Linking Surface Stress to Surface Structure: Measurement of Atomic Strain in a Surface Alloy using Scanning Tunneling Microscopy

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Annealed submonolayer CoAg/Ru(0001) films form an alloy with a structure that contains droplets of Ag surrounded by Co [G. E. Thayer, V. Ozolins, A. K. Schmid, N. C. Bartelt, M. Asta, J. J. Hoyt, S. Chiang, and R. Q. Hwang, Phys. Rev. Lett. **86**, 660 (2001)]. To understand how surface stress contributes to the formation of this structure, we use scanning tunneling microscopy to extract atomic displacements at the boundaries between regions of Co and Ag. Comparing our measurements to Frenkel-Kontorova model calculations, we show how stress due to lattice mismatch contributes to the formation of the alloy droplet structure. In particular, we quantitatively evaluate how competing strain and chemical energy contributions determine surface structure.

That atoms on a surface can lower surface energy by elastically relaxing to states of lower surface stress has dramatic effects on surface structure. For example, elastic relaxations are responsible for the formation of surface alloys in bulk immiscible systems. Experimental studies of such systems [Au/Ni(110) [1], Ni/Au(111) [2], and Ag/Cu-(100) [3]] suggest that the existence and structure of alloys on these surfaces are determined by a balance between an energy reduction due to stress relaxation and the energetic cost of forming chemical bonds upon alloying [4]. Thus, there is a close link between surface stress and surface alloy structure. In this paper, we quantitatively examine the energetics of surface alloy formation by experimentally measuring strain caused by elastic relaxations in a bulk immiscible surface alloy, and show how it contributes to the energies determining surface structure. To do this, we have measured both elastic relaxations and the configuration of single monolayer films of the CoAg/Ru(0001) surface alloy using scanning tunneling microscopy (STM). Initial investigations of this system [5] indicated the formation of a surface alloy in Co-rich films. It was observed that the structure of the alloy is not atomically mixed but instead consists of Ag droplets (15–25 atoms in size) within a Co matrix [see Fig. 1(a)]. Our measurements and analysis of elastic relaxations on this surface allow us to understand the factors that determine the size of the Ag droplets.

Since the bulk lattice spacing for Ag is larger than Ru and Co is smaller (8% and 7%, respectively), following Tersoff [4] one might expect the formation of an alloy in the CoAg/Ru(0001) system. The argument is that creating a surface with an average lattice spacing similar to the lattice spacing of the substrate could lead to a significant stress reduction. A competing chemical interaction in this system favors Co-Co and Ag-Ag bonds over Co-Ag bonds (causing the bulk miscibility gap) and thus increases surface energy upon alloying. A competition between these two interactions to minimize the surface energy could ac-

count for the particular boundary length and droplet size that is observed to form between Co and Ag, thus governing the length scale of the alloy structure [6,7].

In order to verify and quantify this concept, one must compare the magnitude of the stress relaxation energy to the chemical energy cost of forming Co-Ag boundaries. To extract the stress relaxation energy, we have quantified our observation of strain at boundaries between Co and Ag and analyzed these measurements in terms of a two-dimensional (2D) Frenkel-Kontorova (FK) model. Comparing model strain calculations with measurements of
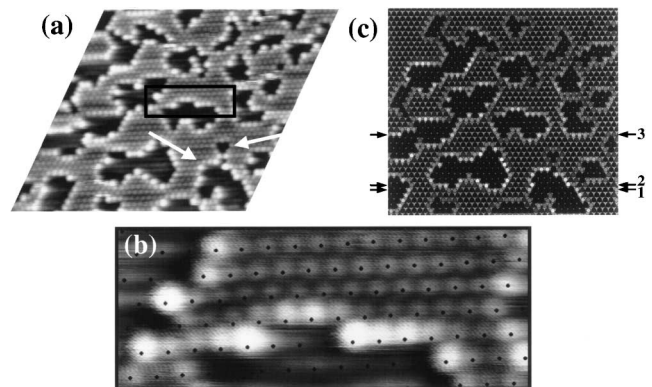

