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A combined LEED and DFT surface structure determination of $Cu_3Au(001)$: Evidence of a surface stacking fault

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ABSTRACT

In this work, we have investigated the surface structure of $Cu_3Au(001)$ using low energy electron diffraction analysis and *ab initio* calculations by density functional theory. Our results indicate a different structure from that usually reported in the literature, where we have observed a stacking fault between the first and third layers of the surface. The rippling effect and the interlayer distances belonging to the first six layers of the surface were calculated and compared with other works too. Specifically, a rippling with gold atoms moving towards the vacuum in the first layer of 0.09 Å was observed and of 0.02 Å in the third layer. A small expansion of the first interlayer distance of 1.3% and a contraction of 0.8% at the second also were observed. Finally, *ab initio* calculations performed in this work are in good agreement with the experimental results.

1. Introduction

Surface structure characterization of binary alloys is very important in materials science. Phenomena such as surface reconstructions, stacking faults, segregation and defects can drastically change the electronic and thermodynamic properties of the surface.

In this context, Cu–Au alloys are extensively employed in studies on surface science because of many reasons: copper and gold are known to be stable towards surface reconstructions and a well-defined surface is relatively easy to be prepared. Its lattice parameter ranging from 3.61 Å (Cu) to 4.08 Å (Au) favors epitaxial ultrathin films growth, where especially the Cu_3Au has been widely used as template for growth of magnetic ultra-thin films as Fe [1–4], Mn [5–7], FeMn [8], NiMn [9] and CoNi [10].

The Cu_3Au has a $L1_2$ phase when below its critical bulk ordering temperature ($T_C = 663\ K$) [11]. Its (001) surface has been studied for a long time, mainly, in order to investigate its structure around T_C [11–21]. Below this temperature, the majority of experimental surface structure studies concentrated only on the first layer and, together with theoretical studies, they indicate a Cu–Au termination [21–27]. They also reveal a rumple between the copper and gold atoms in the first layer [21–23,25–30]. However, these studies, mostly theoretical, do not show a consensus on the magnitude of the rumple, ranging from 2% [25] to 13% [28] related to bulk interlayer distance. Moreover, by overlooking deeper layers and not exploring different models, these studies could not solve completely the alloy's surface structure, and phenomena such as stacking faults and relaxation could not be fully determined.

In the present work, we perform a combined low energy electron diffraction (LEED) and first-principle calculation structural determination of the of $Cu_3Au(001)$ surface. By comparing different models compatible with the surface symmetry observed in the LEED patterns and by allowing atomic relaxations down to six monolayers we have found an unusual behavior for this surface. Our results suggest a stacking fault between the first and third layers and a small gold enrichment of the surface. Finally, confirming these results, DFT calculations showed a good agreement between experiment and theory.

2. Experimental details

The experiments were performed in an ultra-high vacuum (UHV) chamber equipped with X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), with base pressure better than 1.4×10^{-10} mbar. In order to address the influence of the annealing temperature and the sample history on the surface structure, two experiments using different

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$Cu_3Au(001)$ single crystals were done. In the first experiment, an old crystal, which had been used in several studies, was cleaned by cycles of sputtering with Ar^+ ions between 1.0 keV and 1.5 keV for 30 min and annealing at 923 K ($T > T_C$) for 20 min. In the second experiment, a brand new crystal provided by Surface Preparation Laboratory [31], was cleaned by cycles of sputtering with Ar^+ ions between 1.0 keV and 1.5 keV for 30 min and annealing at 595 K ($T < T_C$) for 20 min. The preparation procedure was repeated until no traces of surface contamination could be observed by AES and a well-ordered surface was obtained as confirmed by high quality LEED patterns (Fig. 1).

In both experiments, the LEED patterns at 150 K were digitized as a function of the incident beam energy using a high-sensitivity CCD camera and an automated data acquisition system. In the first experiment (Exp1), the diffracted intensity as a function of electron energy (LEED-IV curve) was then collected for all available beams at nominal normal incidence in the energy range of 40–500 eV. Then, the experimental LEED-IV curves were normalized by the incident electron current and smoothed using a 3-point least-squares cubic polynomial algorithm. Finally, the symmetry-equivalent beams were averaged reducing the number of diffracted beams from 36 to 8 inequivalent beams [(1,0); (1,1); (2,0); (2,1); (2,2); (3,0); (3,1); (4,0)]. The total energy range defined by the inequivalent beams in the first data set was $\Delta E_1 = 2660$ eV.

For the second experiment (Exp2), the same procedure was used and the LEED-IV curves were extracted in the energy range of 25–520 eV. After the averaging procedure, the number of diffracted beams decreased from 46 to 9 symmetrically distinct beams [(1,0); (1,1); (2,0); (2,1); (2,2); (3,0); (3,1); (3,2); (4,0)] defining a total energy range of $\Delta E_2 = 2830$ eV.

3. LEED theoretical aspects

In order to evaluate the theoretical LEED-IV curves, the muffin-tin model was adopted and the muffin-tin potential together with the phase shifts ($l_{max} = 8$) were calculated using the Barbieri/Van Hove package [32]. The full LEED dynamic calculations were performed using the Symmetrized Automated Tensor LEED (SATLEED) computer code [32].

