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Pd growth on Cu(111): stress relaxation through surface alloying?

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Abstract

On the basis of a high-precision reflection high-energy electron diffraction (RHEED) investigation details of the growth of Pd on a Cu(111) single crystal substrate at room temperature are reported. Because of the +7.6% misfit of the Pd lattice spacing as compared to Cu, perfect pseudomorphous growth would result in highly stressed ultra-thin films. RHEED analysis shows that as a function of Pd coverage initially the film starts to grow with the in-plane Cu(111) lattice parameter. With increasing coverage the lattice parameter rapidly changes to the "natural" lateral lattice parameter of Pd(111). We propose that a progressive increase of the equilibrium lateral lattice parameter by alloying (Vegards law) releases the stress in the Pd/Cu(111) system. With a coverage of n > 2 ML (n = number of monolayers, ML) pure Pd layers are formed, since the in-plane lattice parameter equals the expected value for Pd at n = 2 ML. Our conclusion that Pd–Cu surface alloying acts as a relaxation mechanism in this quasi-pseudomorphous growth system, corroborates scanning tunneling microscopy [Surf. Sci. 408 (1998) 43] which also suggests formation of a random surface alloy in the earlier stages of Pd growth on Cu(111).

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

1. Introduction

In heteroepitaxy the lattice misfit between overlayer and substrate usually determines how growth will evolve. In the early stage (first atomic layers) of pseudomorphous growth, the film is stressed or strained to the substrate in-plane lattice spacing and a coherent continuation of the surface-parallel unit mesh of the substrate by the atoms of the overlaying film is observed. With increasing coverage normally film thickness stress/ strain relaxation occurs, which can take place in different ways. More commonly, above a certain critical thickness the stress/strain relaxes due to dislocation formation. Another possibility is that with increasing thickness the lateral lattice spacing smoothly relaxes to the "natural" film lattice spacing. It is also possible that from the very beginning the film assumes its own lattice spacing, contracted or relaxed relative to the substrate (non-pseudomorphous growth). During film

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growth, atom intermixing from and to the substrate may also happen. In spite of lot of work done on surface phenomena of ultra-thin films, often focusing on their electronic, magnetic and optical properties, little attention has been paid to surface alloying [1–3]. Surface alloys are of great interest both for academic and technological reasons. The knowledge of the geometric and electronic structure of a certain alloy, ordered or not, the eventual existence of order–disorder transitions, or of other alloys properties are important issues. How surface alloying may influence metal heteroepitaxy is also poorly investigated until now, especially if it represents a relaxation mechanism in ultra-thin film growth.

This work focuses on the growth dynamics of Pd on Cu(111) during molecular-beam epitaxy, particularly on the evolution of the in-plane lattice parameter and a possible correlation with surface alloying. We used reflection high-energy electron diffraction (RHEED), which yields surface sensitive information of the in-plane lattice spacing with an accuracy of 0.005 Å.

Since the Pd/Cu(111) system has a relatively small bulk misfit ($[a_{Pd} - a_{Cu}]/a_{Cu} = +0.076$) pseudomorphic growth could be expected at least for the first layers. Previous transmission electron microscopy (TEM) and RHEED studies of epitaxial growth of Pd on Cu(111) [4] indicate that, at least initially, Pd grows on Cu(111) by a flat island or layer growth mechanism, and that complete coverage occurs when two complete monolayers have been deposited. RHEED analysis of these bilayer films showed streaked reflections perpendicular to the shadow edge, indication of smooth flat surfaces. In a further work those authors [5] argued that their previous work was done with a contaminated Cu(111) substrate which could explain the bilayer growth mode. Using an atomically cleaner substrate they claimed that a monoatomic flat island nuclei growth mode was achieved. Pessa and Jylhä [6] concluded from angle-resolved photoemission studies of their sample that they obtained high-quality two monolaver thick Pd films with evidence of no diffusion of Pd into the substrate at room temperature. Surface work function studies during Pd deposition on Cu(111) were done by Vook et al. [7]. Up to 0.5 ML the work function initially decreased and then linearly increased until 3.5 ML, and therefore the authors concluded that layer growth occurs at least up to 3 ML of Pd. Several authors [7–9] comment that Pd grows layer by layer, and in [6] it is argued that initially Pd grows pseudomorphically with a misfit of 8% and that over 1 ML the LEED pattern relaxed into the Pd(111) structure. However, a detailed study that addresses the evolution of the lateral spacing is not available in the literature.

