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# Strain Driven fcc-bct Phase Transition of Pseudomorphic Cu Films on Pd(100)

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The pseudomorphic growth of Cu on Pd(100) has been studied by tunneling microscopy. Cu films are found to grow layer by layer with a sharp structural transition from a pseudomorphic face-centered-cubic phase (fcc) to a pseudomorphic body-centered-tetragonal (bct, $a = 2.75$ Å, $c = 3.10$ Å) phase with increasing film thickness. The phase transition is driven by the total strain energy of the Cu film, which scales with the temperature dependent Cu-Pd misfit and the film thickness.

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In the search for new materials epitaxial thin films have attracted considerable attention in recent years. The growth of crystalline films on a crystalline substrate (epitaxy) offers the opportunity to create metastable structures with novel physical and chemical properties [1]. The structure and properties of the film can be manipulated by the geometric and electronic structure of the substrate.

In particular, the fact that substantial changes in the film structure and properties can be induced by subtle changes in the lattice strain simulates the search for model systems to study these effects quantitatively and to test the reliability of theoretical predictions. A promising system for the study of the influence of interfacial lattice strain on film structure is the heteroepitaxial growth of fcc metals on (100) surfaces of fcc or bcc metals. As early as 1924, Bain [2] suggested that upon biaxial expansion of the lattice constant in the (100) plane, a fcc solid may transform spontaneously into a bcc or bct (body-centered-tetragonal) phase through relaxation of the interlayer spacing along the perpendicular $c$-axis (see Fig. 1). The Bain deformation involves the smallest principal strains of the martensitic fcc-bcc (bct) transformation. Thus it appears plausible that by *pseudomorphic* growth [3] on (100) metal substrates with a lattice constant larger than the natural adlayer lattice constant, fcc metals might be forced to grow in a metastable bcc or bct structure.

Pseudomorphic Cu layers on (100) surfaces of fcc metals are particularly attractive systems for the search of a Bain transition in ultrathin films. The stable fcc phase ($a = 2.55$ Å, $c = 3.61$ Å) of bulk Cu has extensively been studied experimentally and theoretically and the properties calculated from first principles agree well with experiment. Total-energy calculations of tetragonal distortions by Morrison, Kang, and Mele [4] predicted the existence of two additional metastable bulk phases, a bct phase ($a = 2.76$ Å, $c = 3.09$ Å) upon applying a large biaxial tensile strain in the (100) plane and a bcc phase ($a = c = 2.86$ Å) upon applying additional hydrostatic pressure. The theoretical work of Morrison, Kang, and Mele stimulated experiments on the growth of metastable Cu phases in pseudomorphic epitaxy on Pd(100). This surface has a square unit cell of side $a = 2.75$ Å and appears favorable to stabilize bct-Cu. The low energy electron diffraction (LEED) experiments of Marcus *et al.* [5] showed that up to about 10 monolayers (ML) a flat pseudomorphic Cu film grows on Pd(100) at room temperature. A detailed structural analysis of the 6 ML film revealed a reduced interlayer spacing of $h = c/2 = 1.62 \pm 0.03$ Å consistent with a bct structure.

The existence of the two metastable bulk copper phases has, however, been questioned in a series of theoretical studies [6] subsequent to the work of Morrison, Kang, and Mele, in particular, the bct phase appeared doubtful and was attributed to an artifact of the computations in Ref. [4]. Marcus *et al.* [7] also changed their original interpretation of the LEED analysis of the pseudomorphic Cu film on Pd(100). Based on a strain analysis they suggested that the Cu film should be described as a highly strained fcc phase, and not as a bct phase.

In this Letter we demonstrate that both fcc- and bct-Cu layers grow pseudomorphically on Pd(100). Below a critical thickness Cu continues the fcc stacking of the Pd substrate. Above the critical thickness the $c$ axis relaxes spontaneously and a bct structure with reduced interlayer spacing is formed. The critical coverage for the onset of bct growth increases from 1 ML at 300 K to 3 ML at 400 K. The Bain transition is driven by the total strain energy of the Cu film, which scales with the misfit and the film thickness.

