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Computational study of stripe alloy formation on stepped surfaces

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The present study deals with two-dimensional (2D) surface alloy formation on stepped crystal surfaces. In specific temperature range, the high diffusion barrier for direct atomic exchange between adsorbed layer and substrate, completely block 2D intermixing on smooth, step-free surface domains. Hence, in a given energy gap the diffusion takes place exclusively via step terrace mechanism. In such systems, the dynamic competition between energy gain by mixing and substrate strain energy results in diffusion scenario where adsorbed atoms form alloyed stripes in the vicinity of terrace edges. The stripe width, L_S, is step-anisotropy dependent and correlates with the relaxation ability of the terraces in specific direction. Atomic terraces having a critical width $L_T < 3L_S$ are completely transparent for the adsorbed atoms. This phenomenon, considered as incomplete 2D alloying, opens up a way various surface pattern to be configured at different atomic levels on the crystal surface. Refining important details of diffusion behavior of adsorbed atoms and accounting for the energy barriers at specific atomic sites (smooth domains, terraces, and steps) located on the crystal surface, the presented computational model reveals a classification order of surface alloying: blocked, incomplete, and complete. Being in agreement with experimental findings, the observed stripe alloy formation could be applied to nanoscale surface design in volume-immiscible systems.

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I. INTRODUCTION

The self-organization phenomena in monoatomic layers adsorbed on crystal surfaces attract special attention in the fundamental surface physics.[1] The reason is the substantial role they play in formation of regular nanoscale objects and superlattices with unique physical characteristics.[2] Therefore, a detailed knowledge of the structure, properties, and mechanism of formation of two-dimensional (2D) atomic layers on crystal surfaces is crucial.

The present study deals with 2D surface alloy formation in atomic submonolayers adsorbed on smooth and stepped fcc (111) surfaces. As a model for studying surface alloying we choose Pb adsorption on Cu single-crystal surfaces because of the large number of experimental data collected in the last two decades.[3–8] Although Pb and Cu are volume immiscible, it has been shown that at low coverage, θ, the formation of 2D surface alloy is an energetically favorable process.[4–7] As a result, stable mixed equilibrium phases are formed with embedded Pb atoms inside the Cu top surface layer. Whereas surface alloying on the less densely packed Cu(110) and Cu(100) surfaces is a well-studied phenomenon, the atomistic mechanism of formation of surface alloy on the most compact Cu(111) crystal orientation is not clear in detail. The goal of the present study is to reveal important details of the diffusion behavior of adsorbed atoms into a step-free surface and across steps and terraces. In the framework of computational model implying many-body tight-binding atomic interactions, we examine the equilibrium properties of one-dimensional (1D) linear interface "adsorbed lattice gas—monoatomic step."

II. COMPUTATIONAL MODEL

The fine atomic structure of epitaxial interface is a result of subtle balance of competing long-range and short-range interactions. The presence of atomic steps, terraces, vacancies, and defects makes the interface layer rather complex physical system, commonly not amenable to pure theoretical treatment. In that case atomistic simulations are successfully applied to study the interface structural properties. The essential advantage of computer simulations is their ability to isolate simultaneously acting physical effects and, therefore, to evaluate separately their contributions to specific behavior of the real systems.

The computational model in the present study is based on classical canonical Monte Carlo (MC) sampling[3,9] with many-body tight-binding second-moment approximation (TB SMA) of electron density of states potential between interacting atoms.[10,11] This semiempirical potential has been extensively applied in contemporary Monte Carlo atomistic simulations of transition metals and intermetallic alloys.[10–12,14] Its advantage relates to adequate reproducing of real physical properties of surfaces and interfaces including point defects, dislocations, vacancies, grain boundaries, etc.[10,11]

