Short-Range Order and Phase Stability of Surface Alloys: PdAu on Ru(0001)

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Structural and thermodynamic properties of thermally equilibrated Pd-Au/Ru(0001) surface alloys are studied within the framework of lattice models based upon first-principles total energy calculations and scanning-tunneling-microscopy imaging of atomic structure. Pd-rich alloys form pseudomorphic solid-solution phases with pronounced chemical short-range order (SRO), consistent with the prediction of a low-temperature order-disorder transition to a $(\sqrt{3} \times \sqrt{3})$-$R30°$ ground state structure. Calculated and measured SRO parameters are found to be in excellent agreement and are quantitatively described by a lattice-model Hamiltonian dominated by short-ranged interactions.

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In heteroepitaxial growth, a recently observed phenomenon is the formation of thin alloy layers (generally referred to as “surface alloys”) that are localized near the film-substrate interface [1–5]. This trend has proven to be remarkably general with cases ranging from Au/Cu(100) [4], where ordering tendencies reminiscent of the bulk are observed, to surprising situations such as Au/Ni(110) [4,5], where two species are immiscible in the bulk but alloy at the surface. Because interfacial structure is a dominant factor in the determination of thin film properties, it is important to develop a detailed understanding of this alloying behavior. Such an understanding requires a thorough investigation of the thermodynamic properties of thin-film alloy systems.

Relative to the bulk, thermodynamic properties of thin-film alloys are modified through interactions with the substrate. In particular, the roles of epitaxial strain energy and elastic-dipole interactions have received considerable attention [6–9]. In addition to these important elastic-energy effects, which generally enhance mixing tendencies relative to the bulk, it is expected that interface modifications to the surface-alloy electronic structure may also affect the energetics of mixing and ordering [3,5,10]. In order to determine the relative importance of these various substrate-related effects for specific thin-film alloy systems, detailed comparisons are needed between experimental measurements for thermally equilibrated samples, and theoretical calculations which incorporate both electronic and atomic-displacement effects on an equal basis. In this Letter, we demonstrate how results of first-principles, density-functional-theory (DFT) energy calculations and scanning-tunneling-microscopy (STM) imaging of alloy atomic structure can be used within the statistical-mechanical framework of lattice models [11–14] to investigate quantitatively the energetic and thermodynamic properties of pseudomorphic surface alloys. We present results for Pd-Au alloys on Ru(0001) where STM and DFT-based results are found to be in excellent agreement and are consistent with a lattice-model Hamiltonian dominated by short-ranged interactions.

Figure 1(a) shows a representative atomic-resolution STM image of a thermally equilibrated monolayer of $Pd_{0.72}Au_{0.28}$ on Ru(0001). The structure in Fig. 1(a) is pseudomorphic with Ru(0001), and the prevalence of chains of Au (black) atoms suggests the presence of chemical short-range order (SRO) in the surface alloy, i.e., a preference for certain near-neighbor environments. This SRO is caused by an energetic preference for certain bond types in the thin-film alloy. As is demonstrated below, from a detailed analysis of the SRO it is possible to derive quantitative information about the chemical interactions in the thin-film alloy system.

To ensure that the alloy structures considered in this work are thermally equilibrated, a detailed study of the interdiffusion kinetics for Pd-Au/Ru(0001) was performed. This study made use of one-dimensional diffusion couples, as described previously [15]. It was found that the diffusivity is of the order of 1 nm^2/s at a temperature of 600 K [16], and becomes negligible (on the time scale of the experiments) at 550 K. Based on these results, the following annealing schedule was developed: After the alloys were aged at 750 K to ensure complete intermixing, an equilibration of the SRO was performed by annealing for 20 s at 570 K. The alloys were subsequently quenched to room temperature, ensuring that the STM measurements were performed for samples representing equilibrated alloys at 570 K.

