

## Structural and Electronic Properties of Two-dimensional C<sub>60</sub>

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We have explored the cohesive property of a monolayer of C<sub>60</sub> molecules (ML-C<sub>60</sub>) by using the total-energy calculations with the density-functional theory. The total energy curve calculated for ML-C<sub>60</sub>, which is obtained as a function of the lattice constant, has two minima, showing the hysteresis in the compression/tension stroke. These two minima in energy correspond to the different structural phases of ML-C<sub>60</sub>, that are the monomer and polymer phases of C<sub>60</sub>. The energy band gap within the framework of the local density approximation varies from 1.0 eV (semiconducting phase) to 0 eV (metallic phase) with the external pressure and without the structural transition from the monomer phase to the polymer one.

Key words: Fullerene, Density functional method, Polymerization, Hysteresis

### I. INTRODUCTION

The interaction between C<sub>60</sub> and the underlying substrate has been investigated with various experimental techniques in recent years. It is known that C<sub>60</sub> molecules interact strongly with metal and semiconductor substrates [1, 2] except for GaAs(110) [3, 4]. The strong interaction between the molecule and the substrate generally overcomes the intermolecular van der Waals interaction [5]. For example, highly strained C<sub>60</sub> film can be stabilized on Au(001) due to a strong molecule-substrate interaction [6]. In the case of C<sub>60</sub> on GaAs(110), commensurate C<sub>60</sub> monolayers are formed at room temperature (RT) [3]. In the commensurate C<sub>60</sub> monolayer on GaAs(110), C<sub>60</sub> molecules can adsorb at two different sites, and this causes the rippling structure of the monolayer. The rippling of C<sub>60</sub> molecules seems to reduce the strain energy due to a small intermolecular distance of 0.98 nm that has been measured along the surface parallel direction.

Recently, it has been investigated that the growth and structure of a monolayer of C<sub>60</sub> (ML-C<sub>60</sub>) on the Si(111) $\sqrt{3}\times\sqrt{3}$ R30°-Ag substrate at

room temperature and this substrate allows formation of a very flat and weakly bound C<sub>60</sub> monolayer [7]. In this system, various well-ordered C<sub>60</sub> arrangements with different strain fields in a molecularly flat C<sub>60</sub> monolayer have been found [7]. Although ML-C<sub>60</sub> can be regarded as one of the solid phase of C<sub>60</sub>, no theoretical investigation has so far been made at the structural and electronic properties of this monolayer phase. In this paper, we report a cohesive property and an electronic structure of ML-C<sub>60</sub> derived from the first-principles density functional calculation.

### II. CALCULATIONS

Although there exist various strained C<sub>60</sub> arrangements in a C<sub>60</sub> monolayer on the Si(111) $\sqrt{3}\times\sqrt{3}$ R30°-Ag surface, the most stable one shows a hexagonal molecular arrangement. It is also known that, in the two-dimensional (2D) rhombohedral phase of solid C<sub>60</sub>, each molecule is connected to each of six neighbors by [2+2] cycloaddition four-membered ring (two covalent C-C bonds between two molecules) [8–11], which is realized by the rehybridization from sp<sup>2</sup> to sp<sup>3</sup>. Hence, we employed the 2D hexagonal unit cell to represent ML-C<sub>60</sub>. The theoretical calculations were performed with TAPP (Tokyo Ab-initio Program Package) [12–14]. The total energy calculations were performed within density

