hcp and bcc Cu and Pd Films

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Epitaxial hcp and bcc Cu and Pd films were grown on W(100). The epitaxial relation of the hcp films is determined by reflection high energy electron diffraction (RHEED) as $(11\bar{2}0) \parallel (100)$ and $[0001] \parallel [011]$. The growth of hcp Cu and Pd is attributed to the much smaller misfit for this hcp orientation in either the $[1\bar{1}00]$ or [0001] direction, respectively, than for any fcc orientation. This misfit difference overcomes the energy difference between hcp and fcc crystal structure. The atomic diameter of Pd is near that of W, which also gives a good fit for bcc pseudomorphic Pd. The energy difference between hcp and bcc determines the structure. X-ray photoelectron diffraction measurements show a bcc Pd film, transmission RHEED hcp islands. [S0031-9007(96)00963-5]

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The difference in physical properties of thin metal films compared to the bulk material has been the key motivation for the extensive research devoted to the growth of thin metal films. These differences are due to the reduced dimensions or a crystalline structure different from the equilibrium structure. A nonequilibrium crystalline film structure may arise when the lattice constant or symmetry of film and substrate material are different. An example of such a situation is the pseudomorphic growth. In the initial stage the film tends to adopt the crystal structure of the substrate and, thus, will have properties different from that of its bulk. The stress due to the difference in the natural lattice constants of film and substrate limits the thickness of such a pseudomorphic layer usually to 1 monolayer (ML), or a few monolayers if the lattice constant difference is sufficiently small. When the energy gain from the lattice fit becomes smaller than the increase of the volume energy of the strained film, pseudomorphic growth breaks down and the layer usually grows in its natural crystal structure with misfit dislocations at the interface to relieve the strain.

When a nonequilibrium crystal structure provides a much better fit to the substrate lattice than any orientation of the natural crystal structure, the smaller stress can make the nonequilibrium structure energetically more favorable than the natural structure over quite a large thickness. In many transition and noble metals the energy difference between the fcc, hcp, and bcc structures is quite small [1–3]. This suggests that nonequilibrium structures may be grown in rather thick layers if well-matching substrates can be found. Nonequilibrium structures which have been obtained in this manner are, for example, bcc Co on GaAs [4], bcc Co on Cr [5], and bcc Cu on Fe [6]. The bcc orientation of the latter two is obtained because the atomic radii of film and substrate are almost equal. In such a situation, pseudomorphic growth can be extended as the substrate has a lattice constant necessary for an atomic volume-conserving bcc oriented film.

A fcc material can also be forced into the hcp structure during growth if an orientation is chosen in which the fcc and hcp 2D unit cells have different sizes and if the misfit of the hcp structure with the substrate is small. This excludes hcp (0001) (basal plane) growth on fcc (111), because the interatomic distances of hcp and fcc modifications are usually similar. For the hcp $(11\bar{2}0)$ (prismatic plane) the situation is different. Its 2D unit cell is almost square; the difference between the two orthogonal axes being determined by the length of the c axis. The square fcc (100) 2D unit cell of the same material differs from it by at least 25%. The $(11\bar{2}0)$ orientation of a normally fcc crystal could, therefore, be grown on a hcp crystal of the same orientation, but hcp crystals that are suitable as a substrate in heteroepitaxy are rare, let alone that they have a suitable lattice constant. Therefore we chose the square bcc (100) surface as a substrate. The misfit for a $(11\bar{2}0)$ hcp–(100) bcc interface with $[0001] \parallel [011]$ may be described by the differences Δ between the two hcp axes parallel to the surface and the bcc substrate. Δ can be expressed in terms of ρ, the ratio of the atomic radii r and r_{bcc} of the film and substrate, respectively:

$$\Delta_{[0001]} = \frac{2\sqrt{\frac{8}{3}}\,r}{2\sqrt{2}\sqrt{\frac{4}{3}}\,r_{\mathrm{bcc}}} - 1 = \rho - 1\,, \tag{1}$$

$$\Delta_{[1\bar{1}00]} = \frac{2\sqrt{3}\,r}{2\sqrt{2}\sqrt{\frac{4}{3}}\,r_{\mathrm{bcc}}} - 1 = \frac{3}{4}\sqrt{2}\rho - 1\,. \tag{2}$$

