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Fast interdiffusion in thin films: Scanning-tunneling-microscopy determination of surface diffusion through microscopic pinholes

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Diffusion of substrate material to the surface of some epitaxial thin-film systems has been reported to occur very rapidly, even at temperatures below 40% of the melting points of film and substrate, where bulk interdiffusion should be negligible. *In situ* scanning tunneling microscopy reveals that the Cu diffusion through ultrathin Co films grown under ultrahigh vacuum onto Cu(100) substrates occurs via a surface diffusion process, not via bulk interdiffusion. During annealing, pores nucleate in weak points of the films, e.g., near step bands of the substrate. As Cu diffuses from the substrate through the pores to the top of the film, pits of up to several tens of nm linear dimensions are formed.

In thin-film science, the very preparation of films is an issue far from general consensus. Even slight variations of growth conditions like deposition rate or substrate temperature sometimes lead to films with quite different microscopic structure. This is so because many thin films are not thermodynamically stable structures: their formation relies on kinetic limitations in the growth processes, which prevent the condensation of three-dimensional islands. Films grown under such conditions often contain a notable density of defects, such as dislocations or a high surface step density. One common approach to fabricate films with a relatively low density of defects is to grow the films under nonequilibrium conditions (preventing island formation) and then to anneal the films (to heal out the defects).

Recently, in several thin-film systems, this approach has been found to produce a somewhat surprising effect: by annealing, not only defects are healed, but also the films become covered by a single monolayer of substrate material, which is thought to somehow diffuse through the films during annealing. Such instabilities have been reported to occur in the systems Fe/Au(100),[1] Au/Ag(111),[2] Ni/Cu/Nu(100) sandwiches,[3] Rh/Ag(100),[4] and Co/Cu(100).[5] A recent theoretical calculation[6] predicts sandwich formation in the system Au/Ag(110) as an energetically favored growth mode.

The present scanning tunneling microscopy (STM) study demonstrates that in the Co/Cu(100) system, the dominant mechanism by which substrate material diffuses to the film surface is not some kind of enhanced bulk interdiffusion, but rather the diffusion of substrate atoms on free surfaces of the film. We have resolved the topographical features caused by the penetration of the film by substrate atoms. The interdiffusion occurs in a way similar to some of the mechanisms proposed by Egelhoff to explain his x-ray diffraction results on the Ni/Cu/Ni(100) system:[3] Cu atoms diffuse up along the walls of microscopic pinholes. Activation energies for surface diffusion are typically significantly lower than activation energies for bulk diffusion, thus our observations offer a simple explanation as to why these segregation processes occur at higher rates and lower temperatures than one would expect from known bulk interdiffusion data.

The Co/Cu(100) system is an important model system for the study of magnetism in the two-dimensional limit. Magnetic and electronic properties determined in experimental studies are highly sensitive to the degree of structural perfection of the films; precise control over film fabrication conditions is therefore essential.[7,8] For the Co/Cu(100) system, room-temperature deposition under UHV conditions is known to lead to pseudomorphic epitaxial growth in a monolayer-by-monolayer mode. The growth occurs via formation of two-dimensional monolayer islands in the typical size range of a few nm.[9] It has been established that by annealing Co/Cu(100) films grown at room temperature, surface smoothness can be improved.[10]

Interdiffusion at the interface has long been thought to be a problem in Co/Cu(100), when the sample temperature was raised to above ~450 K.[7,8,11] It is clear that interdiffusion is not impossible: By heating to approximately 1000 K, the Co films can be dissolved completely into the substrate.[12] However, below approximately 700 K, the phase diagram of Co/Cu (Ref. 13) indicates that the solubility of Co in Cu practically disappears, which means that the interface should be expected to remain sharp. Nevertheless, in Co/Cu(100) growth experiments performed at much lower temperatures, i.e., 460–520 K, the ratios of peaks in the Auger spectra of Co and Cu have been observed to show a temperature-dependent behavior.[7,11] In the cited work, this had been attributed to an interface alloying process. As Li and Tonner[5] have pointed out, annealing of Co/Cu(100) films does not necessarily lead to alloying but results in a Cu/Co/Cu(100) sandwich structure, with one monolayer of Cu capping the Co film. Our results from this work indicate that the underlying diffusion process is based solely on surface diffusion, rather than on bulk interdiffusion: during annealing, substrate material diffuses up along the walls of pinholes, to cover the Co film.