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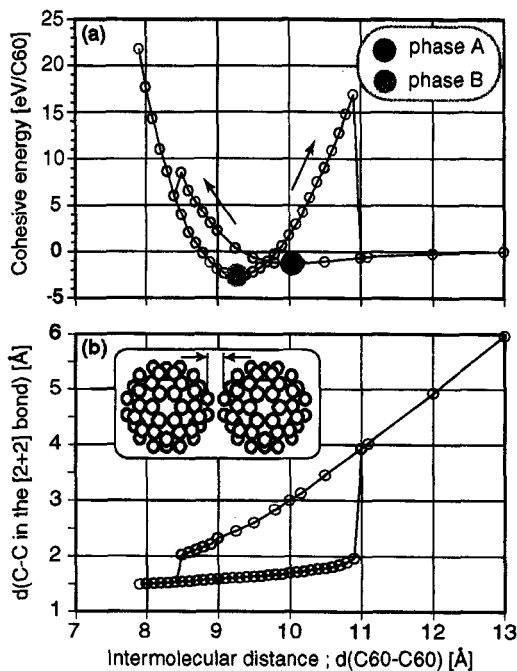


FIG. 1: (a) Cohesive energy per  $C_{60}$  and (b) interatomic distance between C atoms in the interfullerene bond as a function of intermolecular distance,  $d(C_{60}-C_{60})$ . The arrows indicate the direction of the compression/tension stroke.

functional theory [15] in the local density approximation (LDA) [16], using the ultrasoft pseudopotential [17, 18]. The Ceperley-Alder [19] form parametrized by Perdew and Zunger [20] was used for the calculation of the exchange-correlation energy. A supercell geometry was used with a large separation between  $C_{60}$  layers (interlayer distance of 14 Å so as to decouple each  $C_{60}$  layer. The wave functions were expanded in a plane-wave basis set with an energy cutoff of 20.25 Ry. 24 special k points were used to sample the 2D Brillouin zone for the 2D hexagonal unit cell. Both electronic and ionic degrees of freedom were optimized using the conjugate gradient method.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows the cohesive energy calculated for ML- $C_{60}$  as a function of the intermolecular distance between adjacent  $C_{60}$  molecules,  $d(C_{60}-C_{60})$ . In the present calculations, we performed constant volume relaxation with intermolecular distance decreasing from 13.0 Å to 7.9 Å and increasing in the opposite direction with a step of  $\Delta d(C_{60}-C_{60})=0.1$  Å. The atomic arrangement was fully relaxed at each point. Interestingly, the cohesive energy curve has two min-

ima, indicating that the system is bistable. One minimum in energy is shallow at an intermolecular distance of 10.05 Å [denoted as "phase A" in Fig.1(a)], and the other is rather deep at 9.30 Å ["phase B" in Fig.1(a)]. The calculated cohesive energy of the phase A is 1.31 eV per  $C_{60}$ , which is slightly smaller than that of bulk fcc  $C_{60}$ , 1.6 eV [21]; van der Waals like bondings are formed between adjacent  $C_{60}$  molecules in this phase. On the other hand, the cohesive energy of the phase B is 2.66 eV, each molecule being covalently bound to six neighboring molecules. Thus, these two minima in energy correspond to the different structural phases of ML- $C_{60}$ , that is to say, the monomer and polymer phases of ML- $C_{60}$ , respectively.

On the  $Si(111)\sqrt{3}\times\sqrt{3}R30^\circ$ -Ag surface, the most stable structure of the  $C_{60}$  monolayer is a commensurate  $\sqrt{21}\times\sqrt{21}R10.9^\circ$  structure, showing a complete hexagonal arrangement of  $C_{60}$  molecules with an intermolecular distance of 10.16 Å [7]. The intermolecular distance calculated for the monomer phase of ML- $C_{60}$ , 10.05 Å, is very close to the experimental one with an error of 1.1 %. This is one of the reasons why the very flat monolayer of  $C_{60}$  can be formed on the  $Si(111)\sqrt{3}\times\sqrt{3}R30^\circ$ -Ag surface.

In general, in order to reduce strain energy at interface effectively, charge transfer between overlayer and substrate takes place. However, since the interface between the  $Si(111)\sqrt{3}\times\sqrt{3}R30^\circ$ -Ag surface and the ML- $C_{60}$  is perfectly lattice-matched and is expected to be nearly free of stress, such a charge transfer between them may not occur. Indeed, it has been confirmed by core-level photoemission spectroscopy that there is no significant charge transfer from the substrate to  $C_{60}$  molecules in this system [22].