Within a lattice-model framework, the chemical SRO can be described by multisite correlation functions of the form $C_{ij\cdots k} = \langle \delta S_i \delta S_j \cdots \delta S_k \rangle$, where the angular brackets $\langle\,\rangle$ denote ensemble averages, and $\delta S_i = S_i - \langle S_i \rangle$ is defined in terms of an occupation variable S_i which assumes values $+1$ (-1) if site i is occupied by Pd (Au). The *pair* correlation functions are proportional to the familiar Warren-Cowley SRO parameters which are typically measured by diffuse scattering experiments for bulk-alloy solid solutions [18]: $\alpha(r) = 1 - p_{AB}(r)/c_B = C_{i,i+r}/(1 - \langle S_i \rangle^2)$, where $p_{AB}(r)$ is the probability of finding an atom B at a distance r from an atom A, and c_B is the average concentration of B. In a

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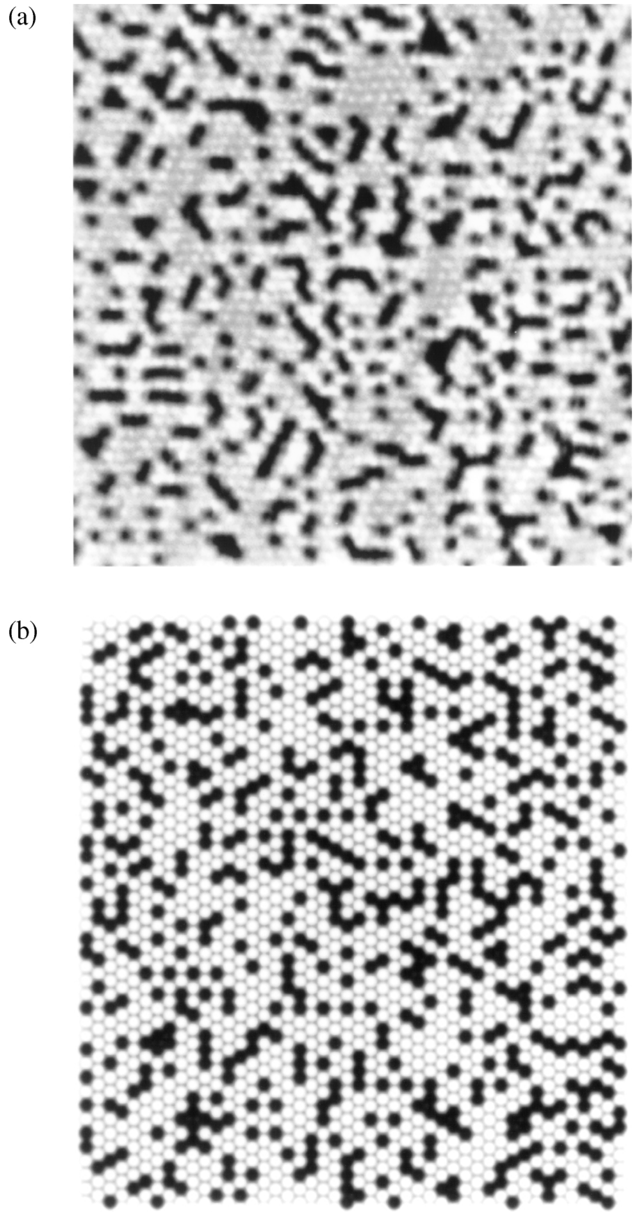

FIG. 1. STM-measured (a) and first-principles-calculated (b) structures for a $Pd_{0.72}Au_{0.28}$ alloy equilibrated at a temperature of $T^* = 573$ K. The STM image is 12 nm by 12 nm in size, and in both (a) and (b) the black and gray atoms are Au and Pd, respectively.

completely random alloy, $p_{AB}(r) = c_B$, so $\alpha(r) = 0$, and more generally $C_{ij\ldots k} = 0$. Thus, the multisite correlation functions measure the deviation from complete randomness due to chemical SRO.

