

EQUILIBRATED SURFACE ALLOYS AND THE INFLUENCE OF STRAIN

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ABSTRACT

Structural and thermodynamic properties of equilibrated ultrathin Pd-Au, Cu-Ag, and Co-Ag alloys on Ru(0001) were studied and are comparatively discussed. These studies provide a framework for a detailed understanding of the energetics of surface alloy formation. Additionally, the differences between the two bulk immiscible systems (Cu-Ag and Co-Ag) and the bulk miscible Pd-Au system are discussed.

INTRODUCTION

In heteroepitaxial growth, an important phenomenon is the formation of surface alloys which are localized near the film-substrate interface. This has been shown to be quite general with systems ranging from Au/Cu(100) [1], where the alloying structure is similar to that found in the bulk, to unexpected cases such as Au/Ni(110) [2], where two metals are immiscible in the bulk but alloy at the surface. Since the structure and integrity of interfaces are known to play an important role in defining the properties of thin film and superlattice systems, developing a detailed understanding of the surface alloying phenomenon is important and has recently received increasing attention. For instance, Tersoff [3] has proposed strain resulting from lattice mismatch as a mechanism for surface alloying of immiscible materials, and recently, Sadigh et al. [4] have shown that results from calculations based on a lattice-model Hamiltonian dominated by short range interactions are in excellent agreement with scanning tunneling microscopy (STM) measurements of PdAu/Ru(0001).

The goal of this paper is to compare three different surface alloy systems, PdAu/Ru(0001), CuAg/Ru(0001), and CoAg/Ru(0001), in order to more clearly show the dominant common mechanisms of alloy formation. In particular, the structure and thermodynamic properties of each system are investigated with careful consideration of the role of surface strain.

EXPERIMENT AND THEORY

Each of the three surface alloy systems we studied were up to one monolayer thick, thermally equilibrated films observed by STM at room temperature. The experiments were performed in an ultrahigh vacuum chamber with a base pressure less than 10^{-10} Torr. Also, each of the alloy films was prepared on the (0001) surface of a Ru crystal which was oriented to within 0.1° of the (0001) direction and mechanically polished with standard techniques. The Ru sample was cleaned in vacuum by a brief sputtering with 500eV Ar ions followed by at least 200 O_2 adsorption-desorption cycles. All film components were deposited by evaporation from resistively heated tungsten baskets except for Co, which was evaporated from a resistively heated Co wire. All depositions were performed at room temperature followed by annealing described in the text.

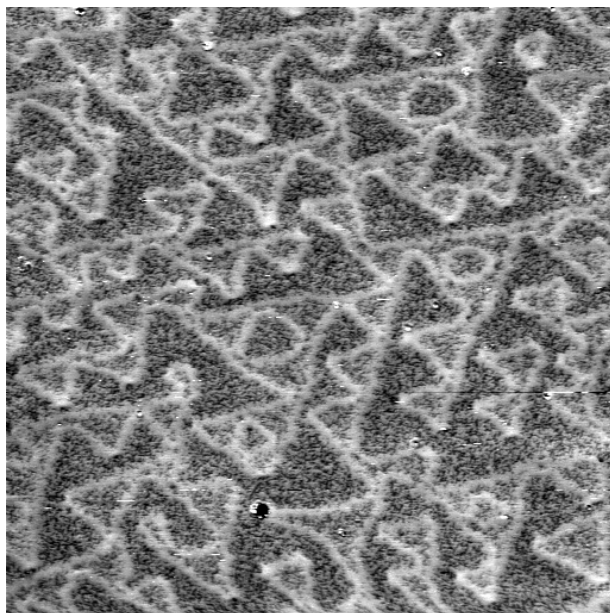


Figure 1(a) 1000Å x 1000Å image of a one-monolayer thick, equilibrated film of AgCu/Ru(0001). The raised white Ag domain walls separate the two types of alloy domains.