The ideal value of $a\sqrt{\frac{8}{3}}$ has been taken for the length of the c axis, with a the lattice constant. In Fig. 1 Δ is shown as a function of ρ. A perfect fit in one direction is accompanied by a misfit of 6% in the other direction. Heteroepitaxial growth under these circumstances is expected to be very anisotropic resulting in strongly elongated crystals, possibly only a few nm wide in the stressed direction. Also in Fig. 1 the value of ρ for Co, Cu, and Pd on a W substrate is indicated. Cu and Pd are representatives of natural fcc materials which have different possibilities for hcp epitaxy, one with small $\Delta_{[1\bar{1}00]}$, the other with small $\Delta_{[0001]}$. Co, for which quite

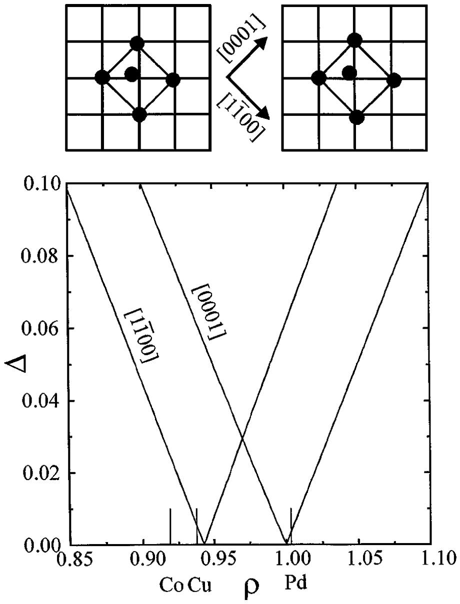

FIG. 1. Lattice misfit Δ as a function of the ratio ρ of the atomic radii for an fcc film on a bcc substrate. Top: Schematic of fit of hcp $(11\bar{2}0)$ orientation to bcc (100) surface for $\rho = \frac{2}{3}\sqrt{2}$ (left) and $\rho = 1$ (right).

recently a $(11\bar{2}0)$ oriented hcp film was reported on GaAs (100) [7], has an atomic radius similar to that of Cu. For Pd, not only the hcp $(11\bar{2}0)$ but also the pseudomorphic bcc orientation gives a good fit as the atomic radius of Pd is about equal to that of W. A competition between the hcp and bcc orientations can be expected, determined by the anisotropic misfit of hcp and the difference in volume energy of hcp and bcc. On the basis of the atomic radii of Rh, Ir, and Pt, a behavior similar to that of Pd is expected, while Ni is comparable to Co and Cu. The radii of Au and Ag are too large to expect hcp or bcc epitaxy on W(100). Nb and Ta with their larger lattice constants provide more suitable substrates for Ag and Au because they have comparable atomic radii.

The heteroepitaxial growth on the W(100) surface has been was monitored with reflection high energy electron diffraction (RHEED). The UHV system used has been described elsewhere [8]. The deposition rates were 0.01 ML/s or less. In Fig. 2 the RHEED patterns for Cu, Co, and Pd layers are shown. Transmission patterns appeared within 0.1 ML at both 150 and 300 K deposition temperatures after 2.5 ML had been deposited. The transmission patterns in Figs. 2(a)–2(c) which were taken with the incident beam parallel to the W[011] azimuth consist of diffuse spots. The elongation of the spots perpendicular to the shadow edge indicates that these patterns arise from very thin small islands. It should be noted that at 150 K up to 40 oscillations in the specular reflected RHEED beam can be seen despite the observation of transmission spots. We will first discuss the Cu and Co results, as for Pd both the hcp and bcc orientations were observed.

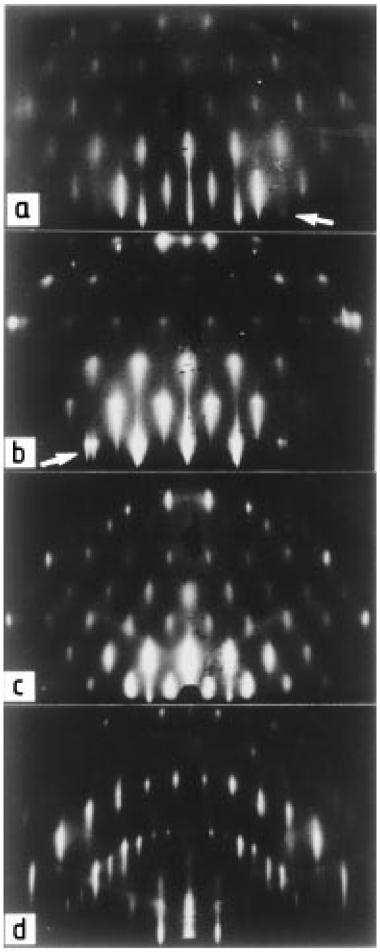

FIG. 2. RHEED patterns observed in the W[011] azimuth of (a) 35 ML Cu deposited at 150 K and annealed for 90 s at 500 K, (b) 3 ML Co deposited at 300 K, and (c) 3 ML Pd deposited at 150 K. The pattern (d) was taken in the W[001] azimuth after deposition of 10 ML Pd at 150 K.

