Surface Alloy Formation by Interdiffusion across a Linear Interface

A. K. Schmid, J. C. Hamilton, N. C. Bartelt, and R. Q. Hwang
Sandia National Laboratories, Livermore, California 94551-0969
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Interdiffusion profiles across a linear interface separating two metals that are miscible as monolayers [Co and Cu on a Ru(0001) surface] have been measured as a function of time. The interface remains sharp even after substantial intermixing, in dramatic contrast to bulk interdiffusion experiments between miscible metals. The unusual concentration profiles are explained by a combination of adatom surface diffusion and exchange of adatoms with atoms in the monolayer films. A simple Monte Carlo simulation of the adatom exchange mechanism quantitatively agrees with observations. [S0031-9007(96)01011-3]

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The formation of 2D surface alloys has attracted recent attention [1–5] because metals that do not form bulk alloys have been found to produce stable mixed phases at surfaces. To date, investigations have concentrated on identifying the mechanisms for the stabilization of these alloys, but little has been done to address the atomistic dynamics of their formation. However, this latter issue is important since mass transport processes at surfaces can differ greatly from those in the bulk [6]. In this paper, we investigate the atomistic mechanisms in the growth of binary surface alloys by studying the interdiffusion of two surface metals across a sharp 1D boundary formed between the species. By examining the composition profile of this interface as a function of annealing time, we show that intermixing occurs predominantly by surface diffusion of adatoms across the surface and exchange [7,8] of these diffusing adatoms with surface atoms. This process preserves the abrupt interface and cannot be described by a single diffusion equation. Free adatom diffusion and exchange with the film layer are common, so this mechanism should operate for a wide range of surface alloys.

The system we have studied is the alloying of Cu and Co on a close-packed substrate, Ru(0001). Intermixing in Co-Cu films and multilayers has previously been studied because the interesting magnetic properties of these layered structures depend sensitively on interface sharpness. Co terminated film structures are unstable toward segregation of a monolayer of Cu to the surface [9–12]. On close-packed films of Co/Cu(111), this instability, paired with the high surface mobility of Cu adatoms, causes intermixing and prevents the formation of perfect interfaces [12].

When deposited individually onto a Ru(0001) substrate, both Co and Cu are known to grow in a Stranski-Krastanov mode in which the first monolayer orders pseudomorphically on the Ru(0001) substrate [13,14]. The surface lattice constants of Ru (Co, Cu) are 2.71 Å (2.51 Å, 2.55 Å), so that the Co (Cu) monolayer films on Ru are under 7% (6%) tensile strain. We consider only films in which the total coverage of both metals is 1 monolayer or less. In this coverage range, we find complete miscibility of the two metals (in contrast to their bulk phase diagram), leading to the conclusion that no miscibility gap exists for temperatures above 500 K.

Our approach to studying interdiffusion is analogous to the traditional method of studying interdiffusion in bulk metals, i.e., to create a sharp boundary between two elements and measure the concentration profiles across the joint after annealing [15]. We start by preparing sharp 1D interfaces. Figure 1 shows a series of ultrahigh-vacuum scanning-tunneling microscope (STM) images illustrating how sharp boundaries are made. (All images shown in this paper were taken at room temperature. At +0.6 V sample bias and 0.2–2 nA constant tunneling current, Co regions appear 0.7 Å lower than Cu regions on the same terrace.) First, a submonolayer amount of Co was deposited and annealed to produce monolayer thick islands [Fig. 1(a)]. Then a submonolayer amount of Cu was added

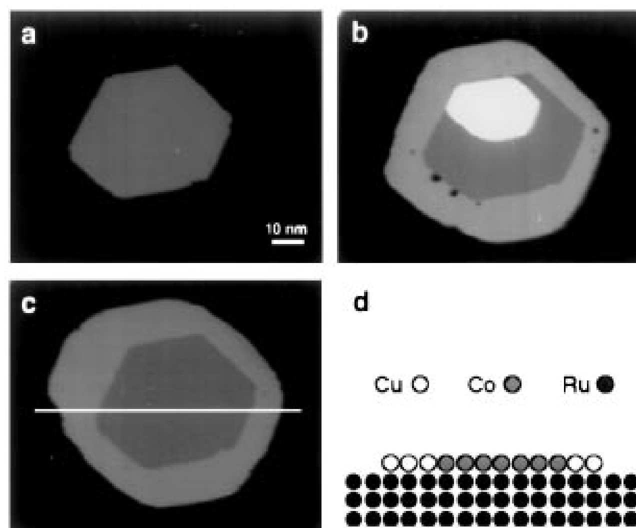

FIG. 1. (a) A monolayer Co/Ru(0001) island, flash annealed to 620 K. (b) The Co island shown in (a) after the additional deposition of Cu. (c) The same island again after annealing to 540 K. (d) Sketch of cross section of structure in (c) along indicated line.

