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Full Length Article

# Structure and energetics of ultrathin Cu adlayers on Ru($1\,0\,\bar{1}\,0$)

J. Brona*, I. Morawski, M. Nowicki, R. Kucharczyk

*Institute of Experimental Physics, University of Wrocław, plac Maksa Borna 9, 50–204 Wrocław, Poland*

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ABSTRACT

Adsorption of ultrathin epitaxial layers of Cu on Ru($1\,0\,\bar{1}\,0$) was investigated by ab initio density functional theory (DFT) simulations combined with directional elastic peak electron spectroscopy (DEPES) measurements. In the low-coverage regime, energetics of the adsorption process indicates that the deposited Cu atoms form instantly a bilayer (BL) and leave some substrate uncovered rather than wet the substrate with a single monolayer. The bilayer-by-bilayer growth is energetically favorable up to 3 BLs, but the third BL already occurs thermodynamically metastable. The DFT-predicted optimal arrangement of Cu adatoms in substrate-lattice-continuation sites was validated by DEPES measurements. This confirms the formation of a stable ultrathin film of hcp-like copper on the Ru($1\,0\,\bar{1}\,0$) substrate.

## 1. Introduction

Despite numerous investigations, the knowledge of epitaxy of fcc metals on hcp metals remains incomplete. In the case of copper adsorption on ruthenium substrates, research has been predominantly focused on the close-packed Ru(0 0 0 1) surface. Scanning tunneling microscopy (STM) measurements revealed that the first Cu monolayer (ML) is pseudomorphic [1,2]. At the coverage of 2 MLs, a striped dislocation pattern was observed, indicating uniaxial contraction of the Cu adlayer. At 3 MLs, a characteristic isotropic pattern of corrugation lines in a triangular arrangement was recognized. At 4 MLs and higher coverage, a large-scale incommensurate lateral superlattice or Moiré pattern was observed, and the Cu overlayer relaxed almost fully to the Cu(1 1 1) lateral spacing in the bulk fcc crystal. Theoretical considerations applying the 2D Frenkel–Kontorova model [3] or the phase-field crystal method [4] yielded the same structures. Low-energy alkali ion scattering [5], high-resolution low-energy electron diffraction [6], X-ray photoelectron diffraction [7,8], STM [9,10], X-ray photoemission spectroscopy [11], scanning tunneling spectroscopy [12], low-energy electron microscopy [13], density functional theory (DFT) [12,14], and $H_2$ diffraction [15] investigations shed more light on the previously recognized Cu overlayer structures. Additionally, two metastable relaxation structures corresponding to a nonrotated and slightly strained Cu film were observed below 450 K and for Cu films thicker than 4 MLs [16]. It was also found that, at elevated temperatures and the coverage higher than 2 MLs, de-wetting of Cu films occurs through the migration of 3D mesa islands across step edges in the ‘downhill’ direction on a (2 ML)-thick wetting layer, whereas no 3D islands exist in the flat substrate regions [17].

Research on the more open ($1\,0\,\bar{1}\,0$) surface of Ru is much more limited. STM, low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES) measurements revealed that the first two Cu bilayers (BLs) grow in registry with the substrate in the bilayer-by-bilayer fashion [18]. When the nominal coverage is higher than 2 BLs, Cu deposited at 800 K forms flat mesa islands with Cu(1 1 1) facets on top. These facets are formed parallel to the terraces of the substrate with the Cu[$0\,1\,\bar{1}$]||Ru[$1\,\bar{2}\,1\,0$] orientation. Mesas lie on a pseudomorphic Cu wetting layer of the thickness of 2 BLs. Directional elastic peak electron spectroscopy (DEPES) experiment showed that Cu(1 1 1) islands formed at the nominal adsorbate coverage of 7 BLs consist of two domains mutually rotated by 180° [19]. If the substrate is precovered with oxygen, a stripe-like (1 × 5) structure arises [20]. The observed stripes are parallel to the [$1\,\bar{2}\,1\,0$] direction, while their width is equal to five times the distance between adjacent Ru($1\,0\,\bar{1}\,0$) substrate atoms along the [0 0 0 1] direction.

In the present paper, the structural and energetic properties of the first two Cu BLs grown on the Ru($1\,0\,\bar{1}\,0$) surface are investigated by ab initio DFT simulations combined with DEPES experiments, with the aim to determine and characterize the optimal configurations of Cu adatoms with respect to the underlying substrate. The Cu/Ru($1\,0\,\bar{1}\,0$) system is relevant for offering the opportunity of growing a stable film of hcp copper, which is interesting from the point of view of basic surface-science research. Indeed, the hcp phase of a native fcc metal might exhibit different properties as compared to its fcc counterpart. A striking example is provided by hcp-like Pb films deposited on the Ru ($1\,0\,\bar{1}\,0$) surface, where the fcc-to-hcp structural modification of Pb is

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* Corresponding author.
*E-mail address:* jacek.brona@ifd.uni.wroc.pl (J. Brona).

