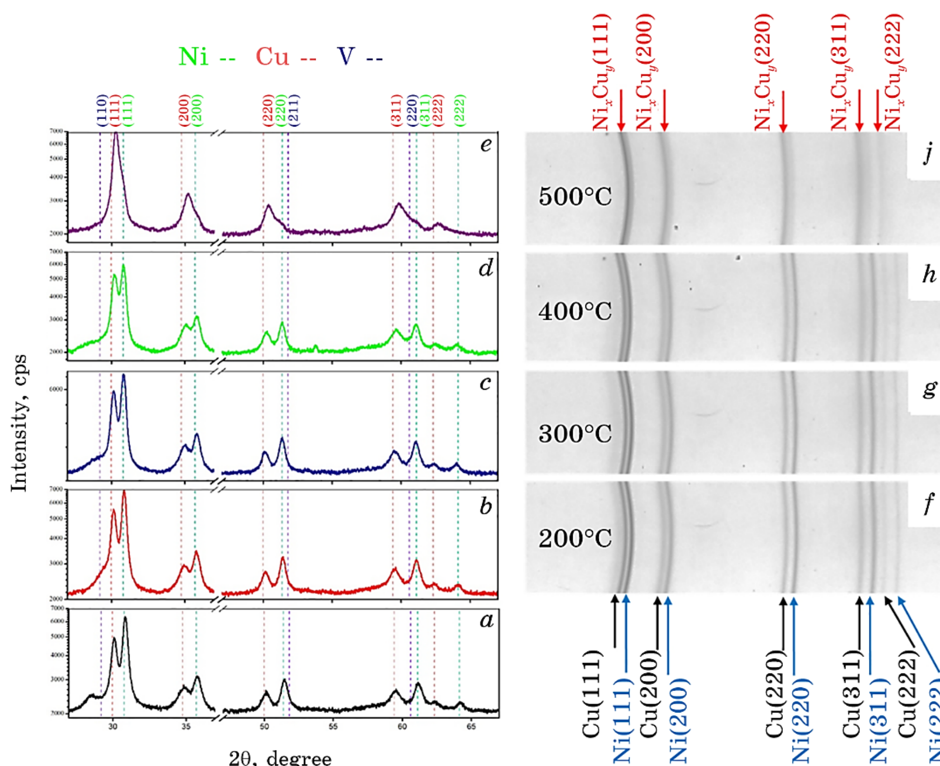

Fig. 3. Diffraction patterns of the Ni/Cu/V thin film system after deposition (*a*) and heat treatment in argon atmosphere at temperatures of 200° (*b*), 300° (*c*), 400° (*d*), 500° (*e*), obtained using synchrotron radiation (wavelength 1.08 Å) and the corresponding 2*D* scans of Debye diffraction rings (*f*, *g*, *h*, *j*).

crease in the Cu lattice period to 0.359 nm at 500°C, while the Ni lattice constant remains unchanged until the formation of the homogeneous solid solution. The crystallites size of Ni is 29–35 nm in the temperature range 20–400°C. The microstrain value decreases from 0.32% to 0.25% when the temperature change from room up to 400°C, which likely indicates on the slight stress relaxation during annealing. The average size of Cu crystallites varies from 10 to 16 nm, and the microstrains, respectively, from −0.1 to +0.1%, within the same temperature range.

Based on the synchrotron radiation XRD data (Fig. 4), and according to the estimation of the lattice constants ratio using Vegard's law [26], a solid solution of $Cu_{77}Ni_{23}$ composition is formed after annealing in argon at 500°C.

