A Mechanism of 13% Lattice Expansion in C_<60> FCC(110) Thin Films Grown on the GaAs(001) As-rich Surface

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A Mechanism of 13% Lattice Expansion in C_{60} FCC(110) Thin Films Grown on the GaAs(001) As-rich Surface*

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We perform a classical molecular dynamics simulation, a first-principle calculation based on LDA, and moreover a simple theoretical analysis to examine the very interesting crystalographic structure of the first layer and overlayer C_{60}s adsorbed on the As-rich substrate of the GaAs(001) surface, which was recently observed with the STM by our group. From the classical molecular dynamics study, we reproduce the pairwise structure of C_{60} adsorbed in the first layer. On the other hand, from the first-principle study, we estimate how much the charge transfer is from the underlayer As atoms to the C_{60}s adsorbed in the first layer. We found that the amount of this charge transfer is large enough to expect that the strong dipole field caused by this dipole layer at the interface induces dipole moments in the C_{60}s adsorbed on overlayers and that the resulting dipole-dipole interaction among the overlayer C_{60} molecules is the origin of the 13% lattice expansion of the overlayer C_{60} fcc thin film observed experimentally.

KEYWORDS: C_{60}, GaAs, surface, numerical simulation

1. Introduction

Quite recently, Xue et al.[1] observed a very interesting structure of C_{60} multi-layer adsorbed on the GaAs(001) As-rich 2×4 surface by means of the scanning tunneling microscopy (STM)[2]. According to their observation, the first layer C_{60} adosorbed on the deep (~ 2.8Å) and wide (~ 8.0Å) trough in between the As-dimer rows has a tendency to line up pairwise when the coverage is increased. At the saturation coverage, each vallay is filled up with C_{60} pairs whose intermolecular distance is 10.54 ± 0.20Å, evenly spaced by 24.0A(Fig.1).

More strikingly, in the second and higher layers (at least up to 10 monolayers), C_{60} forms a highly "strained" FCC(110)-oriented structure. The observed unit cell size, 16Å×11.3Å, and the interplaner distance, 5.9Å, have roughly the ideal axis ratio $\sqrt{2}$:1:1/2 realized in the standard FCC(110), but with a lattice expansion of as much as 13% in all directions compared with the usual bulk FCC C_{60} in which the n.n. C_{60} distance is given by 10.05Å(not by 11.3Å).

Their observation raised two important questions: (1) How does the first monolayer choose such a novel and stable paired-chain structure? (2) What is the origin of the "pseudomorphic" growth of the highly strained FCC(110) crystalline film?

In order to answer these two questions, we have performed a molecular dynamics simulation[3, 1] and an *ab-initio* calculation[4]. Concerning the first question, one possible interpretation was already discussed in the original paper by Xue et al[1]. using a simple analysis based on the intermolecular interactions largely affected by the molecule-substrate interaction. Here we review their theoretical analysis first. Then we propose a mechanism concerning the second question.

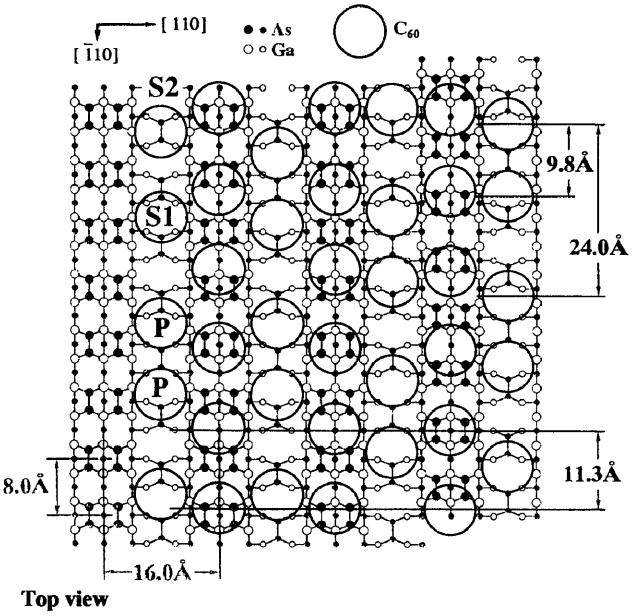

Figure 1. Geometrical structure of the GaAs(001) As-rich 2×4 surface and possible adsorption configurations of C_{60}.

