Interface mixing behaviour of Lennard–Jones FCC (100) thin film

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RESEARCH ARTICLE

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A modified Monte Carlo method combined with quenched molecular dynamics simulation is used to determine mixing energetics and concentration profiles at interface for systems containing mono-and bilayers of adatoms adsorbed on FCC (100) crystal surface. The systems under consideration are constructed via Lennard–Jones potential at temperatures near 0 K. For systems with monolayer of adatoms, intermixing at the interface becomes preferable with increasing magnitude of the potential well-depth ratio of adatom to substrate atom. The increasing tendency of intermixing is linearly enhanced when the adatom becomes smaller than the substrate atom, otherwise, the intermixing trend is non-linear and weaker. For systems with bilayers of adatoms, complex development of concentration profile is observed along with increasing magnitude of the potential well-depth ratio and atomic size difference between adatom and substrate atom. This behaviour is related to the interplay between contributions of asymmetric bond interaction and relaxation to minimise the total energy of the system.

Keywords: interfacial mixing; FCC thin film and substrate; Monte Carlo simulation; molecular dynamics

1. Introduction

Surface and interface alloying, caused by inter-diffusion of atoms located at the vicinity of the interface between substrate and adatoms, may occur when an alloy is formed in the bulk and at the surface [1]. Recent studies show that the interface mixing behaviour of systems may depend on many factors, such as misfit strain [2], crystallographic plane of substrate [3], thickness of overlayer [4], temperature [5] and processing condition [6]. Prediction of the formation of interface alloy in an epitaxial system is often difficult, yet very useful for material designs at nanoscale. This is because, at reduced dimensions, surface and interface effects become more dominant and properties of materials strongly depend on surface structure. Moreover, novel overlayer phases with a structure and periodicity substantially different from that of the bulk are often seen in systems containing very thin adatom coverage [7,8]. An ability to predict mixing at the interface would be useful, for example, in creating novel surface alloys with unique catalytic activity [9,10] and electronic devices utilizing quantum effects [11].

As discussed by Roder [12], classical theory characterised substrate-overlayer systems in terms of γ_A (surface free energy of overlayer), γ_B (free energy of substrate), and γ_{AB} (interface free energy between substrate and overlayer). In this model, intermixing behaviour of the system is determined solely by the sign of γ_{AB}. Intermixing is preferred if $\gamma_{AB} < 0$, and hindered otherwise. However, it has been found that there are shortcomings in the classical theory. First, the value of γ_{AB} is usually a poorly known quality. Second, this model cannot predict the concentration profile at the interface when intermixing is energetically preferred. Tersoff [2] investigated the effect of mismatch strain from atomic size difference between substrate atoms and adatoms on intermixing behaviour using a molecular model. By using a very simplified atomic model, which takes only strain energy into consideration, he found that, in general, the effect of strain promotes two species, which are immiscible in the bulk, to become miscible in thin film configurations, creating an interface alloy.

In this regards, we use molecular statics and modified Monte Carlo simulation to determine the mixing energetics of monolayer thin film systems and the concentration profile at the interface for bilayers thin film systems, which interact via Lennard–Jones (LJ) potentials in temperatures near 0 K. In both cases, adatoms adsorb on the (100) face of the face centred cubic (FCC) crystal surface. The FCC crystal was chosen in particular because of its popularity. Moreover, the (100) surface is one of the key surfaces, and it is of fundamental interest to understand the

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properties of hetero-structure thin film grown on top of that particular surface.

Interfacial free energy is defined as the change in the free energy of the A–B plane, which is created from contact between A and B planes. In this work, we do not measure the interfacial energy to investigate interface mixing preference of systems. Alternatively, we focus on the connection between the mismatch strain caused by the atomic size difference between the thin film and the substrate ($\sigma_{AA}-\sigma_{BB}$) and the ratio of strength of interaction between the film and the substrate ($\varepsilon_{AA}/\varepsilon_{BB}$) on the LJ potential of the interface mixing characteristics of thin film systems. We require that the aforementioned approach be robust and practical in understanding intermixing phenomena at the interface of systems containing a thin layers of adatoms. Even though only noble gas elements can be near perfectly modelled by the LJ potential, extension to other elements such as FCC transition metal elements can be done by application of the recently developed LJ-Embedded Atom Method (LJ-EAM) potential [13].