In our experimental setup, the growth of Co/Cu(100) thin films is observed by *in situ* STM.[14,9] This method can be used not only to judge the surface quality of films, but also as an accurate way to directly monitor film thickness. After preparation in the STM stage, the thin-film samples are transferred to a stage equipped for sample annealing and for Auger electron spectroscopy. For detailed studies of the annealing effects, our STM design allows individual regions on the sample surface to be retrieved again even after sample transfers.

Figure 1 shows topographical STM images of the same region of a 3.2-monolayer Co/Cu(100) film, before [Fig. 1(a)] and after [Fig. 1(b)] annealing. (Images shown in this paper were taken at a constant tunneling current of typically 0.5 nA and 1 V positive bias applied to the sample.) Two main effects are immediately evident.

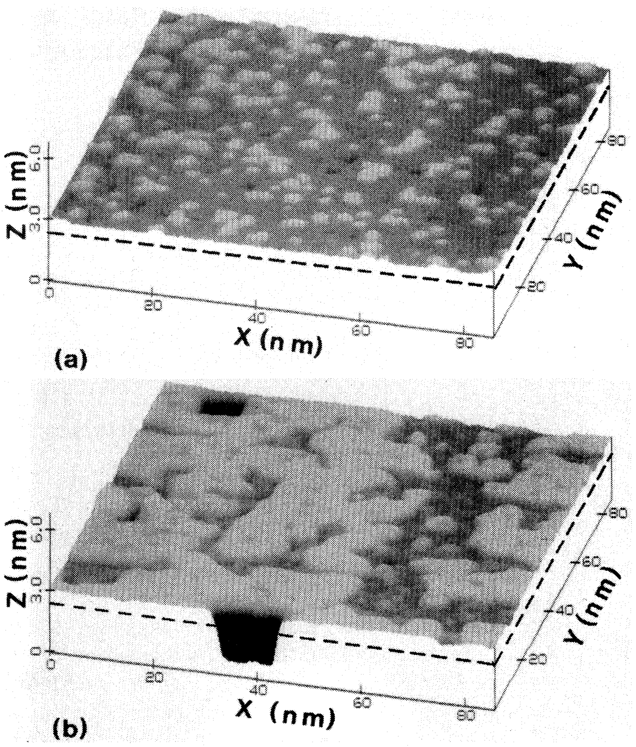

FIG. 1. 85×85 nm^2 STM images showing typical surface profiles of just over 3 monolayers Co/Cu(100). (a) Before annealing: the incomplete top-layer consists of typical islands of the fourth layer of Co. (b) The same location on the sample after annealing for 1000 sec at 490 K: the surface is generally smoother, but also characteristic rectangular pits reaching deep into the substrate have formed. The dashed lines indicate the approximate position of the film/substate interface. Edges of pits usually follow (011) and (01$\bar{1}$) axes.

(1) The film surface roughness, characteristic of the room-temperature growth, is significantly reduced after annealing: monolayer islands belonging to the incomplete topmost layer have increased in size by typically approximately one order of magnitude.

(2) Rectangularly shaped pits have formed in the film surface. Diameters of these pits are typically in the range of 10 nm and many of the pits are found to be at least several nm deep. Their depth is thus much greater than the total thickness of the original Co film.

The first observation is not surprising; it can be attributed to a process analogous to Oswald ripening, i.e., larger top-layer islands have grown at the expense of smaller ones. The second observation is more surprising. It raises the obvious question of where the material, which had previously been filling the location of the pits, has gone. At the temperatures used in these experiments (≤ 500 K), sublimation can be ruled out.