We organize the rest of this paper as follows: In Section 2, we briefly review the classical molecular dynamics simulation of the first layer C_{60}. The result of *ab-initio* calculation is presented in Section 3. Then, in Section 4, we propose a new mechanism of the large lattice expansion observed in the overlayer C_{60} FCC Films. Section 5 is devoted for Conclusion.

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2. Numerical Simulations

For the C_{60} overlayer, equilibrium stacking struncture is, in principle, determined by the balance between the intermolecular potential V_{mm} and molecule-substrate potential V_{ms},

$$\sum_i \frac{\partial V_{ms}(\mathbf{R}_i)}{\partial \mathbf{R}_i} + \frac{1}{2}\sum_{i\neq j} \frac{\partial V_{mm}(|\mathbf{R}_i - \mathbf{R}_j|)}{\partial \mathbf{R}_i} = 0, \quad (1)$$

where $\mathbf{R}_i$ denotes the position of the i-th molecule. The intermolecular potential might be described by a van der Waals type interaction if there was no dipole moment induced by a charge transfer from the substrate. However, in real situation, there is a net charge transfer, and V_{ms} is largely modified by this effect.

In our molecular dynamics (MD) simulation, interatomic interactions between Ga and As atoms in the substrate as well as two carbon atoms inside a C_{60} molecule are treated by means of harmonic potentials concerning the displacements from their ideal positions, while the interaction between two carbon atoms belonging to two different C_{60} molecules is treated by means of the Lennard-Jones 12-6 potential,

$$V_{LJ}(i,j) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \quad (2)$$

with $\epsilon = 28$K and $\sigma = 3.4$Å, which is taken from ref.[5]. The effect of dipole moment is treated afterwards. On the other hand, Ga-C and As-C interactions are described by means of Tersoff's potential[6, 7].

The result for the 20 C_{60} molecules deposited on the surface is shown in Fig.2 . It confirms that the most favorable adsorption site is S1 and P for the individual C_{60} and isolated pair, respectively. The intermolecular distance of the pair estimated in this simulation is 9.8Å, which is comparable with another theoretical result by Girard et al.[8] However, this value differs as much as 2.0Å for a single pair and 0.74Å for the pair in the saturated chain formation. The large differences mean that an additional interaction may be involved.

Realizing the fact that charge transfer between the C_{60} and substrate is significant, one may expect that the induced long-range dipole-dipole repulsion may stretch the intermolecular distance. The detailed analysis using this idea is given in ref.[1], and we just repeat it here.

The equilibrium separation can be quantitatively estimated by balancing the energy increase due to the relaxation of the paired molecules and the energy decrease due to the charge-induced dipole-dipole coupling. The coupling gives rise to an interaction energy with the form,

$$V_{\mathbf{P},\mathbf{P}} = \frac{\mathbf{P}^2}{4\pi\epsilon_0 R^3} \quad (3)$$

where $\mathbf{P}$ is the induced dipole moment and $\mathbf{R}$ is the separation. To a good approximation[8], we introduce the Girifalco Potential $\Phi(\mathbf{R})$ to describe the interaction energy between the two C_{60} molecules on the surface[9],

$$\Phi(\mathbf{R}) = \frac{300\epsilon\sigma}{r_0}\left[\frac{1}{R(R-r_0)^3} + \frac{1}{R(R+r_0)^3} - \frac{2}{R^4}\right], \quad (4)$$

where r_0 is the C_{60} hard-sphere diameter, 7.1Å.