FIG. 1. (a) Atomically resolved image of a CoAg/Ru(0001) alloy film. Dark patches are Ag droplets within the lighter Co matrix. Co atoms at Ag boundaries are imaged substantially brighter than other Co atoms in the figure. The arrows point to two Ag droplets, where the Co atoms around the large droplet are noticeably brighter than those around the small droplet. (b) The hexagonal array of black dots overlaid on a portion of the image in (b) represents hcp sites of the substrate. Co atoms that are imaged bright are clearly displaced from hcp sites while darker Co atoms are not. (c) FK model simulation of the CoAg surface alloy. The gray scale of Co atoms bordering Ag droplets in the simulation is keyed to displacement squared, $(\Delta r)^2$. [The numbers 1, 2, and 3 correspond to the row number for which atomic displacements are plotted in Figs. 2(a)–2(c)].

strain from STM images allows us to determine the forces acting on the surface atoms, which in turn enables us to estimate the stress relaxation energy. By comparing these relaxation energies for different sized Ag droplets in a Co/Ru(0001) film with first-principles local-spin-density approximation (LSDA) calculations of the energetic cost of forming Co-Ag boundaries, we obtain a quantitative connection between surface stress and surface structure.

Atomically resolved STM images of a submonolayer of Co and Ag on Ru(0001), deposited onto the surface while the Ru crystal was heated to 170 °C, are shown in Fig. 1(a) [8]. This image suggests alloying as a possible means of stress relief from an otherwise severely stressed phase-separated, pseudomorphic film: Dark patches of atoms in Fig. 1(a) are Ag within the brighter surrounding Co matrix. Note that the Co atoms adjacent to Ag droplets are imaged substantially brighter than Co atoms located further from these boundaries. Figure 1(b) illustrates that the bright atoms in each row are not arranged in straight lines. Instead, they are displaced from their pseudomorphic positions; the hexagonal array of black dots placed over a portion of the STM image in Fig. 1(a) demonstrates that the brightest Co atoms are shifted a small distance out of the bottoms of the hcp sites, in a direction away from the Ag droplets. The brightness of Co boundary atoms is due to a lateral outward shift of atomic position due to a relaxation of the compressively stressed Ag droplets (discussed in detail below). This shift site leads to a displacement of the Co atoms out of the plane. The relaxation lowers the energy of the system by locally allowing both Co and Ag to have their preferred lattice spacing.

Qualitatively, Figs. 1(a) and 1(b) show the efficiency of alloying in providing stress relief for the surface. In order to more quantitatively interpret the images, we consider two contributions to the surface energy; the interactions between the atoms in the plane of the film, and the interactions between the substrate and the film. The simplest model of these two interactions is the FK model [9]. In this model, the interactions between the atoms in the film are represented by springs, and the substrate interaction is represented by a sinusoidal potential. The surface energy is modeled as

$$E = \sum_i V_S(r_i) + \frac{1}{2} \sum_j k(l_j - b \cdot a_{\mathrm{Ru}})^2,$$

where the first term is the three-dimensional sinusoidal substrate potential at each atom position, i. The second term is a sum over the bonds (springs) that connect each atom to its six nearest neighbors. Here l_j is the length of the bond j, k is the spring constant of the bonds, and $b \cdot a_{\mathrm{Ru}}$ is their preferred equilibrium length (b = preferred lattice spacing of Co or Ag divided by lattice spacing of Ru). The substrate potential parameters were obtained from LSDA calculations [10] using energies for the fcc, bridge, and on-top sites, in reference to the hcp site [11].

TABLE I. List of measured FK parameters found from χ_ν^2 analysis, compared to LSDA predicted values for the same parameters.