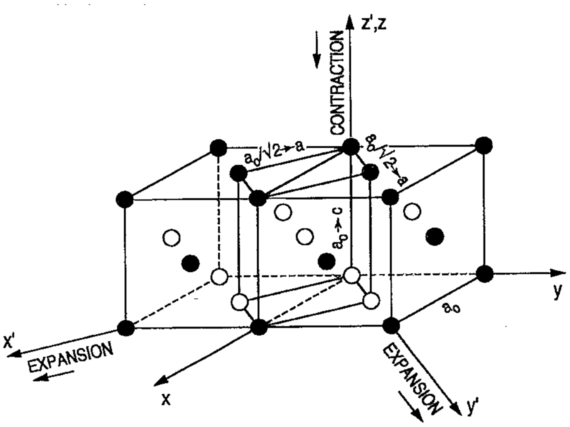

FIG. 1. Lattice distortion and correspondence picture of the fcc-bcc (bct) martensitic transition according to Bain [2].

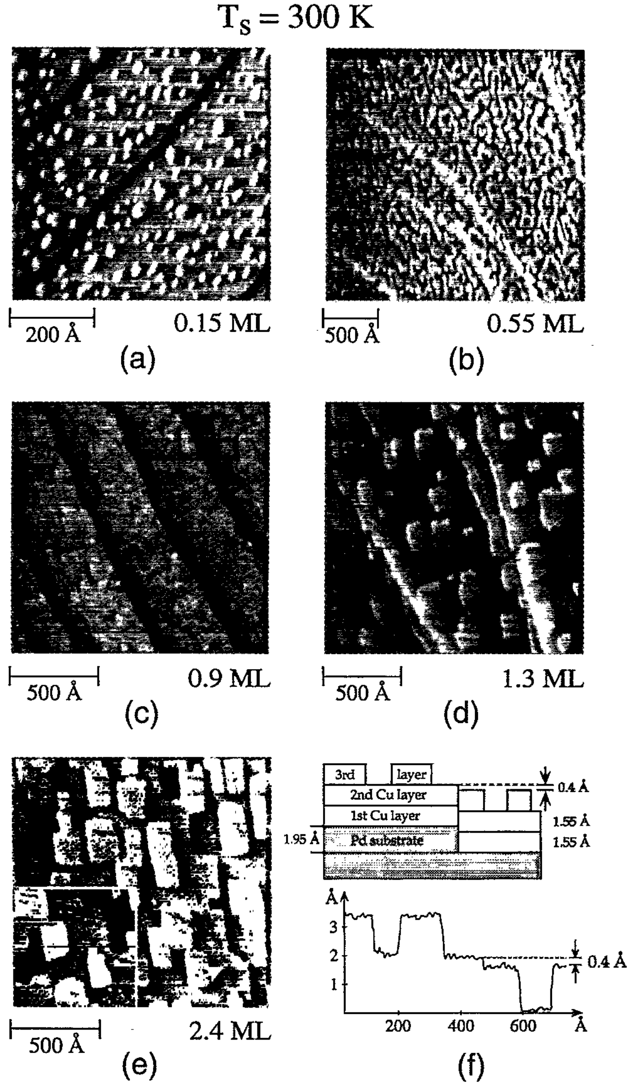

FIG. 2. STM images characterizing the pseudomorphic growth of Cu on Pd(100) at 300 K; the Cu coverage was (a) 0.15 ML, (b) 0.55 ML, (c) 0.9 ML, (d) 1.3 ML, and (e) 2.4 ML. In (f) a line scan from the inset in (e) and the corresponding schematic layer model is shown.