For an isolating pair, the intermolecular distance R_1 is given by

$$V_{\mathbf{P},\mathbf{P}}(R_1) = \Phi(R_1) - \Phi(R_0) \quad (5)$$

where R_0 is the equilibrium distance, 9.8Å, before introducing the charge transfer effect. Starting with the simulation results, the interaction exerted on the individual molecule of a given pair for the saturated layer can be written,

$$\begin{aligned} &V_{\mathbf{P},\mathbf{P}}(R_2) - V_{\mathbf{P},\mathbf{P}}(24 - R_2) \\ &+\sum_N \{V_{\mathbf{P},\mathbf{P}}(24N) - V_{\mathbf{P}',\mathbf{P}'}(24N)\} \\ &+\sum \{V_{\mathbf{P},\mathbf{P}}(24N + R_2) - V_{\mathbf{P}',\mathbf{P}'}(24N + R_2) \end{aligned} \quad (6)$$

where $N = 1, 2, 3...$, and R_2 is the C_{60}-C_{60} distance of the pair at the saturation coverage. $V_{\mathbf{P},\mathbf{P}} - V_{\mathbf{P}',\mathbf{P}'}$ comes from the effect of different screenings for the two molecules that have the same separation as that of the molecule we are considering. The interaction with the equivalent molecules located in other troughs has a net zero effect in the $[\bar{1}10]$ direction and is not included in Equation (4). The last two terms are very small and can be neglected.

Combinig Eqs.(1), (2), (3) and (4), we obtain $R_2/R_1 \sim 0.90$. Now we can predict the distance of the paired C_{60}'s in the paired C_{60}s in the paired-chain using the measured distance for a single pair (and vice versa.) Thaking $R_1 = 11.8$Å, the observed value for the isolating pair, we obtain $R_2 = 10.62$, which is in good agreement with the experimental value, 10.54Å.

3. Ab-initio calculation for a C_{60} adsorption

We use a first-principle code (CASTEP) based on a plane wave expansion and a norm-conserving pseudopotential, to find an optimal adsorption height of one C_{60} molecule adsorbed at the position S in Fig.1 on the trough of the GaAs 2×4 surface. In a tetragonal unit cell, we put 40 As atoms, 44 Ga atoms (altogether 6 layers) with fixing all the positions to ideal ones at and near the surface. On the other hand, the ideal rigid structure is assumed also for C_{60} with an orientation in which the topmost and the lowermost double bonds of C_{60} aline parallelly to the As dimer row. The plane-wave cutoff energy used in this calculation is 300eV. By changing the height of the center of C_{60} from the center of the As-atom on top of the trough, we estimated the total energy of the whole C_{60} and substrate system. The result is tabulated in Table 1.

From this data, we find that the optimal adsorption height, which is defined as the height of the center of the 1st layer C_{60} measured from the substrate As atom, is about $h = 5.7$Å. This value is comparable to the value, 6.2 ± 0.6Å, which can be obtained from the STM data[1], 3.8 ± 0.6Å, for the height difference between the topmost carbon atoms in the first layer C_{60} and the topmost As atoms, by adding the distance, 5.7Å, between the substrate As atoms under C_{60} and the toplayer As atoms

Table 1
Relative total energy values estimated by the present calculations for various adsorption heights

adsorption height h (Å)	4.6	4.8	5.5
relative energy (eV)	7.92	4.08	0.07

adsorption height h (Å)	5.7	5.9	7.3
relative energy (eV)	0.00	0.30	0.97

and subtracting the radius, $D/2 = 3.3$Å, of C_{60}. See Fig.3 for the illustration.

Then, at this optimal adsorption height, we calculated the charge density distribution. The isodensity surface of the resulting total charge density distribution is shown in Fig.4. Now, from this distribution, we can estimate how many electrons transfer from As atoms locating on the bottom of the first layer C_{60} molecules to these C_{60}s. The estimated amount of the charge transfer is about 1.76 electrons per one C_{60}.

