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A photoelectron spectroscopy study of ultra-thin epitaxial alumina layers grown on Cu(111) surface

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ABSTRACT

Thin epitaxial alumina layers were grown on the Cu(111) surface using simultaneous aluminum deposition and oxygen exposure. Different substrate temperatures during the deposition resulted in layers with different thicknesses, growth rates, crystallinity and epitaxy. Low energy electron diffraction measurements confirmed the epitaxial growth for substrate temperatures above 870 K. The Al 2p doublet was studied by means of photoelectron spectroscopy in order to determine the alumina termination at the metal-oxide interface. A strong dependence on the preparation temperature was found and both aluminum and oxygen terminated interfaces were created.

1. Introduction

Copper is one of the most used metals in electronics and microelectronics nowadays. Its high conductivity, moderate price and stability makes it a perfect candidate for conventional wiring as well as for materials used in the process of large scale integration. Copper, on the other hand, suffers heavily from oxidation and for practical use, inert coatings are necessary. For insulating purposes, ceramic materials, such as alumina, are widely used and its high thermal conductivity and hardness make alumina a very suitable material for such coatings. Surface properties of alumina are also exploited in the field of heterogeneous catalysis and non-linear optics. Therefore, there is a considerable interest in creating well-ordered alumina layers on single-crystalline metal surfaces in order to investigate model systems for further use in various branches of industry.

Ultra-thin alumina layers are commonly used as a support for model catalyst systems [1] and well-ordered alumina can be grown by oxidation of intermetallic alloys containing aluminum [2,3]. Such substrates include low-index Ni–Al surfaces [4], but also Fe–Al [5], Co–Al [6], or Cu–Al [7]. Although previous studies clearly show several possibilities of well-ordered epitaxial growth of alumina layers, the requirement of an intermetallic alloy single-crystal narrows the choice of the substrates. Also, using an alloy instead of a pure metal increases the difference with respect to real-life application. Therefore, using a pure metal (Ni, Co, Cu, Fe, etc) substrate is a step towards better understanding of the metal-oxide interface formation, as well as the alumina growth mechanism.

There have been several works reporting ultra-thin alumina growth on single-crystal metallic substrates not containing aluminum. One of the options involved deposition of an Al layer and its subsequent oxidation. Such layers were prepared on Ru(0001) [8] or Re(0001) [9], but they lacked long range order. Recently, epitaxial alumina growth on Fe(110) [10] thin layers was reported. Procedures which used Ni(111) [11] and Ni(100) [12] substrates exploited the formation of a surface Ni–Al alloy. Subsequent oxidation gave results similar to the oxidation of bulk Ni–Al single-crystals [13,14]. Moreover, Jeliazova et al. [15] achieved the alumina growth by direct deposition of NiAl alloy onto a Cu (111) surface and its oxidation.

Another procedure, which uses a single step only, involves simultaneous Al deposition and oxidation. Using this approach, alumina layers were prepared on Ru(0001) and Re(0001) [16] and, recently by our group, on Ni(111) [17]. The preparation uses elevated temperature to ensure good ordering of the layer. However, in the case of Ru(0001) and Re(0001) substrates, the layers exhibit a 3D growth mode. Our layers are prepared using lower temperature and lower oxygen pressure (by two orders of magnitude) compared to the layers formed on Ru(0001) and Re(0001). The growth is therefore

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much slower and the growth mode may differ entirely from the layers presented in [16].

2. Experimental

Photoelectron spectroscopy measurements as well as electron diffraction experiments were performed in an ultra-high vacuum system at the Materials Science Beamline (MSB) endstation, Elettra Synchrotron light laboratory, Trieste, Italy. The base pressure of the vacuum chamber is below 1.10^{-8} Pa. The light source for the MSB is bending magnet 6.1 and monochromatized synchrotron radiation at MSB covers the energy range from 22 to 1000 eV. Two electron emission angles were used for the spectroscopic measurements – close to the sample normal and 60° off-normal.

The endstation is equipped with an X-ray source and Phoibos 150 hemispherical analyzer (both manufactured by Specs GmbH). An Al anode (primary photon energy of 1486.6 eV) was used for all conventional XPS measurements. Al 2p and O 1s spectra were also measured using 106 eV and 630 eV synchrotron light. The analyzer was used in Fixed Analyzer Transmission mode. The total energy resolution of the measurements was 0.1 (105 eV), 0.9 (630 eV) and 1 eV (1486.6 eV) for the respective photon energies. All peaks were fitted by a Voigt function after subtracting linear (O 1s) or Shirley (Al 2p) backgrounds. Spin orbit splitting and branching ratio were fixed to 0.41 eV and 1:2 for Al 2p doublets. Low energy electron diffraction (LEED) measurements were carried out with the primary electron energy ranging from 25 to 125 eV. The diffraction patterns from the screen were recorded by a combination of CCD camera and PC video grabber. Noise reduction algorithm by averaging of the consecutive captured frames was used in order to enhance the recorded image quality.