From digitized versions of STM images, such as the one shown in Fig. 1(a), we have determined values of pair and triplet correlation functions for pseudomorphic Pd-rich alloys with a variety of Au compositions. The degree of SRO is strongest for the most concentrated alloy compositions. In Fig. 2 we show results for a $Pd_{0.61}Au_{0.39}$ surface alloy, obtained from an image containing 2609 atoms [19]. The open circles on the left are the values of $\alpha(r)$ for the first nine pairs. The nearest-neighbor (NN) pair SRO parameter is negative, indicating a preference for unlike-atom bonds in the surface alloy. The $\alpha(r)$ rapidly decrease to zero for distances beyond the second neighbor, indicating that no long-range order is present in the sample. Also shown on the right side of Fig. 2 are the values of C_{ijk} for the three most compact triplets. To the best of our knowledge, these results represent the first time that multisite (beyond pair) SRO parameters have been measured for an alloy solid solution. Such information is extremely difficult to measure for bulk alloys [20], but it can be obtained in the case of surface alloys in a straightforward manner due to the real-space information provided by atomic-resolution STM imaging. The largest value of C_{ijk} shown in Fig. 2 is comparable in magnitude to $\alpha(r)$ for the second-neighbor pair.

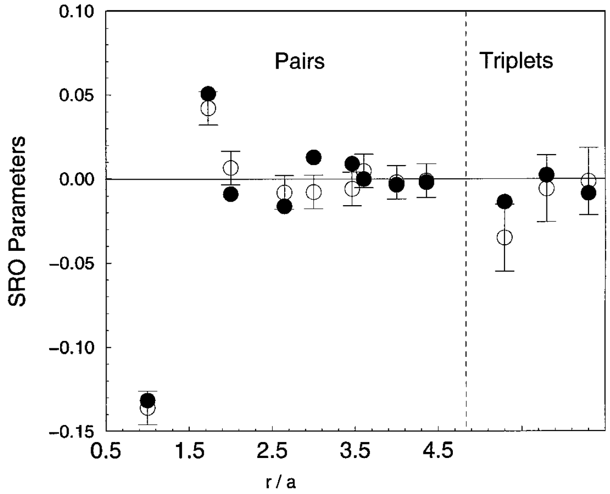

FIG. 2. STM-measured (open circles) and first-principles-calculated (filled circles) SRO parameters for nine pair and three triplet clusters from a $Pd_{0.61}Au_{0.39}$ alloy equilibrated at $T^* = 573$ K. Results for the first two triplets correspond to the two symmetry-inequivalent equilateral NN triangles, while the third corresponds to the isosceles triangle made up of two NN and one second-neighbor pair.

Formally [14], the energy $E(\sigma)$ of any arrangement $\sigma = \{S_1, \ldots, S_N\}$ of Pd and Au atoms on the Ru(0001) surface can be expressed using a two-dimensional, triangular-lattice [21], generalized Ising-model Hamiltonian:

$$E(\sigma) = J_0 + \sum_i J_i S_i + \frac{1}{2}\sum_{i,j} J_{ij} S_i S_j + \frac{1}{3!}\sum_{i,j,k} J_{ijk} S_i S_j S_k + \ldots, \qquad (1)$$

where $J_{i\ldots j}$ is the effective cluster interaction (ECI) for the cluster defined by vertices $\{i \ldots j\}$. From the data presented in Fig. 2 the energetics underlying Pd-Au/Ru(0001) surface-alloy formation can be investigated through an inverse Monte Carlo (IMC) procedure [13]. With this approach it is possible to determine values of the

ECI parameters in Eq. (1) which reproduce the measured multisite correlations at a given temperature. These ECIs can be used subsequently to compute phase diagrams and thermodynamic properties through direct MC simulation. The IMC procedure was carried out for pseudomorphic Pd-Au/Ru(0001) alloys using the SRO parameters from Fig. 2 as input. The resulting ECIs for nine pairs and two NN triplets are shown in Fig. 3 with open bars.

The ECIs in Eq. (1) also can be derived from first principles using the cluster-expansion (CE) approach developed extensively for bulk alloys [11,12]. In this approach, Eq. (1) is truncated to M terms and the cluster interactions are determined from a least-squares fit to N (usually $N > M$) directly calculated energies of simple ordered structures. For Pd-Au/Ru(0001) the total energies of $N = 14$ ordered surface-alloy structures were computed from first-principles density-functional-theory calculations [22]. It was found that four pair and two NN-triplet ECIs were sufficient to produce a lattice-model Hamiltonian which parametrizes very well these DFT results [23].

