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C60-induced Devil's Staircase transformation on a Pb/Si(111) wetting layer

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Density functional theory is used to study structural energetics of Pb vacancy cluster formation on C\textsubscript{60}/Pb/Si(111) to explain the unusually fast and error-free transformations between the “Devil’s Staircase” (DS) phases on the Pb/Si(111) wetting layer at low temperature (∼110 K). The formation energies of vacancy clusters are calculated in C\textsubscript{60}/Pb/Si(111) as Pb atoms are progressively ejected from the initial dense Pb wetting layer. Vacancy clusters larger than five Pb atoms are found to be stable with seven being the most stable, while vacancy clusters smaller than five are highly unstable, which agrees well with the observed ejection rate of ∼5 Pb atoms per C\textsubscript{60}. The high energy cost (∼0.8 eV) for the small vacancy clusters to form indicates convincingly that the unusually fast transformation observed experimentally between the DS phases, upon C\textsubscript{60} adsorption at low temperature, cannot be the result of single-atom random walk diffusion but of correlated multi-atom processes.

I. INTRODUCTION

Pattern formation in heteroepitaxial overlayers via self-assembly at nano and mesoscale has attracted intensive research [1–6]. Among them the compressed two-dimensional (2D) wetting layer of Pb on Si(111) has generated great interest recently because a range of experiments at low temperature (T) have shown superfast diffusion [7–10] and explosive nucleation [11] during phase transformation in this system by fine tuning the Pb coverage (θ). A recent scanning tunneling microscopy (STM) experiment [12] showed that such exceptionally fast and anomalous mass transport can also be induced by the adsorption of C\textsubscript{60} on the Pb/Si(111) wetting layer at T ∼ 110 K with C\textsubscript{60} ejecting Pb atoms to transform the nearby region from an initial to a final Devil’s staircase (DS) phase with slightly higher θ [13,14]. Although theoretical models with long-range elastic interaction included have studied some aspects of the pattern formation [15] and collective diffusion [16] in this compressed 2D system, essential information about the atomic level energy landscape in terms of single vs multi-atom processes is still lacking.

The adsorption of C\textsubscript{60} on the Pb/Si(111) wetting layer [12] offers an opportunity to unveil such energy landscape. C\textsubscript{60} can eject a different number of substrate atoms and generate vacancies of different sizes, i.e., a single vacancy on Al [17,18], Pt [19,20], Ag [21,22], and Au [23–25] (111) surfaces while a seven-atom nanopit on Cu(111) [26,27]. Here, using density functional theory (DFT) [28,29] to calculate the formation energies of Pb vacancy clusters by incrementally removing Pb atoms from the wetting layer in C\textsubscript{60}/Pb/Si(111), we map out the thermodynamic stability of the vacancy clusters as a function of cluster size. The calculated energy landscape clarifies further the puzzling experimental observations.

Some DS phases [13] of the highly compressed wetting layer of Pb/Si(111) are schematically shown in Fig. 1 (with the atomic structures related to the C\textsubscript{60}/Pb/Si(111) experiment [12]). On the left, the surface unit cells of the (√3 × √7) and (√3 × √3) phases are shown [defined in terms of the underlying Si(111) layer]. They contain six (four) Pb atoms per five (three) Si atoms in the (√3 × √7) ([√3 × √3]) unit cell; thus θ = 6/5(4/3) monolayer (ML) or 1.20 (1.33) ML. The DS phases are linear combinations generated from these two phases for 1.20 < θ < 1.33 ML, as θ is increased gradually. In STM and spot-profile-analysis low energy electron diffraction (SPA-LEED) experiments, 12 and 16 DS phases have been atomically resolved, respectively [13]. The observation of such a large number of discrete thermodynamically stable phases within such a narrow coverage range (∼0.09 ML) is one of the best realizations of a DS in nature. For example, the DS(2,1) phase is formed by two units of (√3 × √7) and one unit of (√3 × √3) along the (110) direction appearing as long rows along (112) in STM images. It was also shown [30] that with heating (from 120 to 350 K depending on the coverage of the initial DS phase), the linear phases transform into phases of different symmetry, the so-called hexagonal incommensurate phase (HIC) and stripe incommensurate phase (SIC). A recent STM experiment [12] found that on the DS of Pb/Si(111), even at T ∼ 110 K, the adsorption of C\textsubscript{60} is capable of ejecting on average five Pb atoms (as shown schematically on the right in Fig. 1). The ejected Pb atoms increase locally the Pb coverage and induce ideal structural transformation to the DS phase next in the hierarchy, despite the low T. Because these transformations are extremely fast (with completion times smaller than the STM acquisition speed of several tens of seconds), it was inferred that they must be the outcome of correlated multi-atom processes.

