Nanostructure fabrication by selective growth of molecular crystals on layered material substrates

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Nanostructures consisting of C_{60} molecules were fabricated on a GaSe/MoS$_2$ heterostructure. A submonolayer film of a lamellar compound semiconductor GaSe was grown on a MoS$_2$ substrate to form nanoscale holes or grooves surrounded by monolayer steps. Atomic force microscope (AFM) observation indicates that C_{60} molecules grow only in the bare MoS$_2$ nanoregions at a substrate temperature of 180 °C. C_{60} molecules fill up those holes and grooves, and nanoscale C_{60} domains with polygonal shapes can be formed. This selective growth method can be combined with nanoscale patterning made by a scanning tunneling microscope or AFM to produce nanostructures of molecular crystals with designed shapes. © *1997 American Institute of Physics.*
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Recent progress in thin film growth technology and sub-micrometer scale lithography of semiconductors has enabled the fabrication of nanometer-size low-dimensional structures such as a quantum well or a quantum dot, and has made it possible to explore new physical properties arising from those nanostructures.[1] Moreover, recent advances in scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have realized atomic-scale fabrication on solid surfaces.[2–10] The ultimate purpose of those new techniques is to manipulate atoms or molecules freely, react them as desired, and develop a nanoscale device, that is often called ''molecular device.''[11]

Over the years many organic molecular crystals, including C_{60}, have attracted much attention as candidate materials for high-density optoelectronic devices or as constituents of a molecular device because even a single organic molecule can work as a functional element.[12] Nanoscopic patterning or free arrangement of those molecules as designed is a key issue in those devices. It seems difficult, however, to apply the current photolithography technique to organic materials although it has been successfully used for the fabrication of nanostructures of such inorganic semiconductors as Si or GaAs. Usually organic molecules are bound together by weak forces so that the masking or the lift-off processes in the photolithography easily cause damage in them. Thus a new selective growth method is urgently needed to fabricate the nanostructure of organic crystals.

During the course of searching for a combination of materials suitable for selective growth, we have found that C_{60} molecules can be selectively grown on GaSe and MoS$_2$ substrates. As will be described, C_{60} molecules adsorb only on the MoS$_2$ substrate but not on GaSe at an appropriate substrate temperature. Thus we have tried to fabricate nanoscale MoS$_2$ regions surrounded by GaSe for the selective growth of C_{60}. Both MoS$_2$ and GaSe have anisotropic layered structures, and their unit layers are bound to each other by weak van der Waals forces. This weak bonding at the interface enables the heteroepitaxial growth of GaSe on a MoS$_2$ substrate in spite of large differences in their lattice constants and crystal structures,[13] which we call ''van der Waals

epitaxy.''[14,15] If a submonolayer film of GaSe partly covers the MoS$_2$ substrate, then nanoscale holes or grooves, in which MoS$_2$ surfaces are exposed, are expected to be formed. We have succeeded in making such nanoregions of MoS$_2$ and have found that the GaSe film acts as a mask for the growth of C_{60}. The concept of the present method is shown schematically in Fig. 1.

Masking GaSe films were grown by molecular beam epitaxy (MBE). The MoS$_2$ substrates were natural molybdenite. They were cleaved in air just before loading into a MBE chamber. Before growth of the GaSe, substrates were thermally cleaned at 500 °C for 30 min to remove physisorbed contamination. The substrate temperature for the growth was 540 °C, and flux intensities of Ga and Se measured by a nude ion-gauge-type flux monitor were 1×10^{-5} and 7×10^{-5} Pa, respectively. During growth the crystallinity and coverage of the GaSe film were monitored by reflection high energy electron diffraction (RHEED). In spite of a lattice mismatch as large as 19% (MoS$_2$: $a = 0.316$ nm, GaSe: $a = 0.3755$ nm),
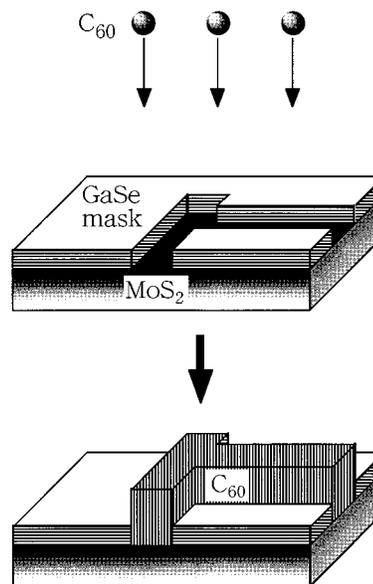
FIG. 1. Schematic views of the selective growth method of the organic molecule nanostructure.