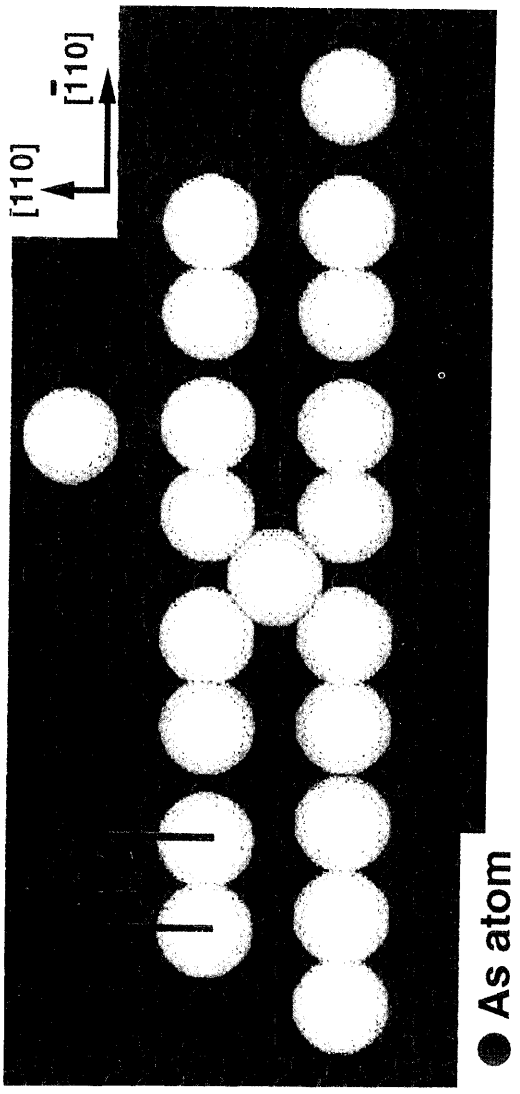

Figure 2. A snapshot of the molecular dynamics simulation. After launching to the center of the surface, C_{60} are diffusing to the optimal adsorption sites.

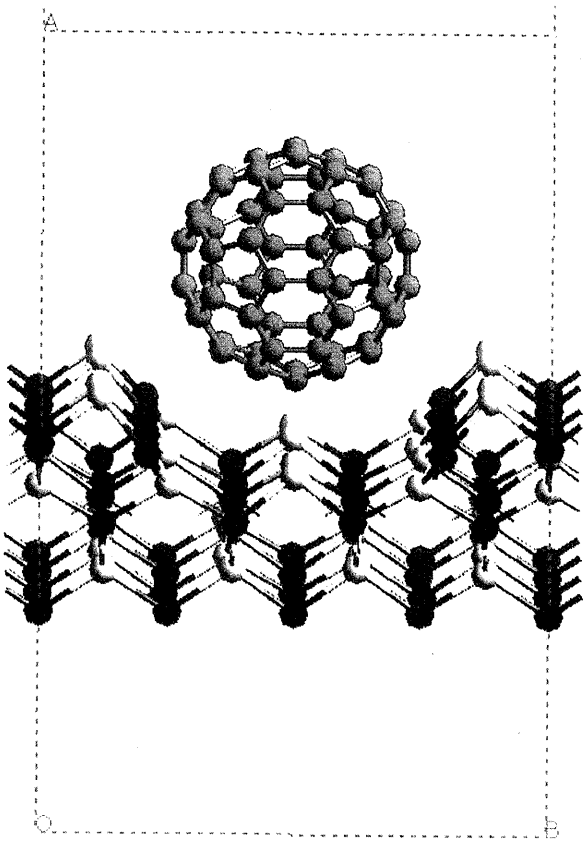

Figure 3. Geometrical illustration of the first layer C_{60}.

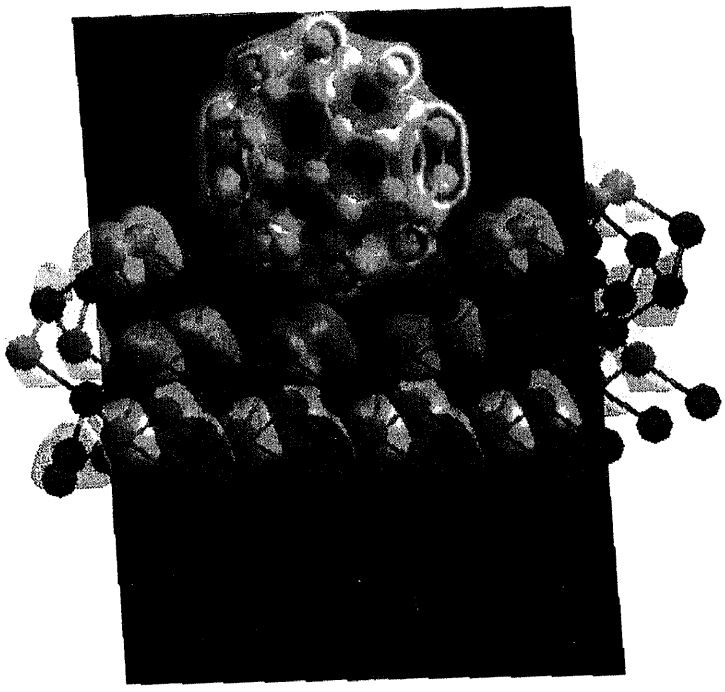

Figure 4. Isodensity plot of the total electron charge density distrubution.