A clue to explain the pit formation is found by recording the Auger electron spectrum of a Co/Cu(100) thin film during annealing. In the data plotted in Fig. 2, the Cu(920 eV) line and the Cu(60 eV) line were scaled by the nearest Co lines: Co(716 eV) *LMM* and Co(53 eV) *MNN*, respectively. The figure shows the evolution of the scaled Auger intensities during the annealing of a 4-monolayer Co/Cu(100) film. To allow a direct comparison of the low-energy Auger intensity ratios and the high-energy ratios, all values plotted in the figure were normalized, i.e., divided by the initial values measured before annealing. At the time $t = 0$, the sample temperature was raised very rapidly (by electron back bombardment heating) to 490 K and then kept constant, within less than $\pm$ 10% of that value, for the rest of the experiment. Two important features evident from this experiment are (1) the Cu(60 eV) signal rises strongly to reach a saturation level and (2) the Cu(920 eV) signal rises very little. Taking the relative rise of the Cu(60 eV) Auger signal alone, several possible conclusions could be drawn: either some intermixing occurred at the Co/Cu interface, or rupture of the film lead to the exposure of Cu substrate material at the surface. Taking account of the 20% increase of the high-energy Auger ratio, intermixing can be ruled out: with the longer mean free path, these *LMM* Auger intensities should show even more drastic changes due to interface intermixing than the low-energy *MNN* intensities, which are sensitive to just the top few monolayers. Looking at the STM images, it is clear that the amount of Cu surface

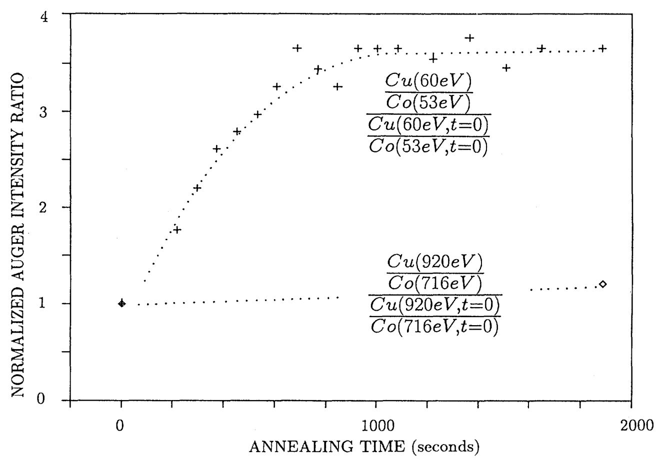

FIG. 2. Auger intensity ratios of the *LMM* and *MNN* lines of Co (at 716 and 53 eV, respectively) and Cu (at 920 and 60 eV, respectively), recorded during annealing. The data were normalized to the initial intensity ratios at the time $t=0$, before annealing. Dotted lines are a guide to the eye.

which is exposed to the vacuum at the bottom of the pits is far too little (below 10% of the total surface) to explain the fourfold increase in the low-energy Auger intensity ratio. The conclusion from these arguments is that a significant amount of Cu must have segregated from the substrate to the surface of the Co film during annealing. A quantitative estimate can be made by calculating relative Auger intensity ratios from electron mean free paths in Cu or Co single crystals. Using reasonable values of ~ 4 Å at 60 eV and ~ 13 Å at 920 eV,[15] we find that the amount of segregated Cu corresponds to roughly one single monolayer.

Closer examination of STM images of the films before and after annealing reveals three main classes of defects as effective nuclation sites for pits: (1) "pinholes," (2) step bands, and (3) rare but severe defects such as clusters of contaminants. All these defects can contribute to the interdiffusion in any particular film. However, the relative importance of the three classes of defects strongly depends on film thickness.

