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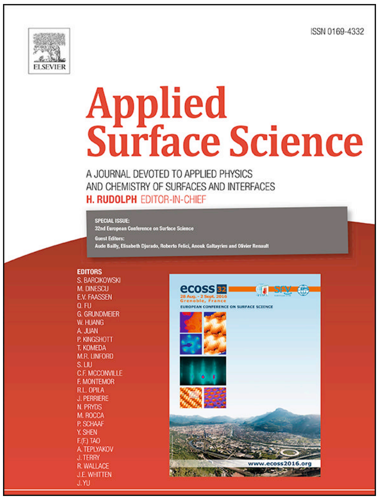

Full Length Article

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Viktor Takáts, Attila Csík, József Hakl, Kálmán Vad

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Diffusion induced atomic islands on the surface of Ni/Cu nanolayers

Viktor Takáts, Attila Csík, József Hakl, Kálmán Vad

Institute for Nuclear Research, Hungarian Academy of Sciences, Bem tér 18/C, 4026
Debrecen, Hungary

Corresponding author: K. Vad
E-mail: vad@atomki.mta.hu

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Abstract

Surface islands formed by grain-boundary diffusion has been studied in Ni/Cu nanolayers by in-situ low energy ion scattering spectroscopy, X-ray photoelectron spectroscopy, scanning probe microscopy and ex-situ depth profiling based on ion sputtering. In this paper a new experimental approach of measurement of grain-boundary diffusion coefficients is presented. Appearing time of copper atoms diffused through a few nanometer thick nickel layer has been detected by low energy ion scattering spectroscopy with high sensitivity. The grain-boundary diffusion coefficient can be directly calculated from this appearing time without using segregation factors in calculations. The temperature range of

423-463 K insures the pure C-type diffusion kinetic regime. The most important result is that surface coverage of Ni layer by Cu atoms reaches a maximum during annealing and stays constant if the annealing procedure is continued. Scanning probe microscopy measurements show a Volmer-Weber type layer growth of Cu layer on the Ni surface in the form of Cu atomic islands. Depth distribution of Cu in Ni layer has been determined by depth profile analysis.

1. Introduction

Materials science plays a significant role in understanding of physical processes in microelectronics. Interconnections between microelectronics parts can be failed due to high current densities, if the line dimensions are significantly smaller than one micron. Deterioration of the quality of interconnections can be evoked by electromigration which is a forced motion of metal ions. Essentially, this is a diffusion process and it is governed by its activation energy. In solid state materials short-circuit diffusions along grain boundaries and dislocations, and surface diffusions have small activation energies. At nanoscale size the diffusion along grain boundaries plays a crucial role as it can cause serious damage or fast aging of materials used in electronic devices, so their study in nanoscale systems is inevitable. In lead-free soldering technologies nickel and copper are frequently used metals. Therefore, study of Ni/Cu nanolayers is important not only from academic point of view but also from technological point of view.

Grain-boundary (GB) diffusion coefficients can be determined by the model of Fisher from diffusion profiles measured experimentally [1]. In this model polycrystalline microstructures were supposed to form large grains where the grain diffusion length was much smaller than the average grain size. In nanocrystalline materials this model required some modifications which were made by Mishin [2], but the essence did not change. In thin films, the mechanism of GB diffusion was worked out by Gilmer and Farell [3]. They described the diffusion in multiple grain boundaries with different flux boundary conditions. They introduced the concept of two surfaces: one of them is in contact with a reservoir and the other is the free exit surface. Finally, the diffusion profile along grain boundaries between these two surfaces was calculated as the average concentration distribution in the film. Hwang and Baluffi presented their results about the accumulation of diffusant atoms on the exit surface of a film formed by parallel grain boundaries [4].

However, due to the lack of desirable experimental results, description of nanoscale GB diffusion has some semi-quantitative nature. Depth profiling and surface accumulation methods are two different methods which give possibilities to study GB diffusion processes at nanoscale. By depth profiling the depth distribution of diffusant can be analyzed. One of the depth profiling techniques is SIMS (Secondary Ion Mass Spectrometry). This technique was used to study GB diffusion along an individually grain boundary of a Cu bicrystal [5]. The other very popular depth profiling technique is the radiotracer method when the diffusivity is determined by radioactive intensity measurements of an isotope used as diffusant. Due to a minimum thickness which is necessary to produce a high enough radioactive intensity to a reliable measurement, the best depth resolution which can be realized by this method is a few micrometers [6,7]. The radioactive tracer concentration cannot be decreased below the sensitivity limit of nuclear detectors with the decrease of thickness. The depth distribution of radioactivity (which is equivalent to the depth distribution of tracer concentration) reflects the penetration profile of diffusant from which the GB diffusion coefficient can be determined. Time evolution measurement of surface accumulation is another experimental method. An increase in surface concentration of diffusant atoms gives information about the quantity which diffused through the grain boundaries during annealing time. The GB diffusion coefficient can be calculated from this time dependence. The surface accumulation can be experimentally studied by Auger and X-ray photoelectron spectroscopy (AES, XPS).

While in radiotracer analyses the depth resolution of tracer concentration distribution is limited by the serial sectioning technique used for depth profiling (a minimum but finite thickness is needed to a measurement), in surface accumulation methods the application of long accumulation time is needed because of the lack of high detection sensitivity of AES and XPS methods. As a solution to this problem, longer annealing times are applied in experiments. Moreover, to get pure grain-boundary diffusivity from the experimental data, a mathematical method is required which is based on the accumulation kinetics of diffusant atoms using segregation factors as input parameters [4]. Surface accumulation is a result of grain-boundary and surface diffusion processes taken place at the same time. However, it is a problem that segregation factors cannot be simply determined experimentally at nanoscale and there are only a very few direct pieces of information about the surface distribution of diffusant atoms.

The detection sensitivity of AES and XPS electron spectroscopy methods used to study the GB and surface diffusions is around 1 at%. In this paper we intend to show that Low Energy Ion Spectroscopy (LEIS) can be an alternative candidate to carry on precise measurements in this field due to the high detection sensitivity of this method (10 ppm instead of 1 at%). The GB diffusion coefficient can be calculated from the appearing time of diffusant atoms which, finally, form small surface islands due to surface diffusion.