Since XRD analysis provides averaged information about the structure of the entire volume of the thin film, for a more detailed study of

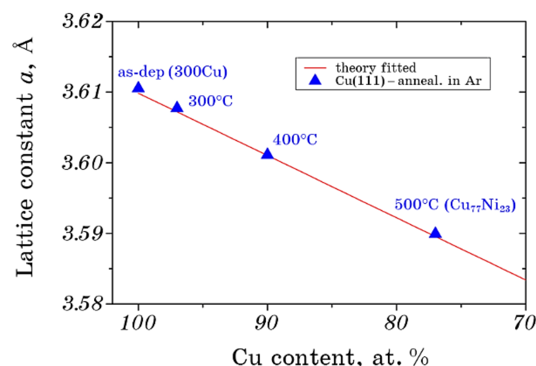

Fig. 4. Lattice constant of Cu-based solid solution as a function of the atomic concentration of Cu in Ni calculated from the synchrotron radiation XRD data.

the diffusion processes as a function of temperature, the layer-by-layer elemental analysis of the nanosize Ni/Cu/V systems using the SIMS technique was performed (Fig. 5). The intensity distribution of secondary ions of the main components (Ni^+, Cu^+, V^+), as well as the secondary complex ions ($NiCu^+$, CuV^+ and NiV^+) was analysed.

The trilayer structure of the film with almost absent mutual diffusion of the components is clearly seen in the initial condition. However, a minor signal of Ni appeared at the Cu/V interface is most likely the result of condensation stimulated fast diffusion of some Ni atoms through the Cu grain boundaries upon deposition [27]. Diffusion of Ni in the initial state is undesirable. It is most likely a result of magnetron deposition and probably can be prevented in further experiments by adjusting of the spattering parameters. The slope of the curves observed at the interfaces is due to the resolution of the used layer-by-layer technique. The leaps of intensity seen in the surface area are associated with oxidation processes, as SIMS technique is highly sensitive to the interatomic interaction and chemical bonding energy [24]. It should be also noted that the thickness of each metal layer in initial state is similar and equal to 25 nm, however their etching time (x-axis) is different, especially for V layer due to the fact that V has the lowest sputtering coefficient (V = 85 Å/s, Ni = 190 Å/s, Cu = 320 Å/s).

The Cu and Ni atoms mutual diffusion is evident when the annealing temperature increases up to 300°C. Besides, the Ni atoms spread more intensively into the Cu layer and segregate in the Cu/V interface region. It follows from the comparison of SIMS and XRD data, that the diffusion interaction at a temperature of 300°C occurs through the grain boundary mechanism, since the angular positions of the corresponding Ni and Cu diffraction peaks remain constant. Cu diffuses to the outer surface and oxidizes, which creates an additional driving

force for diffusion [23, 28]. The diffusion of Cu atoms into V layer starts simultaneously.

The mutual diffusion of Ni and Cu atoms continues at temperature of 400°C. In addition, two diffusion interaction regions at Cu/Ni and Cu/V interfaces are still clearly observed at this temperature. The diffusion of Ni atoms into the Cu layer is more intense, which is con-