2. Simulation method

Our simulation model consists of FCC substrate and mono-and bilayers of adatoms adsorbed on FCC (100) crystal surface. The system under consideration consists of six FCC conventional unit cells in the x–y plane, as shown in Figure 1, corresponding to 72 atoms per layer, with eight layers of substrate stacked in the y direction. The four bottom substrate layers are made static by fixing the positions of atoms according to the

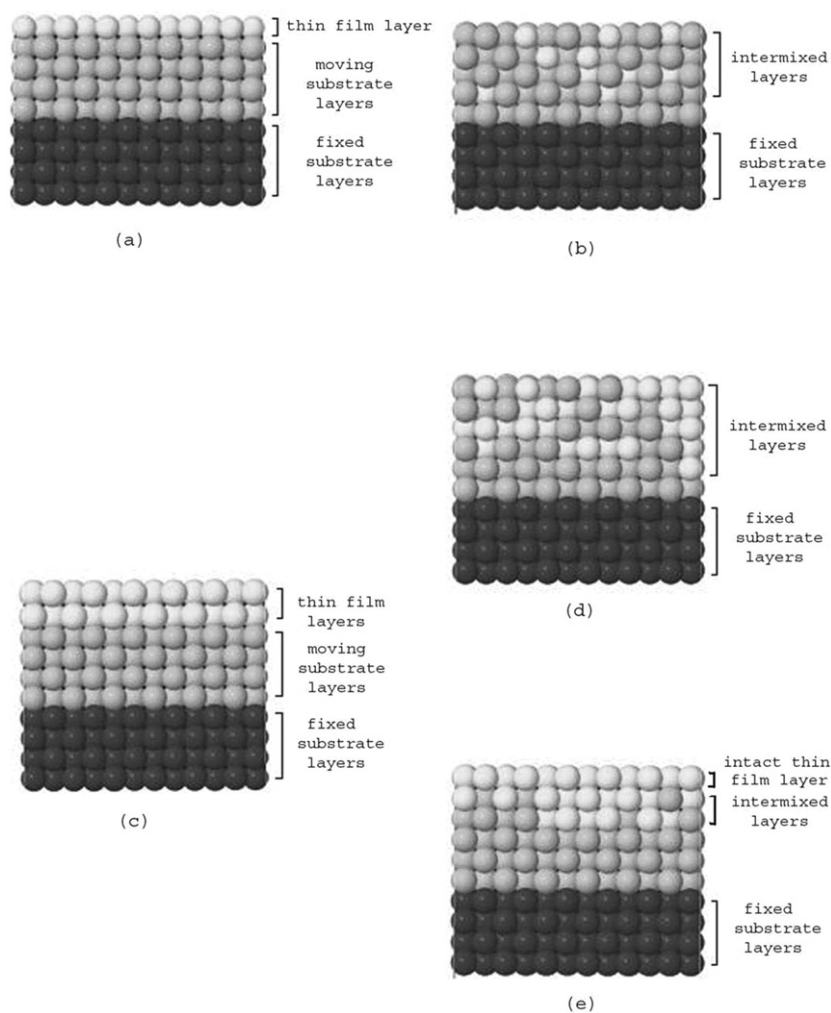Figure 1. Snapshot of the lateral (i.e. x–y plane) face of the simulated systems containing monolayer of adsorbate (a) in initial condition, (b) in fully interchanged condition, and bilayers of adsorbate (c) in initial condition, (d) in final condition where the topmost layer is mixed with substrate atom (e) in final condition where the topmost layer is intact.

lattice constant of bulk FCC crystal [14], and the next four layers are free to move. Periodic conditions ars applied to the *x*–*y* plane. An illustration of the initial condition of the system is depicted in Figure 1(a) and (c) for systems containing monolayer and bilayers of adatoms, respectively.

