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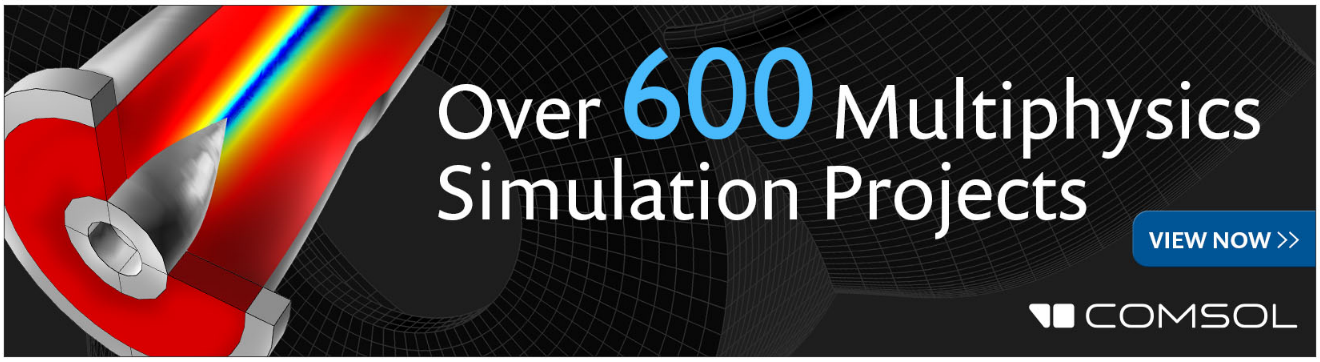

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Electrical conductivity of reconstructed Si(111) surface with sodium-doped C_{60} layers

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Electrical conductance of sodium-doped C_{60} ultra-thin layers (1–6 monolayers) grown on the Na-adsorbed Si(111)$\sqrt{3}\times\sqrt{3}$-Au surface has been studied *in situ* by four-point probe technique, combined with low-energy electron diffraction observations. Evidence of conductance channel formation through the C_{60} ultrathin layer is demonstrated as a result of Na dosing of 3 and 6 monolayers thick C_{60} layers. The observed changes in surface conductivity can be attributed to the formation of fulleride-like NaC_{60} and Na_2C_{60} compound layers. © *2015 AIP Publishing LLC*.
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Fullerene molecules and their composite compounds with alkali metals have attracted a considerable attention for the prospective applications in molecular electronics.[1,2] Due to the high electron affinity of C_{60} molecules, adding alkali atoms to the fullerene-based compounds causes their outstanding electronic features (e.g., superconductivity,[3,4] metallic conductivity, and metal-insulator transition,[5] etc.). When the C_{60} layers are grown on semiconductor surfaces, their properties strongly depend on the surface structure and its electronic states.[6] On the one hand, interaction of the fullerenes with adsorbate-induced reconstructed semiconductor surfaces is of great interest due to exceptional variety of phenomena occurring at C_{60} adsorption.[6–16] For instance, it is possible to modify physical properties of C_{60} layers by forming an appropriate surface reconstruction.[14,15] On the other hand, alkali atoms are known to interact strongly with reconstructed Si surfaces.[17–19] For example, it has recently been reported that originally poor structural and electronic properties of the Si(111)-α–$\sqrt{3}\times\sqrt{3}$-Au ($\alpha\sqrt{3}$-Au hereafter) surface is substantially improved by adsorbing small amount of Na. The resultant homogeneous Si(111)–h-$\sqrt{3}\times\sqrt{3}$–(Au, Na) ($h\sqrt{3}$–(Au, Na) hereafter) surface exhibits a highly ordered atomic structure and advanced properties of nearly ideal two-dimensional electron gas system.[19] Meanwhile, due to the weak coupling of the sodium atoms, interaction of the fullerenes with reconstructed surface that contains alkali atoms seems to be promising for the formation the fulleride-like structures. In this letter, we consider surface conductance of C_{60} layers grown on $h\sqrt{3}$–(Au, Na) surface and its modification caused by additional Na adsorption.