In TB SMA approach the total cohesive energy for an atom i is expressed by

$$E_i = E_i^r + E_i^b, \tag{1}$$

where E_i^r being the repulsive energy

$$E_i^r = \sum_{j, r_{\alpha\beta} < r_c} A_{\alpha\beta} \exp\left[-p_{\alpha\beta}\left(\frac{\mathbf{r}_{ij}}{\mathbf{r}_{\alpha\beta}^0} - 1\right)\right] \tag{2}$$

here α and β denote the chemical nature of atoms, $\mathbf{r}_{\alpha\alpha}$ is the first-neighbor distance of the pure metal, and $\mathbf{r}_{\alpha\beta}^0 = (\mathbf{r}_{\alpha\alpha} + \mathbf{r}_{\beta\beta})/2$ if $\alpha \neq \beta$, $\mathbf{r}_{ij}$ is the distance between atoms i and j, and $\mathbf{r}_c$ is the cut-off distance for the interaction.

E_i^b is the band energy obtained in the from of the second-moment approximation of the electron density of states which is given by

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$$E_i^b = -\sqrt{\sum_{j,r_{ij}<r_c} \xi_{\alpha\beta}^2 \exp\left[-2q_{\alpha\beta}\left(\frac{\mathbf{r}_{ij}}{\mathbf{r}_{\alpha\beta}^0}-1\right)\right]}, \qquad (3)$$

where ξ is an effective hopping integral and q describes its dependence on the relative interatomic distance. In general, the band energy term in Eq. (3) can be considered as a functional expression that represents a sum over the local electronic charge density induced at site i from atoms at site j. Hence, ξ is expected to be sensitive to the number of surrounding atoms. The energy calculation is performed over all atoms within a sphere having radius three times the Cu nearest-neighbor distance. The values of the hoping integral ξ and all related parameters A, p, and q in the interacting potential, Eqs. (2) and (3), are taken from Refs. 10 and 11. These values are consistent with the overall thermodynamic behavior of the system since they reproduce basic physical characteristics of Pb and Cu such as melting point, evaporation energy, elastic constants, etc.[3,10–12]

The physical model is three-dimensional (3D) continuum space with system sizes $L_x=38$, $L_y=22$, and $L_z=5$ lattice units. The initial configuration is Cu(111) stepped crystal surface with random adsorption of Pb atoms at constant coverage. The large atomic terrace allows evaluating the diffusion of adsorbed atoms directly into the outermost surface layer and the diffusion through the steps. The interface energy, pair distribution function (PDF) analysis, and series successive snapshots of system configurations reveal the time evolution of atomic structure of the epitaxial interface. The simulations are performed on canonical ensemble, i.e., system with constant number of particles at constant temperature. Full lattice dynamics for all atoms in adsorbed and substrate layers is applied to allow complete spatial relaxation of the system. The final equilibrium state is realized after an average Monte Carlo time of 5×10^5 MC steps per atom. At that state, for a certain temperature, the total system energy is minimal and fluctuates around a constant value. All simulation details are described elsewhere.[3,12]

III. RESULTS AND DISCUSSION

Two basic types of surface diffusion act upon atomic structure of the epitaxial interface. The first relates to random walk of single atoms and clusters on the crystal surface, whereas the second reflects the ability of adsorbed atoms to penetrate inside the outermost surface layer. At low temperature, T_L, the atomic exchange between adsorbed atoms and substrate is tightly suppressed as a result of high diffusion energy barrier. Hence, after a simple random walk, the atoms attach to the steps, decorating the atomic terraces, Fig. 1(a). In contrast, at high temperature, T_H, the diffusion leads to complete intermixing and formation of two-dimensional surface alloy, Fig. 1(b). Being conspicuous and well worn, the limits of high and low temperature diffusions have been studied in details.[1,13,17] In the present paper, we concentrate our attention on the temperature gap between $T_L \leq T \leq T_H$, where a number of fine effects are observed. These effects could be applied to atomic surface design, for example, regular pattern formation on stepped or vicinal surfaces. The physical model reflects the atomic structure of the epitaxial interface, formed as a results of submonolayer adsorption of Pb on Cu(111) stepped substrate. It is important to note that surface alloying considered here takes place exclusively in the submonolayer range of coverage. Therefore, we simulate the equilibrium properties of the system only in the region of dilute gas at fixed Pb coverage of 0.1 monolayer (ML) at temperature of 300 K.

