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Composition and Order–Disorder Transition in the Cu_3Au (001) Surface Layer Investigated with the Use of DAES and DEPES

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The composition of the first atomic layer of $Cu_3Au(001)$ crystal (about half-and-half copper and gold atoms) changes only slowly even at temperatures much higher than that of the order–disorder transition ($T_C = 663$ K). Theoretical and experimental works show a general trend of these changes but they differ in quantitative findings. In the present work we used directional elastic peak electron spectroscopy and directional Auger electron spectroscopy to investigate changes of atomic order and composition in the first atomic layers of the $Cu_3Au(001)$ crystal during the sample temperature increase. The height of central maximum in DEPES polar profile of the sample investigated was measured as a function of sample temperature. It was found that the measured dependence is linear, but the slope of this dependence changes abruptly around T_C. This change seems to be connected with disappearance of the atomic order in the first and second atomic layers. In DAES the height of the Auger peaks for copper and gold low energy transitions (MVV and NVV, respectively) were measured in the $\mathrm{d}N(E)/\mathrm{d}E$ mode as a function of the primary electron beam incidence angle. The composition of the first, second, and third atomic layers was determined by fitting the ratio of calculated DAES polar profiles for copper and gold to such a ratio for the measured profiles.

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1. Introduction

An ordered Cu_3Au crystal has fcc structure with Cu atoms in face-center positions. This order is stable up to $T_C = 663$ K. At this temperature the order–disorder transition takes place in bulk crystal. Above this temperature all sites are occupied by Cu or Au atoms with stoichiometric probability. Buck et al. [1] have found, using the low-energy ion scattering (LEIS), that the atomic bulk

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*corresponding author; e-mail: rok@ifd.uni.wroc.pl order known from earlier X-ray diffraction (XRD) measurements extends up to the (001) surface first layer having the composition $Au_{0.5}Cu_{0.5}$ and that the first layer composition remains almost unchanged above the order–disorder transition, up to 1000 K. The same has been found by Mróz [2] using low energy electron diffraction (LEED) and directional Auger electron spectroscopy (DAES). LEED and scanning tunneling spectroscopy (STM) were used by Niehus and Achete [3] to determine the structure and composition of the first atomic layer. They observed the c(2 × 2) LEED pattern expected for the ordered Au(0.5)Cu(0.5) first atomic layer. In STM patterns, only steps with the two-monolayer height have been found. On the other hand, Lin et al. [4] have found the two-monolayer steps and the one-monolayer steps as well. In addition, they presented arguments for the difference in the composition of atomic terraces separated by the one-monolayer step. Sundaram et al. [5] have found, using LEED, that disordering of the crystal surface starts well below the bulk crystal order–disorder transition temperature.

In the present work we used directional elastic peak electron spectroscopy (DEPES) and DAES in investigation of order–disorder transition in the surface layer and for determination of composition of the first, second, and third atomic layers. In the DEPES or DAES methods, proposed by Mróz and Nowicki [6], a signal (polar profile) of elastically scattered electrons or the Auger electrons, respectively, is measured as a function of the incidence angle of the primary electron beam (with the energy between several hundreds and about two thousands eV). Maxima in such a profile appear when the primary beam is parallel to one of close packed directions in the sample investigated. Thus, a polar DEPES or DAES profile contains information about the crystalline structure of the sample surface layer.

The height of the central maximum in DEPES polar profile for the $Cu_3Au(001)$ face was measured as a function of sample temperature. It was found that the slope of this dependence changes around T_C. This change can be connected with disappearance of the atomic order in the first and second atomic layers.

Concerning the composition of the first, second, and third atomic layers, we have elaborated an improved method of its determination with the use of DAES profiles.

