Strain Stabilized Alloying of Immiscible Metals in Thin Films

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We report on the structure and composition of codeposited thin Ag and Cu films on a Ru(0001) substrate. All three metals are immiscible in their bulk forms, however, monolayer films of Ag and Cu are observed to alloy on Ru(0001). In the dilute Cu case, preferential formation of the alloy is found. With increasing Cu concentration, domains of the alloy are formed with characteristic shapes. These data point to a mechanism of alloy formation driven by strain relief of the overlayer film. Details of the structure and composition of the film can be understood within this picture.

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The structure and integrity of interfaces are known to play an important role in defining the properties of thin film and superlattice systems. Lattice mismatches between the constituents of the film and the substrate introduce stress into the system, which is known to influence the interface structure greatly. In the simplest situation, this results in the formation of a transition region in which the stress is accommodated by a combination of lattice strain and misfit dislocations, leading eventually to the bulk phase of the overlayer as the thickness of the film increases [1]. The interface structure is complicated by the possibility of mixing between the overlayer material and the substrate. To create sharp interfaces it is attractive to consider materials that are immiscible in their bulk forms. However, because of surface effects, alloying has been observed in such cases [2,3]. The situation is even more complex in superlattice systems where more than one overlayer metal is present. The different stresses introduced by the substrate on the film components alter interaction between the overlayer materials and can lead to the formation of films with novel structures and compositions.

In this Letter, we report on such a process in which the bulk miscibility gap of two materials is drastically altered in a thin film system. Strain induced by the substrate plays a central role in this new alloying mechanism which alters the volumetric barrier to alloy formation between metals with a large lattice mismatch. This is demonstrated in the scanning tunneling microscopy (STM) study of submonolayer Ag and Cu films on Ru(0001). The large lattice mismatch between Cu(111) (2.56 Å) and Ag(111) (2.89 Å), which is approximately 13%, leads to a wide miscibility gap which exists in their bulk binary phase diagram up to the liquid phase boundary. The Ru(0001) substrate, with its lattice constant (2.71 Å) between those of Cu and Ag, mediates this mismatch and the mixing of Ag and Cu in the first layer results in a structure of lower strain and higher commensurability with the substrate. The dispersion of the smaller Cu atoms within the Ag film leads to the formation of a two dimensional alloy phase with a specific stoichiometry. The role of strain in determining the phase diagram of alloy thin film systems is different from the case in three dimensions. We present a simple intuitive picture in which this phenomenon can be understood. Understanding these relationships and their effects on phase transitions and the stability of 2D systems will be vital to the physics of thin film and superlattice systems and provide a platform for the study of binary phase diagrams in two dimensions. This mechanism of alloy formation also leads to the possibility of fabricating new thin film materials with novel physical properties.

The experiments were performed in a UHV chamber with a base pressure less than 10^{-10} Torr. The Ru sample was oriented to within 0.1° of the (0001) direction and mechanically polished with standard techniques. In vacuum, the sample was cleaned by a brief sputtering with 500 eV Ar ions followed by approximately 200 O_2 adsorption-desorption cycles. Ag and Cu were deposited by evaporation from resistively heated tungsten baskets. All depositions were performed at room temperature with subsequent annealing as described in the text. All STM imaging was performed at room temperature. STM images are displayed in gray-scale representation with the brighter areas corresponding to higher corrugation amplitude.

The single component systems of Cu/Ru(0001) and Ag/Ru(0001) have been studied by a variety of spectroscopic and topographic techniques [4–10]. Individually, the first atomic layers of Cu and Ag are known to wet the Ru(0001) surface. Recent work by Schick *et al.* [11,12] indicates that codeposited Ag and Cu on Ru(0001) mix. However, the mechanisms which drive the mixture of these immiscible metals could not be determined.