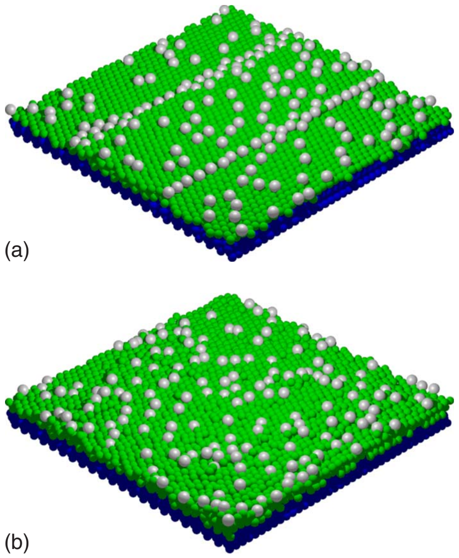

FIG. 1. (Color online) Snapshot of a random atomic configuration of 0.1 ML Pb (light gray balls) on Cu(111) stepped surface with initial Cu terrace width of 16 atoms. (a) low temperatures, $T<200$ K, only step decoration is observed without 2D intermixing between adsorbed Pb layer and Cu substrate; (b) high temperatures, $T>650$ K, complete surface alloying takes place in the interface layer.

In the lattice gas region, $\theta<0.1$ ML, the Monte Carlo simulations, based on coverage-dependent interactions, demonstrate surface alloying for the less dense Cu(110) surface.[4,12,14] The detailed simulation analysis reveals the crucial role of competing atomic interactions which control the fine interface energy balance. In the high coverage range, $0.75<\theta<0.8$ ML, the subtle interplay between the surface strain energy and the energy gain by mixing in the layer, generate a number of exotic 2D alloyed structures.[8,14] For the relatively open Cu(110) surface at Pb coverage 0.1 ML and temperature 400 K, about 80% of the adsorbed atoms are incorporated into the substrate layer. The PDF analysis reveals intermixing only within the outermost surface lattice plane. Increasing the concentration of adsorbed atoms, at coverage 0.5 ML, a reversible effect of demixing has been observed both experimentally and by Monte Carlo simulations.[4,7,12]

The surface alloying process on the most densely packed Cu(111) surface is rather different. At 0.1 ML coverage and $T<400$ K, the time evolution snapshots data show absence of Pb atoms inside the Cu(111) substrate matrix. Being different, with respect to Pb/Cu(110) interface, this result is supported by recent experimental findings for Cu(111).[15] In our simulation experiments, we did not find any direct atomic exchange between adsorbed and substrate atoms on large terraces or smooth, step-free surface areas at

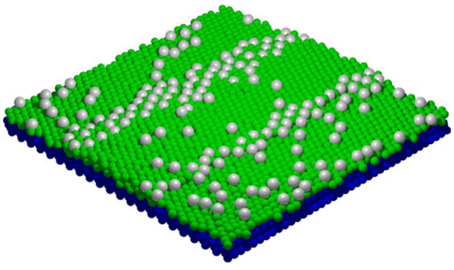

FIG. 2. (Color online) Snapshot of random atomic configuration of 0.1 ML Pb (light gray balls) at 300 K on Cu(111)-stepped surface with initial Cu terrace width of 16 atoms. The formation of 2D stripes due to Pb diffusion across the atomic steps is seen. No surface alloying takes place on a smooth, step-free surface area.

$T < 400$ K, Fig. 2. The observed behavior of the Pb/Cu(111) interface layer is in agreement with recently reported rather high diffusion energy barrier of 1.17 eV for direct embedding of Pb atoms inside the terrace.[16] Let us remind that atomic migration on the substrate is extremely favorable due to the very low surface diffusion barrier for adsorbed Pb atoms, 0.03 eV. Therefore, the high diffusion barrier and low compressibility of the densely packed fcc (111) surface tightly suppress the direct atomic exchange between adsorbed layer and substrate.