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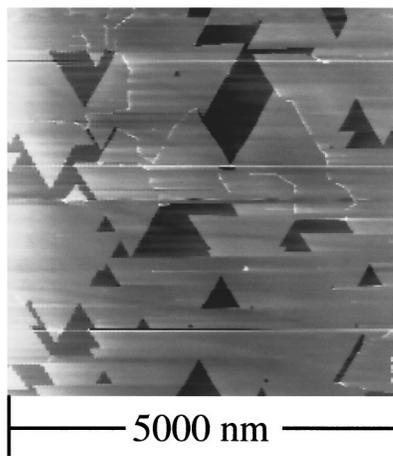
FIG. 2. An AFM image of the submonolayer film of GaSe on the MoS_2 substrate. Darker regions correspond to the bare MoS_2 substrate and brighter regions correspond to the unitlayer GaSe film.

FIG. 3. AFM images of C_{60} nanostructures formed by the selective growth on MoS_2 substrates with GaSe masks. (a),(b) After 1 min growth of C_{60}; (c) after 5 min growth of C_{60}; (d) an enlarged image of the rectangular area in (c); (e) an AFM image where the coverage of the GaSe mask is less than in (c); (f) one of the smallest structures of C_{60}.

sharp streaky RHEED patterns were always observed during the growth.

Figure 2 shows an AFM image of a GaSe film after 5 min growth. AFM (Seiko Instrument SPI-3700 and SPA-300 systems) was conducted in ambient air, and images were taken by a contact mode with a conventional Si_3N_4 cantilever. The AFM observation confirmed that at substrate temperatures lower than 520 °C growth of the second layer starts before the completion of growth of the first layer. To avoid the influence of roughness of the masking GaSe film upon growth of the C_{60} molecules, the substrate temperature was set above 520 °C, and coverage of the GaSe film was controlled so that bare nanoregions of MoS_2 remain on the surface. The substrate temperature should be kept below 560 °C, above which no growth of GaSe is observed.

As shown in Fig. 2, the surface of MoS_2 is covered with triangular domains of GaSe and their coalescent ones. Hexagonal atomic lattice images with an atomic spacing of GaSe can be observed everywhere on those domains, indicating the single-crystalline growth of GaSe. The thickness of each domain was measured as equal to that of a unitlayer of GaSe. Between those domains of GaSe, bare MoS_2 regions could be observed. Sometimes grooves 20–30 nm in width or triangular holes as small as 10 nm in diameter can be created.

C_{60} molecules were evaporated from another Knudsen cell in the same MBE chamber. The substrate temperature was 180 °C and the flux intensity of C_{60} was 4×10^{-6} Pa. Figures 3(a) and 3(b) show AFM images after 1 min growth of C_{60}. At the initial stage of growth, the C_{60} molecules seem to nucleate at the step edges of the GaSe domains, and C_{60} domains grow onto bare MoS_2 regions.

Figure 3(c) is an AFM image after 5 min growth. C_{60} molecules almost fill up the MoS_2 regions, while no C_{60} growth occurs on the masking GaSe. At this stage, the RHEED images show streaks with a much narrower interval than either that of the MoS_2 substrate or that of the GaSe masking film. This streak interval and the symmetry of the RHEED pattern agree well with those of an epitaxial film of C_{60} on a clean MoS_2 substrate that was previously reported.[16] This result suggests that a C_{60} film with a closed-packed
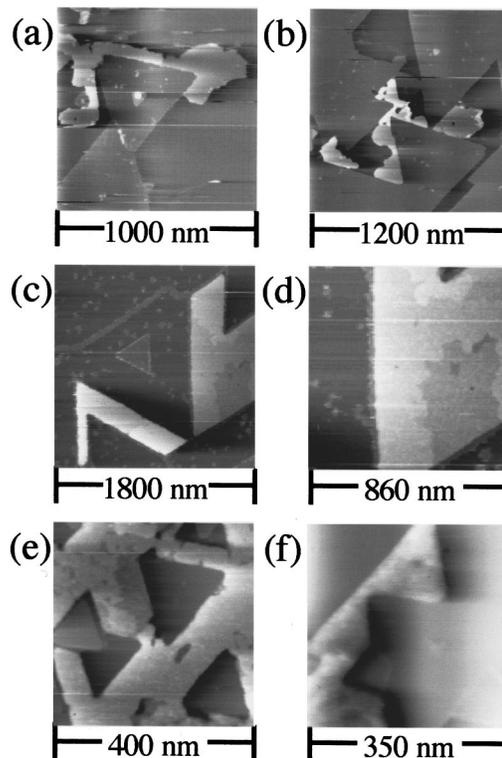
hexagonal structure grows in the bare MoS_2 region.

