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Structural investigation of the c($\sqrt{2} \times 5\sqrt{2}$)R45° surface alloy formed by Ti deposition on Cu(001)

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Abstract

The alloying process of Ti deposited on Cu(001) was studied by means of XPS, LEIS, XPD and LEED intensity analysis. With the sample held at 570 K, a linear decrease of the Cu LEIS signal as a function of the amount of Ti deposited is observed in the early stages of deposition until a constant value is reached. At the onset of the plateau a c($\sqrt{2} \times 5\sqrt{2}$)R45° LEED pattern starts to be visible. XPD and LEED intensity measurements were performed for the c($\sqrt{2} \times 5\sqrt{2}$)R45° phase prepared depositing ca. 1.5 monolayer of Ti. The angle-scanned XPD curves measured for the phase c($\sqrt{2} \times 5\sqrt{2}$)R45° reveal that Ti atoms substitute Cu atoms in the fcc lattice of the substrate. The polar XPD curves show that at least the first four layers of the substrate are involved in the alloying process. We found that the (310) plane of the Cu_4Ti alloy ($D1_a$ type-structure) fits, without significant contraction or expansion of the lattice parameters, the c($\sqrt{2} \times 5\sqrt{2}$)R45° structure. The intensity versus energy curves of the diffracted beams were calculated on the basis of this structural model using the tensor LEED method. The results of the LEED intensity analysis provide a further evidence of the formation of a slab of Cu_4Ti(310) layers.

Keywords: Surface crystallography; Surface alloy; LEED; XPD; Copper; Titanium

1. Introduction

In the copper–titanium phase diagram there exist several intermetallic phases in addition to solid solutions of the two metals [1]. The formation of Cu–Ti intermetallic compounds, solid solutions and amorphous phases is characterised by negative enthalpies [2]. The deposition and annealing of titanium on a copper substrate should allow one to prepare Cu–Ti surface alloys of various structures and compositions [3]. To our knowledge, in the literature there are no studies using the surface science methods about the composition and structure of Cu–Ti surface alloys prepared by depositing titanium on surfaces of a copper single crystal. Besides the interest related to the surface physics of alloys, the copper–titanium bimetallic system has also a technological relevance. The characteristic of copper renders this metal suitable for a variety of metallurgical applications, for instance as continuous casting steel molds. Unfortunately, copper has a rather low hardness and is prone to adhesive and abrasive wear. Its tribological properties can be improved by the application of suitable surface coatings consisting of hard materials. A possible coating can be prepared by depositing titanium on a copper substrate and subsequent annealing to form an alloy [4]. The nature of the deposited metal/copper interface is relevant for the adhesion properties of the coating. In the present work, we studied by means of surface sensitive techniques, the alloying process of titanium deposited on the Cu(001) surface. In particular, we searched for the conditions leading to the formation of an ordered surface alloy, a phase which could be studied by diffraction methods. The composition of the phases formed upon

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annealing Ti deposited on Cu(001) was determined by means of X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering (LEIS). The structural characterization of the surface alloys formed by deposition of titanium was carried out by means of X-ray photoelectron diffraction (XPD) and low-energy electron diffraction (LEED).

2. Experimental details

The experiments were carried out in a ultra-high vacuum (UHV) apparatus with a base pressure in the low 10^{-10} mbar range. The chamber was equipped with a non-monochromatised Al K_α radiation source. This radiation was used for the XPS and XPD measurements. The chamber was also equipped with a hemispherical electron/ion energy analyser, a focused ion gun for the LEIS measurements and a 3-grid rear view LEED optics. The angle between the analyser axis and the X-ray source was 55° and the semicone angle of acceptance of the analyser was 4°. The XPS spectra were measured with a fixed pass energy of 44 eV. The binding energy (BE) scale was calibrated setting the $Cu2p_{3/2}$ peak to 932.6 eV [5]. Prior to the measurement of the peak areas, the inelastic background in the spectra was evaluated by means of the Shirley method [6] and subtracted. For LEIS we used a He ion beam with 1 keV energy impinging on the surface at an angle of 45°, along the [110] direction. The scattering angle was ca. 135°. The sample was mounted on a manipulator which permits polar rotation (around the manipulator axis) and azimuthal rotation (around the normal to the sample surface). The XPD curves were acquired by monitoring the intensity of the $Ti2p_{3/2}$ and $Cu2p_{3/2}$ peaks as a function of the polar and azimuthal emission angles. The background was estimated by measuring simultaneously the intensity at a given peak maximum and the intensity at kinetic energies 5–10 eV higher than the peak.

