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VERY THIN SILVER LAYER GROWTH ON THE Cu(111) FACE AT DIFFERENT TEMPERATURES

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Measurements of work function changes ($\Delta\Phi$) and Auger Electron Spectroscopy were used for investigation of very thin silver layer adsorption on the (111) face of copper crystal. At room temperature the layer-by-layer growth was observed while at temperatures above 850 K $\Delta\Phi$ and the Auger peak height kinetics indicated the presence of silver diffusion to the surface layer of the copper sample.

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1. Introduction

Adsorption kinetics and properties of very thin silver layers adsorbed on the (111) copper face were investigated in a number of papers [1-11]. Contrary to the previous model proposed by Namba and Vook [4] in which the growth of islands of two atomic layer thickness was supposed, it has already been established that at least the first two silver layers grow according to the layer-by-layer Frank-van der Merwe mechanism. Concerning the atomic structure of the first silver layer, all authors investigating this problem agree that the crystallographic axes of the Ag(111) islands are parallel to the corresponding axes of the substrate. Almost all papers deal with investigations at room temperature or at temperatures slightly elevated. Only Vook et al. [3] state that at temperatures higher than 400°C interdiffusion effects occur, but no more details are presented.

In the present paper the properties of the very thin silver layer adsorbed under UHV conditions on the Cu(111) face are investigated with the use of the Auger Electron Spectroscopy and the work function change. Measurements were performed at the sample temperature ranging from room temperature to desorption temperature.

2. Experimental

Measurements were performed in the stainless steel UHV system equipped with the retarding field analyser (RFA). The copper crystal was cut parallel to the (111) face with accuracy of 0.5° , and then mechanically and electrochemically polished. Silver was evaporated from the tantalum cup heated by surrounding tungsten resistive heater. Owing to the proper geometry, it was possible to perform simultaneously silver evaporation and recording of Auger peak heights for silver and copper under the computer control [12]. The $\text{Cu-M}_{2,3}\text{VV}$ and Ag-MNN peaks were recorded and presented as a function of adsorption or annealing time. The sample was heated by radiation with the toroidal shaped tungsten resistive heater placed behind the sample and shielded with a special cover. The heating current did not disturb the measurements even for low-energy $\text{Cu-M}_{2,3}\text{VV}$ Auger transition. Before the silver adsorption the sample surface was cleaned by the potassium ion bombardment from the zeolite source and simultaneous heating at temperature of about 900 K. After such procedure only small traces of sulphur and carbon were visible in the Auger spectrum. This cleaning procedure was repeated a few times to remove contaminations accumulating at the surface during the prolonged measurements.

The work function changes were measured with the use of the so-called "onset method" [13]. In this method the low-energy part of the secondary electron energy distribution is used (Fig. 1). The position of the low-energy onset is determined

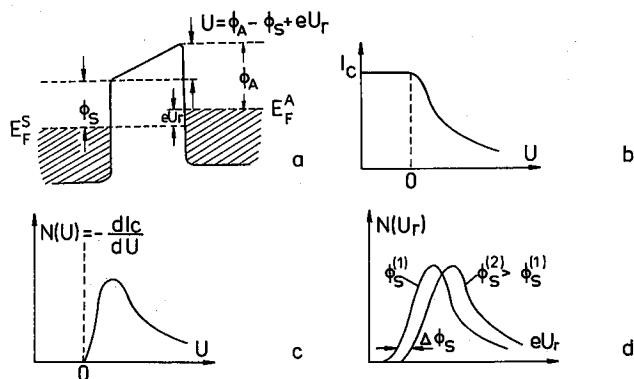


Fig. 1. Explanation of the "onset method". (a) Electron potential energy diagram for the system: sample-analyser. (b) and (c) Dependences of the RFA collector current and its derivative, respectively, on the difference of potentials of the sample and the analyser retarding grid surfaces. (d) Shift of the low-energy part of the secondary electron energy distribution, related to the sample work function change.

by the value $U_r = \Phi_A - \Phi_S + eU_r$ where Φ_A and Φ_S are the work functions of the retarding grid in RFA and the sample, respectively, and U_r is the retarding voltage applied between the grid and the sample. Thus, this onset moves along the eU_r axis when Φ_S changes provided Φ_A value constant. The onset shift is equal to the

work function change. An example of such a shift is shown in Fig. 1d. In our case the eU_r value was changed during the measurements in such a way that the signal of the lock-in amplifier measuring the $N(U_r)$ distribution was constant and equal to about 0.1 of the maximum of the $N(U_r)$ distribution. Changes of eU_r necessary to keep this signal constant were recorded as a function of time and taken as Φ_s changes.