Figure 3(d) shows an enlarged AFM image of the rectangular area in Fig. 3(c). Several steps can be seen in it, indicating the multilayer growth of C_{60} molecules. Even after the third layer has started to grow, C_{60} domains do not flow onto surrounding GaSe regions. Figure 3(e) is an AFM image where the coverage of the GaSe mask is less than that in Fig. 3(c). In this case the fourth or the fifth layer of C_{60} completely covers the bare MoS_2 surface. Triangular GaSe domains are left in holes that are surrounded by C_{60} walls.

Figure 3(f) shows one of the smallest structure. The narrowest width of the C_{60} domain measured by AFM is about 20 nm, which corresponds to the twenty intermolecular distance of the closed-packed lattice of C_{60}.

Usually surfaces of layered materials have very low step density, and the growth of C_{60} molecules on the MoS_2 substrate was found to be dominated mainly by two-dimensional (2D) nucleation.[17] The migration length of the C_{60} molecule reaches tens of micrometers and a supersaturation condition is easily achieved for the proper flux rate of C_{60} and the substrate temperature of MoS_2. In the present case, the size of the bare MoS_2 region is much smaller than the migration length so that C_{60} molecules on the MoS_2 reach step edges of GaSe and nucleate there, or are incorporated into C_{60} domains already formed. C_{60} molecules on the GaSe surface, however, have a far shorter residence time in these growth conditions. Most of C_{60} molecules on GaSe desorb before 2D
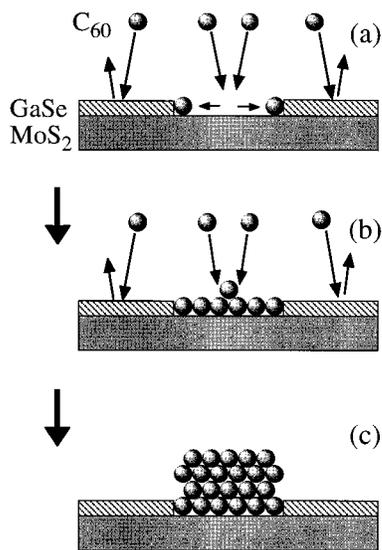
FIG. 4. Schematic views of the formation of the C_{60} nanostructure on the MoS_2 substrate covered with the GaSe mask.

nucleation or before reaching C_{60} domains formed on MoS_2.

Figure 4 depicts schematic views of the present growth mechanism. As shown in Fig. 4(a), C_{60} molecules nucleate at step edges, and their domains spread only onto MoS_2 regions. Eventually those regions are completely filled by C_{60} [Fig. 4(b)]. The attractive interaction between C_{60} molecules is strong enough, thus impinging molecules on C_{60} domains adsorb there and form subsequent layers [Fig. 4(c)]. Successive C_{60} growth occurs only on C_{60} domains, and the fourth or the fifth layer of C_{60} grows without spilling over onto GaSe regions.

In the present system selective growth is achieved by the use of the difference in adsorption energy of C_{60} between GaSe and MoS_2 substrates. Through our preliminary experiments it was found that C_{60} molecules can adsorb on a bulk MoS_2 substrate up to 260 °C, whereas on a thick GaSe film C_{60} molecules do not adsorb above 180 °C. Thus the substrate temperature of the present experiment was chosen in order to create a large difference in the accommodation factor of C_{60} on both materials. Determination of the maximum growth temperature of C_{60} for various layer compounds is now in progress.

So far nanoregions of bare MoS_2 have been naturally formed. The size and the shape of the nanostructure cannot be controlled intentionally. But this selective growth method can be combined with the lithography technique to produce nanostructures with any shape desired. Nanolithography using STM or AFM seems to be an especially good method for the present system. Many groups have reported that STM or AFM can be used to scratch the topmost layer of layered

materials with atomic-scale accuracy.[5,18,19] In our AFM observations, GaSe films were often cut by the cantilever. In some cases small islands of GaSe could be removed from the surface. Therefore a combination of STM/AFM lithography of the GaSe/MoS_2 system and selective growth of C_{60} will enable the formation of a more complicated nanostructure than ever. Furthermore, it may also be possible to expand constituent materials for nanostructure formation, since the difference in the adsorption energy between organic molecules and substrates has been already reported with other combinations of materials.[20]

In conclusion, nanostructures consisting of C_{60} molecules were fabricated on a MoS_2 substrate covered by a submonolayer GaSe film. It was observed by AFM that C_{60} molecules deposited on that substrate at a substrate temperature of 180 °C adsorb only on bare MoS_2 surrounded by the monolayer GaSe, and that almost no growth of C_{60} occurs on GaSe. Then nanoscale domains of C_{60} with polygonal shapes were created on bare MoS_2 regions. It is expected that the present selective growth method will be combined with nanoscale patterning by STM or AFM to produce nanostructures of molecular crystals with any shape that is desired.

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