	Measured (minimum in χ_ν^2) $\pm$ error	LSDA
k_{Co}	1500 meV/Å² $\pm$ 500	1300 meV/Å²
b_{Co}	0.73 $\pm$ 0.24	0.77
V_{Co}	180 meV $\pm$ 60	220 meV
k_{Ag}	1100 meV/Å² (see text)	3800 meV/Å²
b_{Ag}	1.05 $\pm$ 0.35	1.03
V_{Ag}	20 meV (see text)	50 meV

The values of k and b were determined from LSDA calculations as described in Ref. [12] (for the LSDA values, see Table I). Spring constants were also determined from LSDA calculations for three types of bonds; Co-Co (k_{Co}), Ag-Ag (k_{Ag}), and Ag-Co ($k_{\mathrm{Ag\text{-}Co}}$) (we assume $k_{\mathrm{Ag\text{-}Co}}$ is a simple average of k_{Ag} and k_{Co}).

We have used the atomic configuration of a surface alloy directly from the STM image of Fig. 1(a) to create an initial alloy configuration for the FK model with LSDA-calculated parameters. This hexagonal configuration was allowed to relax within the FK model, resulting in the structure shown in Fig. 1(c). In this figure, the brightness corresponds to the lateral displacement of each atom, squared, $(\Delta r)^2$. These results are strikingly similar to the experimental data [Fig. 1(a)] and suggest that the brightness of atoms in the STM image is also due to displacements of surface atoms.

In order to quantitatively compare the model calculations to the STM images, we extract elastic FK spring constants from the data by measuring the strain displacements of individual atoms. We argue [13] that, for a small displacement of an atom in a harmonic region of potential, both the height displacement and the redistribution of the charge density (to lowest order) are proportional to the square of the lateral displacement, Δr. Hence, the STM image intensity I is given by $I = B(\Delta r)^2$, so that the lateral displacement of atoms can be estimated from measurements of the intensity. (Here we have directly attributed our intensity measurements to height without consideration of a possible electronic effect due to the asymmetry of the system, i.e., charge transfer between Ag and Co, which may contribute to apparent height. The plausibility of this assumption will be discussed below.) We define our height measurements of a Co strained atom with respect to that of unstrained Co atoms in the same row of atoms of the image shown in Fig. 1(a). Height measurements were taken for the approximately 800 Co atoms in the figure. To determine the proportionality constant, B, we measured both lateral displacement and height directly from the image in Fig. 1(a) for the atoms of largest lateral displacements [14]. Though there is a large uncertainty in the lateral displacement measurements, we find $B = 1.6 \pm 0.5$ Å^{-1}. Given this estimate of B, it is now possible to make a comparison of atomic lateral
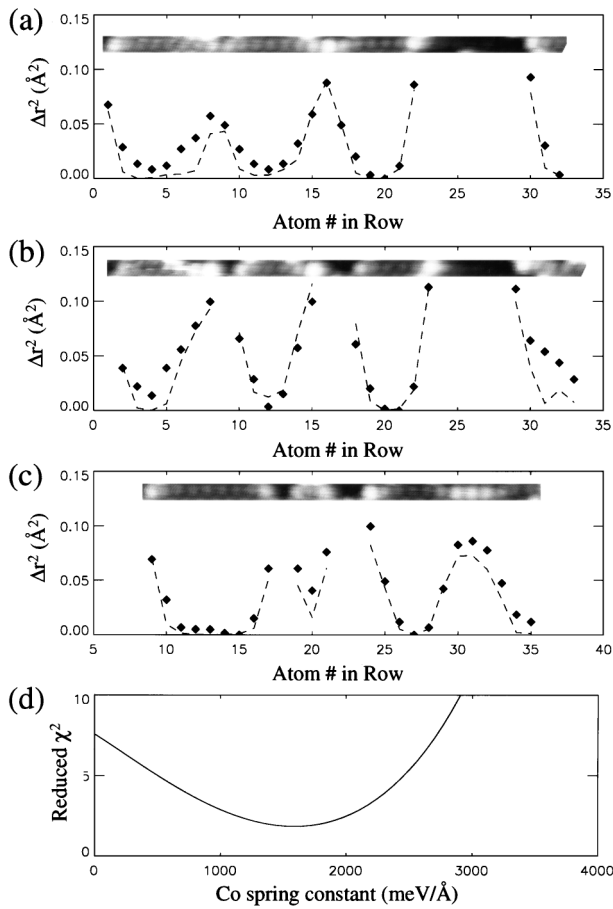
FIG. 2.   (a)–(c) Displacement squared, $(\Delta r)^2$, vs atom number in three different rows of atoms in Figs. 1(a) and 1(b). Atoms are numbered in each row by counting from the left of the image. Dashed lines are data calculated from the FK model; the solid dots are measured data from the STM image. Inset within each plot is a cutout from the STM image of the row of atoms to which the plot refers. Breaks in the plots correspond to a lack of data points for Ag atoms. (d) Plot of χ_ν^2 between measured and FK calculated displacements.

