Strain Relief in Cu-Pd Heteroepitaxy

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We present experimental and theoretical studies of Pd/Cu(100) and Cu/Pd(100) heterostructures in order to explore their structure and misfit strain relaxation. Ultrathin Pd and Cu films are grown by pulsed laser deposition at room temperature. For Pd/Cu, compressive strain is released by networks of misfit dislocations running in the [100] and [010] directions, which appear after a few monolayers (ML) already. In striking contrast, for Cu/Pd the tensile overlayer remains coherent up to about 9 ML, after which multilayer growth occurs. The strong asymmetry between tensile and compressive cases is in contradiction with continuum elasticity theory and is also evident in the structural parameters of the strained films. Molecular dynamics calculations based on classical many-body potentials confirm the pronounced tensile-compressive asymmetry and are in good agreement with the experimental data.

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Heteroepitaxy with different thicknesses ranging from monoatomic layers up to micrometers produces various structures and is one of the most important routes to artificially obtain functional materials and devices. Stress and its relaxation due to an interface lattice mismatch are an essential problem in the heterostructures. Classical continuum theory defines the concept of an equilibrium critical thickness $h_c$, above which the lattice stress relaxes with the introduction of a misfit dislocation (MD) [1]. The critical thickness is determined by energy balance between strain energy buildup and strain relief due to dislocation nucleation in the mismatched structure. The value of $h_c$ predicted by the continuum theory, however, often does not agree with experiments. Moreover, the critical thickness in the continuum elasticity theory is independent of the strain type, be it tensile or compressive. Atomic details of the interface structure, such as surface steps and surface roughness, are usually ignored. Actual stress relaxation of coherent strained films is kinetically limited, typically with high barriers. Recently, atomistic studies on model systems have been done to determine the transition paths and energy barriers from coherent to incoherent states in real epitaxial films [2–4]. One of the main findings has been a striking asymmetry between the tensile and compressive cases, due to the anharmonicity and asymmetry of the atomic interactions [3,4]. Further, the concept of a size-dependent mesoscopic mismatch has been proposed to explain strain relaxations in the early stage of homoepitaxial and heteroepitaxial metal growth on the atomic scales [5].

In this Letter, we present results from a combined experimental and theoretical study on a model system of Cu-Pd heteroepitaxy grown by pulsed laser deposition (PLD). The bulk lattice parameters of Cu and Pd are $a_{Cu} = 3.61$ Å and $a_{Pd} = 3.89$ Å, respectively. The lattice misfit induces a large compressive ($m = -7.2\%$) strain in the Pd overlayer on Cu(100) and a tensile ($m = 7.8\%$) strain for the Cu overlayer on Pd(100). The Pd films on Cu(100) and the Cu films on Pd(100) were grown by PLD in a multichamber UHV system with a base pressure $p < 5 \times 10^{-11}$ mbar, and $p < 2 \times 10^{-10}$ mbar during deposition. Prior to deposition the copper and palladium substrates were cleaned by cycles of Ar$^+$ sputtering followed by annealing at 873 K for the Cu substrate or 950 K for the Pd substrate until clean Auger electron spectroscopy spectra, sharp low-energy electron diffraction (LEED) spots, and atomically smooth terraces under scanning tunneling microscopy (STM) were observed. The substrate temperature was kept at room temperature during deposition. The substrate was placed about 100–130 mm away from the targets. A KrF excimer laser beam (wavelength 248 nm, pulse duration 34 ns, typical pulse energy 300–350 mJ, and pulse repetition rate 3–5 Hz) was focused onto the targets. During deposition the growth process was monitored by reflection high energy electron diffraction (RHEED). All STM measurements were performed in the constant current mode at a 0.2–0.5 V positive tip bias and a 0.1–0.5 nA tunneling current. Compared to thermal deposition, an extremely high instantaneous flux of atoms in PLD favors much larger nucleation density [6,7]. This helps to suppress the formation of a Cu(001)cg(2×2)-Pd ordered alloy in the initial growth stage for Pd/Cu(100) [8] and the phase transition at 1 ML from fcc to body-centered tetragonal structure for Cu/Pd(100) [9]. Even though the present STM setup does not provide a direct distinction of the Pd and Cu atoms, neither pits in the substrate surface nor
eroded substrate step edges show any evidence of Cu-Pd interlayer mixing. Moreover, the surface area covered by the islands for submonolayer coverages, as determined from STM images, is always consistent with the coverage from RHEED. The RHEED data confirm the layer-bylayer growth mode for both systems. It persists up to at least 5–6 ML in Cu-Pd heteroepitaxy.

Figures 1(a)–1(d) display STM images taken at room temperature for Pd films on Cu(100). For submonolayer Pd at 0.5 ML, many islands with a monolayer height of about 1.80 Å were observed as shown in the inset of Fig. 1(a). With increasing Pd thickness such islands are always formed on a completely filled underlayer up to a total thickness of about 3–4 ML, indicating an ideal 2D growth mode. Above 4 ML a striking feature is the appearance of misfit dislocations as marked by many protruding stripes with an average height of \( \Delta h = (0.57 \pm 0.10) \) Å [see Figs. 1(c) and 1(d)], by which the compressive stress in the Pd film relaxes efficiently. They align nearly regularly along the [100] and [010] directions. The average spacing of MD lines is \( (7.09 \pm 0.30) \) nm for 4.8 ML. The layer-by-layer growth persists up to 6 ML, after which the multilayer growth mode occurs.