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accompanied by quenching its reactivity towards oxygen [21,22].

The detailed knowledge of Cu adsorption on Ru(1 0 $\bar{1}$ 0) can also be useful in microelectronics. Indeed, research continues on the optimal method of Cu deposition onto Ru in the damascene process, important for fabrication of microelectronic devices. Direct plating of Cu on Ru was found to be the most promising method [23], and consequently, several papers concerning this topic were recently published (see, e.g., Refs. [24–28]). Adhesion of copper to the Ru substrate and the stability of the resulting adsorbate structure play a crucial role here. Ru layers are usually polycrystalline and consist of various facets [29–33], including the (1 0 $\bar{1}$ 0) one, which makes it desirable to characterize Cu adsorption on Ru(1 0 $\bar{1}$ 0) in more detail.

Furthermore, the Cu/Ru(1 0 $\bar{1}$ 0) adsorption system might be of interest to catalysis. It is well known that the properties of a catalyst could critically depend on its crystalline structure. For example, recent studies of CO dissociation on Ru(0 0 0 1) and Ru(1 1 $\bar{2}$ 1) revealed that the direct dissociation is preferred on the sixfold site of the (1 1 $\bar{2}$ 1) face, while the H-assisted dissociation is favored on the B5 site of the stepped (0 0 0 1) face [34]. The characteristics of a catalyst could also vary upon deposition of other chemical elements. For instance, adsorption of Cu on Ru(0 0 0 1) enhances selectivity towards $O_2$ and $H_2$ dissociation [35]. Other recent examples of the ongoing research on Ru-based catalysts include methanol reactions on Ru(0 0 0 1) and Cu/Ru(0 0 0 1) [36], methanol [37] and ethanol [38] reactions on Ru(0 0 0 1), decomposition of ethanol on Ru(0 0 0 1) [39], Fischer–Tropsch synthesis on Ru(0 0 0 1) surface and Ru clusters [40], CO oxidation on Ru(0 0 0 1) [41], CO dissociation on Ru(0154) [42] and Ru nanoparticles [43], or oxidation of p-cymene on Ru nanoparticles consisting of (0 0 0 1), (1 0 $\bar{1}$ 0), and (1 0 $\bar{1}$ 1) facets [44]. This indicates that the Cu/Ru(1 0 $\bar{1}$ 0) system could be relevant as a novel model catalyst.

## 2. DFT calculations

To investigate theoretically the structural and electronic properties of the Cu/Ru(1 0 $\bar{1}$ 0) adsorption system, and predict the optimal adsorbate structures for an increasing Cu coverage, the Vienna Ab-initio Simulation Package (VASP) [45], which implements plane-wave DFT calculations, has been employed. Computations were performed using the projector-augmented-wave (PAW) method to describe the electron-ion interactions [46] and the Perdew–Burke–Enzerhoff (PBE) form of the exchange-correlation functional within the generalized gradient approximation (GGA) [47]. While the kind of adopted density functional obviously affects the obtained results, and a number of approaches—including various flavors of GGA, meta-GGA and hybrid functionals—have been developed to improve the reliability of DFT simulations for specific purposes (see, e.g., Refs. [48,49] and references therein), the GGA–PBE is a common method of choice that performs reasonably well for metal-on-metal adsorption systems composed of transition metals such as Ru and Cu.