DFT calculations have provided insights to explain the experimental observations on C\textsubscript{60}/metal interfaces [18,20–22,25–27,31–39]. Here we focus on the energetics of the Pb vacancy cluster formation induced by a C\textsubscript{60} ML on Pb/Si(111). We search for the lowest-energy structures in the C\textsubscript{60}/Pb/Si(111) (√7 × √7) surface unit cell as Pb atoms are gradually removed from the system. We construct the formation energy (E\textsubscript{f}) diagram as a function of the size of the Pb vacancy cluster (N\textsubscript{v}), i.e., the number of the Pb atoms being ejected. We show that it is thermodynamically favorable to create Pb vacancy clusters with the size N\textsubscript{v} ≥ 5 per C\textsubscript{60} and
II. COMPUTATIONAL METHODS

The DFT calculations have been carried out using the local density approximation (LDA) [40,41] and DFT-optPBE [42,43] exchange-correlation functionals, a plane-wave basis set and projector augmented wave [44] method as implemented in the Vienna atomic simulation package (VASP) [45,46]. DFT-LDA calculations have been shown to describe well the C$_{60}$/metal interfaces, to explain successfully the puzzle in work function change on noble metal surfaces after C$_{60}$ adsorption [32,33]; and to predict the energetics of the surface reconstructions induced by C$_{60}$ [20,21]; and even the different orientations of C$_{60}$ at the single vacancy on Ag(111) and Au(111) [25]. To estimate the van der Waals (vdW) interaction in the system [38,47], DFT-optPBE has been used to check key results. We use a 400 eV kinetic energy cutoff, 12 Å vacuum layer, and (6×6×1) k-point mesh with a Gaussian smearing of 0.05 eV. Total energies are converged to 1 meV/atom with respect to the size of vacuum and k-point mesh, and the magnitudes of the force on each atom were reduced below 0.02 eV/Å. The $E_f$ of C$_{60}$/Pb/Si(111) are calculated as a function of $\theta$,

$$E_f(\theta) = \frac{1}{N_{\text{surf}}}[E_{C_{60}/Pb/Si(111)} - E_{C_{60}} - N_{\text{Pb}}E_{\text{Pb bulk}} - E_{\text{Si(111)}}],$$

(1)

where the coverage is defined as $\theta = N_{\text{Pb}}/N_{\text{surf}}$, with $N_{\text{Pb}}$ and $N_{\text{surf}}$ being the number of Pb and top-layer Si atoms in the surface unit cell. $E_{C_{60}/Pb/Si(111)}$, $E_{C_{60}}$, and $E_{\text{Si(111)}}$ are, respectively, the total energies of the structure, of free-standing C$_{60}$ ML, and of the Si(111) substrate in the surface unit cell. For Pb, the fcc bulk energy $E_{\text{Pb bulk}}$ is used as energy reference. $E_f$ can also be regarded as a function of $N_{\text{Pb}}$ (or $N_{\text{Pb}}$) per surface unit cell. Similar formula can also be used for the adsorption energy for the case of the wetting layer itself at different $\theta$ without C$_{60}$ and the case of C$_{60}$ on Si(111) without Pb. The low-energy structures at the given $\theta$ are explored by varying the orientation of C$_{60}$ followed by thermal annealing in ab initio molecular dynamics (MD) until no lower-energy structures are found [48]. The Si(111) surface is modeled by a slab of six atomic layers with one side passivated with H.

