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COMPARISON OF PROCESSES OCCURRING DURING SILVER ADSORPTION ON COPPER AND NICKEL AT ELEVATED TEMPERATURES

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A flux of silver atoms reevaporated from the copper and nickel targets during deposition of silver was measured as a function of the target temperature during spontaneous cooling from 1150 K and during heating the target with deposited several silver monolayers from room temperature to 1150 K. Differences in the measured dependences for both targets give the evidence of competition between reevaporation of silver atoms from the copper surface and their dissolution in the copper bulk and are in accordance with the lack of silver dissolution in nickel. Thus, the role of silver dissolution in the copper surface layer during silver adsorption at elevated temperatures is experimentally evidenced. Activation energy for silver dissolution in the copper substrate was estimated to be equal to 1.7–2.4 eV/atom.

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1. Introduction

A mechanism of silver layer growth during deposition in ultrahigh vacuum on metallic substrates depends on the substrate temperature. For silver adsorption on the Cu(111) [1] and Cu(011) [2] faces the silver Auger signal was found to be limited to the value corresponding to about 1 monolayer (ML) when the substrate temperature exceeds 770 K while for lower temperatures this limit was appreciably higher and reached the value expected for the silver bulk. This limitation was interpreted as a result of silver dissolution in the surface region of the copper substrate.

Similar limitation was found for $T > 860$ K in the case of silver adsorption on the nickel (111) [3] and (001) [4] faces. Silver is practically insoluble in the nickel bulk even at $T = 800$ K [5]. Thus thermal desorption of silver atoms was invoked in explanation of this limitation.

Such a difference in the behaviour of silver at hot surfaces of copper and nickel (dissolution and desorption and only desorption, respectively) should influence the silver flux reevaporated from a target during silver deposition. Namely, silver dissolution should compete with reevaporation changing the temperature dependence of the flux mentioned above.

The goal of the present paper was to give a direct experimental evidence of the correctness of the above interpretation. To do this, the temperature dependence of the silver flux reevaporated from copper and nickel surfaces during silver adsorption was measured. The expected difference in this dependence for copper and nickel substrates should support the statement that silver dissolution in the copper surface layer is responsible for limitation of silver coverage on copper to one monolayer for $T > 770$ K.

2. Experimental

The measurements were performed in the stainless steel ultrahigh vacuum system with the limit pressure of about 10^{-9} mbar. During heating the sample and the silver source the pressure increased to about 10^{-8} mbar. Silver was evaporated from a quartz cup heated with the tungsten wire resistive heater. The target (nickel or copper) was a polycrystalline foil with dimensions of $15 \times 15 \times 0.2$ mm^3 and with the purity of 99.999% fastened to two molybdenum wires 0.3 mm in diameter and 40 mm long. Those wires were resistively heated and rose the target temperature up to 1150 K as measured with the Pt–PtRh10 thermocouple (wires of 0.1 mm in diameter) fastened to the rear surface of the target. The error of the temperature measurement is difficult to estimate. One can expect that the real temperature of the sample was higher than that measured with the thermocouple wires. However, those wires were thin and long and we hope basing on the observation of the hot sample surface (no difference in the surface brightness in the thermocouple vicinity was visible) that this error is small.

The target surface was electropolished before location in the vacuum system and cleaned in situ by bombardment with potassium ions from a zeolite source and simultaneous annealing at 900 K. This method was found in separate experiments to be effective in cleaning the copper and nickel surfaces.

The silver atoms flux from the silver source impinged the target with the incidence angle of about 45°. The monopole mass spectrometer (MMS), which is the modification of a quadrupole mass spectrometer, was placed with its ionization area at the distance of 5 cm from the target in the direction making the angle of about 45° with the surface normal and about 90° with the primary silver flux.

In a separate experiment, the primary silver flux was calibrated with the use of a quartz oscillator. The flux of about 10^{15} atom/(cm^2 s) was used in experiments described below.

Two kinds of measurements were performed:

1. The MMS was tuned to the 107 mass (the one of silver isotopes), the clean target was heated to 1100–1150 K, and the silver source was turned on. Then, the target heating current was turned off and the MMS signal was recorded as a function of the target temperature during its spontaneous cooling at a rate of about 10 K/s in the temperature range of 1050–950 K.

2. Several silver monolayers were deposited onto the target maintained at the room temperature. Then, the silver source was turned off, the heating of the target was turned on, the target temperature increased up to 1100–1150 K at a rate of about 4 K/s in the temperature range of 1000–1150 K, and the signal of the MMS tuned to the ^{107}Ag peak was recorded during this increase as a function of the target temperature.

3. Results

Dependences of the height of the ^{107}Ag peak in the MMS spectrum on a temperature of the target during its cooling and heating are shown for nickel and copper targets in Figs. 1 and 2, respectively.