Figure 3 displays the interactions obtained from the first-principles CE (filled bars). The agreement between the first-principles-calculated and IMC-measured (empty bars) ECIs is excellent, particularly for the pair clusters [24]. The Pd-Au/Ru(0001) system is strongly dominated by the NN-pair interaction, while the more distant pair ECIs are much smaller. The next most important interactions are those corresponding to the NN triplets.

The SRO data presented in Fig. 2 provides a basis for critically testing the predictions of the first-principles cluster expansion approach in its application to surface alloys. The first-principles ECIs were used in direct MC simulations to compute SRO parameters for Pd-rich surface alloys. The image in Fig. 1(b) is a representative "snap-shot" from a MC simulation for $\mathrm{Pd}_{0.72}\mathrm{Au}_{0.28}$ at 570 K. The similarity between the chain features in Figs. 1(a) and 1(b) is apparent. To quantify the agreement between STM and the first-principles results for chemical SRO, we show in Fig. 2 CE-MC calculated SRO parameters for $\mathrm{Pd}_{0.61}\mathrm{Au}_{0.39}$ at 570 K. The agreement between the calculated and STM-measured results at the same composition is excellent; the largest discrepancies are found for the triplet C_{ijk} where the experimental error bars are largest. Similar agreement between experiment and theory was also obtained at more Pd-rich compositions.

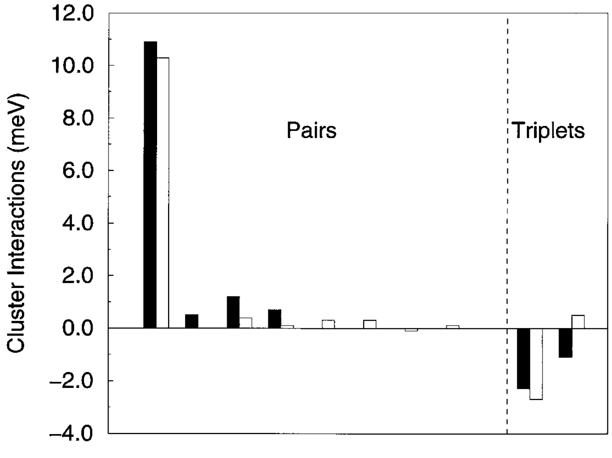

FIG. 3. Cluster interactions for pair and triplet clusters derived for Pd-Au/Ru(0001) pseudomorphic surface alloys from IMC (open bars) and first-principles CE (filled bars) approaches. Results for triplets correspond to the two inequivalent equilateral NN triangles.

The interaction parameters plotted in Fig. 3 have been used in MC simulations to investigate further the thermodynamic properties and phase equilibria of Pd-Au/Ru(0001) alloys. The chemical SRO present in Pd-rich alloys at 570 K is consistent with the presence of order-disorder transitions occurring at lower temperatures. Specifically, from MC simulations using both CE and IMC interactions, we predict a second-order transition to a long-range-ordered $(\sqrt{3} \times \sqrt{3})$-$R30°$ $\mathrm{Pd}_2\mathrm{Au}$ ground state structure below the critical temperatures T_c of 180 and 100 K, respectively. Unfortunately, the predicted values of T_c lie well below the temperature range where kinetics would permit an experimental observation of the order-disorder transition. The $(\sqrt{3} \times \sqrt{3})$-$R30°$ ordered structure is characterized by nearest- and second-nearest-neighbor SRO parameters which are negative and positive, respectively, similar to those plotted for disordered Pd-rich alloys in Fig. 2. This structure is a ground state of triangular-lattice lattice-model Hamiltonians dominated by a nearest-neighbor pair interaction [25]. The $(\sqrt{3} \times \sqrt{3})$-$R30°$ structure has been observed in a number of close-packed surface-alloy systems [26], including Pd on Au(111) [27].

