A Novel Method to Fabricate a Molecular Quantum Structure: Selective Growth of C_{60} on Layered Material Heterostructures

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We propose a new method to fabricate nano-scale devices consisting of C_{60}. C_{60} molecules have a spherical shape with a diameter of 0.7 nm. It may be possible to consider each molecule as a quantum dot to fabricate a single-electron-tunneling device which will work at room temperature. In order to control the position of a C_{60} molecule on a device substrate, we have developed a "selective growth" technique on layered material heterostructure substrates, which utilizes the difference in the nucleation process of C_{60} molecules on various kinds of layered materials. To clarify the selective growth mechanism, the density of C_{60} islands grown on different layered material substrates was measured using atomic force microscopy. It has been suggested that differences in the adsorption and diffusion energies of a C_{60} molecule on layered materials influence the selective growth.

KEYWORDS: nanostructure, molecular crystal, selective growth, C_{60}, MoS_2, GaSe, InSe, van der Waals epitaxy

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1. Introduction

The fabrication of atomic or molecular scale structures is one of the ultimate goals of materials science and technology. Recent progress in this field has enabled us to fabricate nano-structures which show optical or electronic quantum size effects.$^{1)}$ Till now, however, most nano-scale devices consist of inorganic semiconductors such as Si or GaAs, and the quantum dots or wires are fabricated using complicated processes of thin film growth and nano-lithography. Therefore it has been considerably difficult to produce a large number of uniform quantum dots or wires smaller than 10 nm.

On the other hand, many organic molecular crystals including C_{60} have attracted much attention in recent years as candidate materials for ultrahigh-density optoelectronic devices or molecular devices, because even a single organic molecule can work as a functional element in principle. For example, a spherical shaped C_{60} molecule may be treated as a nano-size dot with a diameter of 0.7 nm. So if we can construct a designed circuit pattern of organic molecules on a substrate, it will be possible to fabricate an organic nano-scale device like a single-electron tunneling (SET) device. A SET device composed of a small dot such as C_{60} is expected to work at room temperature.$^{2)}$ The Coulomb blockade and the Coulomb staircase effects have been observed in the SET system which exploits the C_{60} molecule as a quantum dot, and uses a scanning tunneling microscope (STM) to form a double barrier tunnel junction.$^{3,4)}$

It is difficult, however, to apply conventional lithography techniques for the fabrication of a nano-scale circuit of organic materials, because most organic solids are very fragile and their chemical properties are similar to those of resist materials. Thus a new method is urgently required. Until now, our group has been studying heteroepitaxial growth of many kinds of organic molecular crystals, and in the course of experiments we have observed the "selective growth" phenomenon, which can be applied to the nano-fabrication of organic materials.$^{5-9)}$

A schematic view of the selective growth process is shown in Fig. 1. In the present Fig.1

experiment we used C_{60} as a constituent to form nanostructures, and three layered materials, MoS_2, GaSe and InSe as substrate materials. First, a sub-monolayer epitaxial film of GaSe or InSe is grown on a MoS_2 substrate by molecular beam epitaxy (MBE) so that the substrate MoS_2 surface is partly covered with monolayer GaSe or InSe islands. Next C_{60} molecules are deposited on it. Atomic force microscope (AFM) observation revealed that C_{60} molecules grow only on MoS_2 regions but never nucleate on GaSe domains on a GaSe/MoS_2 heterostructure substrate at a substrate temperature of about 180°C.(6) In contrast, the C_{60} molecules grow only on InSe domains on an InSe/MoS_2 heterostructure substrate when the substrate temperature is around 90°C.(8) Figure 2 shows schematic views of these selective growth phenomena. Thus the fabrication of C_{60} nanostructures as small as 10 nm can be achieved using GaSe or InSe domains as negative or positive masks, respectively. The nano-scale patterning of a GaSe or InSe mask is realized by scraping it with an STM or AFM tip.(7)

Fig.2

In this paper we will discuss the mechanism of selective growth. It has been assumed in a previous study(8) that selective growth originates from differences in the adsorption and diffusion energies of C_{60} molecules on MoS_2, GaSe and InSe substrates. Individual values of those energies, however, have not been estimated yet because C_{60} molecules have been grown mainly on the heterostructure substrate to observe the selective growth phenomenon itself. In the present work, we have grown C_{60} molecules on single crystals of these layered materials, and observed the surface by AFM. Then the differences in the adsorption and diffusion energies were estimated by measuring the coverage and the density of grown C_{60} islands on these substrates, and the selective growth process was discussed.