The LEED intensity versus accelerating voltage (I–V) curves of the diffracted beams were collected by means of a video LEED system. The LEED I–V curves were measured at normal incidence of the electron beam in the energy range 50–350 eV. Normal incidence was considered to be achieved when Pendry reliability (R_p) factors [7] between I–V curves of symmetrically equivalent beams of 0.1 or below were obtained. The I–V curves of symmetric beams were averaged to compensate for minor differences due to small deviations from normal incidence. The I–V curves were background subtracted and normalized to constant incident electron current. The LEED intensities were collected at room temperature (RT).

The sample was a plate of 10 mm × 10 mm × 2 mm cut and polished along the (001) surface with an accuracy of ±0.1°. The temperature was measured by means of a chromel–alumel thermocouple placed near to the sample. The surface was prepared by cycles of argon ion sputtering (600 eV) and annealing (700 K for 30 min) until no contamination was detectable by means of XPS and LEIS and a sharp (1×1) LEED was visible.

Ti (99.999% purity) was evaporated using an electron beam evaporator. The pressure during evaporation remained in the low 10^{-10} mbar range. The amount of Ti deposited was estimated by means of XPS and LEIS taking into account the alloying of the deposited metal with the substrate. The coverage is expressed in terms of monolayer (ML). One monolayer of titanium corresponds to the atomic density (number of atoms/unit area) of Cu(001).

The intensity of the diffracted beams as a function of the primary electron beam energy was calculated using the tensor LEED (TLEED) method [8]. The TLEED calculations were performed by means of the Barbieri/Van Hove symmetrized automated tensor LEED package (SATLEED) [9]. The Barbieri-Van Hove program package was used for the calculation of the phase shifts [9]. Ten phase shifts ($l_{\max} = 9$) were used in the LEED calculations. The phase shifts for Cu and Ti were calculated from the muffin-tin potential of a Cu_3Ti alloy with a face centred cubic (fcc) structure. The LEED calculations were performed between 40 and 350 eV. The imaginary part of inner potential was set to 5 eV, whereas the real part was set to 10 eV and optimised in the search procedure. The Debye temperatures of Cu and Ti were set equal to 350 K. In the automated search for the best fit structure, eight non-equivalent beams were used for a total energy range of about 850 eV. The R_p factor was used in the analysis to judge the agreement between experimental and calculated I–V curves [7].

3. Results

3.1. XPS and LEIS results

XPS and LEIS show that the surfaces prepared by evaporation of Ti on the sample held at 300 and 370 K are significantly contaminated by carbon and oxygen. These impurities are attributable to the adsorption and decomposition of CO from the residual atmosphere in the chamber. The deposition with the sample held at ca. 600 K resulted in a much cleaner surface compared to the lower temperature cases. XPS and LEIS spectra did not show the presence of adsorbed carbon and oxygen above the noise level after deposition of Ti. Also the low background in the LEIS spectra at low kinetic energy is an indication of the cleanliness of the surface. Small levels of contamination (estimated to be below 0.1 ML of carbon after deposition of 1 ML of Ti) were observed only after prolonged exposures to the residual atmosphere in the vacuum chamber. The LEIS signal of Cu (normalised to the intensity of the clean surface) as a function of the ratio of the Ti2p and $Cu2p_{3/2}$ XPS peak areas (indicated with R_{XPS} hereafter) is reported in Fig. 1. We report the LEIS signal versus the R_{XPS} instead of versus the exposure since the evaporation conditions were not reproducible in different runs. The Cu LEIS signal decreases with increasing the amount of Ti deposited and remains constant to 0.72 ± 0.04 for R_{XPS}