2. Experimental details

The Cu_3Au (001) sample (René Koper Surface Preparation Laboratory, Zaandam, The Netherlands) was in the form of a disk 10 mm in diameter and 1 mm thick. According to the producer's information, the sample surface was prepared by polishing with diamond 6, 3 and 1 μm on a silk cloth followed by polishing with Al_2O_3 0.05 μm with chemical etching. The composition of the volume of this sample was measured with the use of electron probe microanalysis and the atomic relative concentration of gold was found to be equal to 0.24. The sample

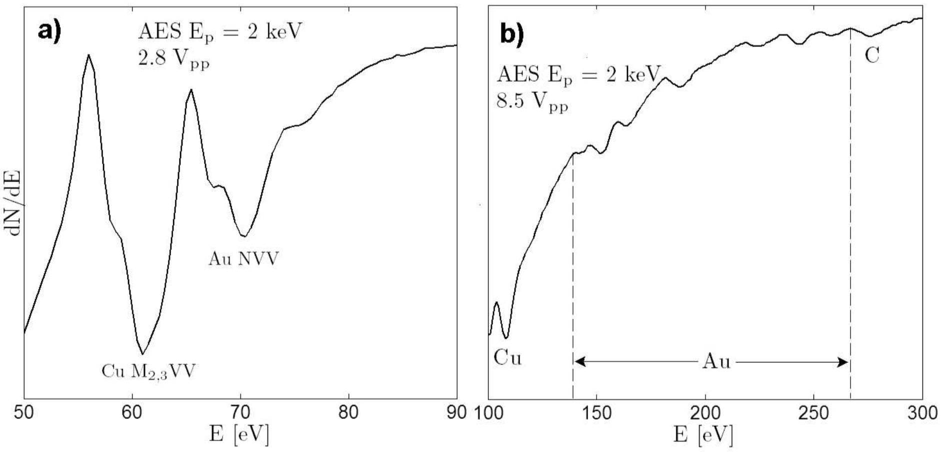

Fig. 1. AES spectra for a clean and ordered $Cu_3Au(001)$ sample. The primary electron energy $E_p = 2$ keV and the modulating peak-to-peak voltage equal to 2.8 V_{pp} (a) and 8.5 V_{pp} were used.

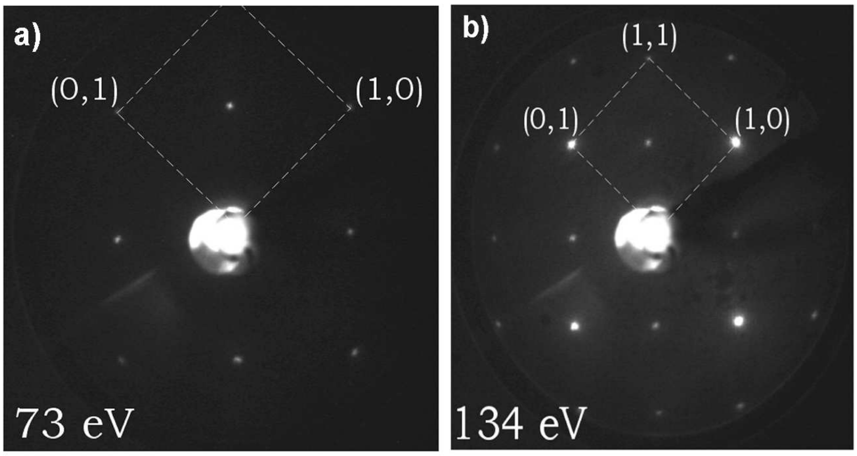

Fig. 2. LEED patterns of the ordered $Cu_3Au(001)$ surface for primary electron energy 73 eV (a) and 134 eV (b).

was mounted on a molybdenum holder. The holder was equipped with a shielded tungsten radiative heater and with a Pt–PtRh10 thermocouple fastened under a ring tightening the sample to the holder. The heater allowed the annealing of the sample above 1000 K. The holder was fastened to the rod of a manipulator enabling its independent rotations around the axis normal to the sample surface and around two mutually perpendicular axes lying at the sample surface. The manipulator was placed in the stainless-steel ultrahigh vacuum system (with the pressure below 10^{-7} Pa) pumped with a titanium ion pump and a titanium sublimation pump. A three-grid, reverse view retarding field analyzer (RFA) was used for LEED patterns observation and for Auger electron spectroscopy (AES), DAES and DEPES measurements. The sample surface was cleaned by argon ion bombardment with an ion energy of 600 eV followed by heating up to about 1000 K. After repeating this procedure many times, only well-pronounced signals of copper and gold and a very small signal of carbon were visible in the Auger spectrum (see Fig. 1) while the c(2×2) LEED pattern indicating the ordered surface (see Fig. 2) was observed.

