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

A. de Siervo [a,c], R. Paniago [b,*], E.A. Soares [b], H.-D. Pfannes [b], R. Landers [a,c], G.G. Kleiman [a]

[a] *Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, C. P. 6165, 13083-970 Campinas, SP, Brazil*
[b] *Departamento de Física, Universidade Federal de Minas Gerais, Av. Antonio Carlos, 6627 C. P. 702, 30123-970 Belo Horizonte, MG, Brazil*
[c] *Laboratório Nacional de Luz Síncrotron, C.P. 6192, 13084-971, Campinas, SP, Brazil*

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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

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.

* Corresponding author. Tel.: +55 31 34995683; fax: +55 31 34995600.
E-mail address: paniago@fisica.ufmg.br (R. Paniago).

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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

experiment. The surface chemical composition was checked by XPS and revealed to consist of atomically clean Cu films. The quality of the surface was verified by the existence of a p(1 × 1) LEED pattern and substrate and film valence band were monitored by ultraviolet photoelectron spectroscopy (UPS).

3. Results and discussion

3.1. Film growth

A first indication that Cu on Pd(1 1 1) grows layer-by-layer was obtained by monitoring the growth dynamically by XPS. Fig. 1 shows the intensity rates of the Cu-3p and Pd-3d peaks as a function of evaporation time. The linear variation of $I_{\text{Cu-3p}}/I_{\text{Pd-3d}}$ and the periodic change on the slope is the sign for FV-growth confirming similar result obtained by Liu et al. [11]. It was also possible to calibrate the evaporation rate, namely 0.1 ML/min—in this case a relative low evaporation rate was necessary to ensure good quality XPS data.

The RHEED experiment was performed in the second UHV-chamber as already mentioned. The evaporation rate of Cu on Pd(1 1 1) could be calculated from the RHEED oscillations of the diffuse scattered intensity near the specular spot as seen in Fig. 2. The oscillations are damped above 2 ML, suggesting that growth proceeds not in a perfect but in a *predominantly* layer-by-layer mode—in other words, new layers might be able to start growing before the preceding layer has been completed. Stroscio et al. [13] have showed that in the Fe(0 0 1) homoepitaxy although RHEED oscillations are observed, at least three layers are seen (by STM) in the growth front. It is important to mention that the growth rate in the RHEED experiment (Fig. 2) was 5 times faster than in the XPS case (Fig. 1). An increase in diffusion coefficient (by increasing temperature) or lowering growth rate might have resulted in a more perfect layer-by-layer growth mode [13]. We can however safely argue that the Cu film grew in a nearly layer-by-layer (FV) mode up to 4–5 ML. Increasing coverage the oscillations were attenuated and the p(1 × 1) LEED pattern at 7.5 ML, was not as clear as for the clean Pd(1 1 1) substrate. On the other hand, the RHEED pattern after ca. 7.5 ML-Cu coverage (Fig. 3b) as compared to clean Pd(1 1 1) (Fig. 3a) exhibits only very little degradation. In addition to that, valence band spectra of 7.5 ML-Cu/Pd(1 1 1) taken by UPS corresponded exactly to what would be expected for Cu(1 1 1)—even the Shockley surface state [14] was observed at normal emission indicating good surface quality. To examine the atom lateral spacing, which is inversely proportional to the streak

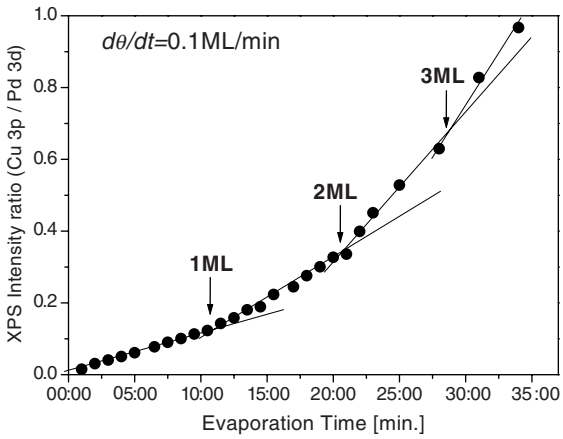

Fig. 1. Intensity rates of the Cu-3p and Pd-3d peaks ($I_{\text{Cu-3p}}/I_{\text{Pd-3d}}$) measured by XPS as a function of evaporation time.