4. A Mechanism of the FCC Lattice Expansion

Now we propose a mechanism of the 13% lattice expansion of the C_{60} fcc structure observed in the overlayers up to at least 10 monolayers. The main idea is to imagine also for C_{60}s in overlayers a dipole moment successively induced by the dipole field which is originally caused by the strong charge transfer from the substrate to the first-layer C_{60}s. The width of the dipole layer (dipole distance) realized in between the first layer of C_{60} and the substrate may be regarded as the same order as the adsorption height, $h = 5.7 \times 10^{-8}$cm. Then, the dipole moment per one C_{60} amounts to

$$P_1 = Q_1 h = 1.6 \times 10^{-26}\text{Coulomb} \cdot \text{cm}, \tag{7}$$

where $Q_1 = 1.76e = 8.4 \times 10^{-10}$Coulomb is the absolute value of the charge transfer from the As-substrate to one C_{60}. The electric field caused by this dipole layer is given by

$$E(\sigma, h, z) = \frac{\sigma}{4\pi\epsilon_0} \int dxdy \left[\frac{1}{x^2+y^2+z^2} - \frac{1}{x^2+y^2+(z+h)^2} \right] = \frac{\sigma}{\epsilon_0} \log\left|\frac{z+h}{z}\right| \tag{8}$$

as a function of the two-dimensional charge density σ, the dipole distance h, and the distance z from the center of the first layer C_{60}. When z becomes large, this electric field behaves as $\sigma h/\epsilon_0 z$. Here the charge density σ is estimated to be $Q_1\rho$ with ρ the two-dimensional number density of C_{60} in the first layer. This dipole field causes the dipole moment in C_{60} adsorbed in the second layer. The amount of the induced dipole moment in the second-layer C_{60} is given by

$$P_2 = \alpha E(Q_1\rho, h, d), \tag{9}$$

where d is the interlayer distance of the C_{60} and α the dielectric polarizability of C_{60}.

Using the values, $Q_1 = 1.76e = 2.8 \times 10^{-19}$Coulomb, $\rho = 10^{16}/(16\times11.3) = 5.5\times10^{13}\text{cm}^{-2}$, $h = 5.7\times10^{-8}$cm, $d = 5.9 \times 10^{-8}$cm, $\alpha/4\pi\epsilon_0 = 83/4\pi\text{Å}^3 = 6.6 \times 10^{-24}\text{cm}^3$ in ref.[10–13], we find

$$E_2 = \frac{1.6 \times 10^{-4}}{4\pi\epsilon_0}\text{Coulomb} \cdot \text{cm}^{-2}.$$

$$P_2 = \alpha E_2 = 1.1 \times 10^{-26}\text{Coulomb} \cdot \text{cm}. \tag{10}$$

Since the diameter D of C_{60} is given by $D = 6.5 \times 10^{-8}$cm, the charge $\pm Q_2$ induced in one C_{60} in the second layer amounts to

$$Q_2 = P_2/D = 1.7 \times 10^{-19}\text{Coulomb}. \tag{11}$$

The induced dipole in the second-layer C_{60}s as well as the first-layer dipole causes, in turn, the dipole in the third-layer C_{60}, and so forth. The amount of the electric field at the third-layer C_{60} is given by

$$E_3 = E(Q_2\rho, D, d) + E(Q_1\rho, h, 2d) = \frac{1.6 \times 10^{-4}}{4\pi\epsilon_0}\text{Coulomb} \cdot \text{cm}^{-2}. \tag{12}$$

