Journal of Alloys and Compounds 484 (2009) 123–129

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Directional elastic peak electron spectroscopy in the investigation of order–disorder transition in the $Cu_3Au(0\,0\,1)$ surface layer: Measurements and SSC calculations

Ł. Rok, S. Mróz*

Institute of Experimental Physics, University of Wrocław, pl. Maxa Borna 9, PL 50-204 Wrocław, Poland

ARTICLE INFO

Article history:
Received 23 February 2009
Received in revised form 19 April 2009
Accepted 20 April 2009
Available online 3 May 2009

PACS:
61.05.J
68.69.Jk
68.35.Rh

Keywords:
Electron diffraction
Surface structure
Binary alloys
Cu_3Au
Low index single crystal surfaces

ABSTRACT

We present the results of directional elastic peak electron spectroscopy (DEPES) application to investigating the order–disorder transition in the surface layer of the $Cu_3Au(0\,0\,1)$ crystal. We measured the DEPES polar profiles for a few sample temperatures ranging from 300 to 1000 K and for a few electron energies ranging from 1000 to 2000 eV. The obtained results were compared with those calculated in the single scattering cluster (SSC) approximation for $Cu_3Au(0\,0\,1)$ clusters characterized by different inelastic mean free paths of electrons, effective Debye temperatures and surface layer atomic structure (including ordering and rippling of gold atoms). Measured and calculated DEPES profiles were found to be sensitive to the order–disorder transition. Reasonable agreement between measurements and calculations was obtained for the effective Debye temperature equal to (220 ± 6) and (172 ± 4) K for $T < T_C$ and $T > T_C$, respectively, and for the rippling of Au atoms in the first atomic layer decreasing during the order–disorder transition from 0.12 to 0.09 Å.

1. Introduction

The directional elastic peak electron spectroscopy (DEPES) was proposed [1] as method for investigating the surface layer atomic structure. In DEPES, the elastically scattered electron signal is measured with the use of a large acceptance angle spectrometer as a function of the primary electron beam incidence angle for electron energies of 600–2000 eV. For crystalline samples, pronounced maxima of this signal appear when the incidence beam is parallel to one of close-packed atomic rows. Having collected the close-packed directions, one can determine the symmetry elements of the crystalline structure in the surface layer. The layer thickness is limited by mechanisms involved in the creation of the maxima mentioned above and does not exceed a few monolayers. Namely, the primary beam directed parallel to a close-packed row of atoms is forward focused [2] on the core of the second or third atom of this row. This focusing increases the probability of the elastic backscattering of primary electrons and leads to the formation of the measured signal maximum. Electrons passing through the first two or three atoms without backscattering are defocused on their further path and the probability of their backscattering on the next atomic cores is much smaller. Besides, the probability of the inelastic scattering of such electrons increases with the elongation of their path in the sample. This simple model was used for qualitative interpretation of the DEPES results for low index copper and nickel faces, both clean and covered with several monolayers of silver [3–6], gold [7], cobalt and lead [8,9], and cobalt on gold [10], including the determination of epitaxial relationship between the substrate and the deposited layer.

To obtain more information from the DEPES results, a single scattering cluster (SSC) approximation [11] was used in a number of papers (for example [12–18]) for the calculation of the DEPES profiles of epitaxially grown layers and, by fitting the calculated profiles to the measured ones, for the determination of crystalline structures and epitaxial relations with the substrate (including the population of particular domains). All those calculations were performed for crystalline samples composed of one sort of atoms and with the use of the R-factor. Recently, polar DEPES profiles were calculated for the ordered $Cu_3Au(0\,0\,1)$, $Cu(0\,0\,1)$, and $Au(0\,0\,1)$ crystals [19] and for the $Si(111)$ crystal both clean and covered with an ordered Ag monolayer [20].

* Corresponding author. Tel.: +48 71 375 94 01; fax: +48 71 328 73 65.
E-mail address: mroz@ifd.uni.wroc.pl (S. Mróz).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.04.102

It is well known that, in the perfectly ordered Cu_3Au crystal, Au and Cu atoms are placed in corners and in the face-centred positions of a face-centred cubic unit cell, respectively. This structure is stable up to the critical temperature $T_C = 663$ K at which the order–disorder transition takes place in the crystal bulk [21]. Above this temperature, gold and copper atoms are distributed randomly in all lattice sites with the stoichiometric probability. It is well established that this transition is of the first-order type.