The experiments were performed with a variable-temperature scanning tunneling microscope (STM) described in detail in Ref. [8]. The Cu films (purity 99.999%) were evaporated with a Knudsen cell at a deposition flux of $1 \times 10^{-3}$ ML/s. All STM measurements were performed in the constant current mode at a 0.2–1.0 V positive or negative tip bias and a 0.5–1.5 nA tunneling current. In most STM images the derivative $\partial z/\partial x$ of lines of constant tunneling current was recorded. The images therefore represent the surface as it appears when illuminated from the left. The inset of Fig. 2(e) and images in Figs. 3(c) 1.5 ML and 3(d) 2.5 ML are grey scale images representing the absolute tip height.

Figure 2 displays a series of STM images characterizing the growth of Cu on Pd(100) upon deposition at 300 K. At $\Theta_{\mathrm{Cu}} = 0.15$ ML [Fig. 2(a)], a high density ($1.4 \times 10^{12}$ cm$^{-2}$) of small, irregular-shaped Cu islands is present on the surface. Their average diameter is about 40 Å; the size distribution is rather broad. Their height of 1.9 ± 0.1 Å corresponds to a monolayer of Cu atoms. With increasing coverage, the islands coalesce and percolation patterns are formed [Fig. 2(b)]. Figure 2(c) shows that at $\Theta_{\mathrm{Cu}} = 0.9$ ML, there is still no indication of second-layer island nucleation. Figures 2(d) ($\Theta_{\mathrm{Cu}} = 1.3$ ML) and Fig. 2(e) ($\Theta_{\mathrm{Cu}} = 2.4$ ML) reveal that Cu grows in a layer-by-layer mode at 300 K; only one layer is growing at a time. As indicated by a sharp $(1 \times 1)$ LEED pattern without any additional spots and flat imaging by STM, the Cu film grows in a pseudomorphic structure. The layer-by-layer growth mode continues up to about $\Theta_{\mathrm{Cu}} = 7$ ML; thicker Cu films become rough and disordered (not shown here). These observations are in agreement with the previous LEED study [5]. It is worth noting that also on Pd(110), Cu films are found to grow pseudomorphic up to 5 ML [9].

Closer inspection of Fig. 2 reveals that above a critical coverage of $\Theta_{\mathrm{Cu}} = 1$ ML, a remarkable change in the film morphology and structure occurs. While small, irregularly shaped islands nucleate at submonolayer coverages, above 1 ML well-shaped square and rectangular islands are formed. The island edges are oriented along the close-packed $\langle 1\bar{1}0 \rangle$ lattice directions. The average island density in the second layer of the 1.3 ML film is $1.1 \times 10^{11}$ cm$^{-2}$, i.e., is reduced by 1 order of magnitude with respect to submonolayer nucleation. More importantly, two different step heights are detected in the Cu multilayer range [see arrow in Fig. 2(e)]. The inset in Fig. 2(e) displays a detail of this image in the absolute height representation. From horizontal line scans [Fig. 2(f)], the step heights are determined to be 1.55 ± 0.1 and 0.4 ± 0.1 Å. The sum of the two step heights is equivalent to the interlayer spacing of Pd(100) (1.95 Å), which suggests the model shown in Fig. 2(f). The step height of 1.55 Å corresponds to the distance between two layers of the deposited Cu multilayer film. This value is in good agreement with the value of the LEED measurements (1.62 ± 0.03 Å) and the theoretically predicted interlayer spacing of bct-Cu (1.545 Å). Since this distance is considerably smaller than the step height of the Pd substrate, the boundary between Cu, which has diffused to a step edge, and the adjacent terrace is visible in the STM image and gives rise to the small 0.4 Å step. The flat imaging of the Cu islands by STM, the observation of a sharp $(1 \times 1)$ LEED pattern throughout the whole Cu coverage range ($\Theta_{\mathrm{Cu}} \leq 7$ ML), and the measured interlayer spacing of 1.55 Å strongly support the assumption of a Cu-bct phase growing on Pd(100) at 300 K above a critical coverage of 1 ML.