displacements between the FK simulation and the STM data for all atoms in Fig. 1. Figures 2(a)–2(c) show plots of lateral displacements from both for a few rows of atoms in Fig. 1. Agreement between the measured and the calculated values is good. The agreement between the FK model and the STM data is also illustrated by the arrows in Fig. 1(a), which point to two differently sized Ag droplets; one is large and the other is small. The Co atoms around the larger Ag droplet are noticeably brighter than those around the small droplet as would be expected if the brightness of the Co atoms is due to displacement, since the elastic forces pushing on the Co boundary atoms are larger around the larger droplet [the FK model reproduces this effect [Fig. 1(c)]]. (The substantial agreement between the results of the FK simulation and the measured data is consistent with recent work demonstrating the smallness of the contribution to the energetic stability of the CoAg surface structure from substrate relaxations

such as in continuum models of periodic self-assembled structures [15].)

Agreement of these displacements supports our previous assumption that the variation in image intensity of Co atoms is to lowest order due to their lateral displacement; electronic effects due to charge transfer can be neglected. This simplifying fact can be rationalized by pointing out that the electronegativities of Co and Ag (1.8 and 1.9 on the Pauling scale, respectively [16]) are similar, suggesting that charge transfer between Ag and Co is small and so limits the contribution of electronic effects to the brightness of Co boundary atoms. Furthermore, one check of the significance of electronic effects to the relative image intensities can be made by studying the few atoms in the STM image [Fig. 1(a)] that differ most from the FK predictions [Fig. 1(c)]. Analysis of these few discrepancies indicates that there is no straightforward correlation between the number of Ag nearest neighbors and the brightness of the Co atoms [14]. If electronic effects, which depend on the configuration of nearby Ag atoms, were significant, one would expect a correlation between Co atom intensity and the number of Ag nearest neighbors as seen, for instance, in the Au/Ni(111) system [17] [the electronegativity difference between Au (2.4) and Ni (1.8) [16] is 0.6, suggesting a significant charge transfer from Ni to Au]. These results lend confidence to the relationship $I \propto (\Delta r)^2$ in the CoAg/Ru system.

We are also able to compare the LSDA calculated spring constants to those extracted from our STM data. Spring constants from our STM image were obtained by repeating the above FK calculations for different values of k_{Co} and comparing the resulting strains of the FK simulations with measured strains from our STM data. This comparison is displayed in Fig. 2(d) by a plot of χ_ν^2 (defined as the sum of the differences at every data point divided by the number of data points) versus k_{Co} for a range of Co spring constants. The minimum in χ_ν^2 at the value of $k_{Co} = 1500$ meV/Å^2 is remarkably close to the LSDA calculated value of 1300 meV/Å^2.

Similar analysis has been done for the other parameters such as b_{Co}, V_{Co}, k_{Ag}, b_{Ag}, V_{Ag}, and $k_{Ag\text{-}Co}$, where V_{Co} and V_{Ag} are the potentials that were calculated for the Ru bridge site. Table I shows the resulting minimums in χ_ν^2, the estimated uncertainty (primarily due to uncertainty in proportionality constant, B), as well as the LSDA predicted values. Our analysis for $k_{Ag\text{-}Co}$ indicates that $k_{Ag\text{-}Co}$ need only be larger than 2000 meV/Å^2. We note however, that the measured values for k_{Ag} and V_{Ag} are inside the large uncertainty of the results from our analysis. The above χ_ν^2 analysis was done by keeping all parameters fixed except one while finding a minimum in χ_ν^2. Ideally, one would want to allow all parameters to vary while finding the minimum χ_ν^2. We have done this for three parameters: k_{Co}, b_{Co}, and V_{Co}, which determine the Co surface stress. The resulting χ_ν^2 minimum for the surface stress of Co/Ru, $\tau = (3/2)k_{Co}(1 - b_{Co})$ is

4.8×10^2 meV/Å^2 and can be compared to the LSDA calculated surface stress of 4.5×10^2 meV/Å^2. This agreement validates the LSDA calculations.