3. DEPES polar profiles and the order–disorder transition

To record a DEPES polar profile, the proper azimuth (in our case, the $[0\bar{1}0]$–[010] one) was chosen with the use of the LEED pattern. Next, the sample was rotated, with the use of a proper motor, around the axis lying in the sample surface plane and perpendicular to the chosen azimuth. During this rotation, the signal from the output of a lock-in amplifier was measured in the $N(E)$ mode and recorded as a function of the incidence angle θ of the primary electron beam. An example of the obtained profile is presented in Fig. 3. Distinct maxima corresponding to the close packed directions [001] (I_0 for $\theta = 0°$) and [011] (I_{45} for $\theta = -45°$) are clearly visible in this figure. Next, the height of the I_0 maximum was measured as a function of the sample temperature T. The temperature changed linearly with time from 520 K to 773 K and back with the rate of 2 K/min. Results are shown in Fig. 4. The enlarged part of Fig. 4 corresponding to the temperature range 600 to 700 K is shown in Fig. 5. It is visible in these two figures that the dependence measured for the increasing temperatures can be well approximated by two smoothly connected linear parts: the first one (with the smaller slope) for

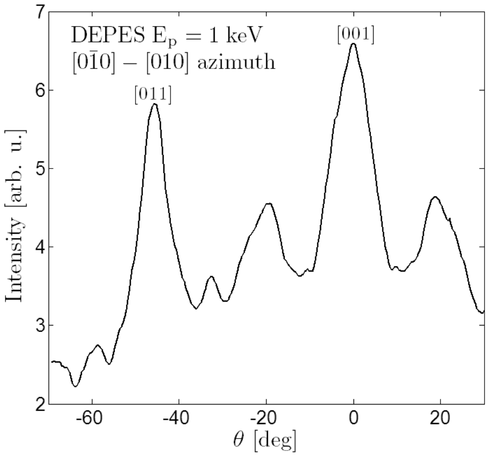

Fig. 3. DEPES polar profile for $[0\bar{1}0]$–[010] azimuth of $Cu_3Au(001)$ and for primary electron energy $E_p = 1$ keV. Maxima visible for incidence angles equal to 0° and −45° correspond to close packed directions [001] and [011], respectively.

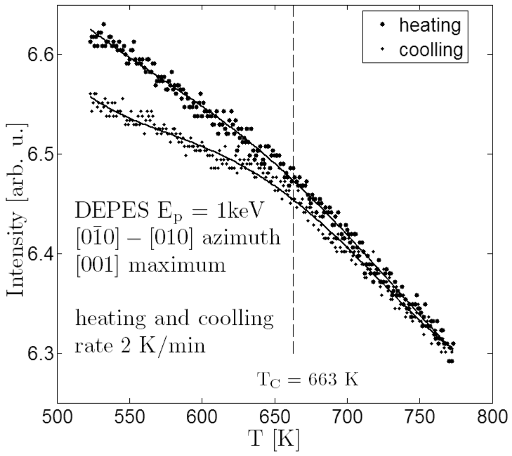

Fig. 4. The height of the I_0 maximum of DEPES polar profile of Fig. 3 as a function of the sample temperature T. Signal was recorded during increase (denoted as heating) and decrease (denoted as cooling) in the sample temperature. The temperature changed linearly with time with the rate of 2 K/min.