1.1. Submonolayer and one monolayer growth

In a recent high-spatial resolution work-function investigation of 1.0 ML-Pd on Cu(111) using STM [8] the authors found no indication of alloying at room temperature. But a more recent STM-work on the submonolayer growth mode of 0.2 ML-Pd on Cu(111) [10] indicates that for temperatures up to 100 °C, the islands consist of disordered alloys formed by exchange of Pd and Cu atoms. Above 160 °C Cu was dug out from the surface and for temperatures of 220-300 °C the presence of subsurface Pd was confirmed by STM. In a recent photoelectron diffraction (PED) work [11] the composition of the first three layers and the interlayer distance of those first layers after ≈ 1 ML of Pd deposition on Cu(111) was investigated. It was shown that after annealing the films at 320 °C for 1 min (in order to improve film ordering) a random alloy formed with approximately 20%/70%/20% Pd concentration in the first three layers. This confirms the result of Bach Aaen et al. [10] that Pd tends to migrate to the second layer at higher temperatures (T > 200 °C).

2. Experimental

The studies were carried out in an ultra-highvacuum (UHV) molecular-beam epitaxy system with base pressure of 1×10^{-10} mbar. Surface structure development of the first monolayers (ML) was monitored in situ by a RHEED system from Staib Instruments (15 keV). We operated the electron gun at 11 keV, with the beam at a grazing incidence angle of about 2°. The Cu(111) crystal

was previously cleaned in UHV by argon ion sputtering with an energy of 900 eV and subsequently annealed at 600 °C. After this treatment, the RHEED patterns of the samples showed very sharp streaks, suggesting atomically flat terraces with an extension of hundreds of nanometers. Pd deposition was performed typically at a rate of 0.72 ML/min by electron beam evaporation. Highpurity (>99.9%) Pd was used as source material and during evaporation the residual gas pressure was below 8×10^{-10} mbar. Chemical cleanliness check of the sample was performed by X-ray photoelectron spectroscopy (XPS) and showed no contamination. Nominal Pd thickness (t_{Pd}) was calculated by *time×growth rate* of each e-beam evaporator.

The RHEED diffraction pattern was recorded on a fluorescent screen using a high-sensitivity CCD-camera and a video recorder linked to a computer using the KSA400 software for imageprocessing. This setup permitted us to analyze in detail the various aspects of pattern evolution, such as streak positions (distances) and widths as a function of time. Intensity profiles were done along predefined regions and the peaks were numerically analyzed through peak-fit procedures enabling an accuracy of a few tenths of a percent in the lattice parameter determination.

3. Results and discussion

In order to clarify how the growth mode evolves we show in Fig. 1 the variation of the (0,0) spot intensity along the [112] azimuth during the growth of 7 ML-Pd on Cu(111) at room temperature. Besides a singular minimum, no RHEED oscillations are observed. Since RHEED oscillations are only seen when the surface regains smoothness after completion of each monolayer, this means that in our case it is not clear that Pd grows atomically smooth epitaxial layers on Cu(111) i.e., Pd does not grow in a "perfect" layer-by-layer mode on Cu(111) but something more complex happens. In addition to that no significant degradation of the RHEED pattern is seen after 10 monolayers, meaning that the Pd film is still quite smooth. Growth of Pd on Pd(111)



Fig. 1. RHEED intensity as function of time of Pd evaporation on Cu(111). Inset: RHEED oscillations that was used to calibrate the evaporation rate.

[12] at room temperature indicates the presence of flat film morphology after 5 ML, which also does not mean that homoepitaxial Pd-growth occurs in a perfect layer-by-layer mode. Several possibilities could be mentioned here which would cause the absence of RHEED oscillations [13,14] such as (i) premature nucleation of the next layer before completing the first, (ii) formation of a steady-state terrace distribution corresponding to the transition from island to step flow growth, and (iii) macroscopic growth rate variations across the sample surface.