The first atomic layer of Ag on Ru(0001) displays a range of structures determined by the local density of Ag in the layer [13]. At full saturation of the layer, a uniaxially expanded structure is formed that consists of an ordered array of misfit dislocation stripes running along the [120] direction, as shown in Fig. 1(a). This strain relief structure has been observed in several other (111) orientation overlayer systems [14,15], as well as on the reconstruction of the (111) faces of Au [16,17] and Pt [18,19]. The stripes of the structure correspond to domain walls separating regions of hcp and fcc stacked

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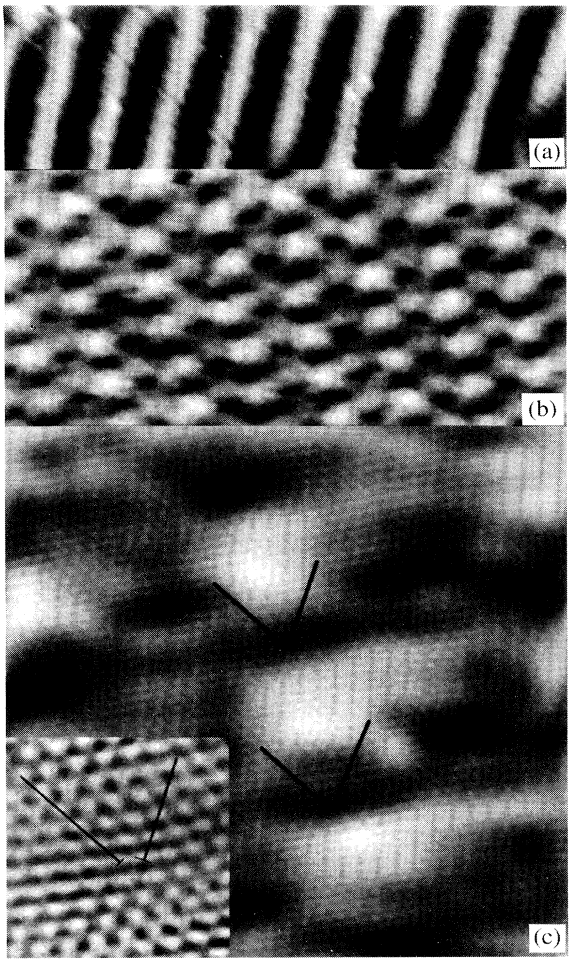

FIG. 1. Dislocation structure of Ag/Ru(0001). (a) 170 Å × 50 Å STM image of uniaxially expanded structure observed at saturation of the first atomic layer. Bright stripes represent transition regions of Ag acting as domain walls between fcc and hcp occupied regions. (b) Misfit dislocation structure of submonolayer Ag/Ru(0001) films (400 Å × 200 Å). (c) Atomically resolved image of structure in (b). Surface edge dislocations are marked by crossed line segments. Details of the dislocation structure shown in the inset.

Ag. In the walls, the Ag atoms occupy bridge sites and allow the lattice to relax along the close packed [100] direction. Below saturation of the first Ag layer, the Ag film relaxes further to form a different network of dislocations shown in Fig. 1(b). The details of this structure can be seen in Fig. 1(c), which displays an atomically resolved image of the unit cell. The dark regions of the surface contain the cores of surface edge dislocations which form an array of structure similar to that observed on the herringbone pattern of Au(111) [20]. It was this Ag structure, Fig. 1(b), that formed the starting point of all the experiments discussed here. A detailed discussion of the Ag strain relaxation mechanisms will be contained in a forthcoming paper [13].