Figure 4 shows that the 2.4 ML Cu-bct phase with its well-shaped island morphology is unstable towards annealing. At 350 K [Fig. 4(b)], the onset of island coalescence is observed. The shape of the isolated islands

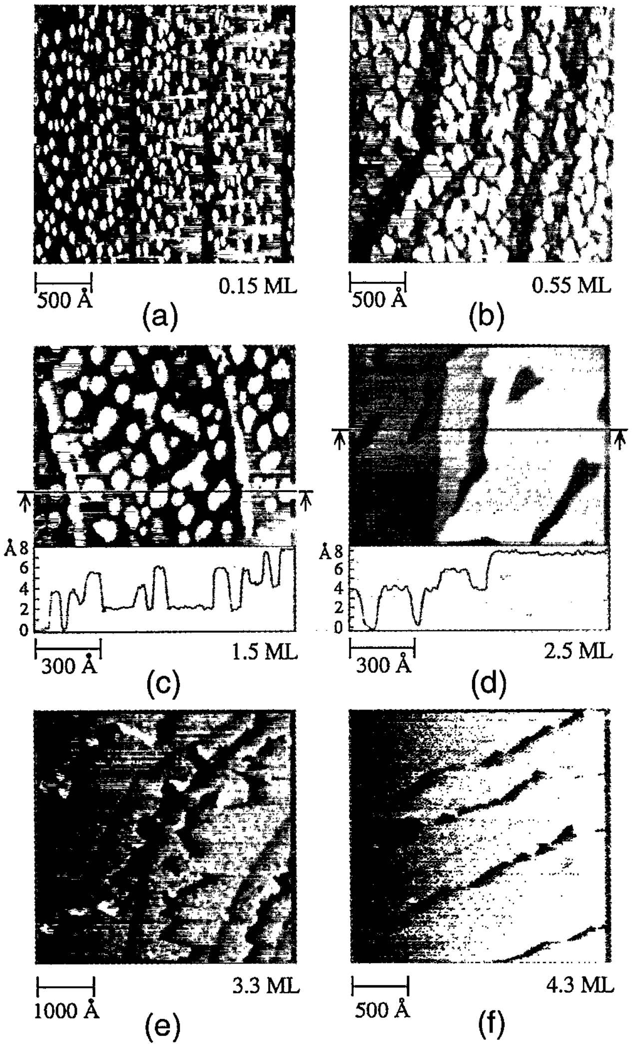

FIG. 3. STM images characterizing the pseudomorphic growth of Cu on Pd(100) at 400 K; the Cu coverage was (a) 0.15 ML, (b) 0.55 ML, (c) 1.5 ML, (d) 2.5 ML, (e) 3.3 ML, and (f) 4.3 ML.

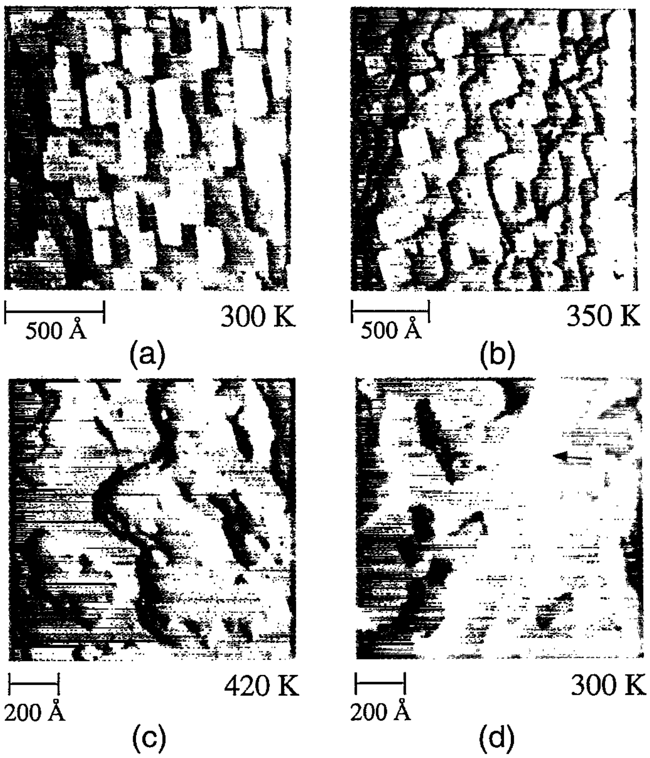

FIG. 4. STM images characterizing the structural change of a 2.4 ML Cu film on Pd(100) upon annealing and recooling. (a) Growth morphology of the 2.4 ML film at 300 K. (b) and (c) Morphology at 350 and 420 K, respectively, and (d) annealing at 420 K and recooling to 300 K.