It is essential to note that the initial configuration of our system is a smooth, step-free surface area and large terrace with steps. Hence, the adsorbed atoms can inhabit sites on the substrate having different energy. The adatoms, therefore, have different ability for intermixing. In contrast to the smooth domains, near the step edges our simulations show very distinct Pb adatom diffusion inside the Cu matrix, Fig. 2. At low temperature, $T < 400$ K, PDF and snapshot data reveal surface alloying on the densely packed Cu(111) surface taking place exclusively in the vicinity of the steps of atomic terraces. Similar experimental STM observation at the periphery of atomic islands on Fe substrate has been recently reported.[19] Thermodynamically stable configuration of alloyed stripes and pure terrace areas is shown in Fig. 2, where the native Cu terrace has a width, L_T, of 16 atomic rows. After initial intensive process of intermixing between adsorbed atoms and substrate atoms located in the vicinity of step, the diffusion inside the terrace dramatically decreases. It is seen in Figs. 2 and 3 that after the third atomic row of the Cu terrace, the concentration of foreign Pb atoms dramatically falls down. The system tends to generate alloyed, finite-sized stripes, with characteristic width, L_S. For equilibrium atomic configurations, we have evaluated the stripe width by the amount of mixed Pb/Cu atomic rows in the vicinity of the terrace edges (in direction toward the terrace center). Hence, in our model, L_S is defined as the number of Cu rows comprising 90% of all Pb atoms incorporated inside the terrace. The time evolution of the Pb atom diffusion into the terrace through atomic steps is shown in Fig. 3. After penetration in depth of 3–4 atomic Cu rows of the both sides of terrace, the Pb migration is completely blocked. It is important to note that observed in Fig. 2 step-striped atomic configuration reflects stable, near equilibrium state of the system. This is manifested by the inset of Fig. 3, where the interface energy reaches minima and fluctuates around a constant value. Evidently, as a result of different elastic strain in complete surface layer and in terrace with finite size, the energy barriers for diffusion into the smooth substrate by direct atomic exchange, E_D^{DIRECT} and for diffusion across the step of terraces, E_D^{STEP}, are different. Therefore, in a specific temperature range we can block completely the direct atomic exchange and open energy window for diffusion exclusively through the steps.

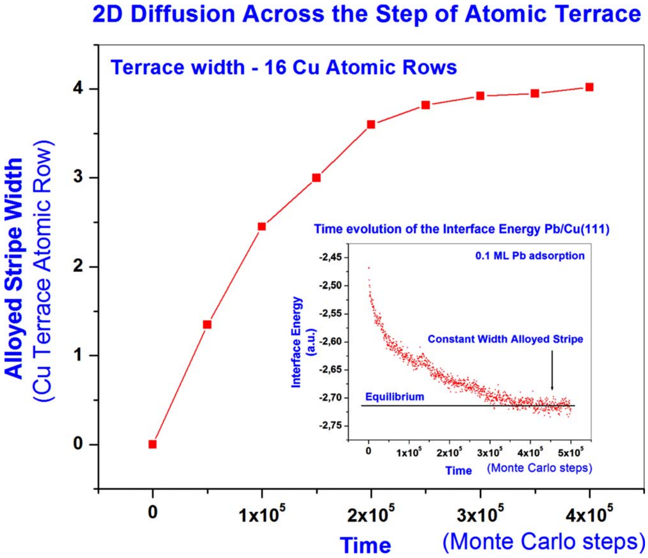

FIG. 3. (Color online) Time evolution of Pb atoms diffusion across atomic steps inside the Cu(111) terrace. After penetration in depth of 3–4 atomic Cu rows of both sides of the terrace, the Pb atoms migration is completely blocked. No surface alloying takes place on a flat, step-free surface area. The inset shows the variation in the interface energy, being indicative of the state of equilibrium.