As we have shown in Ref. 9, one characteristic feature of the room-temperature growth mode of this thin-film system is the existence of voids (or pinholes) in the film, within atomically flat regions of the substrate, even at coverages above 1 monolayer. In the 2-monolayer film shown in Fig. 3(a), the characteristic density of such voids is of the order of several thousand per μm^2. After annealing [Fig. 3(b)], small rectangular pits are found on the sample surface in nearly the same density, indicating that the voids present in the film *before* annealing have acted as sources for Cu adatoms to cover the Co-film surface. Due to the high density, these pinholes appear to be the dominant source of Cu during the annealing of Co films below 2.5 monolayer thickness. For increasing coverages above 2 monolayers, the density of these growth-mode-induced pinholes decreases very rapidly—the pinholes get filled in with Co. At coverages around 3 monolayers, perhaps a few hundred pinholes per μm^2 can be found within flat terraces of the substrate. Correspondingly, after annealing, only very few pits are found within atomically flat terraces of the substrate. In these films, step bands, which are always present on well-annealed substrates before film deposition, are the dominant weak regions which allow the nucleation of pinholes. A characteristic example of this effect can be seen in Fig. 4. Beyond coverages of 4 monolayers, even step bands are no longer permeable to the described surface diffusion process. Yet, these films can transform into sandwiches during annealing, provided there is a sufficient density of defects severe enough to create pinholes. One example of such defects can be clusters of contaminations.

The striking rectangular shape of the pits reflects the crystal symmetry. In all images shown here, (011) and $(01\bar{1})$ axes are horizontal and vertical, respectively; the

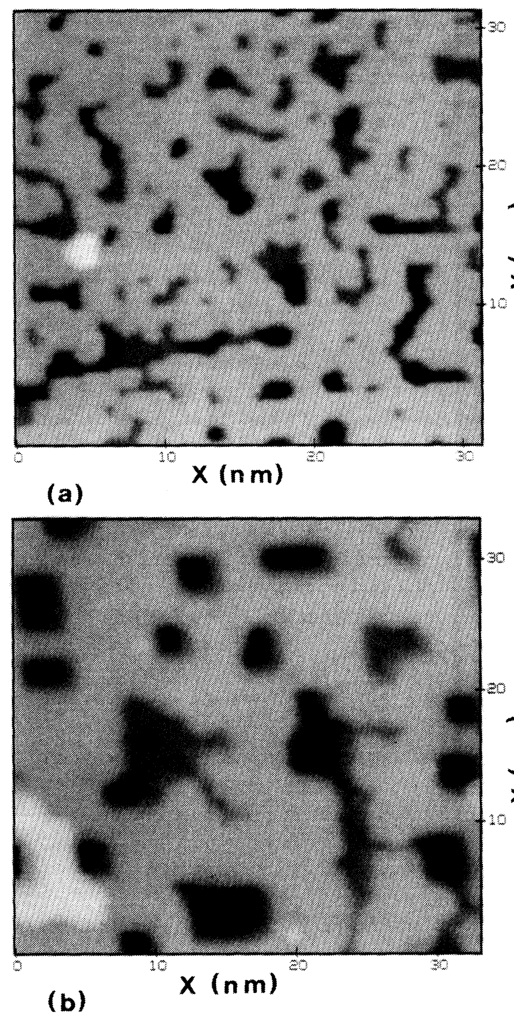

FIG. 3. 30×30 nm^2 regions on a 1.9-monolayer Co/Cu(100) film, before (a) and after (b) annealing 500 sec at 490 K. Gray scaling in (a): Cu-substrate, darkest gray; first monolayer of Co, middle gray; second monolayer of Co, light gray; third monolayer of Co, one small white island. Due to the characteristic room-temperature growth mode (Ref. 9), this 1.9-monolayer film still contains small unfilled voids in a significant density before annealing [irregularly shaped darkest regions in (a)]. During annealing, through such voids Cu adatoms have diffused out to cover the Co film, leaving behind the deep pits [black rectangular features in (b)].

walls of the pits tend to be oriented along these directions. In our STM images, the walls of the pits often appear to have angles of ~50° with respect to the surface plane. We believe that most likely the walls are (111) facets, which would agree with the fact that in fcc crystals, (111) faces have the lowest energy. Due to the problem of tip-shape convolution, however, the possibility of walls even steeper than (111) facets cannot be excluded on the basis of our data.