Changes in the long-range order (LRO) parameter for the surface of the (0 0 1)-terminated Cu_3Au crystal were first investigated by Sundaram et al. [22]. Their observations were made with the use of low-energy electron diffraction (LEED) and showed that the surface LRO parameter decreases continuously with increasing temperature. Disordering starts and ends at temperatures equal to $0.9T_C$ and T_C, respectively. LEED measurement performed by McRae and Malic [23] showed that this process starts already at $T = 0.6T_C$ but ends also at the transition temperature. On the other hand, Jamison et al. [24] used the spin polarised LEED technique for the same purpose and found that the disordering process is not finished at $T = T_C$ but is still in progress well above the critical temperature T_C.

The investigations of the Cu_3Au(0 0 1) crystal surface composition performed by low-energy ion scattering (LEIS) showed that the crystal is terminated by an atomic layer containing equal amounts of gold and copper atoms [25]. All theoretical [26–30] and experimental [25,31–34] papers devoted to changes in the (0 0 1) surface layer composition with increasing sample temperature showed that it changes in a continuous manner during this increase and the stoichiometric composition is not achieved even at temperatures as high as 1000 K.

It is also well known that the (0 0 1) surface of the Cu_3Au crystal shows atomic rippling. Houssiau and Bertrand [35], with the use of the time of flight ion scattering (TOF-IS), concluded that gold atoms in the first atomic layer of the Cu_3Au(0 0 1) crystal are placed 0.12 Å above copper atoms in this layer. In another experimental study, Wang et al. [36] measured *I–V* LEED profiles for 0.5 monolayer of gold deposited on the (0 0 1) surface of the Cu crystal. As was shown in their study, the deposited gold atoms formed with the substrate copper atoms a single, ordered Au–Cu layer. They found that gold atoms in this structure are located 0.1 Å outwards from copper atoms. The latest scanning tunneling microscopy (STM) measurements performed for the Cu_3Au(0 0 1) surface by Dias et al. [37] indicated the rippling value of gold atoms equal to 0.122 Å. The rippling effect in the Cu_3Au(0 0 1) surface was also investigated in theoretical studies. Hayoun et al. [29] used the Monte Carlo method for two *n*-body phenomenological potentials. Their results indicated that gold atoms are placed 0.01 or 0.14 Å above copper atoms, depending on the potential used. However, it should be pointed out that only the potential leading to the rippling value of 0.14 Å gives the realistic composition of the first atomic layer. Lekka et al. [38] found, with the use of molecular dynamic calculations, that gold atoms are shifted above copper atoms by 0.25 Å and that the rippling effect in Cu_3Au(0 0 1) occurs only in the first layer.

In the present paper, polar DEPES profiles are measured and also calculated for the Cu_3Au(0 0 1) sample with the use of the SSC approximation. This crystal was chosen because it is a model for the study of the order–disorder transition in binary metallic alloys. The purpose of this work was to recognize DEPES sensitivity to changes of parameters characterizing the Cu_3Au(0 0 1) surface. We expect that this recognition will open a new application of the DEPES in investigating the composition of complex sample surface layers or structural transitions induced by temperature changes. It is worth the attention, that maxima of intensity in DEPES polar profiles are clearly visible even in temperatures as high as 1000 K, what makes this technique useful in the case of high-temperature structural transitions observed, e.g., in Ni_3Al or Fe_3Al.

2. Experiment

The measurements of polar DEPES profiles and dependencies of DEPES signals at particular incidence angles on the sample temperature were performed in the N(E) mode in an ultra-high vacuum system (titanium ion pump and titanium sublimation pump, $p \approx 3 \times 10^{-8}$ Pa) equipped with an RFA analyzer for LEED observation and AES and DEPES measurements, an argon ion gun for cleaning the sample surface, a sample manipulator enabling independent sample rotations around three mutually perpendicular axes and linear motions along *x*, *y*, and *z* directions, and a resistive heater of the sample controlled by an electronic system with the use of a Pt–PtRh10 thermocouple and enabling the sample heating from RT to about 1000 K with a controlled speed equal, e.g., to 0.5 K/s.