The corresponding layer-by-layer growth mode for PLD Cu films on Pd(100) has also been confirmed by STM images as indicated in Fig. 2. At 0.85 ML, second layer nucleation is not found, while in the 2.1 ML thick film more than 95% of the second layer is accomplished [Figs. 2(b) and 2(c)]. At 2.1 ML, few of the islands in the third layer have a preferential orientation, whereas at 3.05 ML most of the fourth layer islands are rectangular along the (110) directions. With increasing Cu thickness to 6.0 ML, 90% of the sixth layer is completed, where nearly all the pits in the sixth layer and the seventh layer islands are rectangular. Above 6 ML the morphology of Cu films is changed because of the multilayer growth mechanism. A typical image for 9.0 ML is given in Fig. 2(f). Four layers appear simultaneously on the surface. Moreover, only 70% of the ninth layer is completed while the remaining 30% appears as the 10th and 11th layers. It should be pointed out that the height or depth of all (ir)regular islands and pits is about 1.65 Å until 9.0 ML as shown in the inset of Fig. 2(e). This vertical magnitude corresponds to the interlayer spacing of highly strained fcc Cu [10]. In PLD Cu films on Pd(100) we have not found any trace of dislocation nucleation up to 9 ML. Above 9 ML, the multilayer island structure with the (110) orientation is still visible and the film surface becomes more and more rough.

IV-LEED measurements of the specularly scattered electron beam were done to obtain structural information on the films. The average interlayer spacing of PLD films was calculated from LEED intensity of the (00) diffraction beam vs energy curves based on a kinetic model [11]. Figure 3 gives the layer thickness dependence of the interlayer distance for both systems. In the case of Pd/Cu(100) films, the interlayer distance is about \( 1.82(5) \) Å up to 3 ML, very close to the value of the Cu substrate, and increases rapidly above 3 ML to reach the value of bulk Pd. For Cu on Pd(100) up to 10 ML, the value stays constant \( (\approx 1.64) \). This agrees well with the measured height of monolayer islands by STM. Above 10 ML the interlayer spacing gradually increases close to the value of bulk fcc Cu at a coverage of 20 ML.

The actual in-plane lattice constant of deposited films was obtained in situ by measuring the spacing between the

![Fig. 1. STM images for (a) 0.5 ML Pd (200 \times 200 nm²), (b) 1.6 ML Pd (200 \times 200 nm²), (c) 4.8 ML Pd (100 \times 100 nm²), and (d) 6.0 ML Pd (100 \times 100 nm²) deposited at 300 K.](fig1.png)

![Fig. 2. STM images for (a) clean Pd(100) substrate (500 \times 500 nm²), (b) 0.85 ML Cu (100 \times 100 nm²), (c) 2.1 ML Cu (100 \times 100 nm²), (d) 3.05 ML Cu (100 \times 100 nm²), (e) 6.0 ML Cu (100 \times 100 nm²), and (f) 9.0 ML Cu (100 \times 100 nm²) deposited at 300 K.](fig2.png)
account for the observed stress relaxation and tensile-relaxation here is to study the thermal excitation and nature of dislocations of the epitaxial layer after deposition. The object chosen to perform equilibrium molecular dynamics simulation experimental conditions is unfeasible. Instead, we have theoretical modeling of the kinetic growth process under the characterization of the PLD growth conditions, a full thermodynamic equilibrium state. Given the lack of precise considerations or whether it corresponds to a true thermodynamic state. The lines are guides to the eye.

In any growth mode, there is always the question whether the final configuration is dictated by kinetic considerations or whether it corresponds to a true thermodynamic equilibrium state. The exact nature of the misfit dislocations is rather complicated, varying both as a function of film thickness and lateral size. In Fig. 5, we show a typical configuration for a film of 7 ML thickness and lateral size. The in-plane strain shows a very different thickness dependence in the case of PLD Cu films on Pd(100). Until 9 ML only a 0.6% reduction is visible and a residual strain is observed until 20 ML. The most striking discovery in our data is the strong asymmetry in the strain relaxation behavior between the tensile and compressive strained films. This result is in direct disagreement with the continuum elasticity theory, which predicts a symmetrical behavior for tensile and compressive systems.

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opposed to a very slowly decreasing attractive part at large separations. This strong asymmetric feature of the interaction is what leads to the observed macroscopic tensile-compressive asymmetry. We have performed additional studies using very different potentials (of the Lennard–Jones-type) with the same general feature, and the results indeed remain qualitatively unchanged. Interestingly, we find that geometry and dimension play an important role in the tensile-compressive strain relief asymmetry. For the 2D model, misfit dislocations are favored for tensile rather than compressive strained systems [3,4]. Clearly, there is much more to learn in strain relief in heteroepitaxy through further theoretical and experimental investigations.

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