A closer look at the transmission patterns shows that they are due to two superimposed transmission patterns, arising from transmission along the [$1\bar{1}00$] and [0001] directions. The distances parallel to the shadow edge which are determined by the lengths of the [0001] and [$1\bar{1}00$] axes, respectively, are different for the two patterns. For Cu and Co an increased splitting of the spots can be seen with increasing order of the diffraction beams, confirming the existence of the two different periodicities. The width to height ratio of these two rectangular lattices is 1.72 and 1.62 for transmission along the [0001] and [$1\bar{1}00$] directions, respectively. These ratios correspond to the ratios expected for a hcp $(11\bar{2}0)$ oriented film, whose orthogonal [$1\bar{1}00$] and [0001] directions are slightly different. In addition to the transmission pattern, RHEED also shows surface diffraction spots for Cu and Co. Diffracted beams at $(\frac{1}{2}, \frac{1}{2})$ position indicate a $c(2 \times 2)$ unit cell with respect to the W(100) substrate. This pattern was also seen with LEED upon deposition of more than 2 ML of Co and Cu on the W(100) surface at 300 K [9]. The dominating $c(2 \times 2)$ pattern indicates a change in the basic 2D unit cell from the W(100)-(1×1) unit cell to a square unit cell with its axes parallel to the W$\langle 011 \rangle$ directions and a length $\sqrt{2}$ larger than the W lattice constant. This is consistent with a hcp $(11\overline{2}0)$ oriented film for which an almost square unit cell of this size and orientation is expected, see also the inset in Fig. 1.

The two different ratios (1.72 and 1.62) observed for Cu and Co distinguishes this transmission pattern from a fcc (110) oriented film. Such a fcc orientation would be expected from the work of Bruce and Jaeger [10,11]. They found for heteroepitaxy on W(100) heavily faulted fcc (110) epitaxy, the stacking faults indicating an about equal amount of fcc (110) and hcp $(11\overline{2}0)$ orientation. They studied rather thick films (>5 nm) deposited from room temperature upwards and explained the observed epitaxial relations with simple geometric arguments. However, for much thinner layers different structures have been reported [12–15]. This discrepancy between observations on thicker layers and layers up to 10 ML is, on second thought, not surprising. The argument of Bruce and Jaeger for a fcc (110) oriented film with the epitaxial relation $[\overline{1}11]_{\mathrm{fcc}} \parallel [011]_{\mathrm{bcc}}$ or $[1\overline{1}2]_{\mathrm{fcc}} \parallel [011]_{\mathrm{bcc}}$ gives two possibilities for the minimization of the misfit between film and substrate. These two possibilities are the same as those derived for the hcp orientation and depicted in Fig. 1. However, initial growth in the fcc (110) orientation is quite unlikely for the following reason: In the $[\overline{1}11]$ direction the next nearest neighbor distance of the film is 3 times larger than the nearest neighbor distance in the [011] direction of the substrate. This would lead to an alternating fourfold hollow and on-top position of the film atoms, which is quite unlikely to occur. Only a very strong deformation of the fcc lattice angles and/or lengths could eliminate this problem, but this would cause a much higher stress in the film. In thicker films, stacking faults may certainly lead to a partial fcc (110) orientation. A (110) fcc oriented film with the epitaxial relations described above would show a low energy electron diffraction (LEED) pattern different from the $c(2 \times 2)$ pattern observed by us.