2. Experimental

C_{60} molecules were evaporated from a Knudsen cell in an MBE chamber with a base pressure of 2×10^{-8} Pa. The C_{60} source was a powder of 99.8% purity. The flux intensity of the C_{60} beam was calibrated by a quartz crystal microbalance, and set at

1.9×10^{11} molecules·cm^{-2}·s^{-1} in all the experiments. This flux intensity was almost equivalent to the growth rate of 0.1 monolayer·min^{-1}, where "monolayer" (ML) means the full coverage of close-packed hexagonal lattice of C_{60} with the same molecular interval of 1.0 nm as the bulk single crystal.

Single crystals of MoS_2, GaSe and InSe were used as substrates. Two different substrates (GaSe and MoS_2, or InSe and MoS_2) were mounted on a molybdenum plate with indium solder in order to maintain the same dose of C_{60} and the substrate temperature for both the substrates. These samples were cleaved in air just before loading into the MBE chamber, and cleaned under ultrahigh vacuum by heating at 400°C for 30 min. Then the substrate temperature was lowered to the growth temperature, and 0.2–0.3 ML equivalent C_{60} molecules were irradiated.

After the deposition of C_{60}, the samples were taken out of the MBE chamber and observed by AFM (SPI-3800 and SPA-300 system, Seiko Instruments Inc.) under air. Images were taken in a non-contact mode with a Si cantilever to avoid destruction of the grown C_{60} film.

3. Results

The selective growth phenomena have been observed both on GaSe/MoS_2 and InSe/MoS_2 heterostructure substrates. Thus we will compare the density of the grown C_{60} islands on GaSe with that on MoS_2 as well as compare that on the InSe and MoS_2 substrates.

(a) Growth of C_{60} on GaSe and MoS_2 substrates

Figure 3 shows the AFM images of C_{60} islands grown on GaSe and MoS_2 substrates. The substrate temperature was 90°C (a, b), 150°C (c, d) or 170°C (e, f). The total amount of evaporated C_{60} was the equivalent of 0.3 ML in all the experiments. This means that 30% of the area of the substrate surface should be covered with a monolayer of C_{60} islands under the complete condensation conditions.

Fig.3

When the substrate temperature was 90°C (Figs. 3(a) and 3(b)), the C_{60} islands of the first layer were dendritic-shaped both on GaSe and MoS_2 substrates. A small amount of the second layer was also observed. The size of C_{60} islands on the GaSe substrate was larger than that on MoS_2, and the density of grown C_{60} islands on the GaSe substrate was smaller ($5.0\times10^6\,cm^{-2}$) than that on MoS_2 ($20\times10^6\,cm^{-2}$). Although the size and the density of C_{60} domains differ between GaSe and MoS_2, the total amount of grown C_{60} molecules estimated from the AFM images was almost equal to 0.3 ML on both substrates. This result suggests that the complete condensation is valid for the substrate temperature of 90°C.

When the substrate temperature was raised to 150°C, C_{60} molecules still completely adsorbed onto the MoS_2 substrate with a larger domain size and smaller density of islands ($3.3\times10^6\,cm^{-2}$) than at 90°C (Fig. 3(d)). On the GaSe substrate, however, the complete condensation of C_{60} molecules did not occur. As shown in Fig. 3(c), coverage of C_{60} on the GaSe substrate at 150°C was about 0.15 ML. Only 50 % of impinging C_{60} molecules nucleated on GaSe, and rest of them reevaporated from the surface.

When the substrate temperature was further raised to 170°C, no distinct island of C_{60} grew on the GaSe substrate as shown in Fig. 3(e). On the contrary, complete condensation still occurred on the MoS_2 substrate with a larger domain size and smaller density of islands ($1.8\times10^6\,cm^{-2}$) than at 150°C (Fig. 3(f)).

(b) Growth of C_{60} on InSe and MoS_2 substrates

Figure 4 shows AFM images of C_{60} islands grown on InSe and MoS_2 substrates at the substrate temperature of 90°C. The total amount of evaporated C_{60} was the equivalent of 0.2 ML.

Fig.4

It was observed from the AFM images that the C_{60} molecules condensed completely both on the InSe and MoS_2 substrates. The density of C_{60} islands on InSe was larger ($30\times10^6\,cm^{-2}$) than that on MoS_2 ($13\times10^6\,cm^{-2}$), while the size of the C_{60} islands on InSe was smaller than that on MoS_2. It should be noted that C_{60} molecules nucleate on the MoS_2 substrate at 90°C, while almost no island was grown on the MoS_2 region on the InSe/MoS_2 heterostructure substrate at the same substrate temperature.[8)]

4. Discussion

From the measurement of the density and the coverage of C_{60} islands on each layered material substrate, the mechanism of selective growth will be discussed below.