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[Fig. 1(b)]. The Cu attaches to the Co-island edges and also nucleates on top of the Co islands. Upon flash-annealing this structure to 540 K, the Cu on the second layer has diffused down to the Ru surface and joined the Cu at the Co island edge [Fig. 1(c)]. This brief, low temperature anneal does not cause any mixing: The position of the boundary between the Co and the adjacent Cu [Fig. 1(c)] is identical to the position of the original Co island edge [Fig. 1(a)] [16]. Furthermore, no indication of foreign atoms in either material is found: the composition profile across the interface is a step function.

For better statistics, longer interfaces than the ones shown in Fig. 1 are desirable. This was achieved by warming the sample during the deposition of Co to enhance step-flow growth from Ru steps. Figure 2 shows a section of such a long interface between monolayer thick regions of Co (left, darker) and Cu (right, brighter) after annealing the structure at 580 K for 1 min [Fig. 2(a)] and for 5 min [Fig. 2(b)]. Interdiffusion across the Co-Cu interface is clearly visible. The dark spots in the Cu region are incorporated Co, and the bright features in the Co region are incorporated Cu. Note that while both the overlayer constituents readily penetrate several tens of nanometers away from the original interface, the interface itself remains nearly steplike.

Lower magnification images as shown in Fig. 3 reveal another interesting feature. Co (arrows) has diffused into the Cu regions not only in regions near where they share an interface, but also in areas where Cu regions have an open step edge to a bare Ru terrace. Conceivably, Co atoms might have diffused from the Co-Cu interface, across the Cu regions, and become stabilized near the Cu step edge, perhaps by an associated strain field. This type of process can be ruled out, however, by observing voids or vacancy islands in Cu film. If Co migrating through the Cu film was stabilized near Cu step edges, Co would also be found at the edges of such voids. This is not the case, indicating that the Co on the left side in Fig. 3 has come from the Co region on the next lower terrace (which is to the left of the region scanned in Fig. 3).

A clue to the possible interdiffusion mechanism is found by inverting the deposition sequence, i.e., depositing Cu first. Figure 4(a) shows a monolayer Cu island of one atomic thickness on the Ru substrate. Deposition of a submonolayer amount of Co onto this Cu island [Fig. 4(b)] leads to (i) the usual nucleation and growth of monolayer thick Co islands on the open Ru terrace (gray triangular islands on the Ru substrate), (ii) Co growth at the edge of the Cu island, and (iii) the formation of second layer islands on top of the Cu island (white irregular islands on top of the Cu island). Close inspection of Fig. 4(b) reveals alloying in the Cu island. The inset shows a magnified section of the island; the small dark features (arrows) are characteristic Co clusters ranging in size from 1 to 5 Co atoms. Clearly, Co atoms impinging on the Cu have exchanged with Cu atoms and incorporated into the islands. The second layer islands seen in Fig. 4(b) are actually comprised of the displaced Cu atoms. This becomes obvious after briefly annealing the structure just high enough to allow the second layer Cu islands to diffuse off the monolayer island. The resulting alloy island is shown in Fig. 4(c). Note that the boundary between