The experiments were performed in an ultrahigh-vacuum (UHV) chamber with a base pressure of 10^{-10} Torr, equipped with low energy electron diffraction (LEED) and four point probe (4PP) facility for *in situ* electrical conductance measurements. The measuring unit of the 4PP method incorporated electro-chemically sharpened 0.7 mm thick tungsten wires pressed to the surface (in the corners of $\sim 0.6\times 0.6\,\mathrm{mm}^2$ square) by individual springs. Conductance measurements were carried out at room temperature (RT) after 1 h cooling down of samples following the preparation of a desired surface. Substrates ($15\times 5\times 0.45\,\mathrm{mm}^3$ in size) were cut from a P–doped Si(111) wafers with resistivity of 10–25 $\Omega\times$cm. The $h\sqrt{3}\times\sqrt{3}$–(Au, Na) surface was prepared by deposition of ~0.1 monolayers (ML) of Na onto the $\alpha\sqrt{3}$-Au at 350 °C (Ref. 19) (1 monolayer of Si(111) corresponds to atomic concentration of $7.8\times 10^{14}\,\mathrm{cm}^{-2}$). Gold was deposited from an Au-wrapped tungsten filament at a rate of ~1.0 ML/min. Au deposition rate was calibrated by the formation of the known Au/Si(111) surface phases.[20] Sodium was deposited from SAES Getter source at a rate of ~0.3 ML/min. Na coverage was calibrated by LEED observation of the Si(111)3 × 1-Na surface phase formation[21] and metal–to-insulator transition after Na deposition onto Si(111)7 × 7 determined with electrical measurements.[17] Fullerenes were evaporated from Knudsen cell at a rate of 0.1 ML/min. One monolayer of fullerite $C_{60}(111)$ has concentration of molecules equal to $1.15\times 10^{14}\,\mathrm{cm}^{-2}$.[12] Fullerite-like structures were produced by deposition of fullerenes onto the $h\sqrt{3}$–(Au, Na) surface held at RT.

C_{60} adsorption on metal surfaces is known to cause changes in sheet resistivity due to charge transfer from metal atoms to C_{60} molecules.[6] Silicon surfaces covered with monoatomic layers of metals can exhibit the properties of the extra-thin two-dimensional metals, and effect of C_{60} adsorption on their surface conductivity is of great interest. Figure 1 shows the changes in conductance in the course of C_{60} adsorption onto the $\alpha\sqrt{3}$-Au and $h\sqrt{3}$–(Au, Na) surfaces. Both surfaces are metallic due to the presence of S_1 surface state band crossing the Fermi level. But upon Na adsorption onto $\alpha\sqrt{3}$-Au surface, this band demonstrates significant increase of electron filling (from ~0.1 to ~0.5 electrons per $\sqrt{3}\times\sqrt{3}$ unit cell) and decrease of electron effective mass (from 0.3 to 0.03 m_e), which leads to the growth of surface

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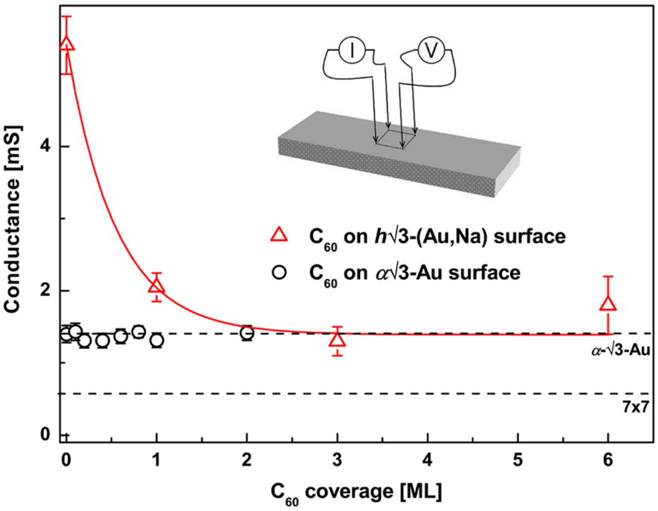