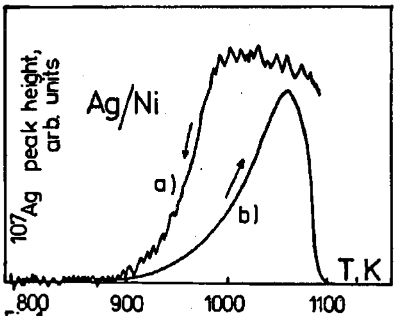

Fig.1

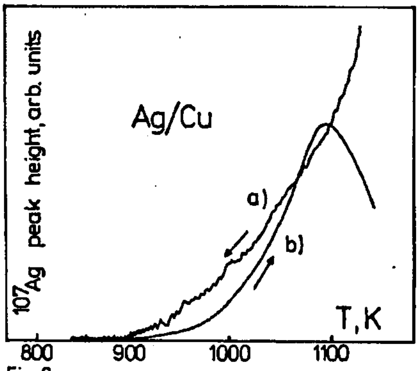

Fig. 2

Fig. 1. Temperature dependence of the height of the ^{107}Ag peak in the monopole mass spectrometer spectrum as a function of the nickel target temperature during spontaneous cooling from 1100 K (curve *a*) and during heating the target with deposited several monolayers of silver from the room temperature to 1100 K (curve *b*). Constant flux of silver atoms was directed onto the target surface during the target cooling. During heating the target, the silver source was turned off.

Fig. 2. As Fig. 1, but for the copper target and for the highest temperature of 1150 K.

For the nickel target, the plateau of this dependence appears during cooling the target from 1100 K to below 1000 K (see curve *a* in Fig. 1). Then, the height drops rapidly to about one third of the maximum value at 950 K and near to zero at 900 K. During heating the nickel target covered with several silver monolayers deposited (see curve *b* in Fig. 1), a silver signal in MMS spectrum appears at about 900 K, reaches its maximum at 1070 K and then rapidly drops to zero at 1100 K.

For the copper target, the plateau mentioned above for nickel does not appear (see curve *a* in Fig. 2). The monotonic decrease in the silver signal with smaller and smaller slope is observed during cooling the target from 1150 K to 850 K where this signal reaches the zero value. Unfortunately, technical reasons restricted the maximum target temperature to about 1150 K and it was impossible to check if the plateau occurs at higher temperatures.

During heating the copper target covered with several silver monolayers deposited (see curve *b* in Fig. 2), the low temperature part of the silver signal temperature dependence was similar to that obtained for the nickel target while the high temperature part has an appreciably smaller slope and the zero value of the silver signal was not reached even at 1150 K.

4. Discussion

The plateau of the curve *a* in Fig. 1 can be explained under supposition that a two-dimensional gas of silver atoms is present at the nickel target surface and that concentration of this gas increases during cooling the target, due to the silver atom lifetime increase. As a result, the flux of reevaporated silver atoms remains constant in the region of the plateau and is almost equal to the primary silver flux impinging the target.

At the low-temperature side of the plateau a condensation of the two-dimensional silver atom gas into islands takes place. Silver atoms forming those islands are bounded stronger than those in the gas and do not reevaporate. Besides, reevaporation of atoms still remaining in the gas now competes with condensation of those atoms on already existing islands. The coverage of the target surface with islands and their capture areas increases rapidly with the target temperature decrease and a multilayer coverage of silver establishes quickly owing to high intensity of the silver flux. As a result, the reevaporated flux drops rapidly to zero.

The rate of silver desorption $v_{\rm des}$ can be described by the relation

$$I = av_{\rm des} = an\nu_{\rm des}\exp\left(-E_{\rm des}/kT\right), \tag{1}$$

where n is the concentration of silver atoms in the outer silver atomic layer (this value is not known because of unknown morphology of the silver layer but it should be constant during the drop of the desorbed silver flux), $\nu_{\rm des}$ is a frequency of silver atom vibrations responsible for desorption, $E_{\rm des}$ is the activation energy for silver atom desorption from the silver multilayer, I is the mass spectrometer signal, and a is a some constant.

Presenting data from Fig. 1 as a dependence of $\ln I$ on $1/T$ one obtains the straight line shown in Fig. 3 and indicated as Ag/Ni. From the slope of this straight line one obtains $E_{\rm des} = (2.76 \pm 0.04)$ eV/atom. This value is smaller than the binding energy of silver atom in a silver crystal (2.95 eV/atom [6]). This difference can be explained by the possible roughness of the silver layer investigated or by systematic error in the temperature determination. Namely, underestimation of the sample temperature for 20 K results in underestimation of $E_{\rm des}$ for about 0.15 eV in our case.