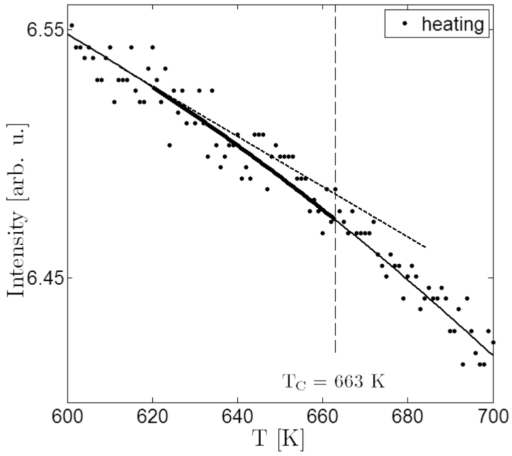

Fig. 5. The enlarged part of the dependence in Fig. 4 for the temperature range from 600 to 700 K, for the increasing temperature. Bold line indicates non-linear part of this dependence while the broken line is an extrapolation of the low temperature linear part (for details see text).

T ranging from 520 to about 620 K and the second one for T ranging from about 660 to 773 K.

4. AES and DAES in determination of surface layer composition

Quantitative analysis of the relative composition of the first three atomic layers with the use of DAES polar profiles was performed with the use of the modification of the method proposed and used for the first time in [7]. In this method, the Auger signals from the alloy investigated and from pure standards of this alloy components are measured, with the use of an RFA analyzer with a central electron gun, as a function of incidence angle θ of the primary electron beam. For the given incidence angle θ, the Auger signal $I_{\mathrm{Aa}}(\theta)$ generated by the component A of the alloy and reaching the RFA collector is given by the relation

$$I_{\mathrm{Aa}}(\theta) = k_{\mathrm{Aa}} n_{\mathrm{a}} C_{\mathrm{Aa}}(\theta), \tag{1}$$

where k_{Aa} is a coefficient characteristic of the given Auger transition in atoms A and of a backscattering factor of the alloy and this transition, n_{a} is the total atomic concentration in the alloy, while $C_{\mathrm{Aa}}(\theta)$ takes into account the relative atomic concentration of atoms A in the particular atomic layers of the alloy sample (Au1, Au2, Au3, and Aubulk for example), the geometry of the sample–analyzer system, and the inelastic scattering of the Auger electrons on their path to the sample surface (characterized by an inelastic mean free path λ). For details concerning $C_{\mathrm{Aa}}(\theta)$ see [7].

The ratio of the Auger signals for pure standards of copper and gold is given by the relation

$$I_{\mathrm{Cus}}(\theta)/I_{\mathrm{Aus}}(\theta) = (k_{\mathrm{Cus}}/k_{\mathrm{Aus}})(n_{\mathrm{Cus}}/n_{\mathrm{Aus}})$$
$$\times[C_{\mathrm{Cus}}(\theta)/C_{\mathrm{Aus}}(\theta)] \approx (k_{\mathrm{Cus}}/k_{\mathrm{Aus}})(n_{\mathrm{Cus}}/n_{\mathrm{Aus}}), \tag{2}$$

because $C_{\mathrm{Cus}}(\theta) \approx C_{\mathrm{Aus}}(\theta)$ for $M_{2,3}VV$ Auger transitions in Cu and Au (for energies 60 and 70 eV, respectively, where inelastic mean free paths are practically identical while relative atomic concentrations are equal to unity in both standards).

Knowing the ratio $I_{\mathrm{Cus}}(\theta)/I_{\mathrm{Aus}}(\theta)$ from measurements performed for pure standards (in our case, this ratio was taken from [2] where it was determined with the use of the same measuring system and under the same conditions) one can determine the ratio $k_{\mathrm{Cus}}/k_{\mathrm{Aus}}$ from relation (2):

$$k_{\mathrm{Cus}}/k_{\mathrm{Aus}} \approx [I_{\mathrm{Cus}}(\theta)/I_{\mathrm{Aus}}(\theta)](n_{\mathrm{Aus}}/n_{\mathrm{Cus}}). \tag{3}$$