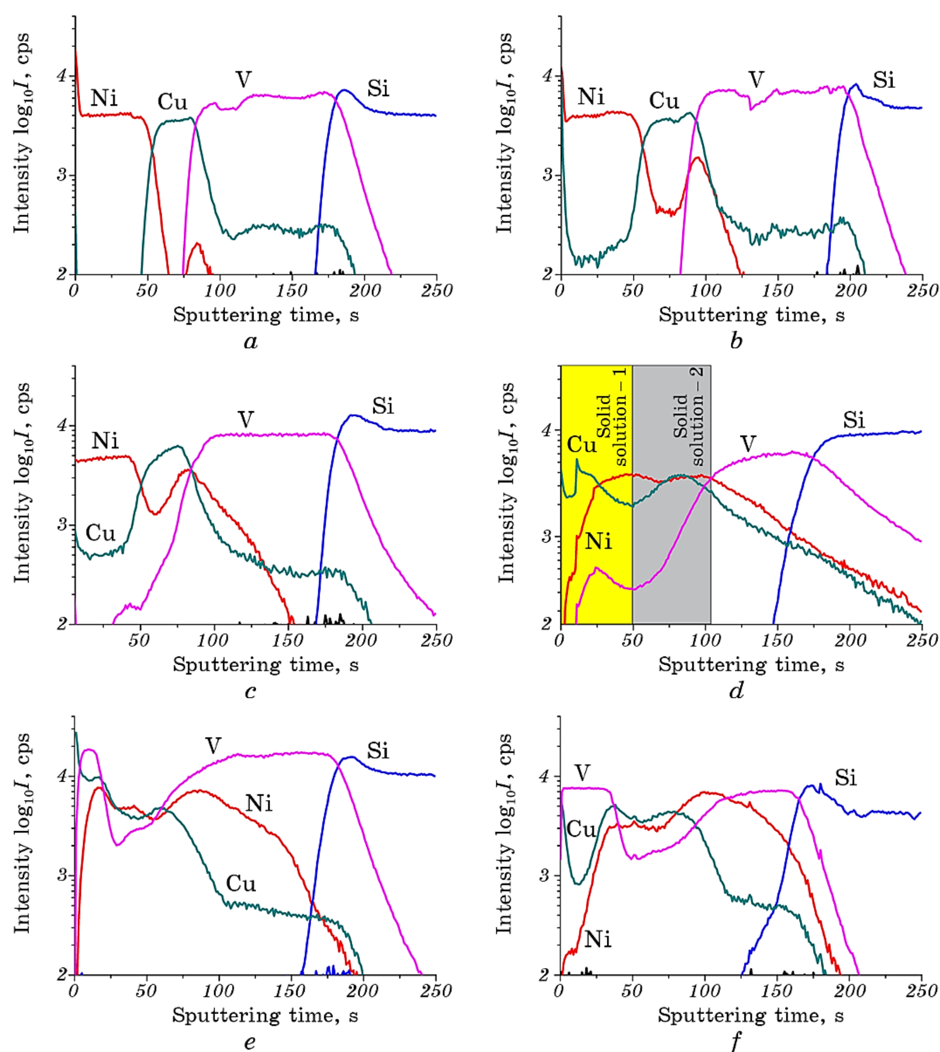

Fig. 5. The intensity of Ni^+, Cu^+, V^+ and Si^+ secondary ions current as a function of the sputtering time of Ni/Cu/V/Si thin films after deposition (*a*) and annealing in an Ar atmosphere at temperatures of 300°C (*b*), 400°C (*c*), 450°C (*d*), 500°C (*e*), 550°C (*f*). The regions of the two Cu–Ni solid solutions formed at 450°C (*d*) are marked in yellow and grey colours.

firmed by the results of synchrotron analysis, where the Cu peak shift is fixed at 400°C and, as a result, a Cu-based Ni–Cu substitution solid solution is formed. The concentration of Ni atoms in the Cu layer is equalized at a temperature close to 450°C. The most pronounced diffusion interaction is observed in the film volume (particularly, in the Cu layer) due to the diffusion mobility of Ni in Cu. In the temperature range of 300–400°C, Ni atoms diffuse through the Cu layer and accumulate at the Cu/V interface, while V acts as a diffusion barrier between the interacted layers and the substrate. As the annealing temperature increases further, a certain critical concentration of Ni at the interface with V layer is accumulated when the Cu and V profiles at this interface are blurred. The position of the Cu/V interface is shifted towards the substrate. At 450°C, not only the two regions of the solid solution with concentration of components are observed, but also the V diffusion towards the free surface begins with its gradual accumulation in the near-surface region. A significant intensification of the vanadium diffusion activity is observed approaching to temperatures ~0.3–0.35 T_{melting}, where $T_{\mathrm{melting}} = 1910$°C. This corresponds to the onset of the diffusion activation by the volume mechanism. A V layer with a small content of Cu atoms is formed in the near-surface area when the temperature reaches 500–550°C. The argon atmosphere contributes to the accumulation of impurities in the film from the residual atmosphere. Moreover, vanadium has a strong susceptibility to oxidation and adsorption of impurities when it comes to the surface under thermal exposure. These two factors can cause the disappearance of diffraction peaks of Ni and Cu at 550°C in Ar due to a decrease in the crystallinity of the studied thin film because of high impurities content. To be fair, the obtained results at 550°C are not sufficient enough to satisfactorily explain the disappearance of diffraction peaks. It should be noted that Cu atoms are observed on the outer surface in the entire temperature range. This may be due to the fact that Cu has a lower surface energy (1.825 J/m^2) than Ni (2.34 J/m^2) and V (2.55 J/m^2) [29]. Therefore, the results of SIMS depth profiling studies showed that the use of top and bottom barrier layers (Ni to prevent oxidation and V to prevent diffusion with the substrate) upon annealing in argon atmosphere turned out to be not very hostile up to 400°C, after which the development of various diffusion processes is irresistibly activated and the thermal stability of the system is violated.