The average stripe width L_S will depend on the diffusion coefficient D through the diffusion energy barrier E_D according to the general relation, $D \propto \exp(-\frac{E_D}{kT})$, k and T being, respectively, the Boltzmann constant and the temperature. At the same time, the simulation results in Fig. 3 reveal diffusion coefficient (for migration across the step) dependent on the position of the atomic row in direction to the center of the terrace. This is a result of different physical boundaries of the stripe. The terrace can relax only in direction out of the step, whereas inside the terrace the elastic strain increases and resists the penetration of foreign atoms. Therefore, the spreading of alloyed stripe depends on a series of diffusion barriers E_D^i for entering in the first, second, third, and ith atomic rows. Being a complex problem, evolved from simultaneously acting effects (elastic strain, nonsymmetric terrace relaxation, step anisotropy, adlayer-substrate atomic interactions, and terrace width), the evaluation of E_D^i and corresponding set of diffusion coefficients D_i is a subject of separate study.[20]

The observed diffusion slowing down argues for different time scale diffusion mechanisms in the system: (i) initial direct atomic exchange in the vicinity of the steps, blocked as a result of the elastic strain and nonsymmetric relaxation of the terrace and (ii) expected vacancy-mediated diffusion inside the terrace that could be realized at some density of

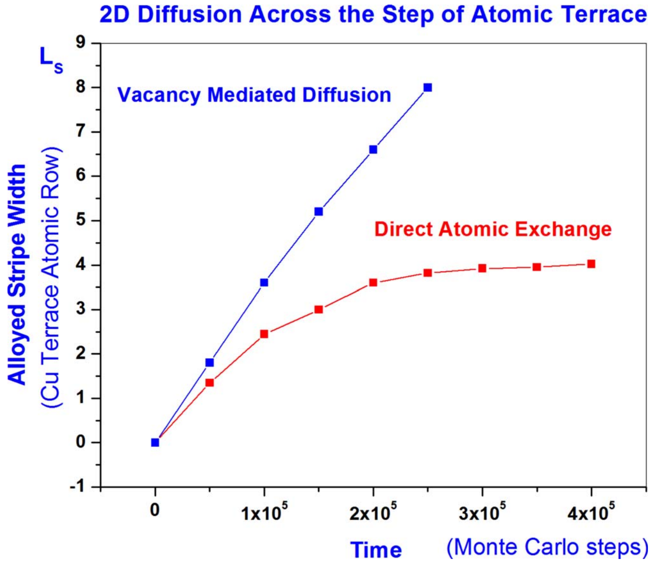

FIG. 4. (Color online) Atomic Pb diffusion across atomic steps inside the Cu(111) terrace. The Pb migration inside the terrace is completely blocked after the third Cu atomic row for dense, vacancyless terrace (lower curve). The diffusion slowing down is not observed on vacancy-populated terrace as a result of easier relaxation (upper curve).