The ratio $I_{\mathrm{Cus}}(\theta)/I_{\mathrm{Aus}}(\theta)$ can be obtained with the use of relations (1) and (3):

$$I_{\mathrm{Cua}}(\theta)/I_{\mathrm{Aua}}(\theta) = (k_{\mathrm{Cua}}/k_{\mathrm{Aua}})[C_{\mathrm{Cua}}(\theta)/C_{\mathrm{Aua}}(\theta)] \approx (k_{\mathrm{Cus}}/k_{\mathrm{Aus}})[C_{\mathrm{Cua}}(\theta)/$$
$$C_{\mathrm{Aua}}(\theta)] \approx [I_{\mathrm{Cus}}(\theta)/I_{\mathrm{Aus}}(\theta)](n_{\mathrm{Aus}}/n_{\mathrm{Cus}})[C_{\mathrm{Cua}}(\theta)/C_{\mathrm{Aus}}(\theta)]. \tag{4}$$

Finally, one can define ratios $R_{\mathrm{calc}}(\theta)$ and $R_{\mathrm{meas}}(\theta)$ for the CuAu alloy as the left- and right-hand sides of relation (4), respectively,

$$R_{\mathrm{calc}}(\mathrm{Au1}, \mathrm{Au2}, \mathrm{Au3}, \mathrm{Aubulk}, \theta) = C_{\mathrm{Cua}}(\theta)/C_{\mathrm{Aua}}(\theta), \tag{5}$$

$$R_{\mathrm{meas}}(\theta) = [I_{\mathrm{Cua}}(\theta)/I_{\mathrm{Aua}}(\theta)][I_{\mathrm{Aus}}(\theta)/I_{\mathrm{Cus}}(\theta)](n_{\mathrm{Cus}}/n_{\mathrm{Aus}}). \tag{6}$$

The ratio $R_{\mathrm{calc}}(\mathrm{Au1}, \mathrm{Au2}, \mathrm{Au3}, \mathrm{Aubulk}, \theta)$ can be calculated for all angles θ used in DAES measurements and for particular supposed compositions of the first, second, and third atomic layers and for the known composition of succeeding layers.

Values of this ratio obtained in such a way can be fitted simultaneously to the ratios $R_{\mathrm{meas}}(\theta)$ obtained from measurements for the incidence angles used. In this way, the relative atomic concentrations of gold, Au1, Au2, and Au3 for the first, second, and third atomic layers, respectively, can be determined.

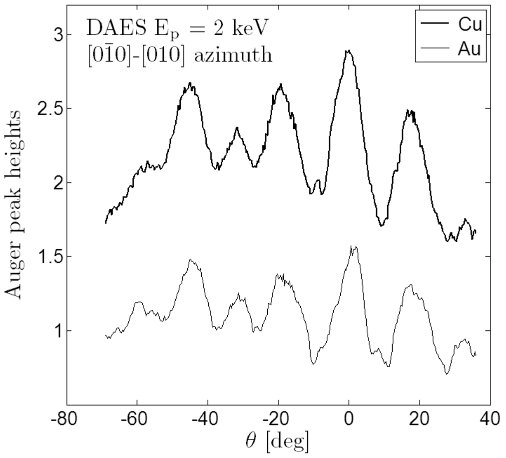

Fig. 6. DAES polar profiles for Cu $M_{2,3}VV$ and Au NVV Auger transitions from $Cu_3Au(001)$ and for primary electron energy $E_p = 2$ keV.

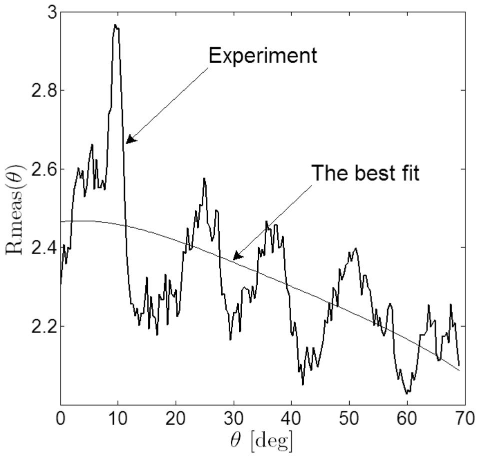

Fig. 7. Ratio R_{meas} of measured DAES profiles of Fig. 6 (denoted as Experiment) and the best fitted ratio R_{calc} calculated for the relative atomic concentrations of gold Au1 = 0.44, Au2 = 0.12, and Au3 = 0.24, in the first, second, and third layer, respectively.