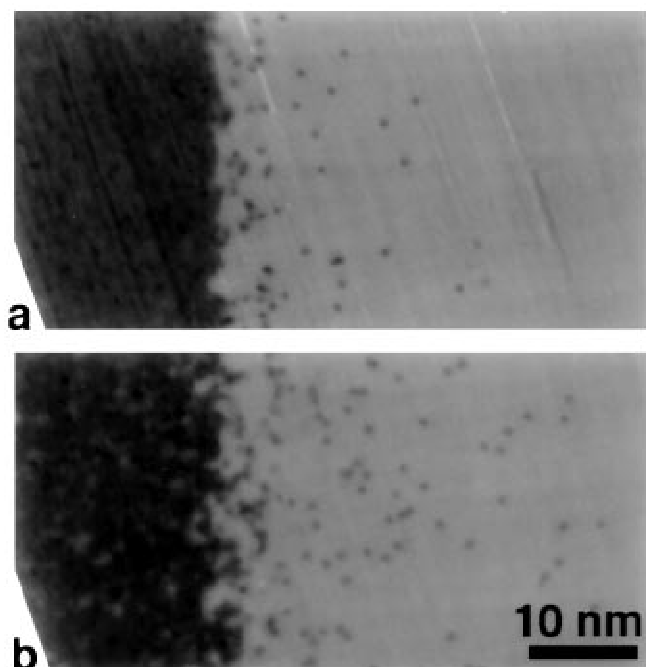

FIG. 2. Early stages of interdiffusion at the one-dimensional interface between adjacent regions of one monolayer Co (left) and one monolayer Cu (right) following 580 K annealing for 1 min (a) and 5 min (b).

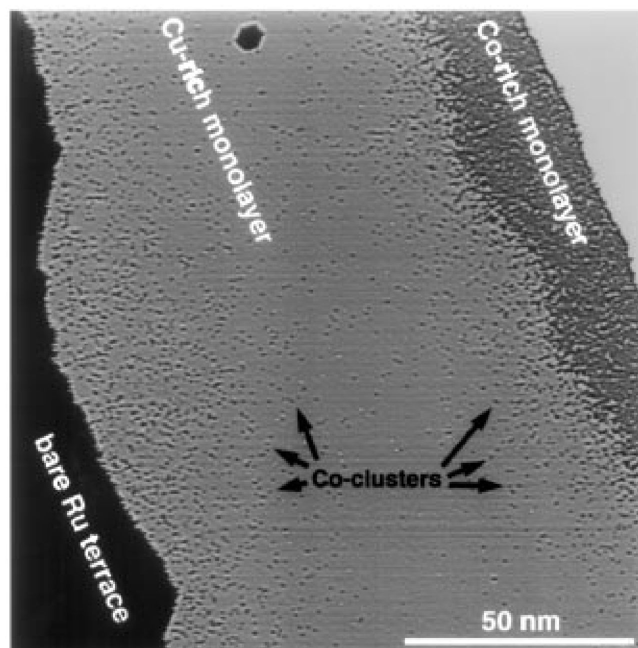

FIG. 3. Lower resolution image of Co-Cu couple after 1 min anneal at 580 K. Note that Co clusters are concentrated in the Cu region not only near the Co-Cu interface, but also near the step edges of the Cu.

the alloyed region (brighter) and the Co step-flow region around it (darker) is identical to the footprint of the original pure Cu island. From this experiment we can conclude that the Co atoms on a single monolayer Cu/Ru(0001) do not diffuse very far and are readily incorporated into the Cu island. Furthermore, the underlying mechanism for this alloying process involves the expulsion of Cu atoms from the monolayer island into the second layer. Other conceivable processes, such as Co adatoms filling vacancies originating from the island edge, can be ruled out. If vacancy annihilation was an important mechanism to the incorporation of Co into the Cu island, then the footprint of the alloyed region in Fig. 4(c) could not be identical to the footprint of the original Cu island [Fig. 4(a)].