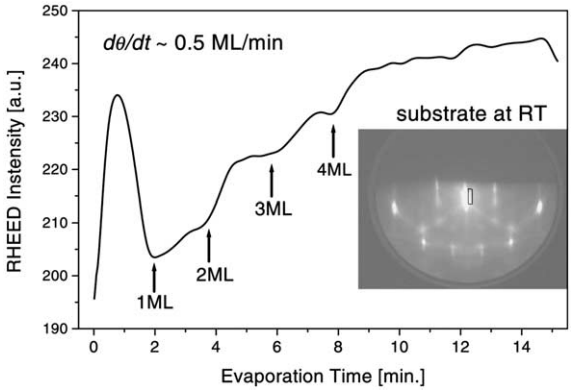

Fig. 2. RHEED intensity of the diffusely scattered electrons near the (0,0) beam spot as function of time during evaporation of Cu on Pd(1 1 1). Insert: RHEED pattern showing the region from where the intensity was read out.

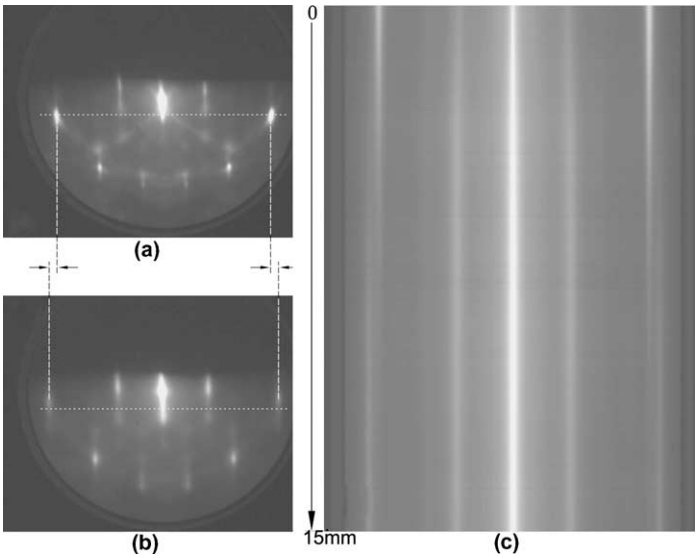

Fig. 3. (a) RHEED image of clean Pd(1 1 1); (b) RHEED image after 15 min of Cu evaporation; and (c) intensity evolution (0–15 min) of the scanned line in (a), corresponding from a clean Pd(1 1 1) crystal to 7.5 ML of Cu on top of it.

separations in the RHEED pattern, the evolution of the streak intensities along the dotted line indicated in Fig. 3a and b, was measured during the 15 min of Cu deposition at 0.5 ML/min and plotted in a single image in Fig. 3c. Profiles (taken for equal time intervals) from 0 to 7.5 ML are plotted in Fig. 4. The two external peaks are the [−2,0] and [2,0] streak positions and one clearly sees that between 2 and 3 ML they disappear from their initial positions and reappear at new positions remaining there up to the end of coverage at ca. 7.5 ML. Because RHEED is only sensitive to surface (ca. two layers at 2° grazing incidence and 11 keV) occurrence of two peaks is interpreted as two different lateral spacings. The change in distance of the [−2,0], [2,0] peaks is interpreted as a relaxation (contraction) of the lateral lattice parameter of the film. We performed a least squares fitting of line intensities and line positions of the two outermost peaks indicated in Fig. 4. Fig. 5a shows the evolution of the line intensities and Fig. 5b the dependence of the lateral (or surface) lattice parameter. Because of the already mentioned attenuation of the RHEED oscillations, which suggests a *nearly* but not perfect layer-by-layer growth mode, the shoulders in the curves of Fig. 4 (between 2 and 4 ML) may indicate that part of the two-layer film is relaxing while the remaining part is still pseudomorphic. Our conclusion is that up to ca. 3 ML the Cu-film grows at the Pd(1 1 1) registry position, and above that the entire film assumes approximately the "natural" surface lattice of a Cu(1 1 1) single crystal.