The results shown in Fig. 3 indicate that C_{60} molecules rarely adsorb on a GaSe substrate while they completely adsorb on MoS_2 at the substrate temperature of 170°C. The difference in the condensation rate of C_{60} between GaSe and MoS_2 suggests the different adsorption energy of a C_{60} molecule on layered material substrates. It is well known that the surface of layered materials is very inactive, and a C_{60} molecule adsorbs on it via van der Waals-like weak forces without a reaction. Although the interaction could be interpreted from the viewpoint of electronic states of constituent materials, the difference in adsorption energy is closely related to the different condensation rates between GaSe and MoS_2. Thus the difference in the adsorption energy enables the GaSe film to work as a negative mask against the adsorption of C_{60}. When C_{60} molecules are deposited on a GaSe/MoS_2 heterostructure substrate above 170°C, they nucleate only on MoS_2 regions (Fig. 5(a)). Molecules impinging on GaSe reevaporate, and only the MoS_2 regions are covered with C_{60}.

Fig.5

In the case of InSe/MoS_2 heterostructure, however, the selective growth observed at a substrate temperature of about 90°C could not be explained by the difference in the adsorption energy of C_{60}. In the present experiment, the impinging C_{60} molecules condense completely on both the InSe and MoS_2 substrates at 90°C, while they nucleate mainly on InSe domains in the case of the InSe/MoS_2 heterostructure substrate. It is assumed that the diffusion energy plays an important role in the selective growth on the InSe/MoS_2 heterostructure substrate. If the diffusion energy is large, the impinging C_{60} molecules cannot migrate in longer lengths. Then the molecules nucleate there and small islands are formed in high density. Actually, AFM observation has shown that the density of C_{60} islands on the InSe substrate is higher than that on the MoS_2 substrate, indicating the larger diffusion energy of C_{60} molecules on InSe than on MoS_2. The migration length of C_{60} molecules on MoS_2 is estimated to be at least 2–3 μm from the AFM image shown in Fig. 4(b). Therefore if the size of MoS_2 regions on the InSe/MoS_2 heterostructure is shorter than the migration length of C_{60} on MoS_2 at 90°C, C_{60} molecules impinging on MoS_2 can migrate onto InSe domains and nucleate there (Fig. 5(b)). In contrast, C_{60} molecules impinging on InSe nucleate just around that position because of the shorter migration length on InSe.

It is supposed that the difference in diffusion energy between InSe and MoS_2 comes from the difference in lattice constants of these materials. Both sulfur and selenium atoms on cleaved surfaces of MoS_2 and InSe form a close-packed hexagonal lattice, and the atomic intervals are 0.316 nm and 0.400 nm, respectively. Detailed analysis of reflection high energy electron diffraction patterns observed during the growth of C_{60} on these layered materials10) suggests that C_{60} molecules are likely to sit on stable points on the surface so that epitaxial growth of C_{60} molecules is realized. When a C_{60} molecule migrates from one stable site to another, the diffusion energy will be smaller on the surface with a smaller lattice constant. To determine the values of the adsorption and diffusion energies, the density of C_{60} islands on layered materials must be measured at many points of the substrate temperature and the flux intensity of C_{60}.11) Details about the epitaxial relationship between C_{60} films and layered material substrates, and the quantitative discussion on the selective growth will be described elsewhere.

5. Conclusion

In order to investigate the mechanism of the selective growth of C_{60} on such layered material heterostructure substrates as GaSe/MoS_2 and InSe/MoS_2, C_{60} molecules have been grown on a clean surface of each layered material single crystal, and growth features have been observed using AFM. Differences in the adsorption and diffusion energies of the C_{60} molecule on these layered material substrates were clarified by measuring the coverage and the density of grown C_{60} islands. It has been proved that the difference in the adsorption energy causes the selective growth of C_{60} on the GaSe/MoS_2 substrate, while the difference in the diffusion energy results in the selective growth on InSe/MoS_2.

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Figure captions

Fig. 1. A schematic view of the process of selective growth. (a) formation of a layered material heterostructure substrate on which two material surfaces coexist, (b) growth of C_{60}, (c) selective growth of C_{60} only on one of two layered materials.

Fig. 2. A schematic view of the selective growth of C_{60} molecules on GaSe/MoS_2 and InSe/ MoS_2 heterostructure substrates.

Fig. 3. AFM images of C_{60} islands grown on GaSe and MoS_2 substrates at different substrate temperatures. (a, b) 90°C, (c, d) 150°C, (e, f) 170°C. Amount of evaporated C_{60} was 0.3 ML equivalent. Note the difference in the scale of images.