As no oscillations were seen it was not possible to calculate the growth rate from this experiment. Calibration of the flux sensor of the Pd e-beam evaporation source was achieved through another experiment where Pd grows layer by layer. RHEED oscillations as a function of the evaporation time for the system Pd(111) + $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -Sb are shown in the inset of Fig. 1. Those RHEED oscillations are not exactly periodic—see that time intervals between maxima are 1.5, 1.0, 1.4, 1.5 min. A Fourier transform of these oscillations delivers two components with comparable amplitudes and periods 1.38 and 1.79 min, corresponding to 0.72 and 0.58 ML/min

deposition rates respectively. The presence of the main peak of the Fourier transform (0.72 ML/min) is corroborated by a simple calculation: we see 5 periods in $\approx 6.9 \text{ min} (5/6.9 = 0.72)$. The 0.58 ML/ min Fourier contribution is most probably due to some non-constancy in the deposition rate. Thus from these RHEED oscillations we assume a growth rate of 0.72 ± 0.05 ML/min. When depositing Pd on Cu(111) the evaporation source was operated at the same power. We also checked the growth rate by examination of the ratio of the XPS Pd-3d and Cu-3p lines according to $I_{\rm Pd}/I_{\rm Cu}(d) = I_{\rm Pd}^{\infty}$ $[1 - \exp(-d/\lambda_{\rm Pd})]/I_{\rm Cu}^0 \exp(-d/\lambda_{\rm Pd})]$ $\lambda_{\rm Cu}$), where $I_{\rm Pd}(I_{\rm Cu})$ is the intensity of the Pd-3d (Cu-3p) line, d is the film thickness, $\lambda_{Pd,Cu}$ are calculated electron mean free paths of the XPSlines, I_{Cu}^0 denotes the substrate line intensity before deposition and I_{Pd}^{∞} the line intensity of a very thick Pd overlayer when the substrate line is no longer visible. It must be pointed out that this $I_{\rm Pd}/I_{\rm Cu}(d)$ formula assumes a layer-by-layer growth mode and an abrupt Pd/Cu interface, what may not be exactly the case here. For films thicker than 5 ML this formula leads to an error of $\approx 10-15\%$ by neglecting Pd-Cu intermixing within 1 ML. The good RHEED quality at d = 5 ML indicates a smooth film and in this way a growth rate of 0.7 ± 0.1 ML/min was estimated, which agrees well with 0.72 ± 0.05 ML/min from the RHEED experiment.

The in-plane lattice spacing a_{\parallel} during Pd deposition was obtained by measuring the distance between two RHEED streaks, i.e., the *k*-space separation of the (-1,0) and (1,0) intensity maxima (Fig. 2) during growth. Its evolution as function of Pd coverage on Cu(111) plotted in Fig. 3b indicates that:

- (a) The film assumes initially the in-plane lattice parameter of Cu(111) and with increasing Pd-coverage it evolves rapidly, but not in a step-wise manner, to the "natural" lattice parameter of Pd(111);
- (b) At approximately 1 ML of Pd the in-plane lattice parameter is almost equal to that of Pd(111), which clearly evidences the fact that the first Pd layer atoms do not occupy the threefold site of the fcc Cu(111) surface.

Observation (b) was also noticed by Pessa and Jylhä [6] from LEED measurements, however they do not report on details of stress relaxation during growth of the first Pd atomic layer. From our RHEED measurements we conclude that one monolayer thick islands relax *progressively* its stress increasing the (lateral) lattice parameter. To explain such observations for submonolayer coverage four possibilities are discussed:

- 1. Pd has grown in the form of 3D islands with a linear variation of the lattice parameter as they increase in size. This hypothesis can be discarded since several works [7–9] indicate quasi layer-by-layer growth mode up to high-coverage.
- 2. For low-coverages the surface consists of monoatomic Pd terraces with an average lattice parameter of uncovered Cu(111). For low-coverages of Pd the mean radius of the terraces is small and as the coverage approaches 1 ML or more, by RHEED we could see only Pd and the lattice parameter tends to the Pd-Pd atom distance. Such behavior would give rise to a significant broadening of the outer two peaks in Fig. 2d between 0.25 and 0.75 ML of Pd coverage, which is definitively not the case. An analysis of the RHEED line shape (Fig. 3a) indicates only a slightly broadening of the intensity profiles, which is not compatible with the coexistence of two different lateral lattice parameters.
- 3. When the islands are still small the absence of nearest neighbor atoms forces the Pd atoms to assume nearly the substrate atom spacing. As the 1 ML thick Pd-islands grow laterally the stress relaxes continuously until it reaches the surface net atom spacing of bulk Pd(111). Such mechanism has already been postulated for fcc-Fe films on Cu(100) [15].
- 4. Pd is being incorporated (substituting) Cu in the first atomic layer. In this case Vegard's law [16] would be appropriate to describe the progressive increase of the equilibrium lateral lattice parameter by alloying.