remains nearly unchanged and the small 0.4 Å step at the former Pd substrate step is still present in the STM image. At 420 K [Fig. 4(c)], the islands have completely dissolved. Cu has diffused to the step edges or forms large patches on the terraces, no straight Cu step edges are present anymore and the topmost two layers form a percolation network. The drastic morphology change of the Cu film is accompanied by a relaxation of the whole film. The small 0.4 Å step has vanished upon annealing to 420 K, which indicates the expansion of the Cu interlayer distance. Only single height steps of 1.85 ± 0.1 Å and double height steps of 3.75 ± 0.15 Å are measured, corresponding within experimental error bars to the interlayer spacing in the Cu(100) fcc bulk structure. The formation of large double-layer structures located on the first flat Cu monolayer (which remains entirely intact) demonstrates that the temperature induced bct → fcc transition involves massive interlayer mass transport including substantial "upward" motion of Cu. The thermal bct-fcc structural transition is a reversible phase transition, as demonstrated in Fig. 4(d). Upon recooling to 300 K, the 0.4 Å step reappears in the STM image [arrow in Fig. 4(d)], indicating the formation of the bct structure with an interlayer spacing of 1.55 Å.

The bct-fcc phase transition of the ultrathin Cu films is not only determined by temperature, but also by the thickness of the Cu film. Figure 3 displays a series of STM images showing the growth of Cu on Pd(100) at 400 K. At $\Theta_{\mathrm{Cu}} = 0.15$ ML [Fig. 3(a)], Cu clusters with an average size of 80 Å are formed. At $\Theta_{\mathrm{Cu}} = 0.55$ ML [Fig. 3(b)], island coalescence has occurred. In the entire submonolayer range the Cu grows two dimensionally and is imaged with a height of 1.9 ± 0.1 Å. After the completion of the first monolayer, one observes the nucleation of small, irregularly shaped Cu clusters [Fig. 3(c)]; the nucleation density ($1.0 \times 10^{12}$ cm$^{-2}$ at 1.3 ML) in the second layer is much higher than upon deposition at 300 K. The surface morphology at $\Theta_{\mathrm{Cu}} = 2.5$ ML [Fig. 3(d)], a percolation network formed after island coalescence, resembles the corresponding submonolayer situation [Fig. 4(b)]. The differences between the growth at this temperature and at 300 K are obvious. The absence of the small 0.4 Å step is accompanied by a striking change in island shape: Instead of large regularly shaped Cu islands, small clusters of irregularly shaped islands are formed on top of the first

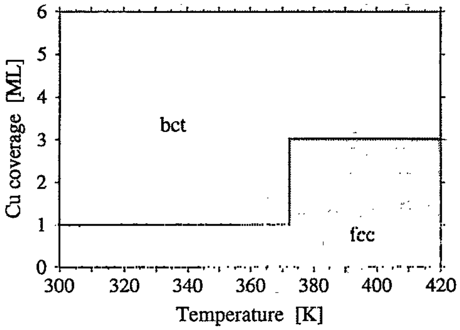

FIG. 5. Schematic coverage-temperature phase diagram of pseudomorphic Cu films grown on Pd(100).

Cu layer. A detailed analysis of the height distribution in the coverage range between 1 and 3 ML at 400 K reveals a double-layer growth of fcc-Cu, as characterized by the simultaneous appearance of monolayer steps of height 1.85 ± 0.1 Å and double-layer steps of height 3.75 ± 0.15 Å [see line scans in Figs. 3(c) and 3(d)].