To collect DAES polar profiles presented in Fig. 6, the Auger peak heights in the $\mathrm{d}N(E)/\mathrm{d}E$ spectrum for Cu and Au in the Cu_3Au sample were measured as a function of the primary beam incidence angle. Namely, the sample was rotated around the axis lying in the sample surface plane and during this rotation the lock-in amplifier signal for the peak minimum was recorded. In the next turn, a similar measurement was performed for the peak maximum. In this way, after subtraction of these two measured signals, the dependence of the Auger peak height on the primary beam incidence angle was achieved for one element. Next, measurements for the second element were repeated in the same manner.

DAES polar profiles for Cu and Au Auger transitions were measured for sample temperatures in the range from 573 to 673 K. As it is known from previous determinations, the concentration of gold atoms in the first two atomic layers at these temperatures seems to be constant. Due to this fact, profiles measured at different temperatures for each component were averaged. Resulting DAES polar profiles for Cu and Au are presented in Fig. 6.

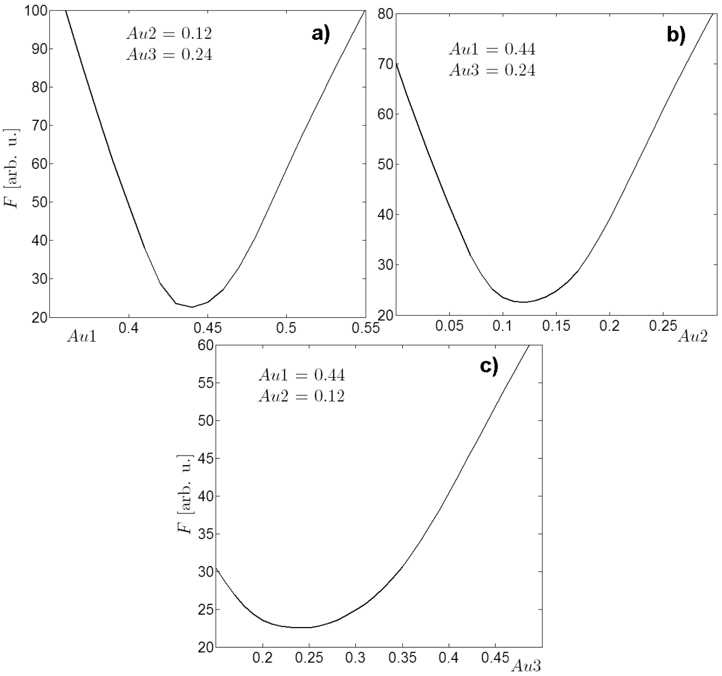

Fig. 8. Fitting factor F (for definition see text) calculated for different combinations of the relative atomic concentrations of gold Au1, Au2, and Au3. Minima of these dependences show the best fit for Au1 = 0.44 (a), Au2 = 0.12 (b) and Au3 = 0.24 (c).

In the next step, a ratio of these two profiles was calculated and, after division by the $k_{\mathrm{Cus}}/k_{\mathrm{Aus}}$ value calculated in [2] and equal to 0.851, $R_{\mathrm{meas}}(\theta)$ ratio was obtained (see Fig. 7). Ratios $R_{\mathrm{calc}}(\mathrm{Au1}, \mathrm{Au2}, \mathrm{Au3}, \mathrm{Aubulk}, \theta)$ were calculated for models of amorphous samples containing 10 layers. In these models, the concentration of gold was changed only in the first three layers and all combinations of Au1 and Au3 from the range 0.15 to 0.6 and Au2 from 0 to 0.35 were used. Succeeding layers (Aubulk) had composition expected in the ordered crystal.