Fig. 4. AFM images of C_{60} islands grown on InSe and MoS_2 substrates at 90°C. Amount of evaporated C_{60} was 0.2 ML equivalent.

Fig. 5. Selective growth process of C_{60} molecules on GaSe/MoS_2 and InSe/MoS_2 heterostructure substrates.

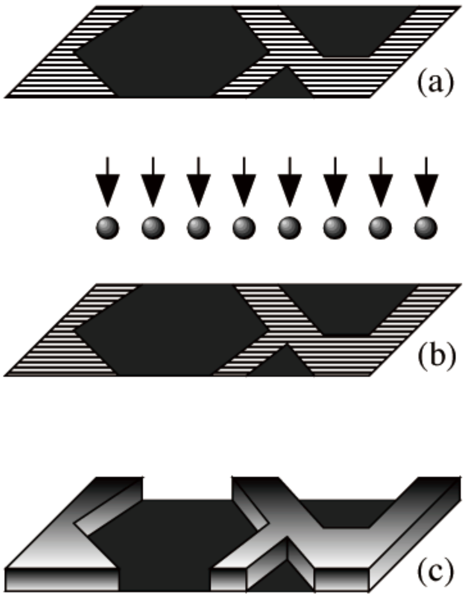


Fig. 1

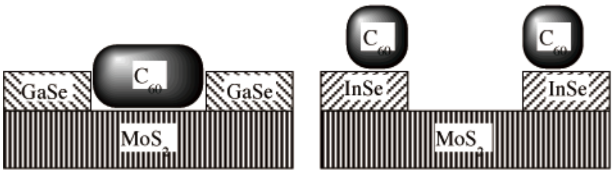


Fig. 2

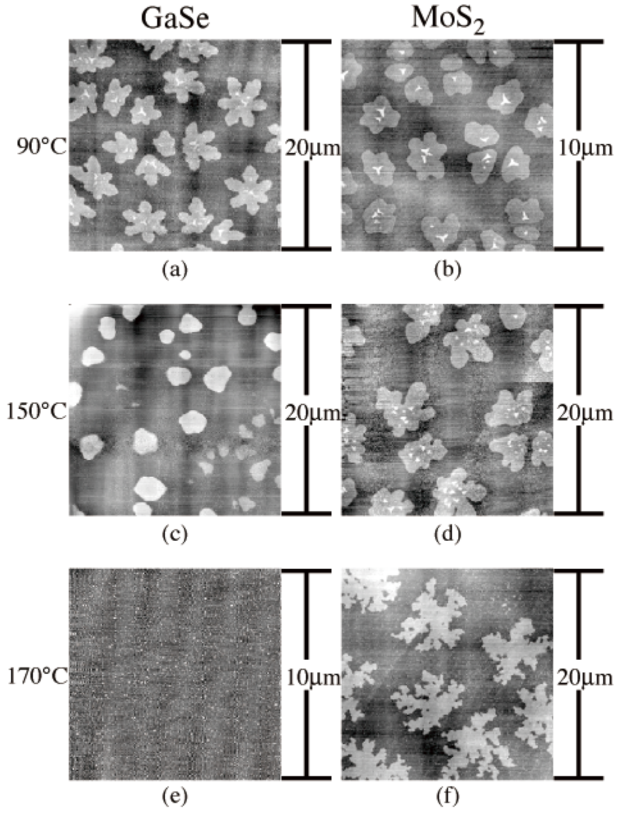


Fig. 3

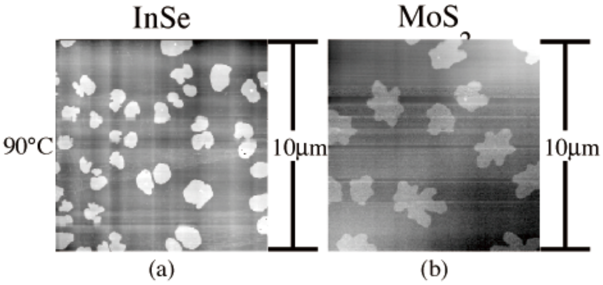
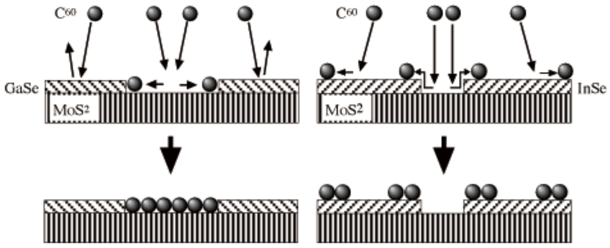


Fig. 4



(a) C$_{60}$ on GaSe/MoS$_2$ (b) C$_{60}$ on InSe/MoS$_2$

Fig. 5