Small amounts of Cu added to the Ag film of Fig. 1(b) mix upon deposition at room temperature to bond directly with the Ru substrate. This mixing is not simply due to kinetic limitations at room temperature as may be expected in a phase segregation system. This is demonstrated in Fig. 2 which displays a film with a concentration ratio of Cu to Ag of $X_{Cu}/X_{Ag} = 0.19$ that has been annealed to 550 °C. The Cu atoms and clusters appear as dark features with a corrugation of approximately 0.15 Å below the Ag layer, consistent with the size difference between the two elements. (Our assignment of these features to Cu is corroborated by comparison of the deposited amount of Cu with the amount observed in these features. Other groups have already shown the ability of STM to distinguish different metallic constituents within the same layer, although the exact nature of the observed contrast is still unclear [20–22].) The Cu and Ag do not phase segregate as would be the case in the bulk. Instead, the Cu atoms preferentially occupy regions in between the corrugation maxima of the pure Ag film pattern, resulting in a rough grid pattern of Cu (Fig. 2). With further deposition of Cu, the dislocation pattern of the Ag layer is disrupted. Figure 3(a) shows a film with $X_{Cu}/X_{Ag} = 0.42$. Two types of Cu-Ag domains form, possessing roughly triangular shapes and separated by raised stripes of Ag. These two domain types are rotated 60° relative to one another. The domain formation becomes more defined as the concentration of Cu increases. The film now consists of two dimensional Ag-Cu mixed domains separated by pure Ag domain walls. The detailed structure of the Ag-Cu domains can be seen in Fig. 3(b). The Cu and Ag mix primarily through the interweaving of chainlike clusters nominally ranging in size from single to 20 atoms. The consistent stoichiometry within the triangular domains at $X_{Cu}/X_{Ag} = 0.5$ indicates that a true 2D alloy phase has been formed and that the small clustering is not the on-

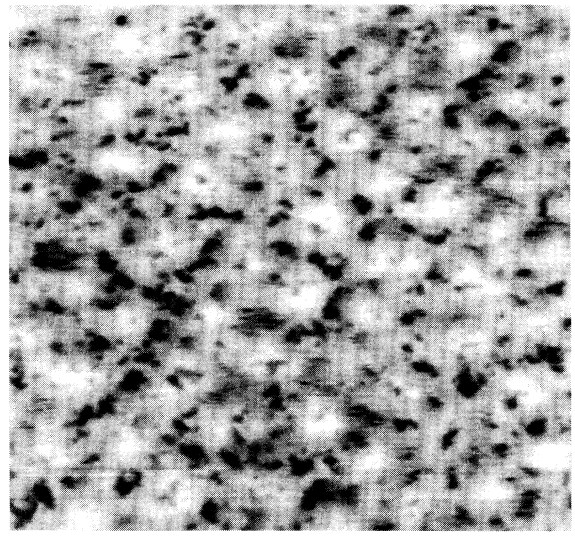

FIG. 2. 300 Å × 300 Å STM image showing film of Fig. 1(b) following deposition of Cu and annealing to 550 °C. $X_{Cu}/X_{Ag} = 0.19$. Dark areas are Cu atoms and clusters.

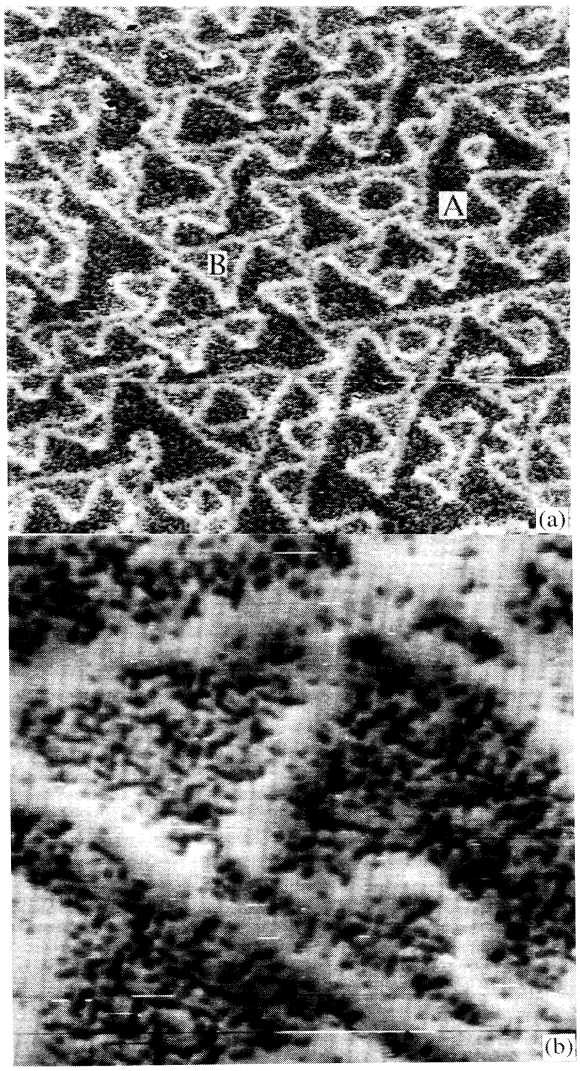

FIG. 3. (a) 1000 Å × 1000 Å image of film with $X_{Cu}/X_{Ag} = 0.42$ following annealing to 550 °C. Two domains of the alloy can be seen and are separated by domain walls made up of pure Ag phase. Details of the alloy domain structure and domain walls can be seen in (b) (200 Å × 200 Å).