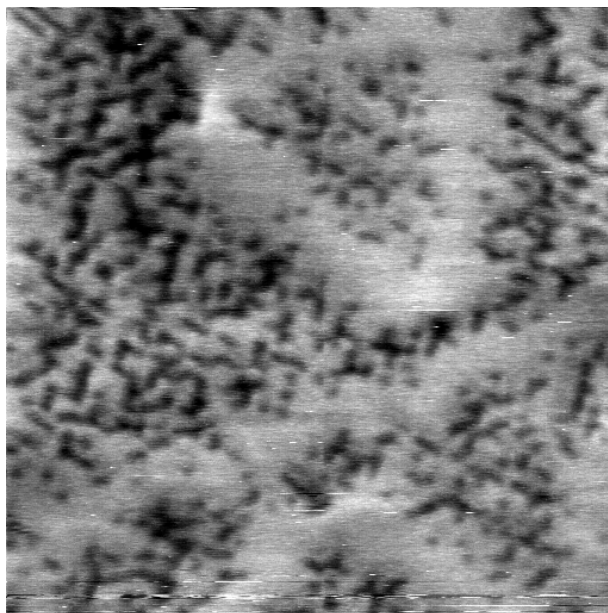


Figure 1(b) 150Å x 150Å image of the same film. The Cu atoms (dark) are in a Ag film.

CuAg/Ru(0001)

We have observed a surface alloy in the CuAg/Ru(0001) system [5]. Although each combination of these three metals is immiscible in their bulk forms, monolayer films of Ag and Cu are observed to alloy on Ru(0001). In the dilute Ag case, preferential formation of the alloy is found. With increasing Ag 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 film. The large lattice mismatch between Cu(111) (near-neighbor distance 2.56 Å) and Ag(111) (2.89 Å), of approximately 13%, leads to a wide miscibility gap in the 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. In this system, the surface strain due to lattice mismatch promotes the formation of an alloy. In the bulk phase, however, the lattice mismatch between Ag and Cu leads to a bulk miscibility gap. Figure 1(a) shows a thermodynamically equilibrated film (annealed to 550° C) with a composition ratio of $X_{\text{Cu}}/X_{\text{Ag}} = 0.4$. Two types of Cu-Ag domains form, possessing roughly triangular shapes and separated by raised stripes of Ag. The two Ag-Cu domain types are rotated by 60° relative to one another and consist of two different types of hollow binding sites, fcc and hcp. The detailed structure of the domains can be seen in Fig. 1(b). The Cu and Ag mix primarily through the interweaving of chainlike clusters nominally ranging in size from one to 20 atoms. An analysis of first, second, and higher order nearest-neighbors in the alloy system has shown that nearest-neighbors of any order have no preference of species. As can be seen in Fig. 1(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 fcc and hcp hollow sites. (The larger domains are likely to be hcp stacked alloy, since in the pure Cu/Ru(0001) film this is the preferred stacking.)

The data described above can be understood on the basis that the alloying of Cu and Ag in this system is driven by strain relief in the Ag film through the incorporation of the smaller Cu atoms. In their bulk states, the large size difference between Cu and Ag hinders the formation of a solid solution. However, a simple hard sphere model of Cu and Ag would lead to an average lattice constant of the mixed film being much closer to the 2.71 Å spacing of the Ru substrate. The atoms in the alloy phase therefore experience an energy reduction via reduced strain energy as compared to the pseudomorphic single component films.

AgCo/Ru(0001)

STM was also used to study submonolayer AgCo films on Ru(0001). Again, it is known that neither Ag nor Co mix with Ru at the temperatures and timescales relevant to the experiment. Also, the single component system of Ag/Ru(0001) forms a dislocation structure on the surface, and the system of Co/Ru(0001) forms a pseudomorphic film.

Depositing 0.25 ML of Co onto a Ru surface already containing 0.25 ML of Ag produces a completely mixed film. However, after annealing the film to equilibrium, we found it decomposes into two distinct phases as shown in Fig. 2. The first phase is a Co-rich, 2-D mixture with a stoichiometry of $\text{Co}_{0.6}\text{Ag}_{0.4}$, with Ag droplets (tens of atoms in size) appearing light against a dark Co background. The second phase is pure Ag with a misfit dislocation structure on the Ru(0001) substrate. This mixed phase is distinct in that films with higher concentrations of Ag always decompose to the same two phases with the stoichiometry of the mixed phase remaining the same and the coverage of the second, pure Ag, phase increasing with increasing amounts of Ag. This behavior indicates the existence of a two-phase field between $\text{Co}_{0.6}\text{Ag}_{0.4}$ and a dislocated Ag layer.