More interestingly, as can be seen in Fig.1(a), the cohesive energy curve shows the hysteresis loop in the compression/tension stroke. Furthermore, the interatomic distance between C atoms in the interfullerene bond similarly shows the hysteresis as shown in Fig.1(b). Such an irreversible energetics is originated from the polymerization and depolymerization processes of ML- $C_{60}$  as follows. Figure 2 shows the optimized atomic structure of ML- $C_{60}$  at each intermolecular distance. At an intermolecular distance of 13.0 Å each molecule in ML- $C_{60}$  is isolated without any interaction between molecules [(i) in Fig.2]. With an decrease of  $d(C_{60}-C_{60})$ , the energy reaches a local minimum [(ii) in Fig.2], corresponding to the most stable monomer phase of ML- $C_{60}$  as we have mentioned before. The energy steadily increases from this equilibrium [ $d(C_{60}-C_{60})=10.05$  Å] until  $d(C_{60}-C_{60})=8.50$  Å [(iii) in Fig.3] in the compression stroke. As we can see in Fig.2, the

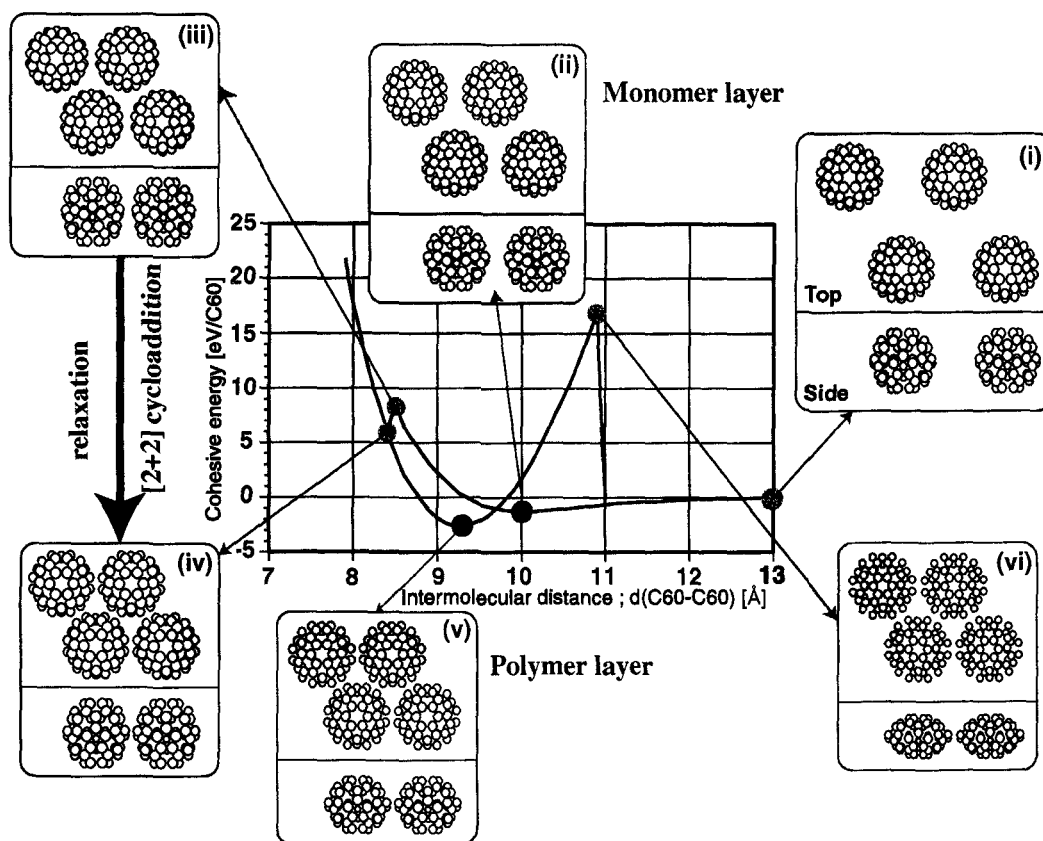


FIG. 2: Optimized atomic arrangement of ML-C<sub>60</sub> at each intermolecular distance (see text).