3.2. Annealing effects

In order to investigate surface alloying, the temperature dependence of a 1 ML-thick Cu film on Pd was annealed and the resulting core-level shifts and ratio of line intensities ($I_{\text{Cu-3p}}/I_{\text{3d}}$) were monitored by XPS. Photoelectron spectra were measured dynamically during heating. In Fig. 6a the energy position of the Cu-3p line for various temperatures is illustrated. At 150 °C a slight change in peak position is noticed and at 230 °C this deviation has already saturated suggesting surface alloying by incorporation of Cu to the first Pd(1 1 1) layer(s). The XPS-intensity ratios of the Cu-3p lines as function of annealing time are shown in Fig. 6b. Saturation of the Cu-3p line intensity at 230 °C indicates that an increase in temperature up to 320 °C does not produce further Cu diffusion into the bulk. A detailed investigation of the com-

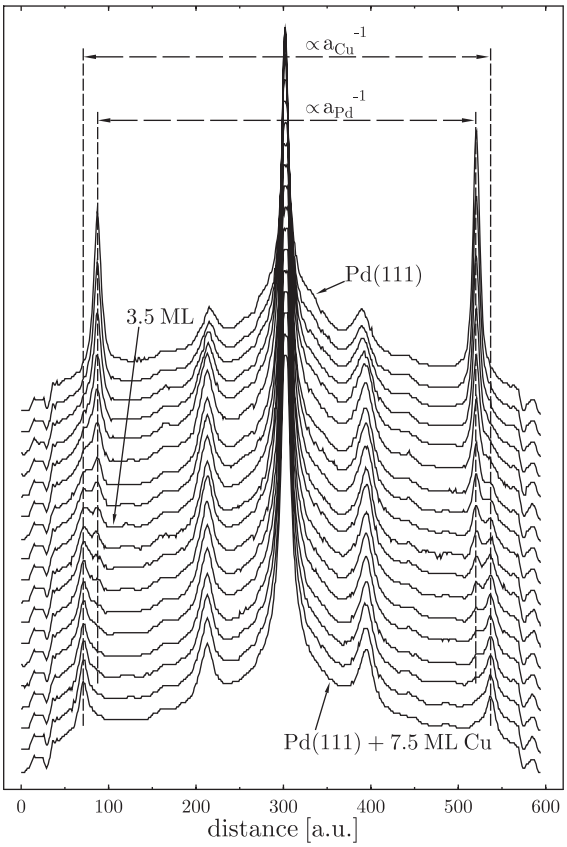

Fig. 4. Evolution of the line profile of the RHEED pattern (indicated in Fig. 3a) from clean Pd(1 1 1) up to 7.5 ML Cu coverage. The two outer peaks are inversely proportional to the surface lateral lattice spacing.