The mixed phase is similar to the CuAg/Ru(0001) system and can be understood on the basis that strain relief of the Co lattice drives alloying of the Co and Ag by the incorporation of the larger Ag atoms. The lattice mismatch between Co(111) (2.50 Å) and Ag(111) (2.89 Å), is nearly 16%. The Ru(0001) substrate with its lattice constant (2.71 Å) between those of Co and Ag mediates the mismatch and results in a structure of lower strain and higher commensurability with the substrate. Therefore, the result is a mixture of Co and Ag with an average lattice constant closer to the 2.71 Å spacing of the Ru substrate, similar to the CuAg/Ru(0001) system. In the AgCo/Ru(0001) system, however, after reaching the $\text{Co}_{0.6}\text{Ag}_{0.4}$ composition, the Co-rich mixture saturates with Ag and any excess Ag segregates into patches of pure Ag on Ru with misfit dislocations which relieve strain caused by lattice mismatch between Ag and Ru. Additionally, since the Ag droplets in the AgCo mixed phase are of the order of tens of atoms in size, there exists a short-range repulsive chemical interaction between Ag and Co despite strain being a long-range driving force for mixing. Indeed, Fig. 2 shows a strong preference for nearest neighbors to be same species.

PdAu/Ru(0001)

Figure 3 shows a representative atomic-resolution STM image of a thermally equilibrated (annealed to 573 K) monolayer of $\text{Pd}_{0.72}\text{Au}_{0.28}$ on Ru(0001) [4]. The structure is pseudomorphic with the Ru surface, and the prevalence of chains of Au (black) atoms suggests the presence of short-range order (SRO) in the surface alloy, i.e., a preference for certain near-neighbor environments. The SRO is caused by an energetic preference for certain bond types in the thin-film alloy. By counting atoms in a digitized version of Fig. 3, it was found that nearest-neighbors have a strong preference to be with the opposite species. That is, Au atoms have a preference to be immediately surrounded by Pd atoms, indicating ordering tendency in the

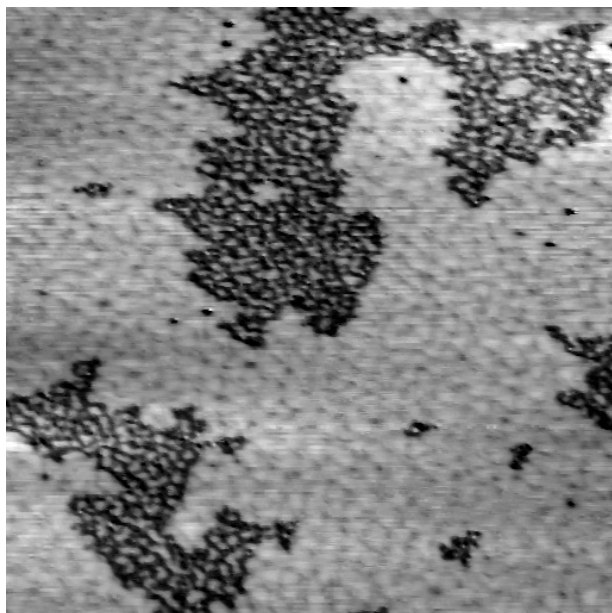


Figure 2 1000Å x 1000Å image of a one-monolayer thick equilibrated film of AgCo/Ru(0001). The dark patches are alloy consisting of Co containing white Ag droplets. The Co patches are within a pure Ag film that is dislocated to relieve strain due to lattice mismatch with the Ru surface.