In order to minimize the magnetic field influence on the low-energy electron trajectories between the sample and the first grid of the RFA, a low potential (about 8 V) negative with respect to the grounded first grid was applied to the sample. Thus, the electrons emitted from the sample were immediately accelerated up to the energy of a few eV. For this reason the onset in Fig. 1d appears at $eU_r \approx 8$ eV. Sensitivity of the method described above was sufficient to measure the work function changes even smaller than 0.01 eV.

For the technical reasons, the sample holder was not equipped with a thermocouple. Thus, the sample temperature was measured with the use of an optical pyrometer for the maximum heater power ($T = 1050 \pm 50$ K was obtained then) and for lower heating current the sample temperature was estimated under supposition that the heater power is dissipated only via the radiation emitted by the sample and its holder. In such a case $P_1/P_2 = T_1^4/T_2^4$, where P_i is the heater power corresponding to the sample temperature T_i . Of course such a temperature estimation can lead to the error exceeding 50 K.

3. Results

Kinetics of the work function changes during the silver adsorption at $T = 300$, 880, and 900 K are presented in Figs. 2a, 2b and 2c, respectively. Figure 2a

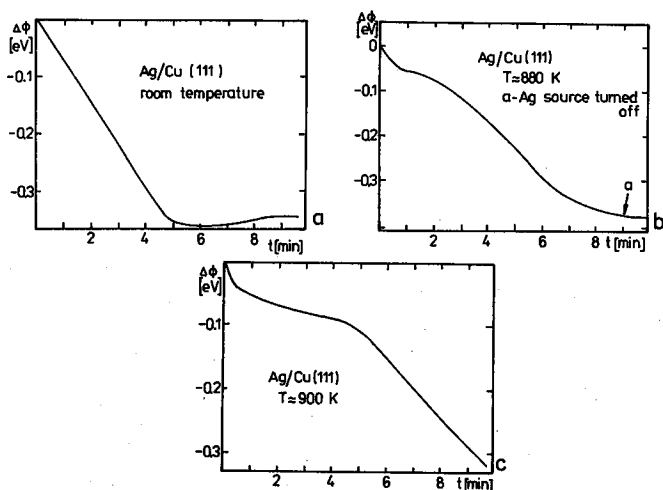


Fig. 2. Kinetics of the work function changes during the silver adsorption at $T = 300$, 880 and 900 K.

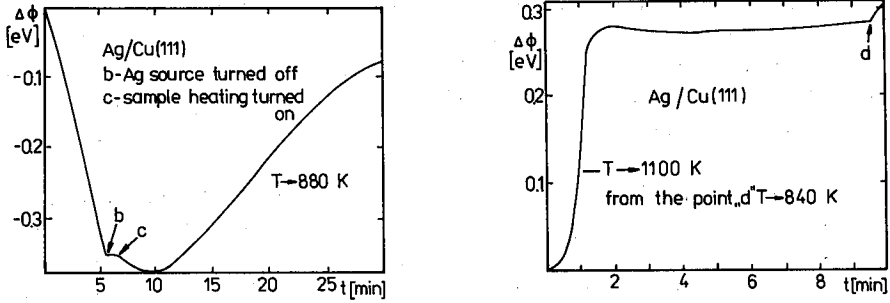


Fig. 3. Kinetics of the work function changes during the silver adsorption followed by the sample temperature rise (below the desorption temperature).

Fig. 4. Kinetics of the work function changes during the silver desorption followed by the sample temperature drop.

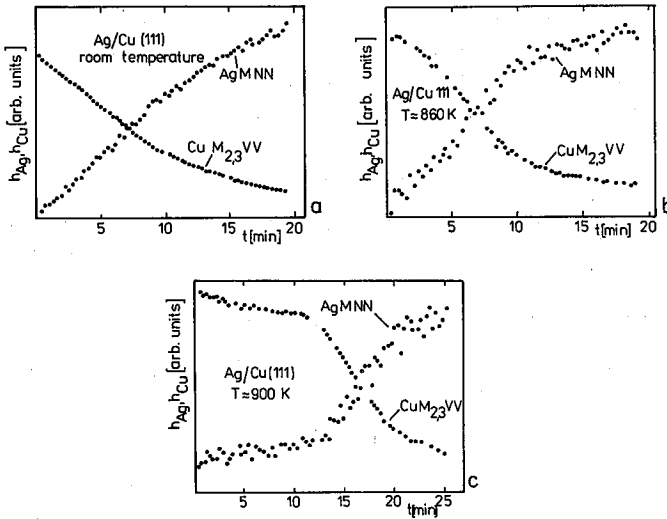


Fig. 5. Kinetics of the Auger peak heights during the silver adsorption on the copper surface at 300, 860 and 900 K.