From the STM data, an estimate can be made of the total volume of Cu, which has left from within the pits. It appears to be less than the equivalent of one flat monolayer. But, the amount of Cu still missing for an interpretation consistent with the Auger data can be found in a systematic error, which is characteristic of topographic STM measurements: due to tip-shape convolution, the volume of pits is usually underestimated.

The interpretation consistent with all our measurements is that during annealing, a surface diffusion process drives Cu from the substrate through pinholes in the Co film to the surface of the sample.

The driving force of this process is the surface free energy σ: literature values indicate $\sigma_{Cu}=1.9$ J m^{-2}, $\sigma_{Co}=2.7$ J m^{-2}, and $\sigma_{CoCu(111)}=0.2$ J m^{-2}.[16,17] Thus, turning a Co/Cu film into a Cu/Co/Cu sandwich lowers the free energy of the system by about 0.6 J m^{-2}. The question remaining to be answered, is the following: why does the system prefer a segregation process, as opposed to three-dimensional clustering of the Co film, which would be expected from the thermodynamical point of view?[18] (Clustering would partially expose the bare Cu substrate and thus lower the free energy even more: ultimately by about 1 J m^{-2}.) The reason lies in the kinetic limitations. For overlayer clustering to occur, the mobility of overlayer surface adatoms must be sufficiently high. In the case of Co/Cu thin films, the mobility of Cu surface adatoms is significantly higher than the mobility of Co adatoms. Therefore, in the given temperature range, the rate at which a single monolayer of Cu can spread over the Co film simply overwhelms the tendency for clustering.

We expect that a large number of other thin-film configurations can transform in the same way upon annealing, provided that the following conditions are met.

(1) Surface free energies relate as $\gamma_{\text{substrate}} < \gamma_{\text{film}}$, while the interface free energy is relatively small.

(2) The mobility of surface adatoms of the substrate species is significantly greater than the mobility of adatoms of the overlayer species.

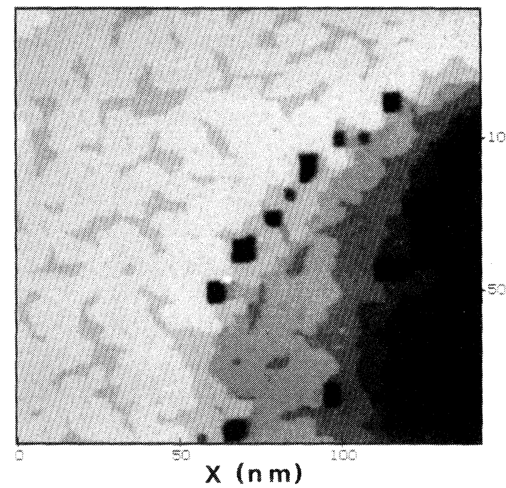

FIG. 4. 150×150 nm^2 image of a 3.2-monolayer Co/Cu(100) film, after annealing 1000 sec at 490 K. A step band, which was already present on the Cu(100) substrate before film preparation, weakened the Co film. As a consequence, pits reaching deep into the Cu(100) substrate (black rectangular features) have formed predominantly in this region.

For most solid elements, the first condition can readily be checked from the literature.[16,17] The second condition is more difficult to judge, as diffusion coefficients are much less well established. Nevertheless, a hint is given by the heat of sublimation, which is fairly well known for many substances; sublimation and surface diffusion are closely related processes, thus the mobility of surface adatoms can be expected to be high, when a materials heat of sublimation is low.[19] Thin-film systems, where similar sandwich transformations may occur thus include, for example, films of Fe, Co, Ni, Pt, . . . , on substrates like Cu, Ag, Mn, and others.