set of phase segregation between the Ag and Cu. The alloy domains are separated by pure Ag domain walls. As X_{Cu}/X_{Ag} increases and the fraction pure Ag decreases, the width of the domain walls remain intact and the decrease is accounted for by reduction in overall wall length. These domain walls are approximately 20 Å wide and appear 0.1 Å higher than the Ag within the alloy phase. These features are identical, within experimental uncertainty, to the domain wall structures found in the uniaxially expanded structure of the pure Ag film [Fig. 1(a)]. In the pure Ag case, the walls separated regions of hcp and fcc stacking, and an analogous assignment is made for the alloy film. This identification is corroborated by the different average heights between the two types of alloy domains. The larger upward pointing triangular structures of Fig. 3(a), (marked *A*), are imaged 0.05 Å lower than the other. This difference is attributed to the occupation of the two types of hollow sites, hcp and fcc. Therefore, the Ag domain walls connect alloy regions of different substrate hollow stacking as in the pure Ag situation.

As can be seen in Fig. 3(a), one type of alloy domain occupies a larger fraction of the surface, which can be attributed to the expected binding energy difference between the two types of hollow sites. (The larger domains are likely to be hcp stacked alloy, since in the pure Cu film this is the preferred site.) As the concentration ratio between Cu and Ag increases to 0.5, the energetically favorable alloy domain grows at the expense of the other, until a uniform Ag-Cu two dimensional alloy covers the surface at $X_{Cu}/X_{Ag} \approx 0.5$. Throughout our experiments, no long range ordering within the alloy was observed.

The data described above can be understood on the basis that the alloying of Cu and Ag in this system is driven by the strain relief of the Ag lattice by the incorporation of the smaller Cu atoms. In their bulk states, the large size difference between Cu and Ag hinders their formation of a solution. However, a simple hard sphere model of Cu and Ag would lead to an average constant of a mixed film much closer to the 2.71 Å spacing of the Ru substrate. The atoms in the alloy phase therefore experience an energy reduction via two related effects: (1) reduced strain energy as compared to the pseudomorphic single component films, and (2) the atoms in the alloy phase can be accommodated in Ru hollow binding sites thereby eliminating misfit dislocations. This can be qualitatively described within the following simple, intuitive picture [23]. The alloy mixing energy is defined as the difference between the alloy energy at its equilibrium lattice constant $E_{alloy}(a_{alloy})$ and the pure components at their respective equilibrium lattice constants $E_{Ag}(a_{Ag})$ and $E_{Cu}(a_{Cu})$, i.e.,

$$E_{mix} = E_{alloy}(a_{alloy}) - [c_{Ag}E_{Ag}(a_{Ag}) + (1 - c_{Ag})E_{Cu}(a_{Cu})].$$

The phase segregating nature of the bulk alloy arises when $E_{mix} > 0$. We contend that the primary effect of the Ru(0001) substrate is to alter the energies of the pure films and the alloy by constraining their lattice constants to nearly that of Ru(0001). This can be seen by adding and subtracting the energies of the pure films strained to the lattice constant of the alloy, referred to as $E_{Ag}(a_{alloy})$ and $E_{Cu}(a_{alloy})$, giving

$$E_{mix} = \{E_{alloy}(a_{alloy}) - [c_{Ag}E_{Ag}(a_{alloy}) + (1 - c_{Ag})E_{Cu}(a_{alloy})]\} + \{c_{Ag}[E_{Ag}(a_{alloy}) - E_{Ag}(a_{Ag})] + (1 - c_{Ag})[E_{Cu}(a_{alloy}) - E_{Cu}(a_{Cu})]\}.$$