2. Theories

The theory of the atomic motion inside grain boundaries can be described by random walk statistics. The root mean squared displacement of large number of diffusant particles in grain boundaries can be given by the well known Einstein-Smoluchowski relation, $\sqrt{< r^2 >} = \sqrt{6Dt}$, where $< r >$ is the mean displacement, D is the coefficient of diffusion, t is the time [8]. In a thin film the mean displacement $< r >$ corresponds to the film thickness h, and t is the time when diffusant atoms appear on the exit surface of the film, i.e. in our Ni/Cu//Si thin film arrangement when Cu appears on the Ni surface. The diffusion coefficient can be calculated very simply, $D=h^2/6t$. The same result was received by Holloway and McGuire, who elaborated their model for the ideal case when the exit surface is an infinite capacity sink for diffusant atoms and the surface diffusion is very high [9].

The precise measurement of the appearing time depends on the experimental details, especially on the detection level of the method applied in the experiment. For example, a radiotracer measurement requires extremely high sensitivity of the counting facilities and a radioisotope with high activity. To avoid this problem, Hwang and Balluffi [4] analyzed the GB diffusion on the basis of surface accumulation kinetics under the condition of kinetic regime *C* (kinetic regime *C* accords with Harrison's classification [10] or see e.g. the work of Kolobov *et al*. [11]). In this regime the volume diffusion is negligible and material transport takes place only along grain boundaries. Under a quasi-steady state condition in grain boundaries and when the surface diffusivity is high, the surface accumulation process can be written in the next formula:

$$c_S = \frac{s' c_{S0}}{s''}\left[1 - \exp\left(-\frac{\delta D_{gb} t}{s' \delta_s d_s h}\right)\right] \qquad (1)$$

where c_S and c_{SO} are the concentrations at the accumulation and diffusion source surfaces, *s'* and *s''* are the segregation factors at the interfaces between the GB/accumulation surface and GB/source surface. δ is the width of a grain boundary, h is the thickness of the film, δ_s is the thickness of diffusant atoms layer at the accumulation surface, t is the time, d_s is the thickness of a grain, and, finally, D_{gb} is the grain-boundary diffusion coefficient [12]. In Equation (1) the concentrations are supposed to be average concentration values. If the segregations are small, we can assume that $s'=s''=1$ and the Equation (1) can be written in the following form:

$$c_S = c_{S0}[1 - exp(-\omega t)] \text{ ,where } \omega = (\delta D_{\mathrm{gb}})/(\delta_s d_s h) \qquad (2)$$

The grain-boundary diffusion coefficient can be calculated from the time dependence of the average concentration c_S at the accumulation surface (see e.g. the papers of Z. Erdélyi *et al*. and G. Erdélyi *et al*. [13,14]). For this purpose the accumulation kinetic plot is fitted by an exponential function and is parameterized. The surface segregation coefficients *s'* is defined by relative concentration ratio of diffusant atoms at the accumulation surface and in the grain boundary near the accumulation surface, and *s"* is also defined by relative concentration ratio of diffusant atoms at the source surface and in the grain boundary near the source surface.

It can be seen that determination of a grain-boundary diffusion coefficient based on the surface accumulation method requires more parameters than a simple measurement of the appearing time of diffusant atoms. The *C*-type kinetic regime corresponds to very low temperatures and short diffusion times which suppress any diffusion from the internal part of GBs into the bulk direction of the material. Moreover, the diffusion length along the nanocrystalline GBs is very small. Therefore, due to the lack of nanometer depth resolution of a conventional sectioning method, the flux of diffusants at low temperatures and in short times cannot be detected at very small grain size (10-100 nm). So, GB diffusion experiments are typically performed in the Harrison's *B* regime where the so-called triple product $P = s\,\delta\,D_{gb}$ can be determined from the penetration profiles of diffusant atoms (s is the segregation factor, δ is the grain boundary width, D_{gb} is the grain-boundary diffusivity).

In a thin layer the grain-boundary diffusion coefficient can be determined directly by measuring the appearing time of diffusant atoms on the exit surface. LEIS is a sensitive technique for detecting the first few atoms appeared on the surface. If appearing time t and the film thickness h are known, the diffusion coefficient can be calculated by the equation of $D_{gb}=h^2/6t$. Until now, the main inspiration of applying the accumulation method against appearing time method was just the lack of a high sensitive technique [4].

3. Experimental procedure

The experimental procedure consists of three steps.

Sample preparation and characterization

Nanocrystalline Ni and Cu layers were deposited by DC magnetron sputtering of Ni (99.99%) and Cu (99.99%) targets onto polished crystalline silicon wafers. During layer preparation the substrates were at room temperature, and the target-substrate distance was 70 mm. Layer thicknesses were monitored by a quartz microbalance. The vacuum of the system was $3\cdot10^{-7}$ mbar and the Ar working pressure was $7\cdot10^{-3}$ mbar. Both the copper and the nickel layer had a thickness of 25 nm, i.e. the layer structure was Ni(25nm)/Cu(25nm)//Si. Thicknesses and quality of the layers were checked by depth profile analyses. The characterization of grains of Cu and Ni layers was made by X-ray diffraction measurements. The average crystallite size in the Cu layer was 10.5 nm, and in the Ni layers it was 8.7 nm. After preparation, the samples were transferred from the preparation chamber to an assembly of machines where the measurements were carried out. These machines - a secondary neutral mass spectrometer, an X-ray photoelectron spectrometer equipped with a low energy ion source, and a scanning probe microscope – have a joint vacuum space and the samples are in ultra high vacuum during measurements ($3\ 10^{-10}$ mbar). The procedure of measurements was started by surface cleaning of samples with low energy (350 eV) argon ion beam. The layers contained oxygen and argon impurities due to the preparation technique. The oxygen originated from the residual gas of the working chamber, the argon from the plasma used for sample preparation. The concentration of impurities was checked by LEIS and it proved to be negligible. Sample surfaces were investigated by the scanning probe microscope having atomic resolution which could be used as STM, AFM and Kelvin probe force microscope. The surface roughness of Ni layer was determined by STM and we received 0.6 nm RMS value (Fig. 1).