FIG. 1. Conductance changes in the course of C$_{60}$ adsorption onto $\alpha\sqrt{3}$-Au and $h\sqrt{3}$-(Au, Na) reconstructed surfaces. Inset: schematic diagram showing the electrical conductance measurement of the sample with 4PP method.

conductivity.[19] During C$_{60}$ adsorption onto the $\alpha\sqrt{3}$-Au surface fullerenes self-assemble into the close-packed molecular layers leaving the underlying substrate structure intact[12,13] and no significant changes in surface conductance are observed (Fig. 1). In contrast, conductivity of the $h\sqrt{3}$–(Au, Na) sample falls drastically with C$_{60}$ adsorption down the $\alpha\sqrt{3}$-Au conductance level. This is believed to indicate that adsorbed fullerenes interact with Na atoms which are weakly bonded with surface, hence very mobile at RT.[19] Saturation of conductance occurs when all Na atoms are already trapped around fullerene molecules due to their high electron affinity. Acting as electron acceptors, fullerene layer decreases the electron filling of the metallic surface state band of $h\sqrt{3}$–(Au, Na). At the same time, C$_{60}$ molecules do not affect significantly a conductance channel induced by $\alpha\sqrt{3}$-Au surface phase with its relatively low electron band filling.

Note that the decrease in surface conductance is typical for metal films after C$_{60}$ adsorption: the charge transfer from metal atoms to fullerene molecules results in depletion of charge carriers in metal film, hence conductivity fades. However, this charge transfer is expected to produce conducting C$_{60}$ layer,[22] which would be indicated by corresponding changes in the sample conductance. Assuming that Na atoms act as dopants for C$_{60}$ layer, an additional adsorption of Na was carried out to enhance the "doping" effect. For this purpose, sodium was adsorbed onto the preliminary formed C$_{60}$/$h\sqrt{3}$–(Au, Na) structures, where C$_{60}$ layers contain one, three, and six monolayers of fullerenes.

Figure 2(a) illustrates the Na dosing effect on the conductance of C$_{60}$(1 ML)/$h\sqrt{3}$–(Au, Na) structure (i.e., $h\sqrt{3}$–(Au, Na) surface covered by 1 ML C$_{60}$). The reference data for Na adsorption onto the bare $h\sqrt{3}$–(Au, Na) surface shows that it causes a rapid decrease in surface conductance. Angle-resolved photoelectron spectroscopy data in Ref. 19 revealed that this is mainly due to destruction of the S$_1$ surface state band. The same behavior is observed for the C$_{60}$(1 ML)/$h\sqrt{3}$–(Au, Na) structure suggesting that Na atoms penetrate through the C$_{60}$ monolayer.[23] If this layer is sufficiently transparent for sodium atoms they can interact with reconstructed surface changing its properties as in the case without the fullerene layer. In both cases, the final conductance values are comparable to the background conductance of pristine Si(111)7 × 7 sample.