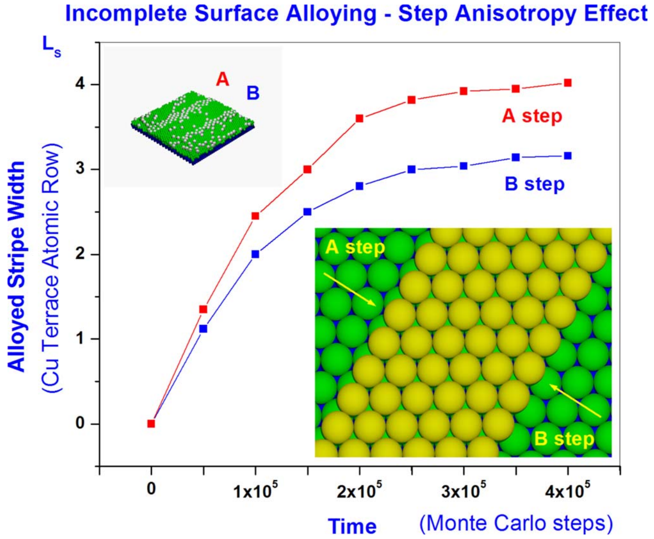

FIG. 5. (Color online) Step anisotropy effect at incomplete surface alloying. Snapshot of a random MC atomic configuration of 0.1 ML Pb on Cu(111) at 300 K and initial substrate terrace width of 16 atomic rows. The larger alloyed stripe width at step A is a result of the eased atomic relaxation of the terrace in that direction. The inset (down right) shows atomic arrangement of A and B steps with feasible directions for relaxation toward the threefold symmetry hollow sites on the substrate level. Light gray balls indicate Cu terrace atoms.

vacancies. Experimental results supporting this diffusion scenario have been recently reported.[16] The validity of the vacancy-mediated mechanism of diffusion inside the terrace has been proved in the present simulation model. In the initial atomic configuration (smooth surface and large, 16 atomic rows terrace on top) 5% atomic vacancies were randomly generated into the terrace. In that case three diffusion processes act simultaneously in the system: (i) migration of Pb atoms into the Cu terrace through the steps, (ii) direct filling of vacancies by simple jump of Pb atoms adsorbed on top of the Cu terrace, and (iii) exchange of Pb atoms on top of the terrace with Cu atoms in the vicinity of the vacancy. In contrast to the previous configuration of compact, vacancyless terrace, we did not observe any decrease in Pb diffusion inside the Cu terrace, upper curve of Fig. 4. Approaching the final equilibrium state, the system forms completely alloyed 2D Pb/Cu islands, on the top of pure, nonalloyed surface. Therefore, the presence of vacancies significantly accelerates the diffusion of adsorbed atoms inside the terrace because it reduces the elastic strain away from the steps.

To distinguish different alloying mechanisms, (i)–(iii), we have excluded the direct atomic vacancy filling. That has been done by generation of fixed number of vacancies into atomic terrace with already formed Pb/Cu alloyed stripes, as that shown on Fig. 2. In such thermodynamically stable configuration, the concentration of Pb adatoms on top of the terrace is negligible and, therefore, Pb atoms that are mostly inside the Cu terrace can participate in diffusion process. In that case, the migration of, blocked in the stripes, Pb atoms starts again and increases, because the vacancies reduce the elastic strain away from the steps. Moving toward the terrace center, the alloyed Pb atoms, assist the process new Pb atoms, adsorbed on flat substrate, to enter into the terrace across the steps. Hence, the presence of vacancies destroys the stripes as a result of the easier relaxation of the entire terrace. These results clearly demonstrate that diffusion of foreign atoms inside the terrace (far from terrace edges and steps) is a largely vacancy-assisted process. This diffusion scenario takes place at high T, near the upper temperature limit of the region $T_L \leq T \leq T_H$, where the density of atomic vacancies is large.[20]

Having established that after diffusion into the terrace, Pb atoms form stable 2D stripes, we now explore how the stripe width depends on the step orientation and on the terrace width, too. Because of the symmetry and the specific atomic arrangement on fcc(111) surface, the terrace ends with two kind of steps, A and B, Fig. 5 (inset down right), each of them having different step-free energy and relaxation ability.[17,18] The MC simulation data show that as a result of the surface anisotropy, the atomic shift toward the nearest-neighbor hollow site for Cu atom of the A-step (left step direction) costs less energy compared to that for peripheral Cu atom of the B-step (right step direction) on the terrace. This follows as well as from simple analysis of the geometrical atomic configuration, presented in the inset down right of Fig. 5. The energy barrier for Cu terrace atom from A step to move toward the nearest threefold symmetry hollow site on the substrate (see A arrow on the inset of Fig. 5) is lower compared to the identical Cu atom from B-step. Hence, the relaxation of terrace Cu atoms in direction *A* is facilitated. In support of that, the simulation snapshot analysis reveals larger stripe width L_S^A at the terrace step A, compared to L_S^B at the terrace step B, Figs. 2, 5, and 6(a). At constant $T = 300$ K we found $L_S^A \approx 1.4 L_S^B$. The elastic strain generated by foreign atoms diffused into the terrace matrix is reduced preferably in the A-step direction. Therefore, the step aniso-