In-situ XPS/LEIS measurements and sample annealing

The XPS and LEIS measurements were performed alternately during annealing times. Both photoelectrons during XPS measurements and helium ions (He^+) scattered on the sample surface during LEIS measurements were detected by the same hemispherical energy analyzer (type Phoibos, SPECS, Berlin). The base vacuum in the instrument was $5 \cdot 10^{-10}$ mbar. The partial working pressure during LEIS measurements was 10^{-7} mbar due to the He^+ ion beam. XPS spectra were obtained by X-ray irradiation of the sample surface using an aluminium Kα source with 10 kV accelerating voltage and 10 mA emission current. The ion energy and intensity of the He^+ beam used to LEIS measurements were typically 1 keV and 45 nA. Such low bombarding energy and intensity prevented an unnecessary sputtering of the sample surface during measurements. The sputtering rate of the He^+ ion beam was checked by an AMBIOS XP-1 type profilometer in a separated measurement of crater depth and we received 0.05 nm/min. Moreover, between two LEIS measurements the ion beam was blanked by an electrostatic beam blanker and the sample was rotated 10 degree around the axis perpendicular to the film surface. The beam was focused into a spot of 3 mm in diameter and shifted from the centreline axis of the sample with 3 mm. The sample rotation before measurements eliminated the surface ion-etching effect since each measurement was made on a virgin area of the sample surface.

The first aim of our experiments was to determine the appearing time of Cu atoms migrated through the Ni layer along grain boundaries. This was the time when Cu appeared on the Ni surface. LEIS made it possible for us not only to measure this appearing time with high sensitivity, but to measure the surface concentration change of Cu atoms, too. The basic equation of low energy ion scattering can be found in the paper of H.H. Brongersma et al. [15]. According to this equation the mass resolution linearly depends on the initial energy of projectiles. This suggests that an increase in primary energy increases the mass separation. However, peaks in a LEIS spectrum also broaden with increasing energy. If the scattering is inelastic, the peak width scales with the square root of the primary energy. If the scattering between projectiles and target atoms is elastic, the peak width scales linearly with the energy. At low ion energies, like in our case, the scattering process can be considered to be elastic, at least in first approximation, so the peak width broadens with the energy similar to the mass separation, i.e. higher energy does not result in better mass resolution, only the surface damage increases. Thus, it is desirable to carry out measurements at small projectile energies, although in this case the separation between adjacent masses is not so good and overlaps between peaks appearing in kinetic energy spectrum. The peaks, which are overlapped with each other, must be decomposed in order to get the exact amount of constituents. The decomposition was made by CasaXPS software.

Annealing of samples was made in the vacuum chamber of the XPS instrument using a temperature controller type Eurotherm 3504 in combination with pyrometer temperature measurements (Sensortherm prodact, type Metis MI18). In front of the pyrometer onto the vacuum chamber flange, a zinc selenide window was mounted to receive an appropriate optical transmittance in the range of infrared wavelength. The pyrometer was optically focused on the heatable tungsten sample holder and measured its temperature, so the emissivity coefficient was chosen for tungsten. Temperature measurement was checked by a thermocouple prior to annealing procedures. Finally, the samples were annealed at temperatures ranged between 423 K and 473 K with 10 K steps. The temperature at the beginning of a measurement was reached in 30-40 s and it was stable within 1 K during the whole measurement.

Cap layer and depth profile analysis

At the end of annealing, an 8 nm thick Ni top layer was sputtered on the sample surface for the purpose of depth profile analysis. The depth distribution of Cu along grain boundaries and the concentration on the sample surface were measured by a Secondary Neutral Mass Spectrometer (SNMS) in direct bombardment mode. A low-pressure radiofrequency plasma was used for both sputter and post-ionization purposes [16,17]. At the beginning of plasma sputtering, some time is needed to stabilize the sputter process. The 8 nm thick Ni cap layer served as a buffer layer to this stabilization. Without cap layer the determination of the correct Cu intensity on the film surface could not be achieved. Ar^+ ions with the kinetic energy of 350 eV were applied to sputter the sample surface through a Ta mask having a round-shaped open area with a diameter of 2 mm. The low energy of bombarding ions could not evoke a significant intermixing of atoms during sputtering. The surface roughness and crater shape were observed by the profilometer used in LEIS experiments. While the surface roughness determined the depth resolution [18], the crater shape gave information about the lateral homogeneity of the ion bombardment. The high detection sensitivity of SNMS gave a possibility to measure the depth distribution of diffusant atoms along short-circuits, i.e. along grain boundaries and dislocations, already at low temperatures when the lattice diffusion was completely frozen out and before the diffusant atoms migrated at the accumulation surface.

4. Results and discussion

The mass numbers of Ni and Cu are very close to each other, so at low kinetic energies used in our experiments their peaks in the energy spectrum were overlapped and their intensities could be determined by decomposition of the mixed peak. In order to make the decomposition correctly, prior to our annealing measurements, we carried on some calibration measurements on copper and nickel standard samples to determine the peak shapes, peak positions and relative sensitivity factors. Using these data, the peak decomposition was made by the commercial software CasaXPS. Fig. 2 shows both the mixed NiCu peak in the LEIS energy spectrum and the decomposed Ni and Cu peaks.

Time evolution of Ni and Cu peaks gave information about the time dependence of the coverage of Ni layer by Cu atoms. The appearing time was determined from this time dependence by extrapolation of Cu peak area to zero. Using the appearing time determined in this way, the GB diffusion coefficient could be calculated from the equation of $D_{gb}=h^2/6t$. Since the GB diffusion coefficient D_{gb} is Arrhenius type as generally diffusion processes, D_{gb} can be written in the form of $D_{gb}= D_{gb0} \cdot exp(-\Delta H_{gb}/RT)$, where ΔH_{gb} is the enthalpy of GB diffusion, R and T are the gas constant and temperature. This expression can be changed into the form of $lnD_{gb}=lnD_{gb0}$ - $(\Delta H_{gb}/R)\cdot 1/T$. In Fig. 3 lnD_{gb} is plotted against $1/T$. As it can be seen, the experimental data show this linear type relation and the enthalpy could be determined from the linear fit, ΔH_{gb} = (55±3) kJ/mol, which is much lower than that of 256 kJ/mol measured by radiotracer method in polycrystalline materials in B-type kinetic regime [19].

Time evolution of Cu peak intensity yields information about the surface coverage of Ni layer by Cu atoms. The surface coverage denoted by θ is 1 at monolayer coverage. Fig. 4 shows the time dependence of surface coverage. At a constant temperature, the surface coverage increased linearly in time until it reached a maximum value of θ = 0.45. This linearity completely differs from the exponential type function which is suggested by the Equation 2. Holloway and McGuire [9] showed theoretically this linear increase in surface concentration of diffusant atoms at the accumulation surface when the diffusion kinetic was clearly C-type and when both the source and the sink boundary conditions for diffusant atoms were infinite. The linear increase of surface concentration reflected a 2D surface accumulation process. The maximum value did not change during further annealing, at least under the period which was three times longer of the time needed to reach the maximum. The slope of linear part represents the speed of surface coverage increase which was determined by the atomic flux diffused through the Ni layer and appeared on the Ni surface. The results are shown in the inset of Fig. 4. Temperature dependence of the slope could be well fitted with an exponential function according to the exponential temperature dependence of the GB diffusion process. The character and the slope of the curve measured at 473 K differed from those of the other curves, as it can be seen in Fig. 4. At 473 K the maximum value of coverage was higher than $\theta = 0.45$ and its slope did not fit to the exponential curve in the inset. The reason of this behaviour is the mixing of different diffusion kinetics which will be explained below.