The last term in this equation represents a purely strain contribution due to the difference between the substrate lattice constant and the equilibrium lattice constants of the pure components. This term is always positive in the alloy, thus hindering mixing. In the case of bulk Ag and Cu, the elements are allowed to relax to their bulk lattice constants and this term is large enough to inhibit mixing. In the thin film situation, the influence of the substrate is to restrict the lattice constants of the alloy *and* the phase segregated (pure) Ag and Cu films to nearly that of the Ru(0001), i.e., $a_{Ag} \approx a_{Ru}$, $a_{Cu} \approx a_{Ru}$, and $a_{alloy} \approx a_{Ru}$. This greatly reduces this strain term. As a result, the alloy mixing energy is primarily determined by the alloy energy relative to the strained pure metals (the first term on the right). If this term is negative, alloying can occur. Indeed, embedded atom method calculations indicate that E_{mix} in this thin film situation is (slightly) negative [24]. In our case, however, all experiments were performed at or above room temperature and an entropy contribution would further favor alloying, leaving the possibility that E_{mix} may also be slightly positive. These arguments are qualitative and do not rule out other mechanisms of alloying. In any case, strain relief is playing an important role in the stability of the two dimensional alloy.

Strain relief also determines the film structure and local composition as the Cu concentration increases. Within the alloy domains, the atoms reside in hollow binding sites and are locally strain relieved. The existence of two types of alloy domains [(Fig. 3(b)] corresponds to the two types of hollow sites available for occupation, fcc and hcp. Energetically only one type of hollow is preferred, as is indicated by only one domain existing as the Cu-Ag mixture reaches 1 to 2 composition. The question remains as to why the minority alloy domain forms [region *B* of Fig. 3(a)] for $X_{Cu}/X_{Ag} < 0.5$. Below this saturation composition, the unaccommodated Ag does not phase segregate. Instead the Ag forms domain walls occupying transition sites between the hcp and fcc hollows. These sites are of lower coordination and, following the arguments of pure Ag film, allow a greater degree of strain relaxation as compared to hollow sites [13]. Therefore, the energy gain in reducing the strain in the Ag phase overcomes the cost of forming the minority alloy domain and the interfaces between the two phases.

In conclusion, we have demonstrated that the reduction of strain can be the driving mechanism in the formation of alloys in multicomponent thin film systems. This has been shown for the case of monolayer films of Ag and Cu on Ru(0001). Although Ag and Cu are immiscible in their bulk phases, their lattice mismatches with the Ru substrate lead to the formation of a strain relieved Ag-Cu alloy with near 2:1 stoichiometry. We have also observed that strain relief also plays a dominant role in the structure of the Ag-Cu domains. This phenomena is expected to be important in superlattice systems in which stresses of opposite signs are applied to the constituents of the film. It may also be a mechanism by which novel materials can be produced.

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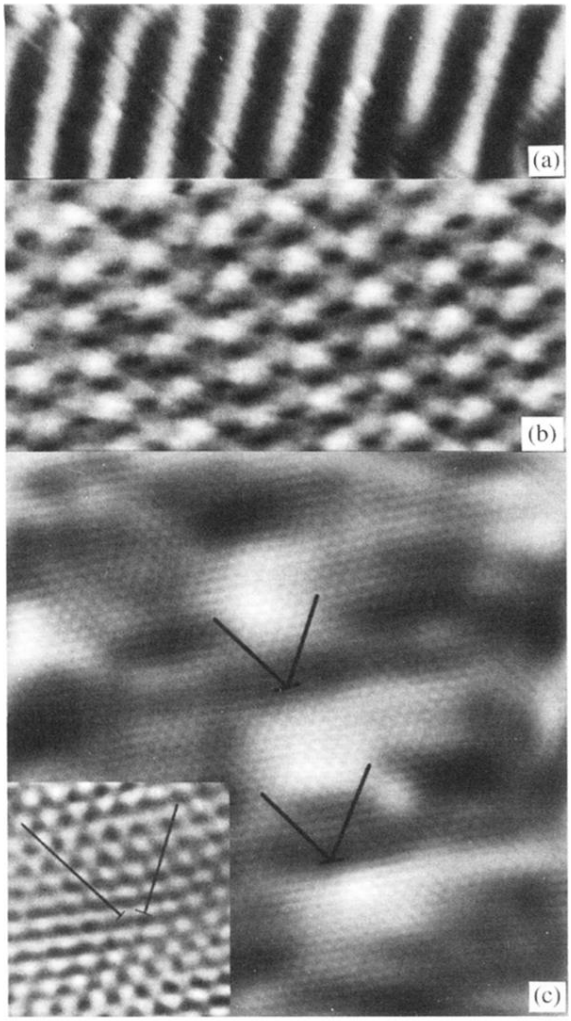