shows almost linear decrease of the work function up to the first monolayer completion (when $\Delta\Phi_S = -0.37$ eV is reached). Next, the work function remains practically constant. In Figs. 2b and 2c this linear decrease is preceded by the flatter part of the kinetics, which elongates as the temperature increases. Figure 3 shows work function changes for almost completed silver monolayer adsorbed at room temperature. At the point "b" the silver source was turned off and the point "c" denotes beginning of the sample temperature increase up to 880 K. This temperature is not high enough to remove silver from the surface (see Fig. 2b, where the silver source was turned off at the point "a" and after this moment the

work function remained constant). Nevertheless, in Fig. 3 the work function increases after the temperature enhancement. Figure 4 presents kinetics of thermal desorption of the silver layer of about one monolayer thick for the sample temperature rising from the beginning of the measurement and reaching 1100 K. The fast, one-stage desorption visible in this figure leads to the work function increase by about 0.28 eV. At the final state of the process presented in Fig. 4 the silver peak is still present in the Auger spectrum and disappears only after heating for more than 30 min at 1000 K. In Figs. 5a, 5b, 5c kinetics of Auger peak heights changes for $T = 300, 860$ and 900 K, respectively, are presented. At room temperature the kinetics for the copper peak and for the silver peak as well consists of two linear parts while at $T = 900$ K in both cases those two parts are preceded by the almost horizontal part.

4. Discussion

Our results obtained at $T = 300$ K are consistent with the Frank-van der Merwe mechanism. Linear work function changes observed up to the silver monolayer completion (Fig. 2a) can be explained as due to constant interatomic distances in silver islands during the growth of a monolayer. The work function decrease $\Delta\Phi \approx 0.35$ eV agrees well with the value of about 0.39 eV measured for the same adsorption system with the use of a different method [9]. Kinetics of Auger peak heights presented in Fig. 5a indicates clearly the layer-by-layer growth. The peak heights were measured without the background subtraction. The role of the background is especially significant for the Cu- $M_{2,3}VV$ (62 eV) transition, when the silver coverage exceeds one monolayer. Nevertheless, the subtraction of approximately constant background could not change the linear shape of the kinetics and the ratio of slopes of the neighbouring parts of this kinetics should remain unchanged. In principle, the inelastic mean free path for Auger electrons can be calculated with the use of this ratio. However, in our case it does not seem to be possible because of the large acceptance angle of our RFA and complicated [11] angular distribution of the Auger electron emission from the Ag/Cu(111) surface. In the case of the adsorption at elevated temperatures both $\Delta\Phi$ and the shape of the Auger peak heights kinetics are changing. Namely, the part with the much smaller slope precedes the linear part observed at room temperature (Figs. 2b and 2c for $\Delta\Phi$ and 5b and 5c for Auger peaks). This change can be interpreted as due to silver alloying in the surface layer of the copper sample, in spite of the negligible mutual solubility of silver and copper, for the bulk samples. The higher is the sample temperature, the larger amount of silver can be incorporated into copper. The first part of the $\Delta\Phi$ kinetics with the large slope visible in Figs. 2b and 2c is probably related to the silver adsorption on surface defects. The silver diffusion towards the copper starts only when these defects are filled with silver. However, the results presented in Fig. 5 do not support this interpretation, because the Auger peak kinetics do not consist parts with the large slope for low coverages of silver. In Fig. 3 the silver monolayer adsorbed at room temperature is annealed at a temperature high enough to enable the silver diffusion. During this annealing the work function increases slower and slower. Probably, this increase is a result of

silver diffusion, but not evaporation. The work function decrease observed immediately after the start of heating, as is shown in Fig. 3, is probably related to the temperature dependence of the work function. The same dependence is a reason for the $\Delta\Phi$ enhancement after the temperature drop in Fig. 4 (point "d"). Figure 5 illustrates the silver thermal desorption, which seems to be a one-step process for a regular silver monolayer. The heating applied here is not sufficient for the complete silver removing. Probably remaining silver was adsorbed on the surface defects and dissolved in the sample surface layer.

5. Conclusions

1. The results obtained in the present work confirm the layer-by-layer mechanism of very thin silver layer growth at room temperature.

2. $\Delta\Phi$ kinetics at room temperature shows that the atomic structure of silver islands is unchanged during the first monolayer growth.

3. Results obtained for elevated temperatures can be interpreted as a result of the silver diffusion to the surface layer of the copper sample.

Acknowledgements

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