The interaction between adatom–adatom (A–A), substrate–substrate (B–B), and adatom–substrate (A–B) are represented by the truncated (12,6) LJ potential,

$$U_{pq} = \begin{cases} 4\varepsilon_{pq}\left[\left(\frac{\sigma_{pq}}{r}\right)^{12} - \left(\frac{\sigma_{pq}}{r}\right)^{6}\right] & r > r_c \\ 0 & r > r_c \end{cases} \qquad (1)$$

where $p = \{A, B\}$ and $q = \{A, B\}$. The Lorentz–Berthelot mixing rule [15] is employed to determine the magnitudes of σ_{AB} and ε_{AB} and to provide systems with reasonable mixing behaviour. In this study, we vary the value of σ_{AA} from 0.9 to 1.06 and ε_{AA} from 0.5 to 1.5 while both σ_{BB} and ε_{BB} are fixed at 1, thus the potential well-depth ratio of adatom to substrate atom is represented by ε_{AA} hereafter. We set temperature as low as 0.02 in simulation units (i.e. k_BT/ε) to restrict systems to the limit of low temperature to investigate intermixing energetics dominated by potential energy contributions.

The general method of simulation follows the Torelli *et. al.* [4] simulation procedure, which is a process of random exchange by Metropolis-MC mechanism between substrate atoms and adatoms followed by quenched molecular dynamics (MD) to relax the system. The purpose of the atomic exchange process and quenched MD are to hinder kinetic bottleneck of the conventional MD simulation at very low temperature. Quenched MD is done by evolving the system in time in such a way that when the negative product of the vectors of velocities and forces is produced we set the velocities to zero. In this case, systems are relaxed to local minimum in total energy closest to the starting configuration. The attempted exchange process is accepted if the total energy of the system after exchange and relaxation decreases in comparison to that of the initial configuration.

For systems with monolayer of adatoms, we restrict the exchange process to be between adatoms positioned on the topmost layer and substrate atoms positioned on the topmost layer of the substrate. Our intention is to measure the total energy change as four pairs of atoms from the two targeted layers are progressively exchanged; thus, we do not apply the acceptance criteria for this type of simulation. The simulation stops when the bilayers are fully interchanged, as illustrated in Figure 1(b). We define the total energy change, which represents the energy of mixing at specific value of fraction exchange *i*, as

$$\Delta E_i = \frac{E_{x=i} - E_{x=0}}{|E_{x=0}|} \qquad (2)$$

where *E* is the total energy of the system, and $x = i$ and 0 represent the progressively intermixed system and the initial system, respectively. Intermixing would be favoured if the total energy of the system decreases along with increasing fraction exchange; negative ΔE_i means that intermixing is preferred.

For systems of bilayers of adatoms, we use Metropolis-MC with species-exchange technique to investigate the preferred intermixed system by collecting concentration profiles of adatoms in the range σ_{AA} from 0.9 to 1.06 and ε_{AA} from 0.9 to 1.4. In this case, the exchange process is restricted to a pair of atoms of different species but the second atom is the nearest neighbour of the first atom. Since we do not measure the energy barrier of the exchange process, actual time required to reach a complete concentration profile is not our concern. Typically, for bilayer systems of interest, we performed $\sim 2 \times 10^6$ MC sweeps in accordance with the quenched MD and particle exchange method, which is equivalent to about a week of operation on an IBM $\times$ 3550 2.66 GHz platform, and for the monolayer system, it took around one third of the time for bilayer simulations.

3. Results and discussion

For all systems under consideration, we observe commensurate layers of adatoms, which are ordered into a two-dimensional phase in FCC registry of the substrate. Exceptions are for the cases when the size of adatom is the largest (i.e. $\sigma_{AA} = 1.06$), where stripes of commensurate domains separated by highly localised walls are observed. The structures are in agreement with Patrykiejew and Sokolowski's findings [16] for systems in such conditions. We illustrate the change of total energy for systems containing one monolayer of adatoms as a function of fraction exchange, which is calculated using Equation (2), in Figure 2. Note that we classify the regions from $\varepsilon_{AA} = 0.8$ to 0.9 as region I and the region from $\varepsilon_{AA} = 1.0$ to 1.1 as region II for both (a) and (b) in Figure 2.