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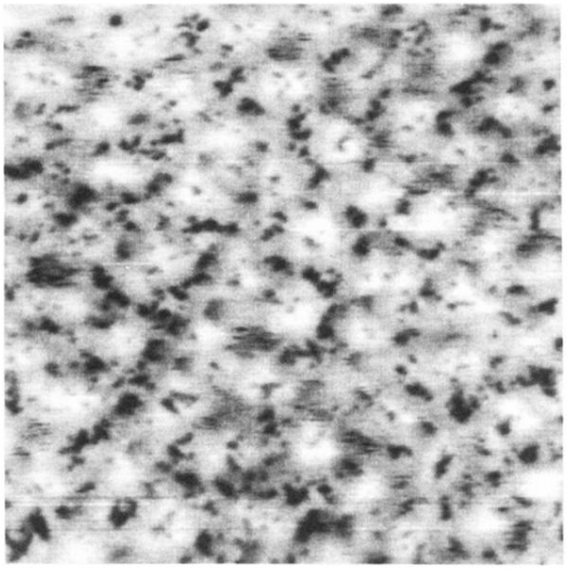

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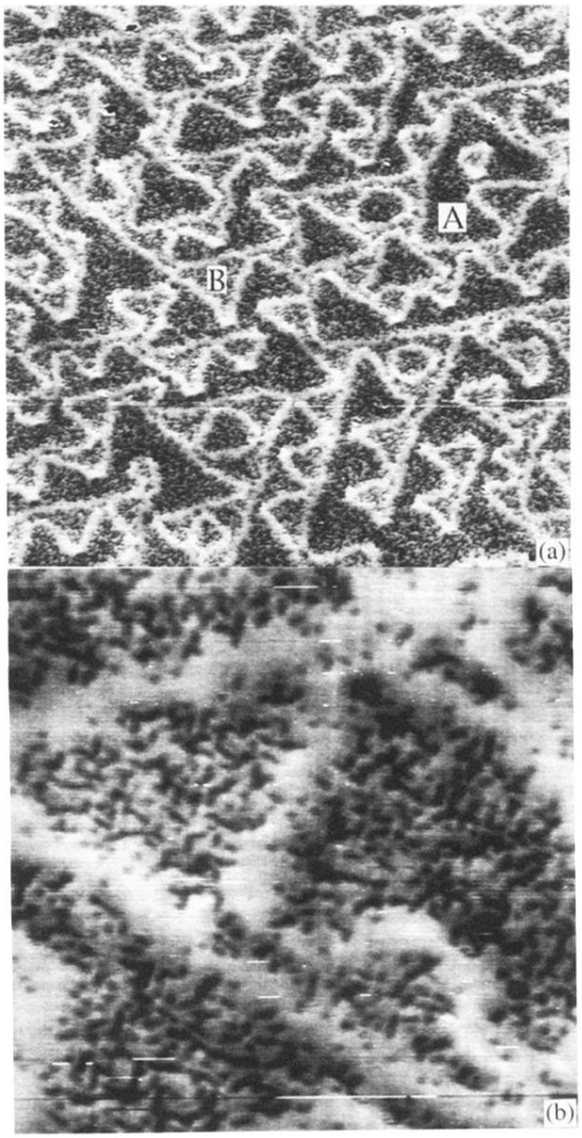

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