The reason we find the fourth possibility the most reasonable in relation to the third one is

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Fig. 2. RHEED images along the $\langle 112 \rangle$ azimuth of (a) clean Cu(111) and (b) after 10 min evaporation of Pd; (c) streak intensities (profile) along the dotted line indicated in (a) and (b); (d) evolution of the line profile of the RHEED pattern from clean Cu(111) up to 7.2 ML Pd coverage. The distance of the outer peaks is inversely proportional to the surface lateral lattice spacing.

because STM [10] indicates random surface alloying for submonolayer growth at room temperature. From a pair-correlation analysis of the Pd positions the authors argue: "it is safe to conclude that all the Pd atoms are alloyed into equivalent positions, undoubtedly substitutional sites". The work of Hasegawa et al. [8] shows STM and work function images of a 1 ML Pd-film on Cu(111) and did not explore what happens for d < 1 ML. If this work did not evidence any intermixing for d = 1 ML it is not the case not agreeing with this result, because that could even be an indication of de-alloying at this coverage (1 ML)—of course assuming that there is alloying for submonolayer growth. Another indication that Pd has the tendency to alloy with the Cu(111) substrate is the already cited PED study [11], although the authors gently annealed the sample at 320 °C. It should also be mentioned that for the Pd/Cu(100) system, alloying of Pd in the first layer is observed experimentally by STM [17,18] and LEED [19] studies. Also, simulations on Pd/Cu(100) based on the BFS-method [20] suggest the formation of an ordered alloy. In the case of

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Fig. 3. (a) Average of the linewidths (FWHM) of the (-1,0) and (1,0) intensity profiles in a horizontal direction in Fig. 2a and b as function of Pd coverage/growth time—below 0.4 min (0.3 ML) linewidth evaluation is not possible because of saturation of line intensity (see Fig. 2d); (b) evolution of the inplane lattice parameter a_{\parallel} .

Pd on Cu(110) STM [21,22] measurements indicate that ordered (2×1) PdCu islands are formed. In the bulk the PdCu system exhibits two ordered alloys, namely PdCu with structure B2 and Cu₃Pd with structure L1₂ [23,24]. In summary Pd alloying at least in the first layer is a general trend.

3.1. Comparison with Pt/Cu(111)

Pt and Pd are isoelectronic and have nearly the same lattice parameter (3.92 and 3.89 Å, respectively). The structure of the Pt/Cu(111) interface has been studied by PED [25–27] and the authors concluded that no alloying occurs at room temperature, and reported the formation of a Cu₃Pt alloy at 350 °C. More recent RHEED [28] and low-energy ion scattering (LEIS) [29] investigations of Pt on Cu(111) indicated that the lattice parameter during the growth of the first monolayer is basically equal to that of pure Cu. With more than one monolayer deposited the lattice parameter increases steeply to 2.65 Å, and then increases monotonically up to the Pt(111) atom

distance after more than five monolayers. We understand the abrupt lattice parameter increase as a transition from the pseudomorphous to the non-pseudomorphous growth mode, being 1 ML the critical thickness for perfect epitaxial growth of Pt on Cu(111). It could be also an indication of surface alloying at 1 ML but we found no report of Pt–Cu alloying at room temperature in Refs. [28,29]. The shape of our (through RHEED) calculated "lateral spacing evolution" of Pd/Cu(111) behaves differently as compared to the Pt/Cu(111) case (see Fig. 2 of Ref. [28] and Fig. 3 of Ref. [29]). In the present paper the lateral spacing change is gradual, with no indication of two components as is clearly seen in the Pt/Cu(11) case.