3.1. *Interface mixing energetic of systems containing monolayer of adsorbate in configuration of FCC (100) thin film*

Under no misfit (i.e. $\sigma_{AA} = \sigma_{BB} = 1$) condition, as we gradually increase the exchange number of adatoms with
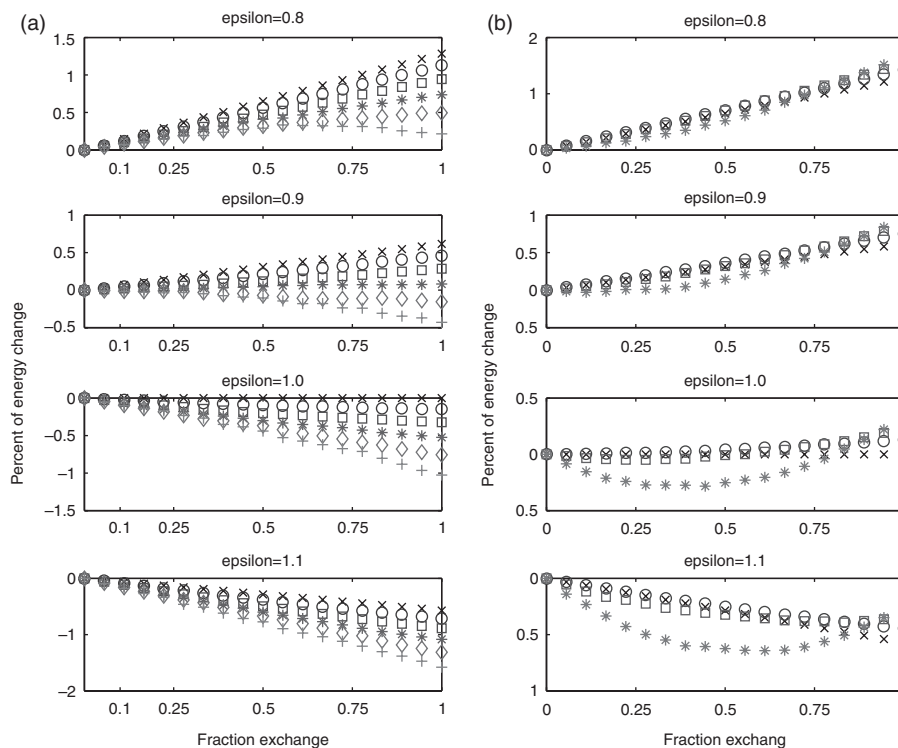
Figure 2. Plot of percentage energy change (see Equation (2)) by the fraction exchange (i.e. exchange of multiple of four adatoms with substrate atoms) for systems containing a monolayer of adsorbate and (a) $\sigma_{AA} < 1$ (b) $\sigma_{AA} > 1$. For (a): ($\times$, $\sigma_{AA} = 1$), ($\bigcirc$, $\sigma_{AA} = 0.98$), ($\square$, $\sigma_{AA} = 0.96$), (*, $\sigma_{AA} = 0.94$), ($\diamond$, $\sigma_{AA} = 0.92$), and (+, $\sigma_{AA} = 0.90$). For (b): ($\times$, $\sigma_{AA} = 1$), ($\bigcirc$, $\sigma_{AA} = 1.02$), ($\square$, $\sigma_{AA} = 1.04$), and (*, $\sigma_{AA} = 1.06$). The solid line denotes no mismatch strain, dotted line small mismatch strain ($0 < |\sigma_{AA} - \sigma_{BB}| \leq 0.04$), and dashed line high mismatch strain ($|\sigma_{AA} - \sigma_{BB}| \geq 0.06$).