C<sub>60</sub> molecules are considerably compressed under the high strain energy of 9.81 eV per C<sub>60</sub> which is measured from the energy of the most stable monomer phase. The polymerization is attained via [2+2] cycloaddition at  $d(\text{C}_{60}\text{-C}_{60})=8.40$  Å with structural relaxation [(iv) in Fig.2]. Thus, the adiabatic activation energy for the pressure-induced polymerization of ML-C<sub>60</sub> is estimated as 3.27 eV per [2+2] cycloadduct, which is slightly smaller than that for the dimer of C<sub>60</sub>, 4.15 eV [23]. After the polymerization, the global equilibrium geometry appears at  $d(\text{C}_{60}\text{-C}_{60})=9.30$  Å [(v) in Fig.2]. In the tension stroke, the energy increases again until  $d(\text{C}_{60}\text{-C}_{60})=10.90$  Å [(vi) in Fig.2], at which the C<sub>60</sub> molecules are remarkably elongated along the direction of the intermolecular bond. The energy abruptly drops at  $d(\text{C}_{60}\text{-C}_{60})=11.0$  Å, which corresponds to bond breaking between adjacent C<sub>60</sub> molecules and structural stabilization. The energy barrier for this bond breaking is estimated as 6.52 eV per [2+2] cycloadduct, which is measured from the energy of the most stable polymer phase. Such an appearance of the distinct hysteresis in the energy curve is attributed to the large degrees of freedom of fullerene cage [23].

Next, we investigate the energy gaps for the

monomer phase of ML-C<sub>60</sub>. The present LDA calculation indicates that the most stable monomer phase of ML-C<sub>60</sub> [ $d(\text{C}_{60}\text{-C}_{60})=10.05$  Å] have an energy gap of 0.97 eV. This means that the ML-C<sub>60</sub> has a typical semiconducting character at ambient pressure. Since the LDA generally underestimates the energy gap, we cannot make a precise discussion about the absolute value of the energy gap. Nevertheless, we may note that the calculated energy gap is in good agreement of the experimental one obtained from the recent scanning tunneling spectroscopy measurement for the ML-C<sub>60</sub> on the Si(111) $\sqrt{3}\times\sqrt{3}$ R30°-Ag surface,  $\sim 1$  eV [24].

By application of external pressure, the energy gap decreases and reaches zero at  $d(\text{C}_{60}\text{-C}_{60})=9.25$  Å without the structural transition; the ML-C<sub>60</sub> with  $d(\text{C}_{60}\text{-C}_{60})=9.25$  Å possesses metallic character in the *monomer phase*. The present result stands in marked contrast to the reports which have been made so far: *only* the three dimensionally *polymerized* C<sub>60</sub> fullerite becomes metallic [25]. In general, electric conduction of semiconducting materials is sensitive to the value of the band gap. Indeed, it has been reported that the electric conductivity of solid C<sub>60</sub> changes with the external pressure, with which

the band gap becoming narrow [26]. Thus, these findings will offer us a good opportunity to control the electric conductivity of  $C_{60}$  with the external pressure.

#### ACKNOWLEDGMENTS

We acknowledge helpful discussions with Dr. J. Onoe and Professor R. Sekine. We would like to express their thanks to Dr. J. Yamauchi for valuable suggestions concerning the computational method. Numerical calculations were performed on Fujitsu VPP700/E at RIKEN. This work was partly supported by RIKEN Special Postdoctoral Researchers Fellowship.

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(Received December 8, 2000; Accepted February 8, 2001)