4. Conclusions

Our RHEED analysis at room temperature clearly revealed that epitaxial Pd films on Cu(111)do not grow by the Frank-Van der Merwe mode but exhibit a more complex growth mechanism. We pointed out three possibilities for the absence of RHEED oscillations and our conclusions are as follows: (i) all authors agree with a quasi layer-bylayer growth, so premature nucleation may not be the case. (ii) Although theoretical works suggest that strained surfaces (induced by misfit) may promote step-flow growth mode [30], the present work shows that there is no surface stress. (iii) Most probably *macroscopic* growth variations across the sample are responsible for the absence of RHEED oscillations-to be sure, the influence of the macroscopic growth parameters (e.g. sample temperature and flux to the surface during deposition) should be better investigated.

Due to the lattice mismatch between Pd and Cu (7.6%), which means a compressive stress for the Pd layers on Cu(111), perfect pseudomorphous growth is not observed, not even in the earliest stages of growth (n < 1 ML). By monitoring the in-plane atom spacing of the overlayer film we concluded that the equilibrium value of bulk-Pd(111) is attained after about 2 monolayers. Our most striking result is the observation of a drastic, but progressive, variation of a_{\parallel} in the film surface in the early states of Pd growth (n < 1 ML) which

can only be understood if one assumes surface alloying. This is in accordance with [10] where Pd-Cu intermixing at room temperature submonolayer growth was observed. The absence of superstructure peaks on the RHEED patterns during Pd evaporation led us to the conclusion that a random alloy is formed in those earlier stages of growth. We cannot exactly determine over how many ML the alloy is established. We presume it happens only in the first layer but more detailed investigations are needed to answer that. The work of Bach Aaen et al. [10] concludes that Pd atoms are alloyed into equivalent positions, undoubtedly substitutional sites at room temperature, as they mention. Besides that it is argued that at lower coverage the Pd atoms are incorporated mainly in the upper terraces at steps. They even propose the process for that-Pd atoms stay on the terrace where they land, migrate to the ascending step and form an alloy with Cu released from the step, the step retracting in this process. Such process has already been observed for Pb on Cu(111) by STM [31]. Coming back to Bach Aaen's work, STM images of a 0.2 ML Pd covered Cu(111) crystal at RT show dark lines within the brims and islands (Fig. 2b of [10]) where alloying takes place. In their discussion it is argued the following: "the nature of the line structure observed in the brims is unknown, but the lines are reminiscent of fcc to hcp-stacking domain boundaries observed as strain relief mechanisms on (111) surfaces for unmatched metal-on-metal system overlayers". If alloying increases continuously the lateral atom spacing as we are suggesting, at submonolayer Pd coverage the "alloy film" or "alloy islands" would be stressed and produce as well misfit dislocations within the brims and islands.

The origin of the completely different behavior of the PdCu and PtCu systems at room temperature is an interesting issue. Up to 1 ML of Pt on Cu(111) growth appears to be pseudomorphous, with no indication of alloying. But above 1 ML the change to a non- (or quasi-) pseudomorphous growth mode is evidenced by the discontinuous change in lateral lattice spacing—from 2.55 to 2.65 Å. In the Pt/Cu(111) case, only after more than 5 ML the lateral atom spacing of Pt (2.77Å) is attained, while only 2 ML are needed for the Pd/ Cu(111) system. Despite of Pd and Pt being chemically closely related and having almost the same lattice parameters as already mentioned, some differences between them exist. First, Pt has a very large surface stress in contrast to Pd. Second, Pt(111) supports a partially occupied surface state band, while Pd(111) has its surface state located above the Fermi level. At this point we can only wonder if one or both facts are responsible for the different growth behavior of Pd and Pt on Cu(111).

Thus, we propose that a random alloy interface relaxes the strain in the Pd/Cu(111) system up to one monolayer and that with further increasing coverage, pure Pd layers are formed, since the inplane lattice parameter equals the expected value for Pd. The question remains if above some Pdthickness, the Pd–Cu transition interface is "dealloyed", and a sharp Pd–Cu interface is established as it happens for example in the Ag/ Cu(100) system. We hope this and other questions on the Pd–Cu surface/interface growth may stimulate further theoretical and experimental work.

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