Any model of these observations must account for two important facts: (1) The position and the sharpness of the interface remains constant even when considerable mass has crossed it and (2) Co found on the Cu step edge (as in Fig. 3) must be coming from the next lower terrace. The model we propose involves adatom diffusion on top of the surface and adatom exchange with surface atoms. Recent experiments have proven that mobile adatoms are common on metal surfaces in thermal equilibrium [17], and play an important role in dynamic phenomena such as step fluctuations, Ostwald ripening of epitaxially grown islands, and surface faceting. Figure 5 shows a schematic of the important mechanisms of our model. When the sample is heated, Cu atoms detach from the edges of 2D Cu regions to form a dilute lattice-gas of Cu covering the sample surface [Fig. 5(a)]. The lattice-gas covers three different environments (not necessarily equally): bare Ru regions, Cu-covered regions, and Co-covered regions. On these areas, the Cu adatoms can diffuse rapidly and may possibly exchange with surface atoms. On the bare Ru, the adatoms simply perform hopping diffusion; no evidence for Co or Cu alloying with the Ru substrate is observed. On Cu monolayer patches, atomic exchange events may occur, but our experiments are not sensitive to them. On the Co monolayer regions, Cu adatoms primarily perform hopping diffusion without exchange, as is evident from experiments such as shown in Fig. 1, where, at relatively low temperature, second layer Cu islands diffused off of Co islands without intermixing. On the other hand, the interdiffusion experiments described above indicate that at slightly higher temperatures Co adatoms are released from the Co monolayer regions [point (2) above]. We propose that these Co adatoms are released by thermally activated atomic exchange with Cu adatoms from the Cu lattice gas [Fig. 5(b)]. This exchange process is most likely the lowest energy path for the release of Co adatoms. The Co adatoms then migrate on the Co region, eventually reaching either a bare Ru or a Cu covered region [Fig. 5(c)]. Once on the bare Ru, they continue to diffuse until they become attached to the edge of a Cu region. In the case of diffusing onto the Cu-covered region, they can easily exchange into the Cu film [Fig. 5(d)], as is evident in the experiment shown in Fig. 4.

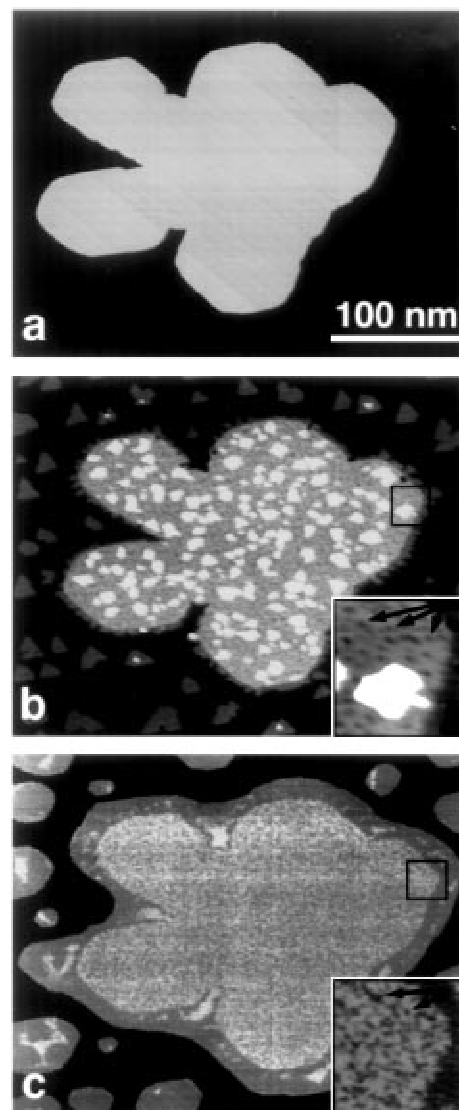

FIG. 4. The deposition of Co on top of a preexisting monolayer island of Cu leads to atomic exchange at room temperature. (a) Initial Cu island. (b) Deposition onto Cu island. The small dark features in the Cu island are clusters of Co. (c) After flash annealing to 620 K, the second-layer material has migrated to attach to the edges of Co islands on the Ru surface, indicating that the second-layer islands in (b) are mostly Cu. Note that the outline of the original Cu island in (a) is preserved in (c).

The concentration profiles from the data of Fig. 2 are shown in Fig. 6. These profiles are inconsistent with simple Fickian interdiffusion (as expected for vacancy diffusion, for example): For an initial step function profile, the solution to the diffusion equation, assuming a constant diffusion constant and no miscibility gap, is an error function. However, attempts to fit our profiles to error functions were unsuccessful: Concentration gradient driven diffusion does not preserve the observed sharp interface, and does not reproduce the long tails of the profiles (as shown by the inset in Fig. 6). To check the

