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## Adsorption of Sm on C<sub>60</sub> Film\*

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*Using photoemission spectroscopy, we have studied the adsorption of Sm on C<sub>60</sub> film. At the first stage of Sm adsorption, the C<sub>60</sub> valence band shifts to the high binding energy side. The maximum shift is about 0.4 eV. In the meantime, there appears a new structure at the upper side of the highest occupied molecule orbit (HOMO) band, which comes from the hybrid of the Sm 4f<sup>5</sup> state and C<sub>60</sub> HOMO band. As Sm coverage increases the Sm electron is in a kind of Sm<sup>2+</sup> state due to the forming of Sm cluster on the surface.*

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Since the discovery of the superconductivity of alkali fullerene compound,<sup>1-5</sup> there has been a vast interest in the interaction between fullerene C<sub>60</sub> and metals. This novel material interaction with metal will form a kind of solid material which has some new physical and chemical properties. For example, interaction of alkali metals<sup>6</sup> and alkali earth metals<sup>7</sup> with C<sub>60</sub> will form a kind of compound which has superconductivity. In contrast, some of the metals which have *d* electrons such as Au, Cr, In, will form cluster on the C<sub>60</sub> film. For Ti, La etc. the first layer on the C<sub>60</sub> film is formed by chemical adsorption with weak interaction between the *d* electrons and the HOMO of C<sub>60</sub>.<sup>8</sup> As we know, there are very few works reported on *f*-electron metal interaction with C<sub>60</sub>. In this letter, we report our recent result of Sm adsorption on C<sub>60</sub> film due to the *f* electron interaction with C<sub>60</sub>.

The experiment was performed on the beamline U20A at National Synchrotron Radiation Laboratory at University of Science and Technology of China. Purified C<sub>60</sub> powder is evaporated from a BN crucible and deposited onto a cleaned GaAs(100) substrate. Both the depositing and doping processes are carried out at room temperature. The pressure during C<sub>60</sub> evaporation process is lower than  $3 \times 10^{-9}$  Torr. The Sm was purchased from the common commercial products with a purity of 99.99% and is put into a evaporator in the sample preparing chamber which is connected to the analyzing chamber. After degassing for about 5 h, Sm is deposited onto the C<sub>60</sub> film by heating with a constant current. The pressure during the Sm evaporation

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process is about  $5 \times 10^{-10}$  Torr. After the evaporation process the  $O_2$  contamination is negligible from the XPS examination. The energy resolution of photoemission measurement is about 0.4 eV at photon energy of 100 eV.

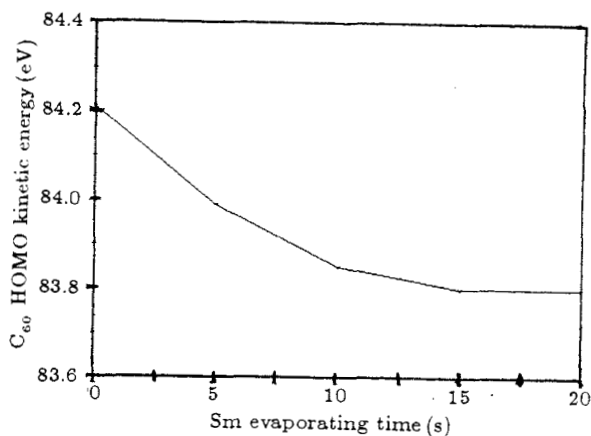


Fig. 1.  $C_{60}$  HOMO band shifts with the Sm adsorption process, the adsorption rate is about 1.8 Å/min.

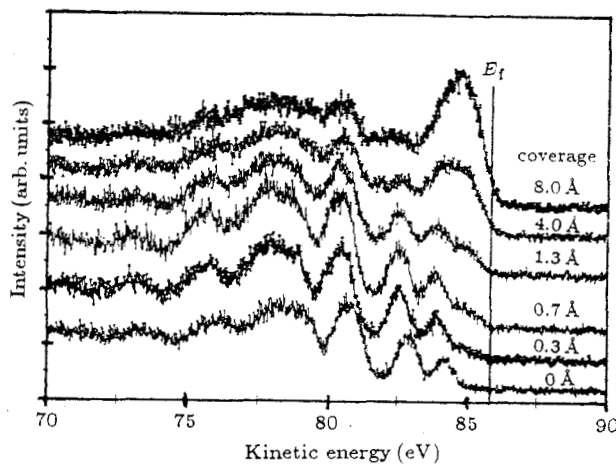


Fig. 2. Valence band of  $C_{60}$  with the doping of Sm. The Photon energy used is 90 eV, the Sm coverage is indicated in the figure.