However, deposition of ≥3 ML Cu at 400 K results in a surprising change of the growth morphology and structure [Figs. 3(e) and 3(f)]. No Cu islands are observed anymore, even on the largest terraces, thus Cu grows in a step-flow mode. The reappearance of small 0.4 Å step is noticed [see Fig. 3(e)], indicating the relaxed Cu interlayer spacing of 1.55 Å. At 4.3 ML, the step edges are smooth and reflect the symmetry of the bct islands found at 300 K. We can thus conclude that at 400 K, the growth of the Cu-bct phase sets in at a critical Cu film thickness of 3 ML. Studies at intermediate deposition temperatures show that below about 370 K, the height of the second Cu layer already corresponds to the interlayer spacing in a bct lattice, whereas at higher deposition temperatures Cu forms a three layer thick fcc film before bct growth starts. This result has been represented graphically in the schematic phase diagram shown in Fig. 5. Note, that at the high temperature end, the phase diagram is limited by the onset of interfacial alloying, which sets in at about 450 K [10].

The delicate balance between the two phases can be explained in an intuitive picture relating the Cu film structure to the total strain energy of the film. Below a critical total strain energy the pseudomorphic film grows fcc with substantial tensile strain; above the critical value this strain is partially relieved by adopting a bct structure with relaxed interlayer spacing. The total elastic energy of a pseudomorphic film is directly proportional to the misfit strain energy, which is proportional to the square of the strain. The misfit strain at the Pd/Cu interface depends on the temperature, since the thermal expansion of both metals is different. The thermal expansion coefficient of Cu is 40% larger ($16.5 \times 10^{-6}$ K$^{-1}$) than the value of Pd ($11.6 \times 10^{-6}$ K$^{-1}$). With increasing temperature the structural misfit between the fcc-Cu and Pd substrate thus decreases. Although this thermal expansion effect is not tremendous, in terms of biaxial strain at the interface it can be decisive in the stabilization of either the fcc or the bct phase, when the system is near the critical strain energy for inducing the phase transition. On the other hand, the total strain energy of the film increases linearly with the film thickness. Based on this idea, the fcc-Cu film has less misfit strain at 400 K and is consequently stabilized up to higher coverages of 3 ML, whereas at 300 K the misfit strain is sufficiently large to increase the total strain energy at 1 ML above the critical value to induce the fcc → bct transition.

We conclude that Cu can grow pseudomorphically on the Pd(100) surface in two crystalline phases, fcc and bct, the actual structure being determined by the total strain energy of the film. While the fcc phase is under considerable tensile strain, the bct phase is nearly strain free. This important conclusion can be drawn from the nucleation behavior and the morphology of both phases. While a large density of small, irregularly shaped islands nucleates in the case of fcc-Cu [Fig. 3(c), 1.5 ML-fc, 400 K, $n_s = 1.0 \times 10^{12}$ cm$^{-2}$], a low density of regularly shaped islands [Fig. 2(d), 1.3 ML-bct, 300 K, $n_s = 1.1 \times 10^{11}$ cm$^{-2}$] is observed in the nucleation of bct-Cu. This difference is a direct consequence of lattice strain in the (100) plane. Large planar strain reduces substantially the contour and kink energy of epitaxial islands [11,12], favoring irregular island shapes and promoting the detachment of atoms from the island perimeter. This enhanced detachment rate generates an increased nucleation density in strained growth [12], which naturally explains the nucleation behavior of the fcc phase with its large lattice misfit of 7.8% ($a_{\text{fcc,Cu-film}} = a_{\text{Pd}} = 2.75$ Å, $a_{\text{fcc,Cu-bulk}} = 2.55$ Å). On the other hand, the very low nucleation density and the well-shaped island morphology of bct-Cu is indicative of a structure under small planar strain. This strongly suggests that bct-Cu is a metastable phase with a local minimum in total energy at a planar lattice constant close to $a \approx 2.75$.

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