The copper intensity on Ni surface was measured by XPS, too. But in our experiments we did not experience any linear type increase and any definite saturation value in the intensities. The reason is that while in the case of XPS the information depth is a few nm (i.e. 95 % of photoelectrons come from about 5 nm thick surface layer for Al $K\alpha$ radiation) and the detection sensitivity is not better than 1 at%, in the case of LEIS the information depth is the topmost atomic layer and the detection sensitivity is about 10 ppm. While XPS has some 3D character, LEIS gives information directly about the surface. In addition to copper concentration, we also measured the Ni surface concentration by both LEIS and XPS. The XPS intensity of Ni was constant during annealing, the LEIS intensity changed opposite to Cu concentration. The XPS was not suitable for Ni concentration measurements because the thickness of the Cu layer on the Ni surface was much lower than the XPS information depth and the Cu layer did not absorb the electrons escaping from the Ni layer, i.e. the small amount of Cu on the surface did not influence the Ni signal.

Before and after annealing procedures, the surface concentration of copper and its depth distribution in Ni layer were measured by SNMS depth profiling. The results measured on as-prepared and annealed samples are shown in Fig. 5. The real purposes of these measurements were to observe directly the depth distribution of Cu in the bilayer nanosystem and to check the atomic mixing at the interface between Cu and Ni layers of as-deposited samples. This latter information was very important since the atomic mixing and, so, the interface roughness between Cu and Ni layers depends on the preparation conditions, namely on the incident energy of vapour atoms during deposition [20]. If the incident energy is high, like in our case which was about 10 eV, the surface roughness and atomic mixing are also high. In Fig. 5 the Cu and Ni depth distributions measured experimentally are denoted by open symbols. In depth profile analyses based on sputtering, the measured depth distribution of an element depends on the surface roughness. The effect of surface roughness can be estimated by calculation. Thus, using the experimentally measured surface roughness as an input parameter, we calculated a Ni distribution in the Cu film (the cyan curve in Fig. 5).

Due to surface roughness, the elements of an A/B interface are mixed by sputtering even if they were not mixed before. Here the atomic mixing means that both elements are sputtered and detected at the same time, and it differs from that of which is evoked by ion bombardment in a surface layer. A sharp change in concentration of an element at a rough interface results in the same effect as a diffuse change in concentration at a smooth interface. The interface width depends on the surface roughness. In order to get the real depth distribution of an element, it is important to know the effect of surface roughness, i.e. how it modifies the real distribution. So, we supplemented our SNMS measurements with calculations of depth distributions induced by surface roughness. These calculations were made for an A/B interface with approaching the surface roughness by a Gaussian distribution [21]. In our calculations a thin surface layer was defined as a calculation volume and the ratio of A and B elements inside this calculation volume was determined. The surface layer was not smooth, so both elements could be found in the calculation volume. Finally, the interface layer was scanned by this calculation volume in the depth direction to receive the calculated depth distribution of elements. If there was not any atomic mixing during preparation, the calculated values should be overlap with the experimental values. If there was some atomic mixing, the calculated values differ from the experimental values. As it can be seen in Fig. 5, the calculated and measured curves differ from each other, i.e. Cu and Ni atoms were mixed during deposition. Molecular dynamics simulations performed on Ni/Cu/Ni multilayers support this experimental result [20]. The SNMS depth profile analyses gave also information about the sample quality. The analyses showed that there was not any degradation in layer quality due to annealing up to 473 K temperature.

Annealing procedures resulted in interdiffusions between the Ni/Cu layers already at low temperatures. The Ni atoms diffused into the Cu layer, and vice versa. But while the Si substrate worked as a diffusion barrier for Ni atoms, the Ni surface was free for Cu atoms. Therefore Cu atoms could diffuse through the Ni layer and accumulate on the exit surface called accumulation surface. In Fig. 5 the peak in the Cu intensity (red line) near the surface shows this accumulation. The intensity gradient inside the Ni layer is proportional to the concentration gradient of Cu in the grain boundaries. Similar concentration gradients were calculated for thin films containing uniformly spaced grain boundaries by Gilmer and Farrell [3].

The annealing temperatures applied by us were so low that the diffusion was confined to GBs forming a pure *C*-type kinetic, except the highest temperature where B-type kinetic was also launched besides *C*-type. That is why at the highest temperature the diffusion coefficient and atomic flux do not fit well with the curves in Figs. 3 and 4. To our knowledge, this was the first experimental arrangement by which the temperature border between *C*- and *B*-type diffusion kinetics could be measured so precisely. It should be noted that the appearing time measured by us belongs to many GBs, so we could only determine an average value for GB diffusion coefficient.

The other important result is the saturation of surface coverage with Cu atoms which is independent of the temperature (Fig. 4). In previous works of GB diffusion measurements published in scientific papers no surface saturation was suggested. E.g. in the papers of G. Erdélyi *et al*. [14] and J.C.M. Hwang *et al*. [22] the authors definitely supposed a uniform distribution of diffusant atoms on the accumulation surface in the form of one or two homogeneous atomic layers. Our experimental result, that the surface coverage of Cu is lower than 1, shows just the opposite of this statement. The model which helps us to understand our results is the DDA model (Deposition, Diffusion and Aggregation model) applied by A.-L. Barabási *et al.* to describe the atomic morphology on a flat surface during submonolayer deposition [23]. In this model, the atoms are deposited by MBE (molecular beam epitaxy) with a constant flux. In our experiments the atomic flux is provided by grain-boundary (short-circuit) diffusion through a thin layer. The atoms which diffused along grain boundaries leave the GB surface area and continue their motion on the surface with much higher diffusivity like the atoms deposited by MBE. It does not matter how the atoms get onto the surface, by grain-boundary diffusion or deposition, their motion and surface arrangement are independent of the preparation method.