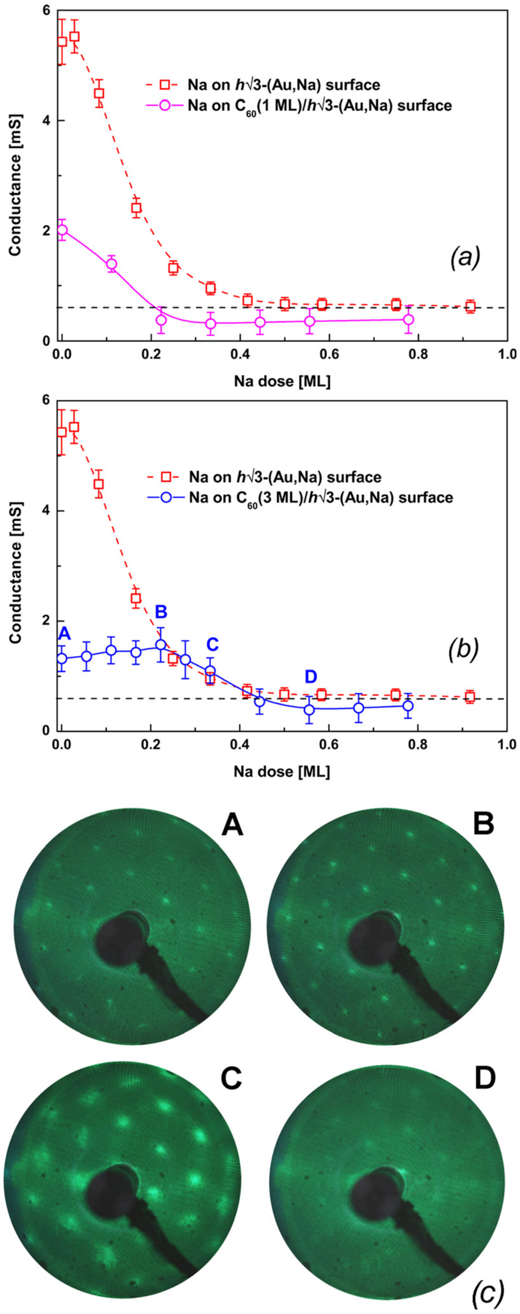

FIG. 2. Na dosing effect on electrical conductance of (a) C$_{60}$(1 ML)/$h\sqrt{3}$-(Au, Na) and (b) C$_{60}$(3 ML)/$h\sqrt{3}$-(Au, Na) structures and bare $h\sqrt{3}$-(Au, Na) surface (red dashed line, given for reference). Conductance of the pristine Si(111)7 × 7 sample is indicated by black dashed line. (c) LEED patterns ($E_p = 36$ eV) are denoted as A, B, C, D in accordance with the points indicated at the plot in (b).

With increasing C$_{60}$ layer thickness, it is expected to detect the conduction path through a continuous C$_{60}$ layer.[13] In the case of Na deposition onto the C$_{60}$(3 ML)/$h\sqrt{3}$–(Au, Na) (Fig. 2(b)), the conductance slightly increases with Na dose up to ∼0.2 ML Na. Evolution of the sample surface structure during Na dosing is illustrated by a set of successive LEED patterns in Fig. 2(c) taken at 0, 0.22, 0.33, and

0.56 ML Na and denoted as A, B, C, and D, respectively. One can see that the sharpest LEED pattern (B) is observed at 0.22 ML Na, where the sample conductivity is maximal. Smearing (C) and fading (D) of the LEED reflections correlate with decrease of the conductance. It can be noted that a LEED pattern similar to that shown in (C) was observed for the polymerized phase of Li_4C_{60}.[24] It has been recently reported that the Na-C_{60} fullerides can occur upon polymerization as NaC_{60} and Na_4C_{60}.[25] In the case of C_{60}(3 ML)/$h\sqrt{3}$–(Au, Na) structure, after depositing 0.22 ML Na the surface contains ∼0.32 ML Na (as $h\sqrt{3}$–(Na, Au) surface already contains ∼0.1 ML (Ref. 19)). Thus, one obtains Na:C_{60} ratio equal to ∼0.7:1 which is close to 1:1, stoichiometry of the NaC_{60} compound.