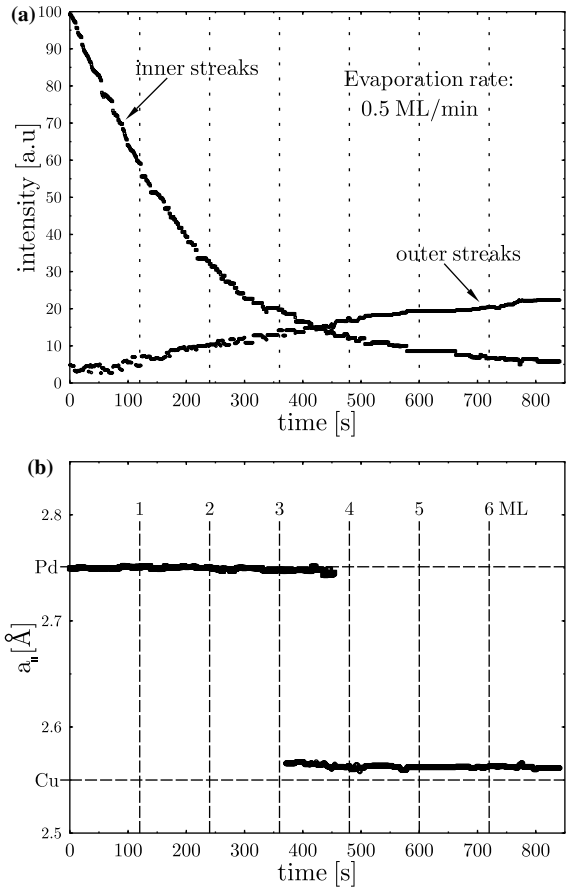

Fig. 5. (a) dependence of the line intensities of peaks [−2,0], [2,0] and (b) of the lateral lattice parameter ($a_{\|}$) as a function of time and Cu coverage.

position of the first layers upon annealing based on photoelectron diffraction [15] will be published else where, for the present analysis it is sufficient to note that alloying occurs only above room temperature (RT). The complementary system Pd/Cu(1 1 1) however shows surface alloying even at 300 K [16,17].

4. Conclusions

From the analysis of the RHEED pattern evolution, the epitaxial growth of Cu films on Pd(1 1 1) at room temperature has been investigated. The observed (damped) RHEED oscillations indicate that new layers might be growing before the preceding layer has been completed suggesting a nearly layer-by-layer growth mode up to ca. 4–5 ML. FV growth mode has also been inferred from XPS measurements. Those results are in contrast to previous LEED-work on this system [12] where the authors exclude SK growth in favor of island nucleation (VW). In fact only a careful STM investigation of the Cu/Pd(1 1 1) growth is able to settle controversy.

RHEED data indicate pseudomorphous growth up to ca. 3 ML. Above that a discontinuous change in lateral lattice spacing is observed and RHEED oscillations become drastically attenuated. A perfect 3 (or 4) ML thick film probably does not even exist and a 2–4 ML thick growth

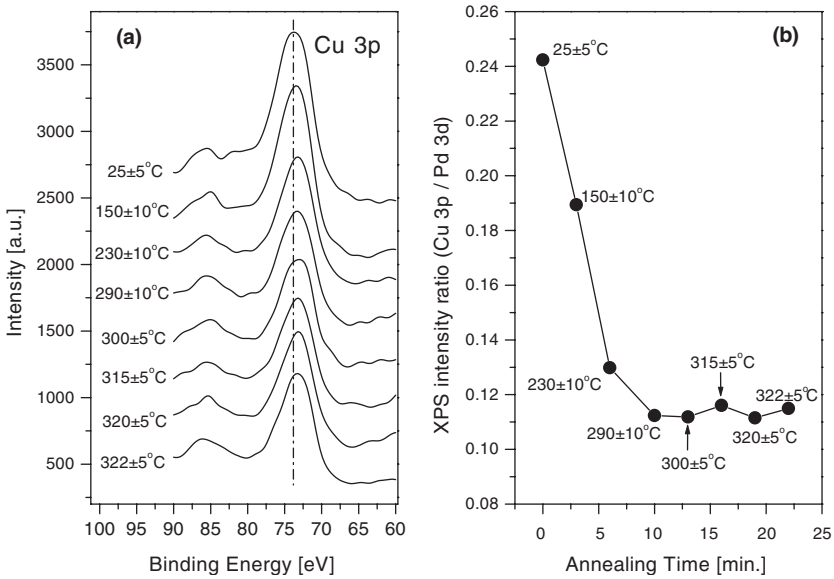

Fig. 6. (a) XPS spectra of Cu-3p after annealing a 1ML-thick Cu film on Pd(1 1 1) at the indicated temperatures; and (b) intensity rates of the Cu-3p, Pd-3d lines as function of annealing temperature and corresponding time.

front might be the real picture. At least it can be safely concluded that the Cu film, which was (−7.1%) strained by the Pd(1 1 1) sub-net, relaxes to the Cu(1 1 1) surface "natural" lattice parameter above 4 ML.

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