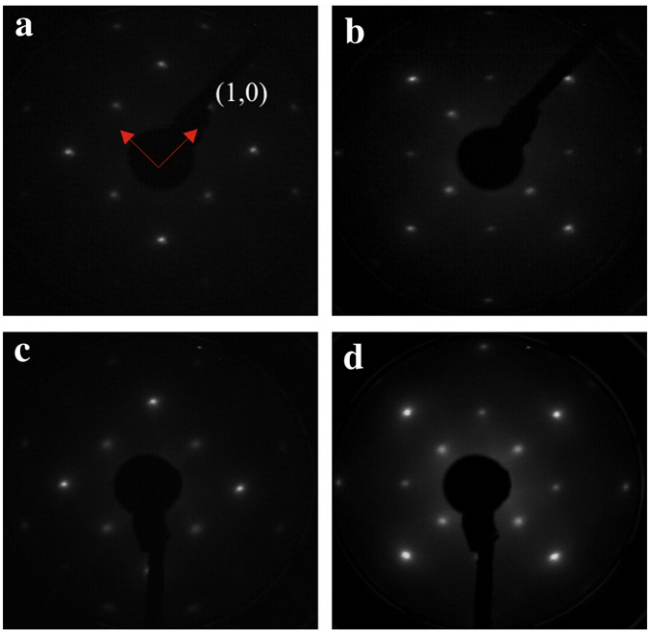

Fig. 1. Figures a) and b) show the LEED patterns at 137 eV and 187 eV respectively for the first data set, while figures c) and d) show the LEED pattern at the same energies, but for the second data set.

The surface temperature was set to 150 K and the gold (Θ_{Au}) and copper (Θ_{Cu}) Debye temperatures were assumed to be 100 K and 240 K, respectively. The imaginary part of the optical potential was kept fixed at $V_{0i} = -7.0$ eV, while the real component was optimized during structural relaxation.

Several different structural models with 6 surface layers were tested, all of them compatible with a p4mm symmetry of the LEED patterns showed in Fig. 1. The main trial models were: unfaulted copper–gold atoms in the first layer at substitutional sites (model A); copper–gold atoms at substitutional sites in the first layer but having a staking fault with respect to third one (model B); a single layer of copper atoms on the topmost surface plane (model C); a pure layer of copper atoms on the topmost surface plane with a stacking fault between the second and fourth layers (model D); half monolayer of gold atoms on the first layer at hollow sites (model E), half monolayer of gold atoms on top sites (model F) and a pure layer of gold atoms on the topmost surface plane (model G).

The theoretical and experimental LEED-IV curves were compared and the agreement between both curves was quantified by the Pendry R-Factor [33], with variance of $varR/\overline{R} = \sqrt{8V_{0i}/\Delta E}$.

Initially, an optimization of the structural parameters was performed for each model, in order to determine which model best fits our experimental data. Afterwards, the Debye temperatures of gold and copper atoms on the surface were optimized for the most promising structural model, as a first attempt to improve the R-factor value. On suite, the gold concentration in the first three layers was varied using the Average t-matrix Approximation (ATA) method [34]. Finally, after the optimization of these non-structural parameters, a new structural optimization was carried out as a final refinement of the best structural model according to our experimental data.

4. DFT methodology

Two types of first-principles calculations using density-functional theory (DFT) were performed: surface energy and stacking fault energy calculations, with slightly different methodological parameters. Surface energy calculations were performed using the Quantum ESPRESSO package [35] and employing ultrasoft pseudopotentials [36] and the Perdew–Burke–Ernzerhof (PBE) [37] exchange-correlation functional. The maximum kinetic energy used for the plane-wave basis was 45 Ry. We used periodic boundary conditions in a symmetric slab geometry with 9 atomic layers and a 16.6 Å vacuum layer. Brillouin zone sampling using a $(7 \times 7 \times 1)$ Monkhorst–Pack [38] scheme was employed. Our supercells have $\sqrt{2} \times \sqrt{2}$ in the lateral directions, with 4 atoms per layer, which allow us to vary the atomic composition in each plane in 25% steps. We calculated 25 different structures by varying the composition of the two outermost layers. Atomic positions were fully relaxed until the forces were smaller than 0.001 Ry/au.

Due to the small values of stacking-fault energies (in the tens of meV range), for such calculations a refined set of parameters was used and other tests were done. Convergence with respect to the number of layers was investigated by performing calculations from 5 to 17 layer slabs. A larger cutoff energy of 100 Ry and a finer Monkhorst–Pack [38] grid $(16 \times 16 \times 1)$ were used. Besides calculations using Quantum ESPRESSO, we also performed additional calculations using the SIESTA code [39]. For SIESTA calculations, we used norm-conserving Troullier–Martins [40] pseudopotentials, a mesh cutoff of 300 Ry to define the real space grid, a double-zeta basis set augmented by polarization orbitals and a Monkhorst–Pack sampling of $(16 \times 16 \times 8)$. Also, the lattice parameters and the atomic positions were fully relaxed until a 0.01 eV/Å force accuracy.

In order to compare the surface energy of systems with different stoichiometries and then to address the segregation of Au atoms to the surface, we used the formalism described by Moreira et al. [41]