The Cu_3Au(0 0 1) sample was provided by René Koper Surface Preparation Laboratory, the Netherlands. The sample surface was prepared by polishing it with the 6, 3, and 1 μm diamonds and by chemical etching with 0.05 μm Al_2O_3.

The sample surface was cleaned in UHV conditions by argon ion bombardment with an ion energy of 600 eV, followed by heating up to about 1000 K. After this procedure was repeated many times, only well-pronounced signals of copper and gold and a very small signal of carbon were visible in the Auger spectrum while the c (2 × 2) LEED pattern indicating the ordered surface was observed.

3. Theory

We use single scattering cluster (SSC) approximation, where the wave field $\Psi(\boldsymbol{k}, \boldsymbol{r})$ generated at the point $\boldsymbol{r}$ in the cluster by the plane wave $e^{i\boldsymbol{kr}}$ diffracted on atoms forming the cluster was calculated from the formula:

$$\Psi(\boldsymbol{k}, \boldsymbol{r}) = e^{i\boldsymbol{kr}} \left[e^{-r_z/\Lambda \cos\theta} + \sum_j e^{i\boldsymbol{kd}_j} e^{-r_{zj}/\Lambda \cos\theta} e^{-d_j/\Lambda} f_j(\boldsymbol{k}, \boldsymbol{d}_j, T) \frac{e^{ikd_j}}{kd_j} \right], \quad (1)$$

where r_z is the component of the vector $\boldsymbol{r}$ normal to the sample surface, θ is the primary beam incidence angle (measured with respect to the surface normal), Λ is the inelastic mean free path for the electrons used, $\boldsymbol{d}_j$ is the vector connecting the position of the *j*-th atom with the point determined by the vector $\boldsymbol{r}$, r_{zj} is the distance from the *j*-th atom to the surface, and f_j is the complex form factor for the electron scattering on the *j*-th atom. In the point-scattering approximation, the form factor can be expressed as:

$$f_j(\boldsymbol{k}, \boldsymbol{d}_j, T) = \sum_{l=0}^{\infty} t_l^j(T) c_l(kd_j)(2l+1) P_l(\cos\theta_{kd_j}), \quad (2)$$

where t_l^j is the temperature-dependent scattering *t*-matrix that describes the scattering amplitude and the vibrational properties of the *j*-th atom [39], c_l is the dimensionless polynomial factor that multiplies the asymptotic form of spherical Hankel functions, P_l is the *l*-th Legendre polynomial and θ_{kd_j} is the scattering angle between the vectors $\boldsymbol{k}$ and $\boldsymbol{d}_j$.

To calculate, in arbitrary units, the DEPES signal reaching the analyzer collector $I(\boldsymbol{k})$, the squares of the wave functions $\Psi(\boldsymbol{k}, \boldsymbol{r}_s)$ are multiplied by the corresponding escape probability $A(r_{zs}/\Lambda)$ given by the relation:

$$A(r_{zs}, \Lambda) = \int_\Omega \exp\left(\frac{r_{zs}}{\Lambda \cos\theta'}\right) d\Omega, \quad (3)$$

where θ' is the angle between the direction of the emitted electron trajectory and the normal to the sample surface while the integration includes the solid angle Ω subtended by the analyzer entrance which, in an RFA analyzer with an axial electron gun, depends on the primary beam incidence angle. Now the signal $I(\boldsymbol{k})$ is calculated by the summation over all nonequivalent atomic sites

$$I(k) = \sum_s |\psi(k, r_s|^2 A(r_{2s}, A) \quad (4)$$

Calculations including changes in the atomic structure of the Cu_3Au(0 0 1) crystal were performed for a cluster in different stages of order. First of all, a cluster representing an ordered crystal was built. This cluster had the lattice constant a = 3.7476 Å [40], and