The Cu/Ru(1 0 $\bar{1}$ 0) surface was modeled within a standard supercell approach. Ru substrate was represented by a [1 0 $\bar{1}$ 0]-oriented slab consisting of 12 atomic layers (which constitute 3 lattice periods in this crystallographic direction), with 6 top layers allowed to relax and 6 bottom layers kept frozen in their bulk-like positions. Cu adatoms were deposited on the fully relaxed surface only. The slab asymmetry was compensated by appropriate dipole corrections. A (1 × 1) surface unit cell was assumed for all considered Cu coverages, in accordance with LEED observations of the adsorbate geometry [18], hence only the adsorption of complete atomic monolayers of Cu (up to 6 MLs) was simulated. In this work, the adsorbate coverage is defined in a geometric fashion relative to the atomic structure of the substrate, so 1 ML corresponds to the atomic density of a Ru(1 0 $\bar{1}$ 0) plane. Supercell of the same size was used in all computations. A sufficiently thick vacuum spacer, equal to about 14 Å for the thickest considered Cu overlayer and respectively greater otherwise, was taken to prevent artificial interactions between the neighboring slab surfaces in the assumed repeated-slab scheme. Unconstrained atom positions were optimized by the conjugate-gradient method until the forces acting on movable atoms reduced to $10^{-2}$ eV/Å or less, whereas the electronic relaxation was performed using the Davidson-block algorithm with the total energy converged to within $10^{-5}$ eV. Atomic coordinates of all relevant structures referred to in the text are provided as supplementary material (see Appendix A). Selected adsorbate structures were further relaxed to satisfy one and/or two orders of magnitude stricter convergence criteria on maximum forces and total energy. This had a marginal effect on the optimal atomic positions (coordinate shifts not exceeding 0.002 Å) as well as the system energetics (energy changes below 1 meV per supercell). Moreover, vibrational spectra computed at the zone center (Γ point) for energetically favorable hcp-like arrangements of adatoms in the substrate-lattice-continuation sites exhibited no imaginary frequencies, thus confirming their equilibrium character.

The energy cutoff of 350 eV, determining the plane-wave basis, was found acceptable (higher tested). The Brillouin zone was sampled by a (13 × 9 × 1) Γ-centered Monkhorst–Pack grid (other tested). With this set of parameters, optimization of the bulk unit cell of Ru yields the lattice constants equal to $a = 2.728$ Å and $c = 4.297$ Å ($c/a = 1.575$), in a good agreement with the experimental values of $a_{\mathrm{EXP}} = 2.706$ Å and $c_{\mathrm{EXP}} = 4.282$ Å [50]. The slight lattice expansion compared to experiment ($\Delta a/a_{\mathrm{EXP}} = +0.81\%$ and $\Delta c/c_{\mathrm{EXP}} = +0.35\%$) was also found in other DFT computations for the Ru bulk hcp phase (see, e.g., Refs. [50–52]).

As has been checked, results obtained for the Cu/Ru(1 0 $\bar{1}$ 0) adsorption system with and without spin-polarization corrections differ negligibly: although the Cu adatoms exhibit a small magnetic moment for the considered range of adsorbate coverage, differences in adsorption energies are of the order of 1 meV, and the structural relaxations also coincide within a fraction of percent. Nevertheless, the spin polarization was taken into account throughout the calculations.

## 3. DEPES measurements

The DEPES experiment [53–55] was performed in an ultrahigh vacuum chamber with the base pressure below $10^{-10}$ mbar. A retarding field analyzer equipped with an axially fixed electron gun was applied. The manipulator enabled independent polar and azimuthal rotations of the sample as well as its shift in the $x$,$y$, and $z$ directions. A single-crystal Ru(1 0 $\bar{1}$ 0) sample of 4 N purity (MaTecK) was used. The cleanliness of the substrate was monitored by AES, and the long-range order of surface atoms was checked by LEED. The sample was cleaned by repeated cycles of oxygen adsorption and thermal desorption in order to remove the surface carbon. This procedure resulted in a surface for which no contaminants were detected by AES, and a sharp (1 × 1) LEED pattern characteristic of the bare Ru(1 0 $\bar{1}$ 0) surface was obtained. Cu was deposited from a Knudsen cell. The amount of adsorbed Cu was determined from AES uptake curves [18].

The DEPES distributions were recorded for four energies of the primary electrons, viz., 900, 1200, 1500, and 1800 eV. The intensity of elastically backscattered electrons was measured as a function of the incidence angle of the primary electron beam. The polar angle $\theta$ was varied from $-75°$ to $+75°$ with the 0.25° step, whereas the azimuthal angle $\phi$ was changed every 2° between 0° and 180°. In order to present the obtained $I(\theta,\phi)$ data as a two-dimensional map, stereographic projection was done with coordinates transformed according to $x = 2\tan(\theta/2)\sin(\phi)$ and $y = 2\tan(\theta/2)\cos(\phi)$, while the signal intensity was reflected by color.

Theoretical DEPES distributions were simulated within the multiple scattering approach [54–56], using the structural information about the system provided by DFT. The degree of coincidence of the simulated DEPES pattern $I_{\mathrm{SIM}}(\theta,\phi)$ to the measured one $I_{\mathrm{EXP}}(\theta,\phi)$ was expressed by the $R$ factor based on the Pearson's product-moment sample correlation coefficient [54,57], viz.,