A free atom moves on the surface until it meets another one and they form atomic clusters with much smaller surface diffusivity. By meeting with newer atoms, the cluster diameter increases and the diffusivity decreases. Finally, these clusters form islands having fixed surface positions. If free atoms meet such an island, they stick to the edge of this atomic island and become also immobile. The real process is determined by the ratio of F/D_S, where F is the atomic flux arriving on the surface and D_S is the surface diffusivity. In our experiments F is the slope of the linear part of the time dependence of surface coverage (Fig. 4), so it can be easily determined experimentally. Both processes are temperature controlled, i.e. they depend on energy barriers of ΔE_S and ΔE_{gb} ($D_S = D_{S0} \cdot exp(-\Delta E_S/RT)$ and $D_{gb} = D_{gb0}$

$\cdot exp(-\Delta E_{gb}/RT)$, where ΔE_S and ΔE_{gb} determine the surface and GB diffusivities, D_{S0} and D_{gb0} are constants). At temperatures of our measurements ΔE_S is lower than ΔE_{gb}, and, as a consequence, D_S is higher than D_{gb} by 3 or 4 orders of magnitude. In other words, surface diffusion is much faster than GB diffusion [24]. However, the temperature dependence of the two types of diffusion is approximately the same, so the temperature dependence of the ration of F/D_S can be neglected, at least in the first approximation. That is why we experienced a temperature independent maximum value in the time dependence of surface coverage functions (Fig. 4). We believe that this maximum value ($\theta = 0.45$) is not a universal constant, it rather depends on the material itself. As we mentioned previously, this maximum value stayed constant during further annealing. In this period, Cu atoms on the accumulation surface diffused to already existing Cu islands, stuck to them, and formed the second, third, etc., atomic layer of islands. It is well known that Volmer-Weber type film growth produces three dimensional islands on a substrate [25]. In our case, Ni layer had a nanocrystal structure which supported the Volmer-Weber type film growth instead of layer by layer growth. A Cu island on the surface of a Ni nanolayer is shown in Fig. 6. The copper content of these islands was identified by Kelvin probe force microscope based on non-contact SPM technique. We could measure local contact potential difference between the island and other part of the film due to different surface structures and atoms, but the irrefutable evidence for high copper content of surface islands is the peak in copper intensity in Fig. 5 at the film surface. The thickness of the surface Cu layer measured by SNMS was about 7 nm which equals the peak-to-valley height of surface islands measured by STM.

In the paper of Rasuli *et al.*, the Cu diffusivity through a Ni layer was measured by AES surface accumulation method [26]. The authors claimed that Cu diffused through the Ni layer, if the Ni layer thickness was lower than 4 nm (see the Fig. 3 in [26]). Contrary to this result, in our experiments we measured the time dependence of surface concentration of Cu when the Ni layer thickness was 25 nm. The authors of the paper Rasuli *et al*. did not see Cu on the Ni surface at higher thicknesses because the sensitivity of their experimental method was probably too low [26], while in our work the sensitivity of LEIS was about 4 order of magnitude higher.

5. Conclusion

Experimental determination of diffusion coefficients in pure *C*-type kinetic regime was presented. A combined measurement technique of LEIS and SNMS gave a unique possibility to measure the fast diffusion in nanolayers at low temperatures. Furthermore, the advantage of this technique was that determination of D_{gb} did not require a complicated calculation with segregation factors in order to remove the effect of *B*-type diffusion kinetic and, as a result of this, the diffusivity could be studied in a simply way, only by measurement of the appearing time. The temperature range of pure *C*-type diffusion kinetic could be determined very precisely. Fast atomic motions in grain boundaries resulted in short appearing times. By STM measurements we could prove that diffusant atoms on the accumulation surface did not form a continuous layer. Instead, a Volmer-Weber type layer growth was realized in nanoscale islands form.

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Figure captions

Fig. 1. The grain structure of Ni nanolayer measured by STM.

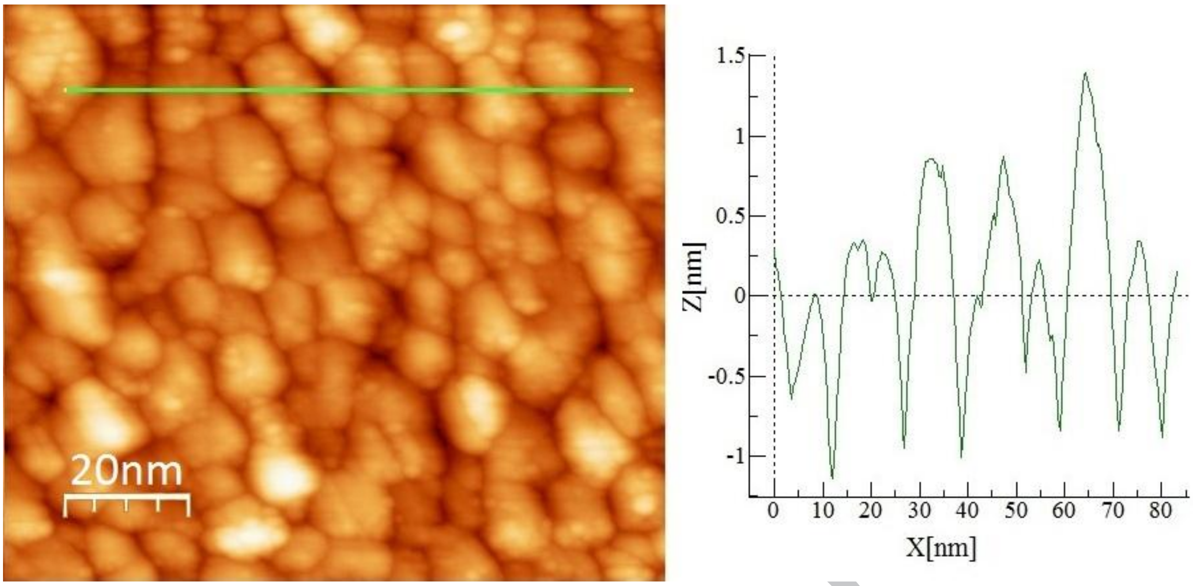
Fig. 2. The mixed NiCu peak in a LEIS spectrum and its decomposition. The sample was annealed at 443 K during 35 min.