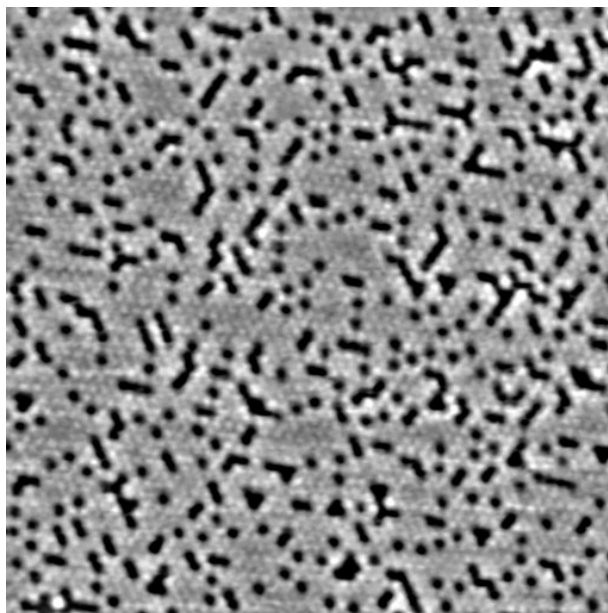


Figure 3 Atomically resolved image (130Å x 130Å) of a one-monolayer thick equilibrated film of PdAu/Ru(0001). The dark Au atoms are imbedded in the light Pd film.

system. Second nearest-neighbors in the alloy were found to prefer the same species. Higher orders of nearest-neighbors were found to have no preference, indicative of a lack of long-range order. These data confirm that Pd and Au have negative formation enthalpies and therefore atomic mixing lowers the film's configurational energy. Analogous to what we have observed on the surface, the PdAu alloy is known to exist in bulk phase as well. This points to the secondary contribution that surface strain makes to the formation of the surface alloy in this case.

RESULTS

Of the above studied alloy systems, Pd-Au is the only one whose constituents are miscible in their bulk phase. The observations showed that the structure of this surface alloy is similar to the bulk alloy phase and is dominated by nearest-neighbor interactions of ordering type. These factors point to strain having a minimal effect on the surface structure, with the alloying is primarily due to chemical interactions between the alloy constituents.

The remaining two systems have large miscibility gaps in their respective bulk phase diagrams. The observation that both Ag-Cu and Ag-Co form surface alloys and are immiscible in their bulk phases points to strain, due to lattice mismatch, as the driving force for alloy formation in these systems. However, it was also observed that the Ag-Cu alloy mixes on an atomic scale while the Ag-Co mixture consists of Ag droplets (tens of atoms in size) within a Co film. In the Ag-Cu alloy, a nearest-neighbor analysis shows that there is no preference for a particular species, leading to the conclusion that strain is the largest interaction determining the structure, which is consistent with the observed atomic mixing. However, since the Ag-Co phase is not atomically mixed, strain is the mechanism determining the structure of the system on larger length scales. In this system, there exists an additional short-range interaction that is chemical in nature and favors clustering on shorter length scales.

CONCLUSIONS

In conclusion, we have presented and compared results of STM experiments on equilibrated one-monolayer surface alloys of PdAu/Ru(0001), AgCu/Ru(0001), and AgCo/Ru(0001). It was found that two dominating interactions involved in the formation of surface alloys are strain and chemical affinity between constituents of the film. The formation of surface alloys has been found to be quite general in that alloy or mixed phases formed both in systems where the constituents of the alloys were and were not bulk immiscible. These studies contribute generally to the development of a detailed understanding of the surface alloying phenomenon.

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REFERENCES

1. D.D. Chambliss, and S. Chiang, Surface Science, **264**, L187 (1992).
2. L.P. Nielsen, F. Besenbacher, I. Stensgaard, E. Laegsgaard, C. Engdahl, P. Stoltze, K.W. Jacobsen, and J.K. Nørskov, Phys. Rev. Lett. **74**, 1159 (1995).
3. J. Tersoff, Phys. Rev. Lett. **74**, 434 (1995).
4. B. Sadigh, M. Asta, V. Ozolins, A.K. Schmid, N.C. Bartelt, A.A. Quong, and R.Q. Hwang, Phys. Rev. Lett. **83**, 1379 (1999).
5. J.L. Stevens and R.Q. Hwang, Phys. Rev. Lett. **74**, 2078 (1995).