The low-temperature part of the curve *b* in Fig. 1 has the slope appreciably smaller than the slope of the curve *a* in this region. This can be easily understood if we have in mind that this time all silver atoms are condensed in a solid layer at the beginning. The near surface transition layer (for more details see [7]) appears at the vacuum–silver boundary at $T \approx 900$ K enabling fast silver evaporation. Thickness of this layer increases with the temperature rise leading to the increase in the silver evaporation rate. However, the thickness of the whole silver layer is smaller and smaller and, at least, only the transition layer mentioned above is

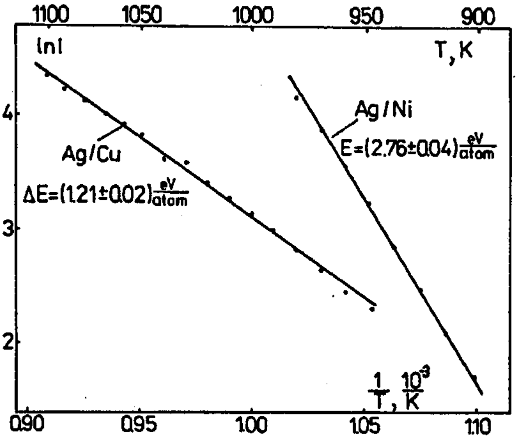

Fig. 3. Dependence of the mass spectrometer signal I (in logarithmic scale) for silver on the inverse temperature during spontaneous cooling of nickel (Ag/Ni) and copper (Ag/Cu) samples with constant flux of silver atoms (about 10^{15} atoms/(s cm^2)) impinging the sample surface.

present on the nickel substrate. Further evaporation diminishes the thickness of this layer. As a result, the evaporation rate drops to zero when silver is completely evaporated.

The absence of the plateau in the curve *a* of Fig. 2 can be explained if the silver dissolution in the copper target volume is taken into account. Namely, this time silver dissolution in copper competes with its desorption. Let us suppose that in the temperature range of 1100–950 K the equilibrium coverage with silver $n(T)$ is smaller than that corresponding to one monolayer. The equilibrium at the surface will be now ruled by the relation

$$v_0 = v_{\rm dis} + v_{\rm des} = n(T)\nu_{\rm dis}\exp\left(-E_{\rm dis}/kT\right)$$
$$+n(T)\nu_{\rm des}\exp\left(-E_{\rm des}/kT\right), \qquad (2)$$

where $\nu_{\rm dis}$ and $\nu_{\rm des}$ are frequencies of silver atom vibrations responsible for dissolution and desorption, respectively, while $E_{\rm dis}$ and $E_{\rm des}$ are activation energies for dissolution and for desorption of silver atom from the copper surface, respectively, and v_0 is a flux of silver atoms impinging the sample surface.

Supposing that $(E_{\rm des} - E_{\rm dis})/kT \gg 1$ and $\nu_{\rm dis} \approx \nu_{\rm des}$, one obtains

$$n(T) \approx (v_0/\nu_{\rm dis})\exp\left(E_{\rm dis}/kT\right) \qquad (3)$$

and

$$I = av_{\rm des} = av_0(\nu_{\rm des}/\nu_{\rm dis})\exp\left(-\Delta E/kT\right), \qquad (4)$$

where $\Delta E = E_{\rm des} - E_{\rm dis}$. This leads to the Arrhenius plot

$$\ln I = b - (\Delta E/k)(1/T). \qquad (5)$$

Indeed, presenting data from Fig. 2 as a dependence of $\ln I$ on $1/T$ one obtains a straight line shown in Fig. 3 and indicated as Ag/Cu. From the slope of this straight line one obtains $\Delta E = E_{\rm des} - E_{\rm dis} = (1.21 \pm 0.02)$ eV/atom.

This time, $E_{\rm des}$ is the activation energy for desorption of a silver atom from the copper surface. The reliable value of $E_{\rm des}$ should lie between 2.95 eV/atom (binding energy of silver atom in silver) and 3.6 eV/atom (activation energy for silver atom desorption from nickel surface [4]). Thus, it results from our measurement that

$$1.7\ {\rm eV/atom} \approx 1.74\ {\rm eV/atom} \leq E_{\rm dis} \leq 2.39\ {\rm eV/atom} \approx 2.4\ {\rm eV/atom}. \qquad (6)$$

This estimation is in a good agreement with the value of about 2 eV/atom given in [8].

The maximum of the curve *b* in Fig. 2 appears at about 1100 K (about 50 K higher than for nickel). This shift can result from competition between desorption and dissolution of silver. The lack of the drop of the curve *b* in Fig. 2 to zero at highest temperatures may be due to desorption of silver atoms previously dissolved in the copper bulk. Namely, the enabled concentration of silver in the subsurface region of the copper target is known to depend on the silver concentration at the surface [9, 10] and, at given temperature, increases with this concentration increase. Thus, after desorption of silver from the surface, silver atoms from the bulk diffuse back to the surface and desorb giving the flux observed at highest temperatures.

In conclusion, results presented in Figs. 1, 2, and 3 support the statement that silver atoms dissolve in the copper volume during annealing at temperatures exceeding 770 K with an activation energy of 1.7–2.4 eV/atom and that such dissolution in nickel does not occur.

Acknowledgments

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