Figure 3 shows the changes in electrical conductance in the course of Na deposition onto C_{60}(6 ML)/$h\sqrt{3}$–(Au, Na) structure. As one can see here, the curve shape is similar to that in the case with 3 ML C_{60} but at a greater dose scale. Wide maximum of conductance is observed at 1.8 ± 1.0 ML Na. Estimation reveals that 1.8 ML Na dissolved in the 6-ML C_{60} film corresponds to the Na_2C_{60} compound, which is known to be a stable Na_2C_{60} fulleride phase with Na atoms occupying the tetrahedral sites in the fullerite fcc lattice.[26,27] Wideness of the electrical conductance maximum seems to indicate a disorder in the alkali atoms distribution in the film. With further increasing Na dose, the wide maximum in the conductance is followed by a wide minimum observed at 3.0–5.0 ML Na (which corresponds to Na_xC_{60} compounds with x varying from ∼3 to ∼6). Remarkably, the above main features of the conductance behavior are similar to those observed for the thick (500 Å) Na_xC_{60} films.[28] When Na dose becomes larger than ∼5.0 ML, sample conductance starts to grow. The most plausible reason is the formation of the metallic Na layer due to agglomeration of excess Na atoms beneath the fulleride film.[13] The fact that deposition of more than about 4 ML Na onto the $h\sqrt{3}$–(Au, Na) surface results in conductivity increasing even without presence of C_{60} layer on the substrate sounds supportive for this assumption.

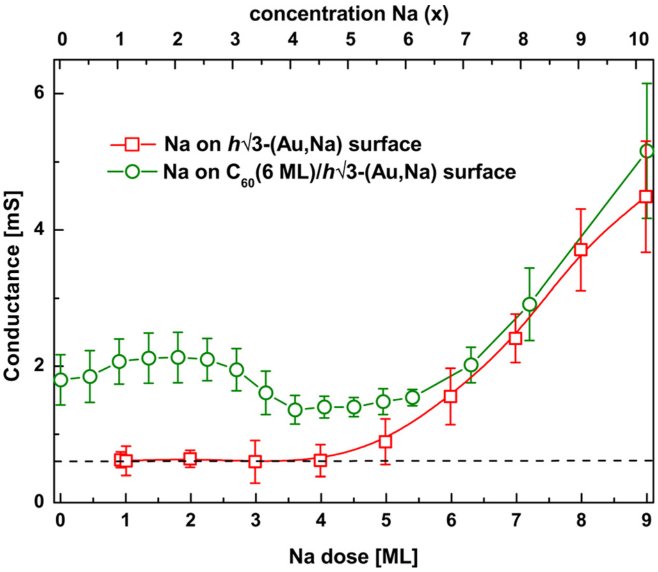

FIG. 3. Na dosing effect on electrical conductance of C_{60}(6 ML)/$h\sqrt{3}$-(Au, Na) (green circles and line) and bare $h\sqrt{3}$-(Au, Na) surface (red squares and line, given for reference). The concentration of Na (upper axis) is denoted as x in Na_xC_{60} fulleride.

Resistance of Na_2C_{60} fulleride ultra-thin layer can be estimated by assuming that resistances of this layer and substrate make a parallel connection. An estimation yields the resistance of 3 ± 1 kΩ. This value is comparable to the resistance reported for C_{60} monolayers formed on Cu films.[22] Note that transport in such layers is dominated by multiple scattering events; hence, the resistivity for layers is higher than that for the bulk material.

In summary, effect of Na dosing on the properties of the ultra-thin C_{60} layers grown on Na-adsorbed Si(111)$\sqrt{3}\times\sqrt{3}$-Au surface has been explored using 4PP electrical conductance measurements in conjunction with LEED observations. It has been found that changes in the sample conductivity can be understood in terms of formation of the fulleride-like films. Formation of a fulleride film with a particular stoichiometry depends not only on the Na dose but also is affected by the thickness of the original C_{60} fullerite film. No fulleride film forms with 1 ML C_{60} film, NaC_{60} compound develops with 3 ML C_{60}, and Na_2C_{60} film grows with 6 ML C_{60}. Thus, our results demonstrates the possibility for the formation of various ultra-thin conducting fulleride-like films by alkali-metal dosing of fullerite layers grown on reconstructed Si surface.

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