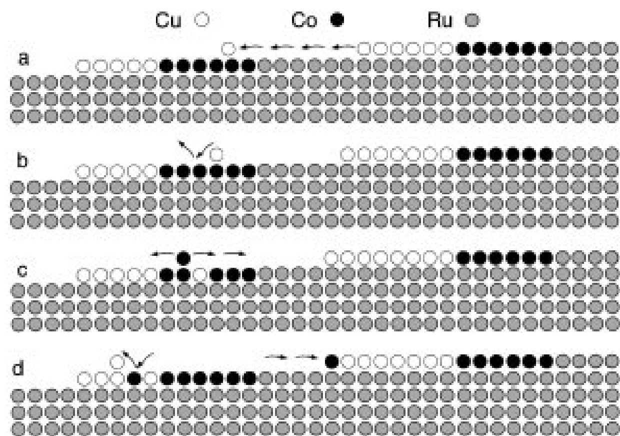

FIG. 5. Schematic diagram of proposed interdiffusion mechanism. See text for description.

validity of the proposed interdiffusion model, we have compared the results of a computer simulation of the model with experiment. We start with atoms of type A at all sites on a 2D grid to the left of the interface and type B at all sites to the right. To simulate the adatom sea, a single atom of type A is placed on top of one of the A atoms. This atom is allowed to diffuse across the top of the surface with hops in random directions occurring with equal time intervals. Exchanges with the surface layer are made with one probability when an A atom sits over a B atom and another probability when a B atom sits over an A atom. By suitably choosing these probabilities, the model profiles can reproduce the experimental measurements as shown in Fig. 6. In particular, the interface remains sharp as observed experimentally.

A semiquantitative understanding of the foreign atom concentration profiles can be obtained by investigating their detailed shapes. In the simulation, the mobile adatom concentration profiles are accurately described by the steady state exponential produced by a constant flux of adatoms diffusing onto a region with a uniform distribution of sinks. Such a constant flux is expected at the early stages of interdiffusion where the probability of a foreign adatom encountering a like foreign atom in the film is negligibly small as in our experiments. The exponential adatom profile leads to the observed exponential profile of immobile foreign atoms incorporated into the monolayer film (Fig. 6). The decay length of the exponential is approximately $(a/2)\sqrt{r_h/r_e}$, where r_h is the Co adatom hop rate, r_e is the exchange rate of a Co adatom on Cu, and a is the lattice constant. From the fits to the data, we deduce that $r_e/r_h \approx 3 \times 10^{-4}$. (The analogous ratio for Cu on Co is too small to be accurately determined. In the simulation the ratio was chosen to be 5×10^{-5}, but it could well be smaller.) The ratio of the two annealing times in the simulations was 3.2. This is in reasonable accord with the actual ratio of 5, given the many simplifying assumptions of the model, such as ignoring possible diffusion barriers across the Co-Cu interface and the potential of altered exchange probabilities near incorporated foreign atoms.

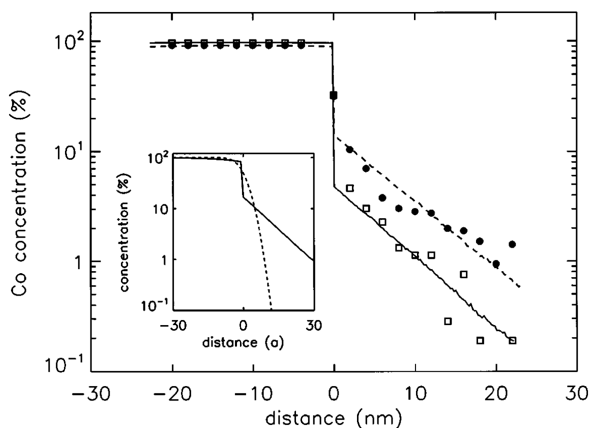

FIG. 6. Co concentration profiles across Co-Cu interfaces annealed to 580 K for 1 min (open squares) and 5 min (dark circles). Simulation results are superimposed as a solid line for the 1 min anneal and as a dotted line for the 5 min anneal. The inset compares a simulation profile (solid line) with the error function form characteristic of concentration gradient driven interdiffusion (dashed line) for the same interdiffused mass.

In conclusion, we have performed a quantitative measurement of mixing in 2D diffusion couples. While mass transport in bulk substitutional alloys is usually dominated by vacancy diffusion, we have found a two-dimensional system in which the contribution of vacancy diffusion is overridden by a mechanism involving adatoms on the free surface as a fast diffusion channel. Since there is no reason to suppose that adatoms of Co or Cu are in any way special, we believe that the proposed mechanism will often occur in surface alloy systems.

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