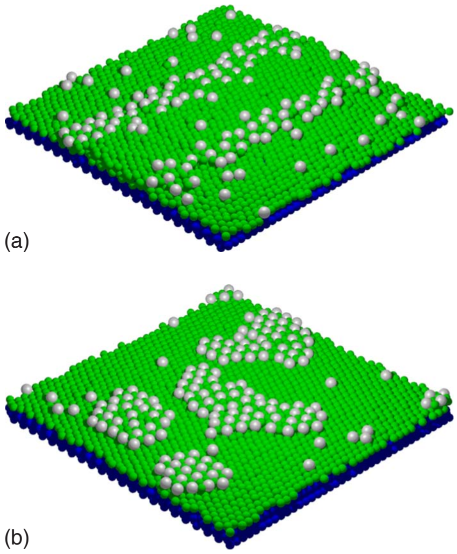

FIG. 6. (Color online) Snapshot of random atomic configuration of 0.1 ML Pb (light gray balls) at 300 K on Cu(111)-stepped surface. (a) Initial Cu terrace width of 16 atomic rows. The formation of stripes due to Pb diffusion across the atomic steps is seen. No surface alloying takes place on a flat, step-free surface area. (b) Initial Cu terrace width of six atomic rows. The terrace width is comparable with the size of alloyed stripe. Two level surface patterns are formed: completely Pb-Cu alloyed islands and pure outermost surface layer.

tropy influences the stripe width due to the different relaxation of the elastic strain generated by "larger" foreign Pb atoms into the terrace.

The average width of stripe, L_S, at 300 K is about three atomic Cu rows. We found that the stripe width L_S does not depend on the terrace width L_T for $L_T > 3L_S$. The decrease in L_T more than three times L_S makes the terrace unstable and completely transparent for Pb atoms. On Cu substrate with terrace width L_T of six atomic rows we have observed totally alloyed Pb-Cu domains. In that case the terrace is destroyed and the system forms 2D-mixed islands on pure outermost surface layer, Fig. 6(b). Therefore, at constant T, the variation in the terrace width L_T gives the opportunity to form various surface patterns: (i) alloyed Pb/Cu stripes followed by smooth, pure terrace areas (one-level patterns) for $L_T > 3L_S$, Fig. 6(a); (ii) totally alloyed Pb/Cu terraces (islands) and pure nonalloyed substrate domains (two-level patterns) for $L_T < 3L_S$, Fig. 6(b). Since the diffusion and relaxation are temperature assisted processes, after variation in T at constant L_T we have found a variation in stripe width, too.[20]

The presented MC computational model and the simulation results reveal a classification order of surface alloying, Fig. 7. Depending on the energy of adsorbed atoms, E_D^{ATOM}, and the energy barriers at specific sites on the crystal surface (steps, terraces or smooth atomic surface area) the surface alloying could be classified as follows: complete alloying ($E_D^{ATOM} \geq E_D^{DIRECT}$), incomplete alloying ($E_D^{STEP} < E_D^{ATOM} < E_D^{DIRECT}$), and blocked alloying ($E_D^{ATOM} \leq E_D^{STEP}$). Here E_D^{STEP} is energy barrier for diffusion across the steps and E_D^{DIRECT} is energy barrier for direct incorporation into a smooth surface. The suggested classification scheme opens up a way for fine tuning surface design and pattern formation. Hence, in bulk-immiscible systems, adsorbed foreign atoms can pattern stepped or vicinal crystal surfaces in the following modes, Fig. 7: (i) pure substrate layer and pure terraces decorated at steps by 1D foreign-atom lines (blocked alloying), (ii) pure substrate layer and stripe-alloyed 2D terraces or islands (incomplete alloying with atomic exchange at steps), (iii) pure substrate layer and completely alloyed 2D islands (incomplete alloying with vacancy-mediated atomic exchange into the terrace), and (iv) complete alloying (full intermixing at the epitaxial interface)

