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Growth study of Cu/Pd(1 1 1) by RHEED and XPS

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Abstract

An X-ray photoelectron spectroscopy (XPS) and reflection high-energy electron diffraction (RHEED) investigation of the growth of Cu films on a Pd(1 1 1) single crystal at room temperature is presented. Dynamically taken XPS-data as function of the deposition time show a linear variation of $I_{\text{Cu-3p}}/I_{\text{Pd-3d}}$ and a periodic change of its slope indicating a nearly layer-by-layer growth process. RHEED oscillations are seen for the 3–4 first layers, also suggesting a smooth growth mode. From the evolution of the RHEED-streaks separation the in-plane Cu-atom spacing is precisely determined. Up to a coverage of ca. 2–3 monolayers (ML) Cu grows pseudomorphously on Pd(1 1 1), despite the −7.1% strain imposed by the substrate lattice parameter. Non-pseudomorphous epitaxial growth is evidenced above ca. 3–4 ML by a discontinuous change in lateral lattice spacing observed by RHEED which indicates a relaxation to the Cu(1 1 1) “natural” surface lattice parameter. In addition it is concluded that surface alloying does not take place at least at room temperature (RT)-XPS spectra taken dynamically during annealing show that alloying occurs only above RT.

Keywords: Copper; Palladium; Low index single crystal surfaces; Molecular beam epitaxy; Reflection high-energy electron diffraction (RHEED); alloying

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1. Introduction

In thin film heteroepitaxy the main driving force for growth is the lattice misfit between the film A and the substrate B. Not only misfit but also the substrate temperature, growth rate, thermodynamic and chemical properties of A and B (e.g.

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surface free energy), will determine which growth mode will be established: (FV) Layer-by-layer growth, or Frank-van der Merwe; (VW) Island growth, or Volmer–Weber; (SK) Wetting layer and island growth, or Stranski–Krastanov. Layer-by-layer growth is possible in many lattice-matched systems, by which in an ideal case a layer is completely filled before the next layer starts to grow. If the misfit is not exactly "matched" (e.g. >5%) usually the film starts to grow pseudomorphously and above a certain critical thickness relaxes to the "natural" film lattice spacing. In this case non-pseudomorphous growth gives rise to dislocation formation but eventually layer-by layer growth still goes on. RHEED is one of the most useful techniques that could be used to monitor growth modes during thin film deposition [1,2], and because of its extreme surface sensitivity (at a grazing incidence angle of ~2°) [3] as compared to other techniques one can precisely investigate strain relaxation processes. By RHEED analysis it is possible to determine with an accuracy of tenths of a percent the lateral lattice parameter evolution. Intensity oscillations of the RHEED-spots, or the attenuation or absence of those oscillations, indicate the growth mode (FV, VW or SK) during all stages of growth. On the other hand X-ray photoelectron spectroscopy (XPS) is widely used in monitoring growth processes, in general by continually observing the evolution of the XPS signal during growth, the attenuation of the substrate signal and increase of the adsorbate signal.

In this paper we report on a RHEED and XPS study of the heteroepitaxy of Cu on Pd(1 1 1) having a bulk misfit $f_o = (a_{Cu} - a_{Pd})/a_{Pd}$ of -7.1%. The surface free energy of Pd is ca. 2.05 J/m^2, much greater than the sum of the free energy of Cu (1.85 J/m^2) and the interface energy (0.01 J/m^2) [4], which means FV growth mode is expected for the Cu/Pd(1 1 1) system. Layer-by-layer growth was already observed at room temperature for Cu on Pd(1 0 0) [5,6], Pd(1 1 0) [7,8], and Pd(1 1 1) [9,10]. In an extensive work on X-ray photoelectron spectroscopy (XPS) [11] the chemical shift of the Cu/Pd core levels are correlated with cluster formation and annealing induced alloying. It is well known that when the interatomic interactions between substrate and film are stronger than those between the film atoms layer-by-layer growth mode is expected to occur. In contrary, SK or VW growth mode is observed when the deposit atoms are more strongly bound to each other. Despite of the Pd–Cu bond being stronger than the Cu–Cu or Pd–Pd one, this in principle favoring FV growth mode, in a low energy electron diffraction (LEED) study [12] island growth (VW) was indicated. Hitherto also very little is known about diffusion or surface alloying in this system. Hence, a high-precision RHEED-analysis, combined with XPS, can contribute to the understanding of some unclear issues on the Cu/Pd(1 1 1) system.

2. Experimental

The studies were carried out in two ultrahigh vacuum (UHV) system equipped with evaporation facilities, both operating at a base pressure of 1×10^{-10} mbar. In the first UHV-chamber it was possible to monitor dynamically the growth by X-ray photoelectron spectroscopy (XPS), using conventional Al-Kα radiation as well as the SGM beamline of the Brazilian Synchrotron Light Laboratory (LNLS). Surface structure development of the first monolayers (ML) was monitored in situ by a RHEED system in the second UHV chamber. The 11 keV-beam impinged on the sample at a grazing incidence angle of about 2°. The reflected and diffracted beams were observed on a phosphor screen with a CCD- camera and the "RHEED movie" was treated with the KSA400 software. The Pd(1 1 1) crystal was previously cleaned in UHV by means of argon ion sputtering with an energy of 900 eV and subsequently annealed to 600 °C. After several sputtering-annealing cycles the RHEED pattern of the sample showed very sharp streaks, indicating atomically flat terraces. High purity (>99.9%) Cu deposition was done from an electron beam evaporation source. In both UHV-chambers the same source was utilized with approximately the same evaporator-sample distance. During growth the residual gas pressure was below 9×10^{-10} mbar (6×10^{-10} mbar) at an evaporation rate of 0.5 ML/min for RHEED and (0.1 ML/min) for the XPS