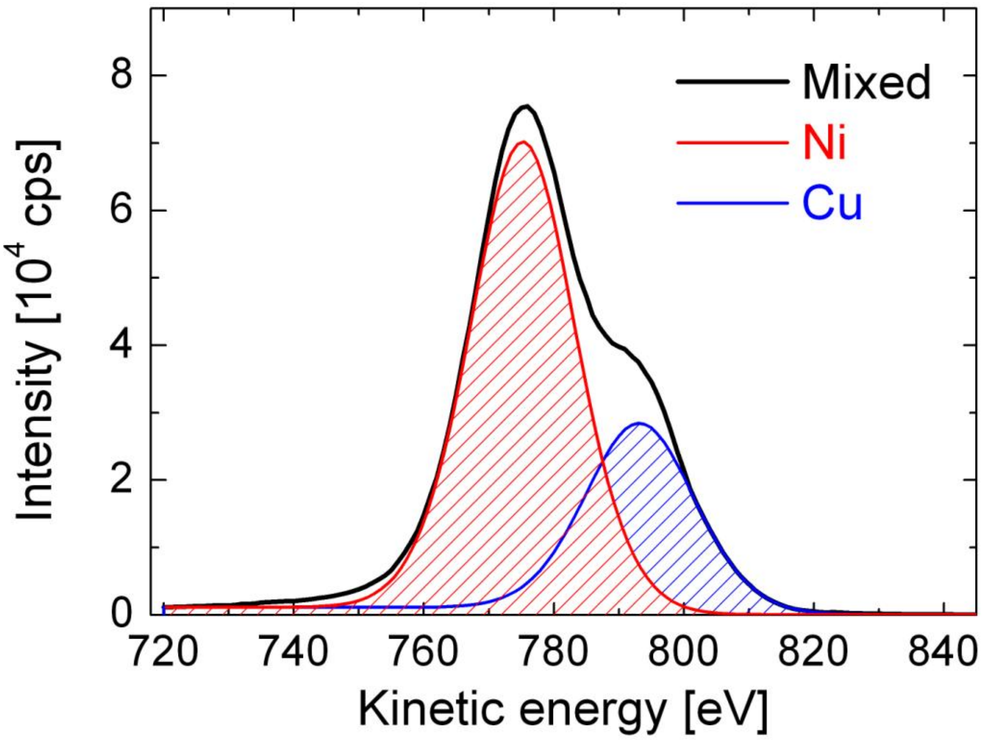
Fig. 3. Temperature dependence of GB diffusion coefficient of Cu in Ni nanolayers. The experimental errors equal with about the diameter of the dots.

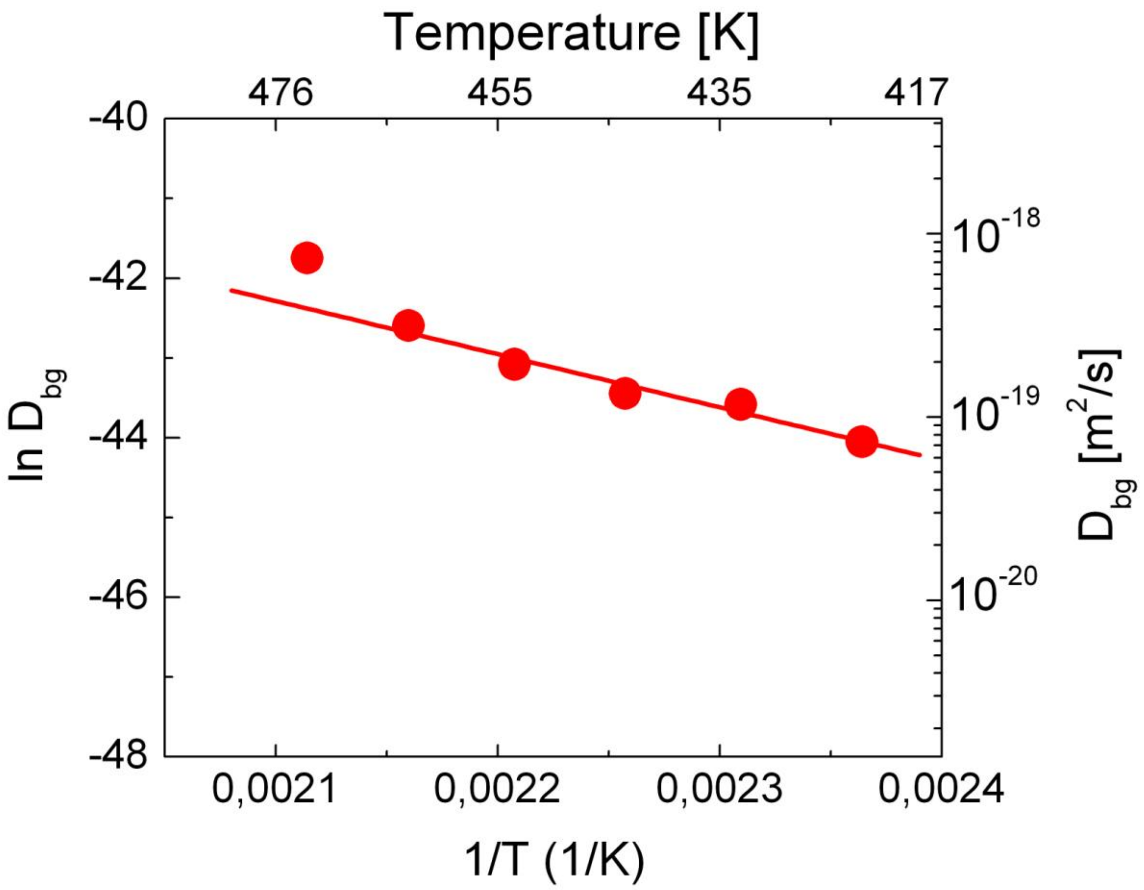
Fig. 4. Time dependence of surface coverage (θ) at different temperatures. Inset: temperature dependence of the atomic flux diffused through the Ni layer. The experimental errors are not shown in figure because the size of error bars is not higher than the size of symbols.