Then, we can estimate the induced dipole moment of the third-layer as

$$P_3 = \alpha E_3 = 1.3 \times 10^{-26}\text{Coulomb} \cdot \text{cm}, \tag{13}$$

and in turn the induced charge, $\pm Q_3$, in the third layer C_{60} as

$$Q_3 = P_3/D = 2.0 \times 10^{-19}\text{Coulomb}, \tag{14}$$

In similar way, we can estimate the induced dipole moment of C_{60} in the fourth layer as $P_4 = 1.7 \times 10^{-26}$Coulomb·cm. This is a very striking result because the induced dipole mement does not decrease at all but increases gradually, instead. Strictly speaking, the present way of determing recursively the induced dipole moment in each layer is not correct, since the induced dipole mements in all the layers should be determined selfconsistently by taking into account the influence from all the existing C_{60} layers. At least from the present simple analysis, it is clear that the induced dipole moments of C_{60} in overlayers does not decrease or only slowly decreases with the height from the interface.

Now we can estimate the magnitude of the resulting dipole-dipole interactions among the overlayer C_{60}s:

$$V_{\mathbf{P},\mathbf{P}} = \frac{\mathbf{P}^2}{4\pi\epsilon_0 R^3}, \tag{15}$$

where ϵ_0 is the dielectric constant in the vacuum and is given by $8.854 \times 10^{-21}\text{Coulomb}^2/\text{dyne}\cdot\text{cm}^3$. The 13% lattice expansion observed by Xue, et al. makes all the C_{60} layers commensurate to the substrate exactly. Such deformation in overlayers can be possible, only if the energy decrease due to the dipole-dipole interaction energy given by Eq.(15) exceeds the energy increase due to the Lennard-Jones-type intermolecular interaction energy, $\Phi(R)$, due to the lattice expansion. This criterion is expressed as

$$V_{\mathbf{P},\mathbf{P}}(R_1) \geq \Phi(R_1) - \Phi(R_0), \tag{16}$$

where R_0 and R_1 are, respectively, the equilibrium nearest neighbor intermolecular distances in the pure C_{60} crystal and that in the overlayer C_{60}s adsorbed on the As-rich substrate. The intermolecular potential energy, $\Phi(R)$, in Eq.(16) is given, for example, by the Girifalco potential[9],

$$\Phi(\mathbf{R}) \sim -\frac{300A}{r_0^2}\left[\frac{1}{R(R-r_0)^3} + \frac{1}{R(R+r_0)^3} - \frac{2}{R^4}\right] \sim -\frac{300A}{r_0^2}\frac{1}{R(R-r_0)^3} \tag{17}$$

where r_0 is the C_{60} hard-sphere diameter, 7.1Å, and $A = 3.2 \times 10^{-59}\text{erg}\cdot\text{cm}^6$. From the knowledge of the ideal C_{60} crystal we have $R_0 = 10.05$Å, while from the STM data[1] we have $R_1 = 11.3$Å. Using these values and $P \sim 1 \times 10^{-26}$Coulomb·cm, we can derive a rough estimation of the left-hand-side of Eq.(16) as 6.2×10^{-13}erg, while for the right-hand-side we derive $\Phi(R_1) = -2.3 \times 10^{-13}$erg and $\Phi(R_0) = -7.0 \times 10^{-13}$erg. Thus, Eq.(16) is certainly fulfilled. This fact guarantees that the lattice expansion occurs due to the induced dipole moments of the C_{60}s adsorbed in overlayers.

5. Conclusion

In conclusion, we have performed the first-principle calculation based on LDA to estimate the charge transfer from the underlayer As atoms to the C_{60}s adsorbed in the first layer. The amount of this charge transfer is so large that this GaAs-C_{60} interface forms a very strong dipole layer. Then, from a simple analysis given in Section 4, we have shown that the strong dipole field caused by this dipole layer at the interface may induce almost the same amount of the dipole moment in C_{60}s adsorbed on overlayers. Since the resulting dipole moment largely affect the intermolecular potential between C_{60}s, we conclude that the 13% lattice expansion of the C_{60} overlayer films on GaAs As-rich substrate observed experimentally by the STM is due to the induced dipole-dipole interaction between the overlayer C_{60} molecules.

6. Acknowledgments

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