In order to enhance the Sm 4*f* emission, in the experiment we choose the photon energy to be 90 eV which corresponds to the maximum photon ionization cross section of Sm 4*f* electrons.<sup>9</sup> When the Sm coverage is very small, the  $C_{60}$  HOMO band shifts to the high binding energy side (low kinetic energy side) as Sm is deposited onto the  $C_{60}$  film. This is due to the adsorbing of Sm which makes the energy band discontinuity near the interface. Figure 1 illustrates the

shift of the HOMO band of  $C_{60}$  as a function of the Sm coverage. Although in most of the metal adsorption system one can observe the band bending phenomena, the direction of the band bending of Sm- $C_{60}$  system is different from other  $d$ -electron metal- $C_{60}$  system where the  $C_{60}$  HOMO band shifts to the low binding energy side<sup>8</sup> and it is in agreement with that of alkali- $C_{60}$  system.<sup>6,9</sup> The reason for this difference is till unclear. Here we can see that only after about 20 s, when the coverage is about 0.6 Å, the Fermi energy is already pinned. This means that at this stage the Sm adlayer is formed. The maximum of the shift is 0.4 eV. At this stage the ratio of molecules of Sm and  $C_{60}$  at the surface is about 3:1. There are more Sm molecules in the surface due to the giant lattice constant. In order to cover the whole surface there should be more adatoms than the substrate atoms. This is in agreement with Ti doped  $C_{60}$  where for the first layer there are about 7 Ti atoms per  $C_{60}$  molecule.<sup>8</sup>

Figure 2 illustrate the valence band of  $C_{60}$  during the process of Sm doping. During the Sm adsorption process we observed a new structure formed at a binding energy of 0.4 eV. This structure comes from the hybrids of C 2*p* and Sm 4*f* and also possible ensemble effects of hybridizing with Sm 6*s*. This phenomenon is also very similar to the alkali- $C_{60}$  compound where a new structure also appeared at the Fermi edge. In our experiment we do not see any metallic Fermi edge during the doping process. This is also in agreement with alkali doped  $C_{60}$  system,<sup>6,10</sup> although some others observed a metallic Fermi edge at  $A_3C_{60}$  phase during the alkali doping.<sup>11</sup> We suggest that at this early stage there formed a kind of Sm fullerides. As Sm coverage grows up to more than 5 Å, there appears a  $Sm^{2+}$  emission with an electron structure of 4*f*<sup>5</sup>, which superposes to the  $C_{60}$  valences band, and there appear some states at the Fermi energy. The possible origin of these states may be due to the following effects: (a) Sm metallic overlayer formed on the surface, (b) Sm cluster formed, or (c) Sm 4*f* hybrids with  $C_{60}$  2*p* has a metallic Fermi edge at some phase. From the spectra, we noticed the fact that the  $C_{60}$  valence band decreases very quickly as the Sm coverage increases, so we can say that these states are not due to the hybrid of Sm and  $C_{60}$ . Also we do not observe a high state at a binding energy of about 5 eV due to the metallic Sm 4*f*<sup>6</sup> states. We know that the Sm 4*f*<sup>5</sup> is a kind of surface state and the 4*f*<sup>6</sup> is a kind of body state. The spectra show that the Sm surface state is much stronger than the body state. We come to the conclusion that the states at the Fermi energy are due to the forming of Sm cluster on the surface. The fact that the substrate core level intensity decreases slower than an exponential function supports our suggestion.

In conclusion, there exist two stages during the adsorption of Sm onto the  $C_{60}$  film. When Sm coverage is less than 5 Å, there appears a kind of Sm-fullerides which has a state at a binding energy of 0.4 eV. The Sm is almost in a two-dimensional manner in this stage. In the meantime, there appears a new structure due to the hybrids of C 2*p* and Sm 4*f* of 6*s*. The interaction between Sm and  $C_{60}$  results in the formation of a kind of Sm fullerides. When the Sm coverage is more than 5 Å, there appears the Sm 4*f*<sup>5</sup> state, but the Sm 4*f*<sup>6</sup> state does not appear till

8 Å. We suggest Sm cluster is formed on the surface at these high coverages.

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