substrate atoms, the change of the system energy linearly and positively increases for the low potential well-depths of adatoms (i.e. $\varepsilon_{AA} = 0.8$ and 0.9) but yields the linear decrease for the high one (i.e. $\varepsilon_{AA} = 1.1$). Note that when $\varepsilon_{AA} = 1.0$, the change of the system energy is zero due to homogeneity of the system. The latter case exhibits the increasing tendency of intermixing around the interface and this result illustrates that the intermixing of the monolayer adsorbate is greatly influenced by the surface energy minimization. For systems located in region I, Lorenz-Berthelot mixing rule [15] always give $\varepsilon_{AA} < \varepsilon_{AB} < \varepsilon_{BB}$. In this region, since the A–A bond is weaker than the A–B bond, atoms of species A would have preference to break their bonds and make bonds with species B atoms. In contrast, since the B–B bond is stronger than A–B bond, species B would remain as they are. On the other hand, for systems located in the region II, Lorenz–Berthelot mixing rule suggests the opposite trend compared to region I (i.e. $\varepsilon_{AA} > \varepsilon_{AB} > \varepsilon_{BB}$). Since the A–A bond is stronger than the A–B bond; atoms of species A prefer to retain A–A bonds. In opposite, since B–B bond is weaker than A–B bond, species B would make bonds with species A atoms.

In the application of atomic size differences between substrate and adsorbate atoms, we observe that the effect of strain is to increase the degree of intermixing. With a different model, similar behaviour was observed by Tersoff [2], who found the effects of atomic mismatch a main cause of surface-confined mixing via MC simulations of modelled atoms that only contain strain energy. He drew the conclusion of the domination of strain on the energetics of the surface by investigating several independent systems of Au on Ni(100). Our approach elucidates the measure of the contribution coming from relaxation of strain energy to the interface mixing behaviour of the LJ system. With compressive misfit strain applied by reducing the size of adatom as shown in Figure 2(a), intermixing is generally enhanced and occurs even at $\varepsilon_{AA} = 0.9$ with adatom size below $\sigma_{AA} = 0.92$. At this state, the surface relaxation is mainly driven by the size of adatom, which induces the lower energy configuration at the top and the second layer by self-induced off-lattice structure. In our study, compressive systems always show lower surface energy than those with no misfit over the varied fraction exchange.
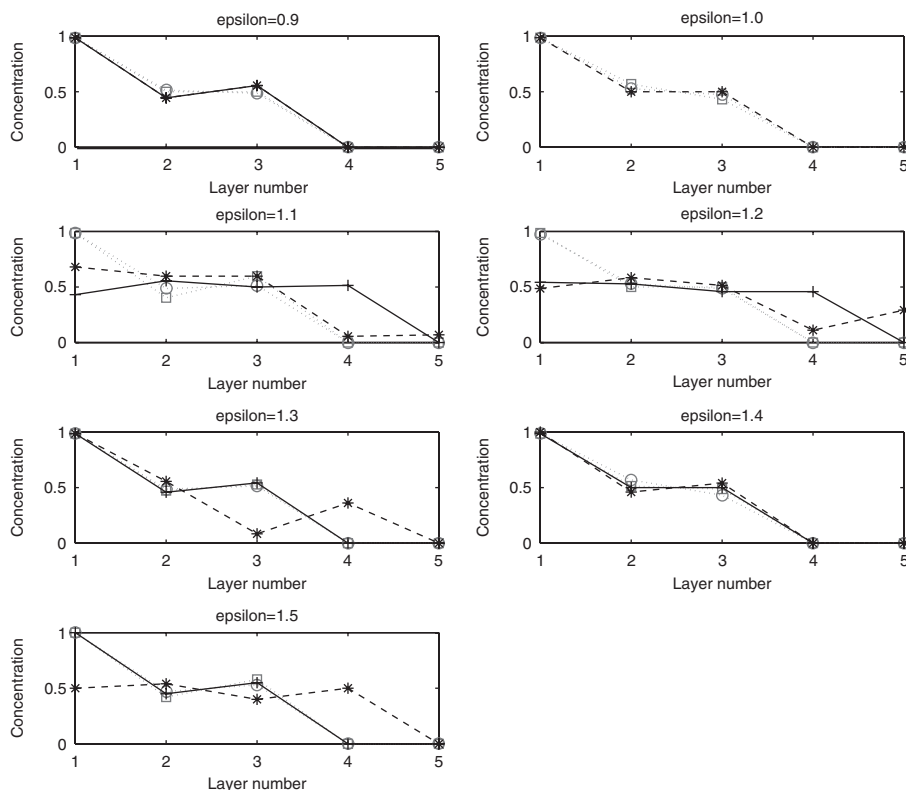
Figure 3. Concentration profile of exchanged adatoms within the fifth layer from the surface in tensile strained systems initially containing bilayers of adsorbate in the range $\varepsilon_{AA} = 0.9$ to $\varepsilon_{AA} = 1.5$. Note that epsilon represents ε_{AA}. Solid line: ($\times$, $\sigma_{AA} = 1$); dotted line: ($\bigcirc$, $\sigma_{AA} = 1.02$) and ($\square$, $\sigma_{AA} = 1.04$); dashed line: (*, $\sigma_{AA} = 1.06$).