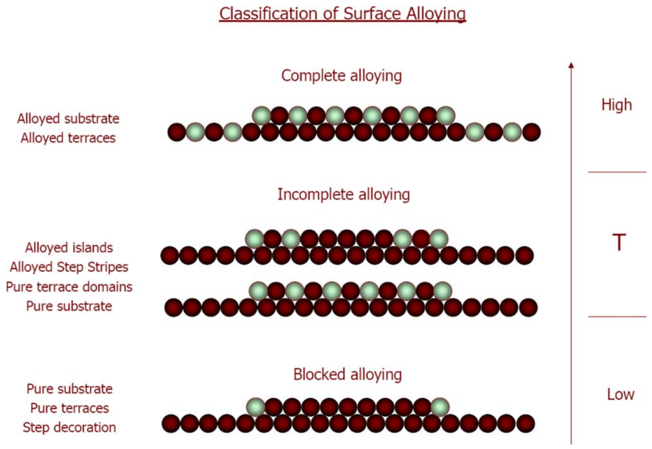

FIG. 7. (Color online) Classification of surface alloying with corresponding atomic configurations at the epitaxial interface (light gray balls indicate adsorbed foreign atoms and dark balls indicate substrate atoms). The presented order opens up a way for fine modification of the atomic surface structure and formation of regular patterns.

All of the presented atomic configurations can be generated simply by temperature variation. Furthermore, in the region of incomplete alloying, $E_D^{STEP} < E_D^{ATOM} < E_D^{DIRECT}$, an additional fine tuning, multilevel pattern formation can be accomplished. In the case of constant T, the alteration of initial terrace width L_T (i.e., by using terraces of different high index vicinal surfaces) can create on the epitaxial interface surface patterns at different atomic levels: (i) one-level patterns: alloyed stripes followed by pure, nonalloyed terrace domains, Fig. 6(a) and (ii) two-level patterns: totally alloyed terraces or islands and pure, nonalloyed substrate domains, Fig. 6(b).

IV. CONCLUSION

The present study reveals diffusion scenario of formation of 2D alloyed stripes on stepped or vicinal fcc (111) surfaces. The stripes formed at the terrace edges are followed by smooth, nonalloyed areas thus creating regular patterns on the surface. Atomic terraces having a critical width $L_T \leq 3L_S$ are unstable and completely transparent for the adsorbed adatoms. The width of stripe is step-anisotropy dependent and correlates with the relaxation ability of terraces in specific direction. The observed effect is a result of subtle interplay between layer strain energy and energy gain by mixing. The blocked direct atomic exchange between adsorbed layer and substrate opens up a way, surface patterns to be configured at different atomic levels: (i) alloyed stripes followed by pure, nonalloyed terrace domains and (ii) completely alloyed terraces or islands on top of pure, nonalloyed substrate. Accounting for the energy barriers at specific atomic sites (smooth domains, terraces and steps) located on the crystal surface, the presented computational model reveals a classification order of surface alloying: blocked ($E_D^{ATOM} \leq E_D^{STEP}$), incomplete ($E_D^{STEP} < E_D^{ATOM} < E_D^{DIRECT}$), and complete ($E_D^{ATOM} \geq E_D^{DIRECT}$). Being in agreement with experimental findings, the simulation results shed light on the crucial role of the competing atomic interactions that control the fine epitaxial interface structure. The observed phenomenon of stripe alloy formation could be applied to nanoscale surface design at volume-immiscible systems. Vicinal surfaces with appropriate terrace width distribution can be used for preparation of regular patterns with unique physical characteristics.

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