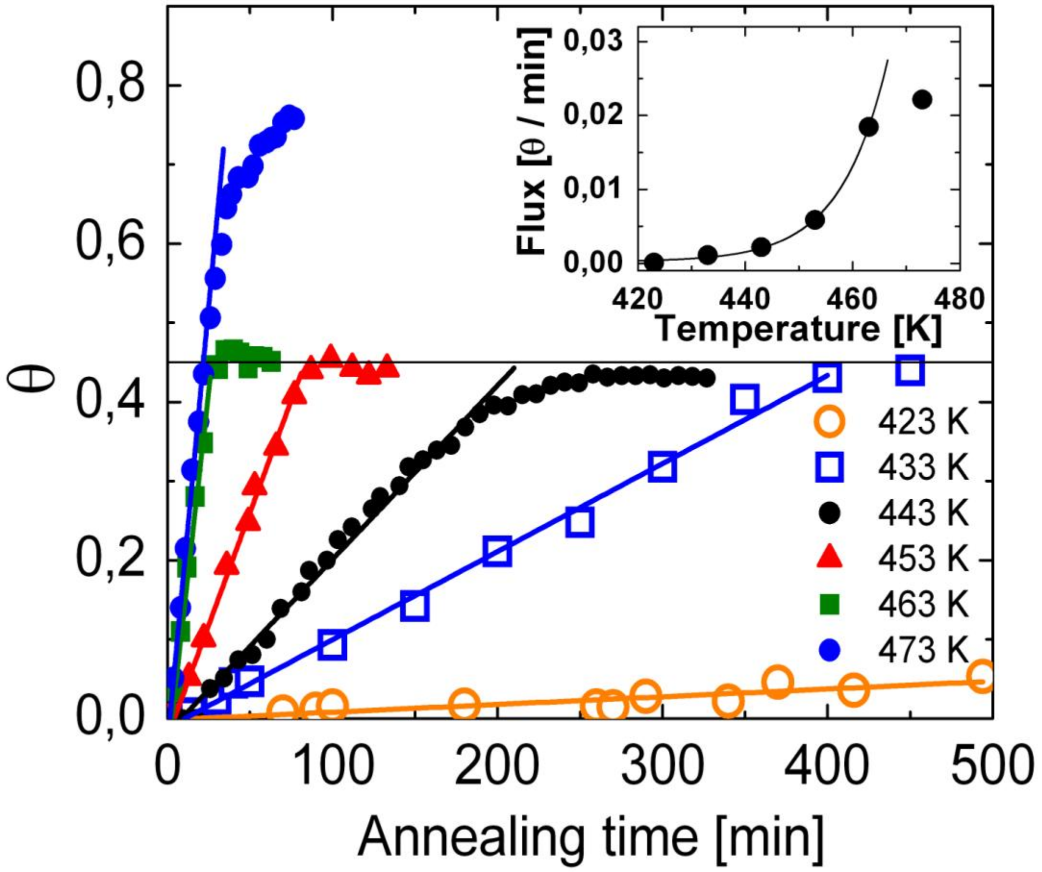
Fig. 5. Depth distributions of Cu and Ni on a silicon substrate were measured experimentally by SNMS. The thickness of the Cu and Ni layers was 25 nm. For simplicity we present only the results of as-deposited and annealed at 463 K samples. The depth distribution of Si and the calculated depth distribution of Ni are also presented in the figure.

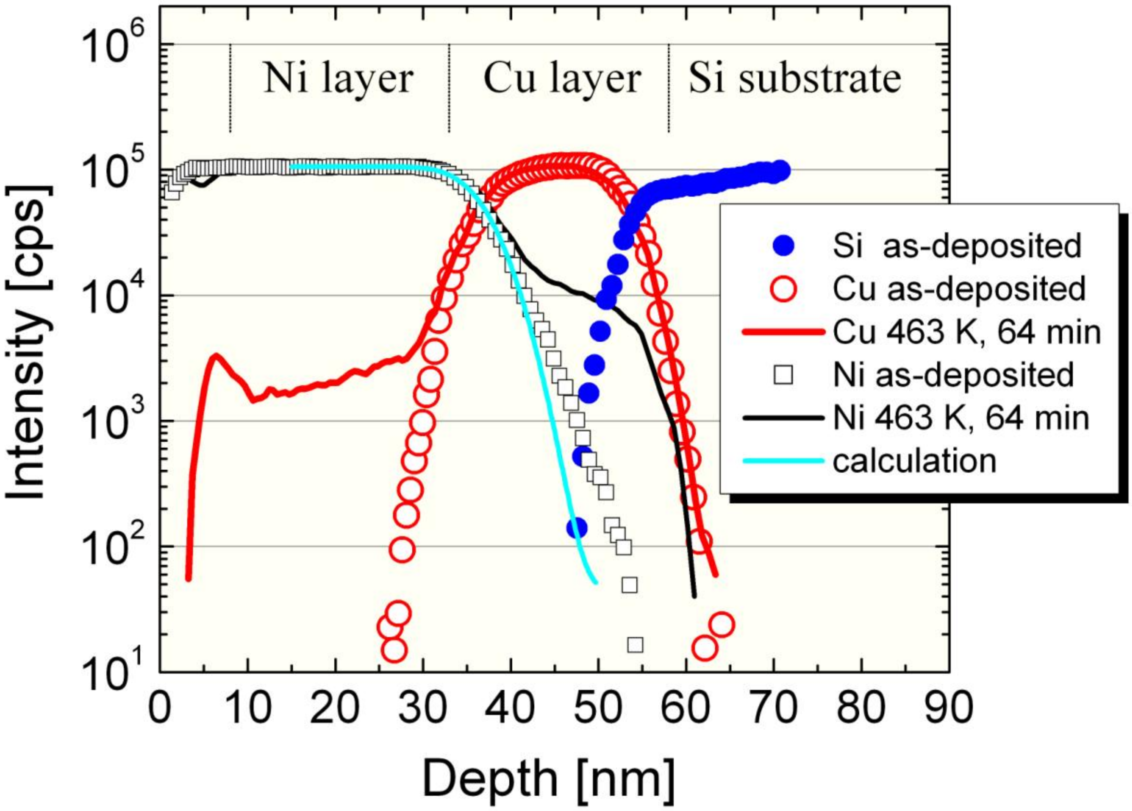
Fig. 6. STM image of a Cu island formed on the Ni layer due to GB and surface diffusions at the beginning of diffusion process. The sample was annealed at 463 K during 8 minutes. This annealing time includes both the warm-up time needed to reach the annealing temperature and the appearing time of Cu diffusant atoms.