In contrast, for systems with tensile strain as shown in Figure 2(b), the effect of mismatch strain is less pronounced for enhancing intermixing. In addition, the difference in mixing energy between systems with and without mismatch strain is virtually indistinguishable, especially for σ_{AA} below 1.04. This shows that adsorbate atoms larger than substrate atoms generally hinder intermixing. As in the compressive system, the increase of ε_{AA} triggers intermixing but the effect of different size is minimal in terms of stability of the system, except at $\sigma_{AA} = 1.06$. Interestingly, this distinct size induces a local minimum, which indicates energetic competition of the strained surface energy with respect to the size of adatom. As ε_{AA} increases, the local minimum shifts to the right, where more adatoms are replaced with substrate atoms in the second layer. At $\varepsilon_{AA} = 1.1$, when approximately half of the adatoms in the top layer ars replaced, the most stable intermixed structure forms in the tensile system. More exchange of atoms still causes intermixing behaviour but yields a less stable system. In terms of surface energetic, the system with all adatoms positioned at the second layer is more stable than the initial system (see Figure 1(a)),

but there exists a more stable intermixed structure based on the degree of fraction exchange. The tensile systems always has higher surface energy than the those with no misfit at the complete fraction exchange.

3.2. Concentration profile of systems containing bilayers of adsorbate in configuration of Lennard–Jones FCC (100) thin film