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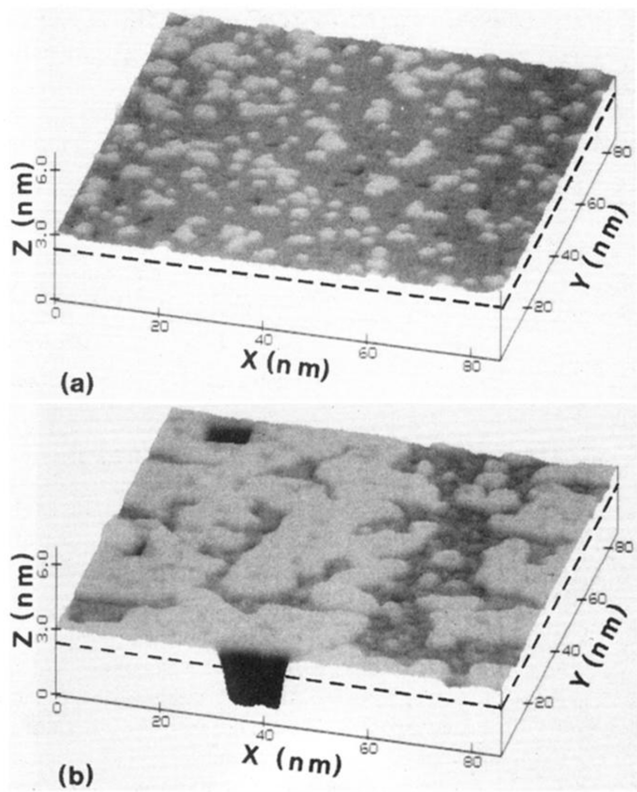

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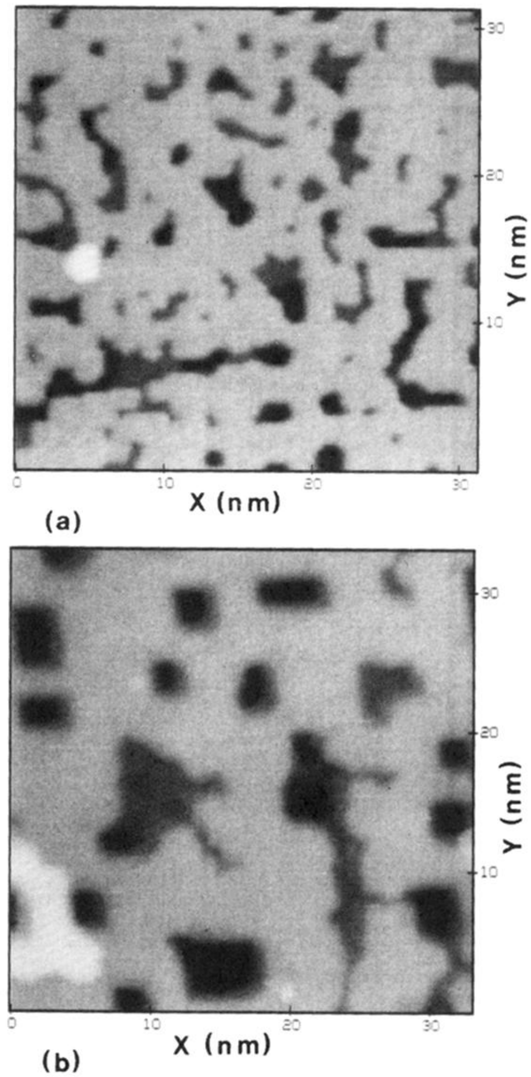

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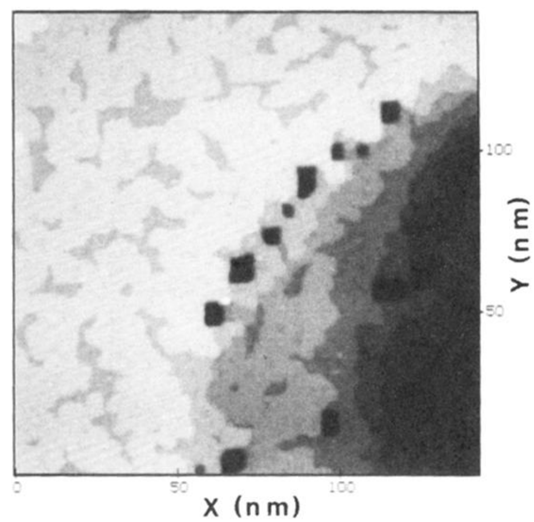

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