The substrate Cu(111) single crystal was purchased from MaTecK GmbH and was cut and mechanically polished with accuracy better than 0.1° with respect to (111) plane. The sample was cleaned by several cycles of annealing up to 940 K and Ar^+ sputtering (1 keV, 20 to 40 min). The cleanliness and ordering of the sample surface was checked by XPS and LEED.

The alumina layers were prepared by a controlled simultaneous oxidation/deposition procedure. Oxidation procedures with varying parameters were used in order to prepare different alumina layers. The sample temperature during oxidation was between 670 K and 940 K. The parameters used in the oxidation procedure are listed in Table 1. Apart from substrate temperature T_S, deposition time t and the partial pressure of oxygen p, the Table contains calculated layer thickness d, which will be further described in the next section. All samples were prepared in a single-step process following the cleaning procedure. Only sample B was prepared in a step-wise manner in three steps (60 min and 2 × 30 min depositions).

Aluminum was deposited using a crucible type evaporator heated conductively by a tungsten wire. The deposition rate was approximately 0.01 nm/min. Every deposition step finished by cooling down the sample in an oxygen atmosphere to below 370 K (for sample C below 470 K) in order to prevent thermal decomposition of the alumina layer. The purity of the O_2 gas was checked by a quadrupole mass spectrometer. The sample temperature was measured and controlled by a K-type thermocouple attached to the rear side of the sample and a temperature controller with PID regulator.

Table 1
Alumina preparation parameters.

Sample	T_S [K]	t [min]	p [10^{-5}Pa]	d [nm]
A	670	60	5	0.47
B	870	120	5	0.91
C	940	120	5	0.37

3. Results and discussion

3.1. LEED results

The crystallographic structure of the prepared alumina layers was studied by means of LEED. Patterns measured with primary electron energy between 70 and 80 eV for samples A–C are shown in Fig. 1. The images at different primary electron energies have been resized in order to have the same momentum scale. The diffraction pattern obtained for the clean Cu(111) substrate contains six main spots forming a hexagon and exhibits three-fold symmetry. Diffraction spots both from the substrate and the alumina layer can be observed in patterns for samples A–C enabling the evaluation of the alumina lattice parameter. The position of substrate spots are marked by empty circles in the patterns.

The contribution of the alumina layer to the diffraction pattern is represented by rings (sample A) or streaky features (samples B and C). The occurrence of rings in the case of sample A suggests that the preparation process led to the creation of a polycrystalline alumina layer. The lower preparation temperature (670 K) was not enough to provide sufficient surface mobility of the deposited atoms and to create a well-ordered layer. A similar phenomenon was observed on alumina prepared on the Ni(111) surface [17].

The intersections of the diffraction lines (the contribution of the alumina overlayers) form a hexagonal pattern and they are the brightest features for samples B and C. The origin of the streaky features lies in the microstructure of the alumina layer. The shape and orientation of the step-edges or boundaries of alumina domains can result in LEED patterns containing lines instead of spots. Similar features were reported in the case of alumina growth on CoAl(100) [18] and NiAl(100) [19].

The brightest diffraction spots originating from the alumina layer are located at the intersections of the streaky features of the pattern. Hexagonal symmetry of the pattern indicates that the alumina layer grows with hexagonal atomic planes parallel to the substrate surface, as it is common for alumina layers grown on (111) surface [2]. From relative orientation of the hexagons in patterns we conclude that rows of oxygen atoms (forming hexagonal sublattice) are aligned parallel to the atoms of the substrate and there is no rotation between their symmetries. Evaluation of the spot position both from alumina and the substrate gives information on oxygen–oxygen distance in the alumina layer, which is approximately 0.27 nm for all samples A–C, i.e. similar to the value for bulk γ-alumina (0.28 nm [20]).

3.2. XPS results

Oxide layer thickness was evaluated using Cu $2p_{3/2}$ XPS peak intensity (spectra not shown). The peak intensity was assumed to decay exponentially with oxide layer thickness, and the inelastic mean free path of the photoelectrons was calculated according to the Tanuma–Powell–Penn formula [21]. The results are shown in Table 1. The differences in the layer thicknesses between samples B and C can be explained by diffusion of aluminum atoms into the substrate. This will be further discussed below, together with the growth rate dependence on the substrate temperature. It is important to emphasize that changes to the Cu $2p_{3/2}$ spectra in terms of position or shape of the peak were negligible.

Al 2p spectra measured for samples A–C are shown in Fig. 2 (a)–(c). Fig. 2 (d) shows the spectrum obtained from an alumina layer prepared by controlled oxidation of Cu-9 at.%Al(111) [22]. By comparing results of analytical fitting, one can clearly see that either one or two components are resolved in each of the spectra (a)–(d). Two components assigned to the alumina layer are present in the case of spectra (a) and (d). The origin of the two oxide components for case (d) is well described in [22,23] and the component with lower binding energy was assigned to Al at the alumina-substrate interface. In the case of sample A, angle-