For the case of bilayers of adatoms, it is possible to distinguish the intermixed systems based on the conditions, where atoms of both layers of the film are mixed with substrate atoms, as shown in Figure 1(d), and where the topmost layer of the film is intact, as shown in Figure 1(e). This variation, which is illustrated by concentration profile in this work, depends on balanced contributions from bond substitution and strain energy. The concentration profiles of systems along with increasing value of ε_{AA} from 0.9 to 1.5 and increasing mismatch strain are shown in Figure 3 for tensile strained systems and in Figure 4 for compression strained systems.
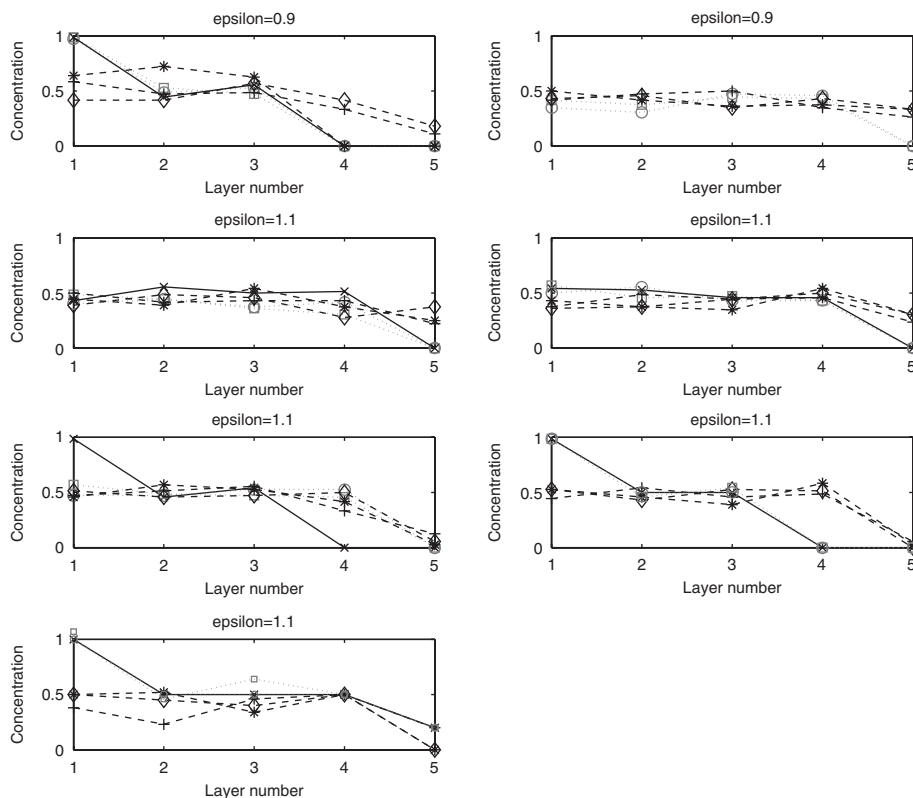
Figure 4. Concentration profile of exchanged adatoms within the fifth layer from the surface in compressive strained systems initially containing bilayers of adsorbate in the range $\varepsilon_{AA} = 0.9$ to $\varepsilon_{AA} = 1.5$. Note that epsilon represents ε_{AA}. Solid line: ($\times$, $\sigma_{AA} = 1$); dotted line: ($\bigcirc$, $\sigma_{AA} = 0.98$) and ($\square$, $\sigma_{AA} = 0.96$); dashed line: (*, $\sigma_{AA} = 0.94$), ($\diamond$, $\sigma_{AA} = 0.92$), and ($+$, $\sigma_{AA} = 0.90$).

Concentration profiles without mismatch strain show the intermixing of the topmost layer with moderately high values of ε_{AA} (i.e. 1.1 and 1.2) with substrate atoms, while an intact topmost layer is observed for small values of $\varepsilon_{AA} = 0.9$ and high values of $\varepsilon_{AA} \geq 1.3$. In the case $\varepsilon_{AA} = 0.9$, after the interface layer is mixed the exchange of atoms stops because of domination of the energetic contribution coming from increasing numbers of the stronger heterogeneous bond (i.e. ε_{AB}) below the topmost layer. On the other hand, in the case $\varepsilon_{AA} \geq 1.3$, the intact topmost layer is caused by domination of the energetic contribution coming from the stronger homogenous bond of the adatom (i.e. ε_{AA}) retaining their bond after the interface layer is mixed. In contrast to the case $\varepsilon_{AA} \geq 1.3$, the exchange continues after the interface layer is mixed and the topmost layer become mixed with substrate atoms for ε_{AA} values of 1.1 and 1.2.

Under small mismatch strain (i.e. $0 < |\sigma_{AA} - \sigma_{BB}| \leq 0.04$), we observed different behaviour between tensile and compressive mismatch strained systems. As depicted in Figures 3 and 4, the concentration profiles

reveal that the topmost layers are intact in the range from small to high value of ε_{AA} for the tensile stress condition but are mixed at moderately high values (i.e. $1.1 \leq \varepsilon_{AA} \leq 1.3$) of ε_{AA} for the compressive strained systems. Thus, the tensile strain avoids the full mixing of the thin film while the compressive strain generally triggers the mixing process. At two limits of ε_{AA} (i.e. 0.9 and 1.5) under these considerations, the topmost layers are intact even with the compressive strains since the interchanged adatoms make the system more stable by making stronger bonds with substrate atoms for the lower limit, and the adatoms are strongly bonded for the higher limit. In the case of tensile strained systems for large mismatch strain ($|\sigma_{AA} - \sigma_{BB}| \geq 0.06$), the topmost layer adatoms show an unusual mixing trend, with mixing occurring at $\varepsilon_{AA} = 1.1, 1.2,$ and 1.5. Our speculation on this finding concerns the complex contribution between the effect of exchanged bond interactions and mismatch strain to minimise the total energy of the system as ε_{AA} is varied. For compressive strained systems, on the other hand, the topmost layer adatoms are mixed under all conditions of interest.