For the study of the C$_{60}$-induced Pb ejection on Pb/Si(111), the ($\sqrt{3}\times\sqrt{7}$) surface unit cell at $\theta = 1.20$ ML cannot accommodate well a quasihexagonal array of C$_{60}$ with a ~10 Å nearest-neighbor distance between fullerenes. Based on the calculated bulk lattice constant of 5.40 Å for Si and 4.88 Å for Pb, the area of the two (111) surface unit cells of 12.8 and 10.6 Å$^2$ have the ratio ~$9/7$. So we construct a ($\sqrt{7}\times\sqrt{7}$) hexagonal surface unit cell for Pb/Si(111) with $\theta = 9/7$ (or 1.29 ML). Figure 2(a) shows the structure and surface unit cell of the ($\sqrt{7}\times\sqrt{7}$) phase. To compare the stability of the ($\sqrt{7}\times\sqrt{7}$) phase to the other known phases for Pb/Si(111), we plot $E_f$ as a function of $\theta$ in Fig. 2(b). The results agree well with previous DFT studies [49] on the known sub-ML phases. We find that the new ($\sqrt{7}\times\sqrt{7}$) structure is quite stable with
respect to the two generating phases of the DS structures, i.e., \((\sqrt{3} \times \sqrt{7})\) at \(\theta = 1.20\) ML and \((\sqrt{3} \times \sqrt{3})\) at \(\theta = 1.33\) ML, and is on the ground-state (GS) hull. Within the \((\sqrt{7} \times \sqrt{7})\) unit cell, we can study the ejection of Pb atoms in C60/Pb/Si(111) as \(N_V\) changes from 0 to 9.

### III. RESULTS

Figure 3 plots \(E_f\) for the lowest-energy structures found by thermal annealing with \textit{ab initio} MD in DFT for C60/Pb/Si(111) as a function of Pb coverage, \(\theta\) (or equivalently \(N_p\) or \(N_V\)), in the \((\sqrt{7} \times \sqrt{7})\) surface unit cell. The \(E_f\) is given both per Si(111)-(1 \times 1) and per C60. The selected atomic structures at \(N_V = 0, 3,\) and 7 are presented in Fig. 4 together with the electron density difference \((\Delta \rho = \rho_{\text{C60/Pb/Si(111)}} - \rho_{\text{C60/Si(111)}})\) to show the strength of the C60-substrate interaction. Without C60 adsorbed, the initial wetting layer has the \(E_f\) = -0.70 eV per Si(111)-(1 \times 1) as also seen in Fig. 2(b). Upon the adsorption of the C60 ML, the \(E_f\) is enhanced to -0.82 eV per Si(111)-(1 \times 1) by 0.12 eV, which corresponds to an adsorption energy of -0.78 eV per C60 on the Pb/Si(111). As shown by \(\Delta \rho\) in Fig. 4(a), the interaction is confined to the Pb atoms in the wetting layer as a charge transfer from Pb to C60, while Si(111) does not bind directly to C60.

In contrast, at the other limit \((N_V = 9)\) when all the Pb adatoms in the \((\sqrt{7} \times \sqrt{7})\) unit cell are ejected, the C60 ML binds strongly on Si(111) forming multiple Si-C covalent bonds at the interface giving an adsorption energy of -5.39 eV per C60, or equivalently, -0.77 eV per Si(111)-(1 \times 1). But overall for the whole system, the \(E_f(N_V = 0)\) is stronger than \(E_f(N_V = 9)\) because of the presence of Pb in the former case.

As Pb is ejected from the unit cell to increase the size of vacancy cluster, \(E_f\) first goes less negative quickly and reaches the maximum at \(N_V = 3\). The \(\Delta \rho\) in Fig. 4(b) shows that although the C60-substrate interaction is enhanced, the interaction is still limited to the Pb atoms in the wetting layer and Si(111) atoms still do not bind directly to C60. The high energy cost is due to the removal of Pb-Si bonds without compensating C60-Si bonds being added. Then as the vacancy cluster size increases to \(N_V = 4\), C60 starts to bind directly to Si, the stronger interaction shift \(E_f\) toward more negative and stabilize the system quickly until it reaches the minimum at \(N_V = 7\). The \(\Delta \rho\) in Fig. 4(c) at \(N_V = 7\) shows the stronger \(\sigma\)-type covalent bonding between Si and C sp orbitals. Finally, as the last two Pb atoms are removed, \(E_f\) is reduced again because the newly exposed Si at the interstitial region among C60 has no nearby C. The Pb vacancy first appears right underneath C60, then expands as a hole when the size of the vacancy cluster increases [see Fig. 4(b) for \(N_V = 3\)] and reaches the interstitial area among C60's [see Fig. 4(c) for \(N_V = 7\)].