The above analysis has shown that the 2D FK model successfully describes the atomic displacements at the boundaries. We can now illustrate how surface stress contributes to determining surface structure by using the FK model to calculate the elastic energy in this system and quantitatively compare it to the boundary energy. From the FK model with STM extracted and LSDA confirmed parameters, we find the surface energy can be lowered by 100 meV/boundary atom due to stress relief at the boundaries between Co and Ag. Using LSDA, we have calculated the unfavorable chemical bonding of Co to Ag to cost 50 meV/boundary atom. That these values are of the same order of magnitude suggests that indeed the structure we observe in this alloy results from the balance found between these two interactions [18]. Furthermore, evaluating the surface energy for different sizes of isolated hexagonal Ag droplets in a Co/Ru(0001) film by using the FK model to find the relaxation energy and using the LSDA to calculate the energetic cost of forming Co-Ag bonds, we find the minimum energy droplet size to be 19 atoms. This minimum energy droplet size is consistent with the sizes observed in thermally equilibrated CoAg/Ru(0001) films [5]. (Ag droplets are also observed at smaller Ag film concentrations, though with a slight decrease in size caused by weakening elastic interactions between droplets [7].) This size is sensitive to surface stress: If we decrease the surface stress by a factor of 2 from the value we estimate, the minimum energy Ag droplet size increases from 19 to 37 atoms [14].

In conclusion, we have shown how the STM can be used to understand the energetic competition between boundary energy and elastic relaxations leading to nanometer-scale structure formation observed in a broad range of surface systems. By parametrizing the forces acting on a surface, we demonstrate how stress due to lattice mismatch contributes to the surface energy in this surface alloy. We are thus able to quantify the energetic balance between stress relaxation and chemical bonding involved in the formation of nanometer-scale surface alloy structures formed from bulk immiscible materials.

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[12] Frenkel-Kontorova model parameters were calculated from the first principles using the Vienna *Ab Initio* Simulation Package (VASP) [10]. Computational details are discussed in Ref. [5]. The substrate potential $V_{Co}(x)$ was calculated by considering the total energy of a Co monolayer on top of a six-layer Ru(0001) slab as a function of the lateral Co position. We used the energies of hcp, hollow, on-top, and bridge sites to estimate $V_{Co}(x, y)$. Spring constant k_{Co} and lattice mismatch b_{Co} were obtained from the total energy of an eight-layer slab of Ru with Co monolayers on both sides as a function of the in-plane lattice parameter a. For each a, the total energy corresponding to eight layers of hcp Ru relaxed in the [0001] direction was subtracted to obtain the contribution associated with Co surface monolayers as the a lattice spacing. The same method was used to find k_{Ag} and b_{Ag}. The LSDA calculated Ag spring constant is larger than one would expect for bulk Ag because this constant was computed at the Ru lattice spacing (the appropriate value for the FK model). This puts the Ag in the hard core of the interatomic potential (i.e., the effective springs are stiffer).

[13] A small lateral shift in atomic position will affect the local density of states, which the STM measures, in two ways. First, the height of the atom will change proportionally to $(\Delta r)^2$. Second, redistribution of the charge density of the shifted atom will, to lowest order, also be proportional to $(\Delta r)^2$.

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[18] This energetic cost was calculated from first-principles LSDA by calculating the formation energy of stripe structures where atoms were kept at the ideal hcp lattice sites and relaxed only in the direction normal to the surface. A caveat to this explanation is that the Ag droplets should be round to minimize the boundary energy when in fact they are not. Presumably the jagged boundaries are due to entropic effects.