The transmission pattern of Pd occurred also after 2.5 ML at both 150 and 300 K deposition temperatures [Fig. 2(c)] . However, in the growth of Pd at 150 K the transmission RHEED pattern disappears at 7 ML and reappears again after 11 ML are deposited. Between 7 and 11 ML only a reflection RHEED pattern can be seen [Fig. 2(d)]. This phenomenon is attributed to changes of the morphology of the film with increasing thickness. A diffraction pattern corresponding to that of Fig. 2(d) has also been observed with LEED [13] beyond 2.5 ML deposition at 300 K. In our RHEED patterns the $c(2 \times 2)$ spots are the strongest, which leads us to describe the pattern as a two domain (2×1) superstructure of a $c(2 \times 2)$ unit cell. This $c(2 \times 2)$ unit cell is the same as that observed in the Cu and Co epitaxy. For Pt on W(100), a similar type of structure, a two domain (3×1)-$c(2 \times 2)$, was reported [15]. These diffraction patterns exclude the fcc (110) epitaxy, but cannot discriminate between bcc and hcp orientation. The film may have, as the bcc W(100) surface, a $c(2 \times 2)$ reconstruction. The transmission pattern of Pd [Fig. 2(c)] is slightly different from that of Cu and Co. The splitting with increasing order of the diffraction spot cannot be seen, but this can be obscured by the large sizes of these spots. However, the odd vertical rows with transmission spots are not in the middle of the even vertical rows in Fig. 2(c). The deviation from the middle position of about 5% of the first odd row is due to the two different azimuths of a hcp $(11\overline{2}0)$ oriented film. The transmitted islands have hcp structure. To investigate the coexistence of the hcp and bcc structure, we measured the angular distribution of the x-ray excited Pd 3d photoelectrons. Figure 3 shows the Al $K\alpha$ x-ray photoelectron diffraction (XPD) pattern measured in the W[011] azimuth for a 20 ML thick film which showed the discussed RHEED hcp transmission pattern. Intensity maxima around 25°, 35°, and 54° indicate a bcc (100) oriented film. The maxima expected for a hcp structure around 30° and 60° which we observed for the hcp Co layer either are obscured by the bcc contributions or are outside the experimentally accessible range. Therefore it seems that the sample is predominantly bcc. However, the islands on the surface are hcp.

The growth of Pd on W(100) may be compared with a recently reported study of the growth of Co on Cr [5], for which $\rho = 1.004$. Starting from a pseudomorphic bcc oriented film, a hcp $(11\overline{2}0)$ oriented film was observed after 50 Å. The close connection between the square bcc (100) and the almost square hcp $(11\overline{2}0)$ makes a change from one to the other orientation possible, with only a small shift of the atom within the unit cell in Fig. 1. The growth of a bcc or bct film has been reported for Cu on Fe [6] with $\rho = 1.03$ and Ni on Fe, with $\rho = 1.004$ [16]. Also in these systems the growth of hcp and bcc orientations should be in competition. The bcc orientation found provides a very good lattice fit in both directions parallel to the surface and is more likely to occur from

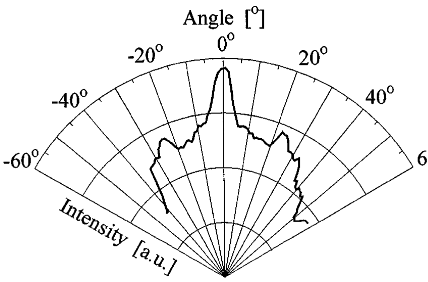

FIG. 3. Pd 3d XPD spectrum of 20 ML Pd on W(100). The polar angle is rotated in the [011] azimuth.

the misfit point of view. The volume energy of the noble metals and the nearly filled *d*-shell metals, however, favors the fcc structure, followed, in general, by the hcp and the bcc structure [1–3]. For Co/Cr this sequence indicates preferred growth of the square bcc lattice in the initial stage. With increasing thickness, the higher volume energy of the bcc lattice leads to a change towards the hcp structure. The elastic properties of bcc Co [17] show that this structure is unstable, so that a change towards hcp after a critical thickness is very likely. For Pd, the volume energy of the bcc structure is calculated to be smaller than that of the hcp structure [1]. This would explain the bcc orientation of the Pd film grown on W(100) found with XPD. However, the transmission patterns show hcp islands, which indicates that hcp is preferred above bcc if the lattice misfit loses its importance. Our measurements thus indicate that hcp has a lower volume energy than bcc. However, the hcp orientation is limited to the islands as the bcc orientation is preferred due to the excellent fit to the W substrate. For the 3*d* transition metals, the optimization of the length of the *c* axes has been shown to give a lower energy for the hcp structure [3] than that obtained by Skriver [1]. Also the inclusion of spin-orbit coupling and spin polarization can lead to different results [2]. In the Cu/W system, the misfit is too large for the bcc structure to be of importance. The energy difference between fcc and hcp structure is very small (<10 meV/atom [1,3]) and a stable hcp Cu film can be expected.

In conclusion, we have provided evidence for the growth of hcp and bcc oriented Cu and Pd films on W(100). The hcp structure can be readily explained by the small misfit between the hcp $[1\bar{1}00]$ and [0001] axes and the W$\langle 011\rangle$ axes. In the case of Pd the atomic radius is equal to that of W, which gives also a good fit for a bcc Pd film as has been measured. The difference in volume energy determines the structure of thicker films in this case. In the initial stage the bcc structure is preferred due to the good pseudomorphy. By choosing a film/substrate combination with ρ close to 0.94 instead of $\rho \approx 1.00$ the mixing of hcp and bcc structure can be overcome.

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