Values of calculated ratios $R_{\text{calc}}(\text{Au1}, \text{Au2}, \text{Au3}, \text{Aubulk}, \theta)$ were fitted to $R_{\text{meas}}(\theta)$ relation by calculation of the sum of absolute values from the difference between experimental and theoretical values for each incidence angle θ:

$$F = \sum \left| R_{\text{calc}}(\text{Au1}, \text{Au2}, \text{Au3}, \text{Aubulk}, \theta) - R_{\text{meas}}(\theta) \right| . \tag{7}$$

The best fit was found for relative atomic concentrations Au1 = 0.44, Au2 = 0.12, Au3 = 0.24 for the minimum value of the fitting factor F as it is seen in Fig. 8. It is also visible in this figure that the method is most sensitive for the first atomic layer but sensitivity for the third layer is still quite good.

5. Discussion

The relative concentration of gold atoms in the first layer Au1, equal to 0.52, was found in the experimental study by Buck et al. [1], for temperature 300 K. This value was almost independent of the increase in sample temperature and just below T_{C} slightly changed to 0.53. On the other hand, the Au1 was measured in the same temperature range [2] and a decrease from 0.49 to 0.46 was found during sample temperature increase from 400 K to T_{C}. In the present work, the Au1 was found to be equal to 0.44. It should be pointed out that this value was obtained from Cu and Au DAES profiles which were averaged from the profiles measured in the sample temperature range from 573 to 673 K. This low value of Au1 could not be explained by copper segregation to the sample surface induced by strong interaction between copper and sulfur atoms because the AES spectra recorded during measurements indicate no sulfur content in the surface layer.

Our result for the Au2 value equal to 0.12 is situated between determinations in papers [1] and [2]. It was found in [1] that the concentration Au2 increases from 0 to 0.03 as the sample temperature changes from 300 K to T_{C}. Similar increase was found in paper [2], but higher values of Au2 equal to 0.14 in 400 K and 0.16 just below T_{C} were observed.

Our present results concerning Au1 and Au2 are supported by STM results presented in [4] mentioned in Sect. 1. Namely, one of two kinds of terraces found in [4] can be enriched with copper, which leads to the measured averaged concentration Au1 lower than 0.5. On the other hand, fragments of the second layer covered with terraces enriched with copper can contain some number of gold atoms.

The gold concentration in the third atomic layer Au3 was found in paper [2] to be equal to 0.5 below the transition temperature T_{C}. Our finding of Au3 value equal to 0.24 can be reasonably explained if we take into account that the transition temperature was crossed several times during measurements. The equilibrium concentration and structure were destroyed in the sample bulk where the time required to restore such an equilibrium just below T_{C} is in the range of 10^6 s. However, the equilibrium in the surface layer can be achieved much faster and a hysteresis is not observed in the measurements performed with the time constant of the order of 10 s [8].

It is visible in Fig. 7 that the dispersion of points in the ratio of DAES polar profiles measured for Cu and Au is rather large. However, the number of points placed below and the above calculated ratio R_{calc} fitted to the points are approximately equal. In addition, the calculated values of the fitting factor F presented in Fig. 8 indicate deep minima (especially for Au1), which indicates that the used method is reasonable.

The temperature dependence of the long range order at the $Cu_3Au(001)$ surface was investigated in [5] by LEED. It was found that the long range order parameter is a continuous function of sample temperature, and the disordering process starts 60 K below T_C. In the present work the height of the I_0 maximum was measured as a function of the sample temperature. As it is described in the previous section, this dependence can be divided into two linear parts (the first one from 520 to 620 K and the second one from 660 to 773 K) connected with the region in which the measured height decrease is non-linear. Presence of this region in the temperature range similar to that reported in [5] indicates that the non--linear part contains information about the order–disorder transition in the surface layer of the sample investigated. However, interpretation of this information will be possible when similar measurements are performed for other primary electron energies and compared with calculations of DEPES profiles made for samples in particular stages of order in the single scattering cluster (SSC) approximation.

Acknowledgments

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