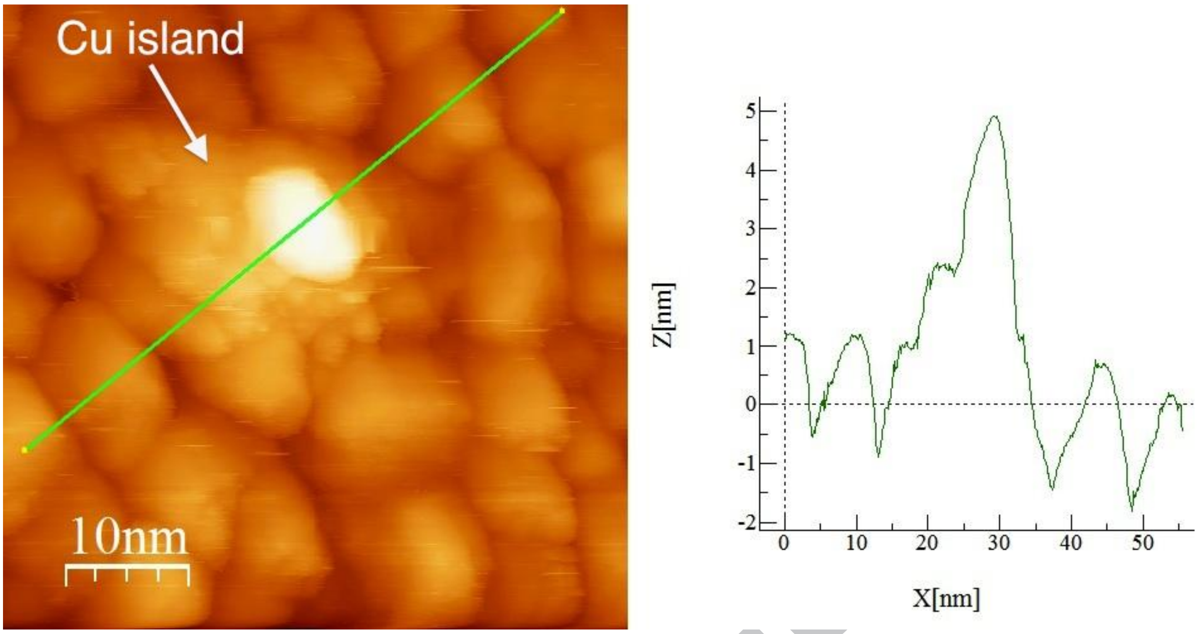

20nm
1.5
1
0.5
0
-0.5
-1
Z[nm]
0
10
20
30
40
50
60
70
80
X[nm]

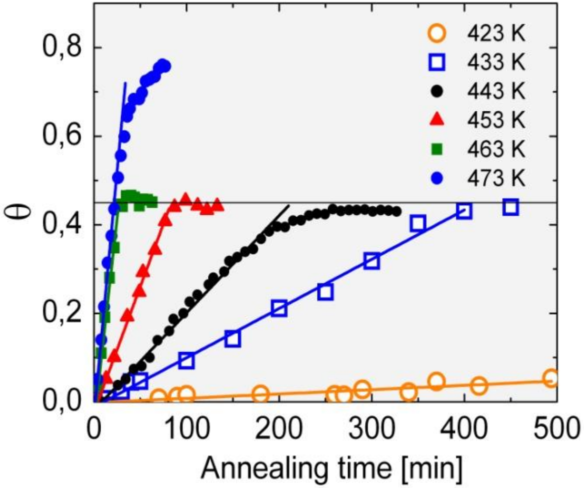

Mixed
Ni
Cu
Intensity [10^4 cps]
0
2
4
6
8
720
740
760
780
800
820
840
Kinetic energy [eV]


Temperature [K]
476
455
435
417
-40
-42
-44
-46
-48
ln D$_{bg}$
10^{-18}
10^{-19}
10^{-20}
D$_{bg}$ [m^2/s]
0,0021
0,0022
0,0023
0,0024
1/T (1/K)

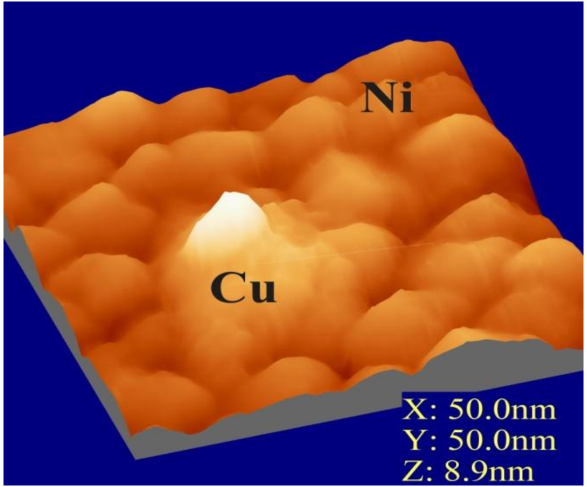

θ
0,0
0,2
0,4
0,6
0,8
0
100
200
300
400
500
Annealing time [min]
423 K
433 K
443 K
453 K
463 K
473 K
Flux [θ / min]
0,00
0,01
0,02
0,03
420
440
460
480
Temperature [K]

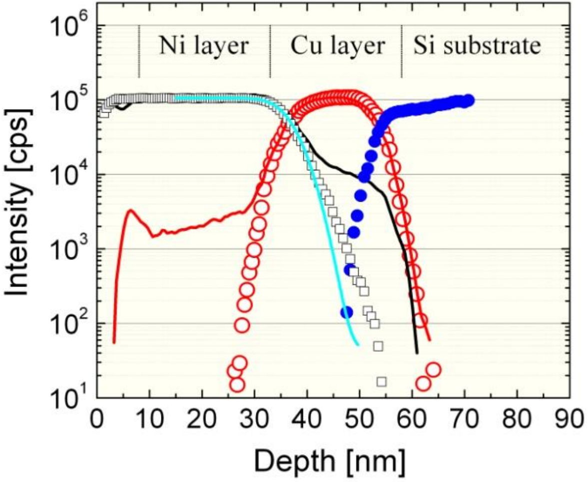

Ni layer
Cu layer
Si substrate
Intensity [cps]
Depth [nm]
10^6
10^5
10^4
10^3
10^2
10^1
0
10
20
30
40
50
60
70
80
90
● Si as-deposited
○ Cu as-deposited
Cu 463 K, 64 min
□ Ni as-deposited
Ni 463 K, 64 min
calculation


Cu island
10nm
Z[nm]
5
4
3
2
1
0
-1
-2
0
10
20
30
40
50
X[nm]



Surface coverage





Depth structure

Highlights

Grain-boundary diffusion at nanoscale.
Surface atomic islands formed by grain-boundary and surface diffusions.
Application of low energy ion scattering for study of nanoscale diffusion mechanisms.