To explain the recent observations on C60-induced transformation of the DS phases [12] at such low \(T\), we connect the GS hull across \(\theta\) and draw the tie line between the two end phases, C60/Pb/Si(111) \((N_V = 0)\) and C60/Si(111) \((N_V = 9)\) in Fig. 3. It reveals the thermodynamic stability of C60-induced Pb vacancy cluster formation on Pb/Si(111) as a function of \(N_V\). Starting with the full Pb wetting layer sandwiched between the C60 ML and Si(111), a single Pb vacancy \((N_V = 1)\) has the energy cost of 0.07 eV per Si(111)-(1 \times 1) or 0.46 eV per C60. Vacancy clusters of two and three cost even more energy with the maximum of 0.86 eV (or 0.80 eV in DFT-optPBE) at \(N_V = 3\). Vacancy cluster of four is stabilized by starting to form a stronger Si-C60 bond, but it is still above the tie line. The stable vacancy clusters are \(N_V = 5, 6, 7,\) and 8, with \(N_V = 7\) being the most stable. The tie line divides the diagram into two regions. The high energy costs of vacancy clusters for \(N_V = 1, 2, 3,\) and 4 make them inaccessible at the low \(T\) ~110 K in experiment [12]. There is a strong thermodynamic driving force to bypass this region and go directly to the stable structures starting with the vacancy clusters \(N_V \geq 5\).

In the DFT-LDA calculations, the lack of vdW contribution to C60-C60 interaction has been avoided by taking the C60 ML (not an individual C60) as the energy reference when calculating \(E_f\) in Eq. (1). To evaluate the vdW contribution to C60-substrate interaction in the system [38,47], we have used DFT-optPBE to further relax the structures and plot \(E_f\) in Fig. 3(b). The vdW interaction enhances the metallic C60-Pb bonding (0.8 eV) more than the covalent C60-Si bonding (0.4 eV) in terms of C60 adsorption energy. But the overall feature in the GS hull and phase stability does not change.

Above we have provided the thermodynamic evidence that the observed transformation of DS phases induced by C60 adsorption via Pb atom ejection at low \(T\) in the Pb/Si(111) is not by single but multi-atom processes. The DFT calculations give the vacancy cluster of \(N_V = 7\) to be the most stable, while the averaged ejection rate from experiment is five Pb atoms per C60. This difference can be justified as the following. In experiment [12], the Pb/Si(111) wetting layer was prepared in large uniform \((\sqrt{3} \times \sqrt{7})\) domains with \(\theta = 1.20\) ML; a minute density of defects is present which originates from unit cells of the low coverage \(\beta-(\sqrt{3} \times \sqrt{3})\) phase with \(\theta = 0.33\) ML [see Fig. 2(b)]. Such defects can form during the thermal annealing of the surface at ~480 K to prepare the \((\sqrt{3} \times \sqrt{7})\) phase. Experiment also found that these defect sites are the preferred nucleation sites for C60 at the beginning of deposition at low \(T\) and thereby the locations to initiate the C60-induced reconstruction. C60 is highly mobile on the \((\sqrt{3} \times \sqrt{7})\) phase and can reach these well-separated defect sites. This initial C60 adsorption at \(\beta-(\sqrt{3} \times \sqrt{3})\) defect sites corresponds to the most stable structure found in the DFT, as shown in Fig. 3 with \(N_V = 7\) or \(\theta = 0.29\) ML. This first group of C60 ejection negligible number of Pb atoms because of the small difference in the initial \(\theta\) and \(\theta\) after C60 adsorption at these defect sites.

With increasing deposition, a second group of C60 molecules reach these nucleation sites adsorbing on the adjacent \((\sqrt{3} \times \sqrt{7})\) phase and the ejection process is initiated at these boundaries. The ejected Pb atoms transform very quickly the surrounding area to the next phase in the DS hierarchy. The Pb ejection stops when all the surrounding area has been transformed into the HIC phase. From this point on, with further increase in deposition, the C60 island grows in a crystalline structure, i.e., this third group of C60 does not contribute further to the ejection rate. So, most C60 islands are built from two parts, i.e., a disordered part which ejects Pb adatoms and a crystalline part which does not. There is a height difference between the two parts of approximately 2 Å. The formation of these two parts is consistent with the energetics in Fig. 4 with the disordered part corresponding to
FIG. 3. (Color online) Formation energy \( (E_f) \) per Si(111)-(1×1) unit cell (or per C\(_{60}\) on the right) in the C\(_{60}\)/Pb/Si(111)-(√7×√7) surface unit cell calculated with (a) LDA and with (b) DF1-optPBE as a function of the number of vacancies \( N_V \) after Pb ejection by the C\(_{60}\). Red circle \((N_V = 0)\) corresponds to the initial Pb wetting layer without C\(_{60}\). The phases with \( N_V = 0 \) and \( N_V = 7 \) Pb are the most stable with energy minima on opposite side of the most unstable phase with \( N_V = 3 \). The ground state hull is shown by the solid line. The tie (dashed) line between full and zero Pb coverages tells the phase stability vs separating into the two end phases. Including the contribution of the van der Waals interaction in (b) does not affect the relative phase stability.