4. Conclusion

We used a modified MC method combined with quenched molecular dynamics simulation to determine the mixing energetics of systems interacting through the LJ potential, which contain monolayer and bilayer films adsorbed on FCC (100) substrate at temperatures near zero K. For systems containing a monolayer of adatoms, we found that the changing magnitude of total energy arises from bond substitution as substrate atoms interchange with adatoms, and is responsible for the increasing tendency towards mixing with increasing values of ε_{AA}. The effect of atomic size mismatch between substrate atom and adatom is to enhance the interface mixing of systems in comparison with systems with the same value of ε_{AA} but without atomic size mismatch. We also observe that the effect of atomic size mismatch to enhance mixing is more pronounced for compression strained systems.

In the case of systems that contain bilayers of adatoms, we found a complex evolution of concentration profile along with increasing magnitude of ε_{AA} and σ_{AA}. Stress at the interface contributes to mixing if the mixed systems are more stable than the initial configuration. We attribute these phenomena to Trushin *et al.*'s [17] findings; the lattice misfit reduces the activation energy barrier. Moreover, force asymmetricity between repulsion and attraction in the LJ potential also plays an important role in inducing the complicated profile, along with increasing magnitude of mismatch compressive or tensile strain. Their findings are basically realised in three dimensions in our work. Entropy and kinetic energy contribution may become prominent at elevated temperature and change the system mixing behaviour. It would be interesting to investigate the contribution from N-body interaction to the interface mixing behaviour of thin adsorbate layer systems using a more complicated potential, such as LJ-EAM [13].

References

[1] A. Christensen, A.V. Ruban, P. Stoltze, *et al.*, Phys. Rev. B **56**, 5822 (1997).
[2] J. Tersoff, Phys. Rev. Lett. **74**, 434 (1995).
[3] W. Zhu, H.H. Weitering, E.G. Wang, *et al.*, Phys. Rev. Lett. **93**, 126102 (2004).
[4] P. Torelli, F. Sirotti, and P. Ballone, Phys. Rev. B **68**, 205413 (2003).
[5] C.-L. Kuo and P. Clancy, Surf. Sci. **551**, 39 (2004).
[6] H.L. Meyerheim, V. Stepanyuk, A.L. Klavsyuk, *et al.*, Phys. Rev. B **72**, 113403 (2005).
[7] M. Yakes, V. Yeh, M. Hupalo, *et al.*, Phys. Rev. B **69**, 224103 (2004).
[8] T. Bernhard, M. Baron, M. Gruyters, *et al.*, Phys. Rev. Lett. **95**, 087601 (2005).
[9] H.E. Hoster, E. Filonenko, B. Richter, *et al.*, Phys. Rev. B **73**, 165413 (2006).
[10] J.S. Filhol, D. Simon, and P. Sautet, Phys. Rev. B **64**, 085412 (2001).
[11] A. Podhorodecki, J. Andrzejewski, R. Kudrawiec, *et al.*, J. Appl. Phys. **100**, 013111 (2006).
[12] H. Röder, R. Schuster, H. Brune, *et al.*, Phys. Rev. Lett. **71**, 2086 (1993).
[13] H.S. Nam, M.I. Mendelev, and D.J. Srolovitz, Phys. Rev. B **75**, 014204 (2007).
[14] J.Q. Broughton and G.H. Gilmer, J. Chem. Phys. **79**, 5095 (1983).
[15] J.S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworth, London, 1969).
[16] A. Patrykiejew and S. Sokolowski, J. Phys. Chem. C **111**, 15664 (2007).
[17] O. Trushin, E. Granato, S.C. Ying, *et al.*, Phys. Rev. B **68**, 155413 (2003).