4. DISCUSSION

It is well acknowledged that annealing in chemically inert Ar is a common pathway to minimize the oxidation of thin-film functional elements in microelectronics technologies, especially for 'noble Me–transition Me' layers combinations [13]. However, the results demon-

strated in present study show that thermal exposure of transition metal thin film in argon can undesirably affect the diffusion-mediated thermal stability compared to the similar vacuum annealing.

Most of the thin-film materials contain impurities that physically or chemically adsorb during condensation or heat treatment from atmosphere being partially in their molecular state. Impurities play a significant role and can accelerate diffusion reactions, especially in the case of nanoscale systems [30]. During thermal treatment in vacuum, degassing of impurities occurs much faster than in an argon atmosphere. This is due to the fact that the partial pressure of saturated vapour impurities in the material in argon atmosphere is much lower than in vacuum, which significantly reduces the probability of their evaporation [31]. Furthermore, volatile chemical compounds have a higher tendency to decompose in vacuum. Annealing of defects and impurities in vacuum, in comparison with argon atmosphere, slows down the diffusion intermixing between conductive and barrier layers. As a result, the Ni/Cu/V thin film structure remains more thermally stable in a vacuum. Due to the annealing of volatile chemical compounds, there is a certain deviation from the original composition, and such non-uniformity of chemical composition has a huge effect on heterogeneous nucleation [32]. In addition, the heat transfer of materials through the surface is higher in argon compared to vacuum, which contributes to a faster establishment of the temperature equilibrium over the entire area of thin-film material. Due to these factors, the stresses arising in the material can additionally accelerate the diffusion interplay between the film components during thermal exposure in an Ar atmosphere compared to the vacuum.

Since the diffusivity of Ni in Cu is higher than of Cu in Ni, the both grain boundary and bulk diffusion of Ni atoms into the Cu layer at 200–550°C is taking place, herewith Cu diffuses only through the Ni grain boundaries. The XRD analysis characterizes a bulk diffusion, and the SIMS technique characterizes both bulk and grain boundary diffusion through the averaged depth elemental distribution. It follows from SIMS data that Cu diffusion into the Ni layer is observed, while Ni crystal lattice remains unchanged according to the XRD data, indicating on the grain boundary mechanism of Cu mass transfer. The presented data and analysis support that vacuum annealing leads to slower interdiffusion between components and, as a consequence, thin film structures retain their thermal sustainability better compared to the argon ambient.

5. CONCLUSIONS

The structural phase transformations and layer intermixing during heat treatment of Ni/Cu/V/Si (100) thin films are studied in the tem-

perature range from 200°C to 550°C for 15 minutes in inert Ar atmosphere and vacuum (10^{-3} Pa) using a combination of structural (XRD) and chemical (SIMS) experimental techniques. The diffusion of Cu atoms to the Ni boundaries and diffusion of Ni atoms in the Cu grains volume in the temperature range of 300–500°C causes the formation of Cu-based solid solutions with different Ni concentrations regardless of the annealing atmosphere. Vacuum annealing compared to Ar reduces the temperature of the Ni in Cu substitutional solid solution formation by 100°C and reduces the Ni concentration in this solution. The V adhesion layer prevents the Cu and Ni atoms intermixing with the substrate and averts the silicide formation below 400°C in argon. Further increase of annealing temperature leads the V diffusion towards the outer surface and its accumulation in the near-surface region. Ni top layer prevents Cu oxidation during annealing in both atmospheres. Studied trilayer structures appeared to be thermally more sustainable under vacuum annealing compared to Ar.

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