in the experiment is shown in Fig. 4 of Ref. [12]. An area transforms to the DS(2,1) phase from the initial (√3×√3) phase with 56 Pb atoms added and the adjacent C\(_{60}\) island contains 11 randomly nucleated C\(_{60}\). The ejection rate of ~5 per C\(_{60}\) is averaged over both the first group of C\(_{60}\) adsorbing on β-(√3×√3) with no Pb ejection and the second group of C\(_{60}\) (before crystallization).

IV. DISCUSSION

The C\(_{60}/\)Pb/Si(111) experiment was used to deduce intriguing results about the diffusion mechanism from the comparison of the final and initial state of the DS transformation, but not all the in-between steps because the STM is not a real time technique due to its slow acquisition speed. As noted in Ref. [12], no diffusing Pb adatoms are ever seen on top of the wetting layer after the ejection, the DS rows are practically completed (within the shortest time approximately tens of seconds to collect the STM image or to record the LEED pattern) and the DS rows mysteriously develop only on one side of the C\(_{60}\) island (which is not possible if the transformation to the next DS phase was due to single Pb adatom diffusion in classical random walk). Because each DS phase involves a complex pattern and the arrival and attachment of the ejected Pb atoms should be in exact locations for this new pattern to be built error-free (as seen in the experiment), this perfect transformation was found to be unusually fast. It leads to a negative activation energy for the diffusion coefficient—if it is assumed to be random walk diffusion of single Pb adatoms; therefore it implies that mass transport must be through the collective motion of the wetting layer—consistent with other unusual observations about Pb/Si(111) found in concentration profile evolution with LEEM [9,10], Pb(111) island nucleation experiments with STM, and coarsening experiments at higher coverage from x-ray diffraction [11]. Our current DFT study supplies the missing evidence on...
the type of atomistic processes for the unusual collective mechanism needed to account for the speed of the phase transformation in Pb/Si(111). There is a highly unstable size range for vacancy clusters with an energy barrier \( \sim 0.8 \) eV, between the two minima in Fig. 3, the phases with \( N_V = 0 \) and 7. It cannot be overcome at 110 K by ejected Pb atoms if they are removed successively, so collective multi-atom processes must be involved.

V. SUMMARY

We have studied the structural energetics of C\textsubscript{60}-induced Pb ejection in the C\textsubscript{60}/Pb/Si(111) system to provide the evidence for multi-atom processes need for the superfast DS transformation observed in experiment. By introducing the Pb/Si(111)-(\( \sqrt{7} \times \sqrt{7} \)) unit cell [which is as stable as the initial (\( \sqrt{3} \times \sqrt{7} \)) and the DS phases], but with the advantage to accommodate a hexagonal C\textsubscript{60} monolayer, we have calculated the vacancy formation energy in C\textsubscript{60}/Pb/Si(111) system as a function of Pb vacancy cluster size (or equivalently the number of ejected Pb atoms). From the formation energy diagram, it is clearly seen that small vacancy clusters of 1–4 have high energy cost and are not thermodynamically favored. Stable vacancy clusters are possible for sizes larger than five (with seven being the most stable), in good agreement with the estimated ejection rate of five Pb atoms per C\textsubscript{60} in the experiment, which is an average over all the C\textsubscript{60} that have joined the island. The large energy barrier \( \sim 0.8 \) eV (Fig. 3) separating the high and low Pb-coverage stable phases excludes random walk diffusion as being the mechanism for mass transport. This confirms that multi-atom processes must be responsible for the unusually fast and correlated diffusion transforming an initial DS to the phase next in the hierarchy, a type of transport process rarely seen in nature.

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