We have demonstrated how the energetic and thermodynamic properties of pseudomorphic thin-film alloys may be studied quantitatively within the framework of lattice models in combination with atomic-resolution STM imaging and DFT total-energy calculations. We find that Pd-Au/Ru(0001) pseudomorphic alloys display a pronounced chemical-ordering tendency consistent with a lattice-model Hamiltonian dominated by short-ranged interactions. For bulk alloys, diffuse-scattering measurements of SRO parameters continue to play an important role in the development of modern theories of bulk-alloy phase stability. However, these scattering measurements are significantly more difficult for surface alloys due to the extremely small scattering cross section associated with an ultrathin film. Therefore, the real-space analysis presented here, which is based upon STM measurements of thermally equilibrated samples, represents a useful alternative which yields additional structural information that is very difficult to obtain by scattering measurements, namely many-body (beyond pair) correlation functions. It is expected that the STM-based approach outlined in this paper, in combination with accurate DFT calculations, will provide a framework for developing a detailed understanding of the energetics of surface-alloy formation.

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[16] A detailed description of the Pd-Au/Ru(0001) interdiffusion study exceeds the scope of this Letter and will be published in a forthcoming manuscript [O. Schaff, A. K. Schmid, N. C. Bartelt, and R. Q. Hwang (unpublished)].

[17] For Au concentrations greater than 50 at. % dislocations appear in the film due to the large size mismatch between Au and Ru.

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[19] In order to quantify the uncertainties associated with finite-sized sampling in our calculation of SRO parameters for Pd-Au/Ru(0001), we performed two independent analyses. First, MC simulations were performed using DFT-calculated ECIs. SRO parameters were computed from 100 independent 2600-atom images extracted during a 10 000-step simulation. These images produced a Gaussian distribution of SRO parameters with a standard deviation of 0.01 for the pair $\alpha(r)$ and 0.02 for the triplet C_{ijk}, giving the uncertainties in Fig. 2. As a further check, we analyzed three different STM images of alloys having compositions within a few at. % of $\mathrm{Pd_3Au}$. The SRO parameters were within a range consistent with the error bars shown in Fig. 2.

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[21] Because of the presence of the hcp substrate in the subsurface layer, the symmetry group is not hexagonal C_{6v}, but trigonal C_{3v}.

[22] Our calculations use the local-density approximation to the exchange and correlation functional [J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981)], norm-conserving pseudopotentials, and a mixed-basis expansion of the electronic wave functions in plane waves and atomic orbitals. Plane waves with kinetic energy less than 8 Ry are used for a convergence of alloy formation energies to better than 0.5 meV. The surface alloy is represented by periodically repeated slabs containing four close-packed layers of Ru sandwiched between two layers of alloy and 7 Å of vacuum. We allowed for full atomic relaxations keeping the in-plane lattice constant fixed to the calculated equilibrium lattice constant of hcp Ru. The Brillouin zone was sampled using a **k** mesh equivalent to the 12 × 12 × 1 hexagonal mesh. Convergence of the alloy formation energies with respect to slab thickness and **k** points is estimated to be within 10%.

[23] The root-mean-square (rms) and maximum errors in the fit of the ($M =$) eight-term CE to the ($N =$) 14 DFT formation energies (ΔE) were 1 and 6 meV/atom, respectively, each less than 10% of the maximum value of ΔE. The predictive power of the CE was tested by fitting ECIs to the seven lowest-energy structures and predicting the remaining seven formation energies; the rms error was 6 meV/atom.

[24] It has been demonstrated [C. Wolverton *et al.*, Solid State Commun. **101**, 519 (1997)] for size-mismatched *bulk* alloys that ECIs obtained from measured SRO parameters at one composition cannot in general be used at other compositions. This effect is due to an explicitly concentration-dependent “volume deformation” term which contributes to the formation energies but does not affect the SRO at a fixed composition. In the case of pseudomorphic *surface* alloys the average lattice constant is fixed by the substrate and the volume deformation term should be relatively unimportant.

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