Nanostructure Fabrication Using Selective Growth on Nanosize Patterns Drawn by a Scanning Probe Microscope

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Abstract

A novel method of fabricating organic material nanostructures using selective growth on patterned layered material surfaces has been developed. First, an epitaxial monolayer film of layered semiconductor GaSe was grown on a cleaved face of MoS_2. Then, nanosize patterns were drawn by scratching only the grown GaSe film using an atomic force microscope (AFM). Next, C_{60} molecules were deposited on the surface. It has been found that if a substrate temperature is appropriately chosen, C_{60} molecules nucleate only on the bare MoS_2 surface and fill up the carved nanostructures. This combination of AFM lithography and selective growth enables the formation of C_{60} nanostructures as small as 10 nm.

Keywords: nanostructure, molecular crystal, MoS_2, GaSe, C_{60}, AFM, STM, selective growth, van der Waals epitaxy

Introduction

Recent advances in scanning probe microscopy (SPM) techniques have realized the fabrication of atomic-scale structures on solid surfaces.[1-9] Many kinds of nanostructures have been created using the very localized interaction between the probe and the solid surface, and it has become possible to study new physical properties intrinsic to those nanostructures. The ultimate purpose of the SPM nanofabrication is to create novel, ultrahigh-density nanoscale devices. To realize this, a further technique is required to arrange a variety of different atoms or molecules freely, react and then assemble them as designed assemblies. In the present paper, we introduce a promising new method to fabricate nanostructures of organic materials.

Over the past few years, organic molecular crystals have been studied by many groups with the aim of applying them to ultrahigh-density optoelectronic devices, because even a single organic molecule may work as a functional element.[10] Nanoscopic patterning of those organic crystals is a key issue in fabricating molecular devices. It seems difficult, however, to apply the current photolithography technique to organic materials even though it has been successfully used in the fabrication of nanostructures of inorganic semiconductors. Solids of organic molecules are usually so fragile that they are easily damaged by masking or lift-off processes used in the photolithography. But we have found a new phenomenon that leads to damage-free formation of organic material nanostructures. We reported elsewhere that C_{60} molecules can be selectively grown on GaSe and MoS_2 substrates.[11] C_{60} molecules adsorb only on the MoS_2 substrate and not on GaSe at an appropriate substrate temperature. Thus, if one can mask the surface of MoS_2 substrate by a GaSe film and remove the mask nanoscopically in a desired pattern, nanostructures of C_{60} crystals can be formed selectively on those nanoscopic regions of bare MoS_2.

Both MoS_2 and GaSe have two-dimensional layered structures, and their unit layers are bound to each other by weak van der Waals forces. This weak interaction at the interface enables the heteroepitaxial growth of a GaSe mask on a MoS_2 substrate in spite of large differences in their lattice constants and crystal structures,[12] which we called "van der Waals epitaxy".[13,14] Furthermore, many groups have reported that a scanning tunneling microscope (STM) or an atomic force microscope (AFM) can be used to remove the topmost layer of those layered materials even with atomic-scale accuracy.[4,15,16] Then by combining the STM/AFM lithography of the GaSe film on the MoS_2 substrate and the selective growth of C_{60}, it is possible to form nanostructures of any desired shape. We succeeded in growing a monolayer film of GaSe on a MoS_2 substrate, scratching it using an AFM cantilever to draw a nanoscale pattern, and growing C_{60} films

selectively on the scratched area. The concept of the present method is schematically shown in Fig. 1

Experimental

GaSe mask films were grown by molecular beam epitaxy (MBE). MoS_2 substrates were natural molybdenite. They were cleaved in air just before being loaded into an MBE chamber. The base pressure of the MBE chamber was 1×10^{-8} Pa. Before the growth of GaSe, the substrates were thermally cleaned at 500°C for 30 min to remove physisorbed contamination. The substrate temperature used for the growth was 540°C, and flux intensities measured by a nude-ion-gauge-type flux monitor were 7×10^{-6} Pa and 3×10^{-4} Pa for elemental Ga and Se, respectively. Details of the growth of GaSe on MoS_2 are described elsewhere.[12] The crystallinity and the coverage of the GaSe film were checked by reflection high-energy electron diffraction.

After the growth of GaSe, the film samples were taken out of the MBE chamber and subjected to the AFM lithography. The AFM system (Seiko Instrument SPI-3700 controller and SPA-300 AFM head) was operated in ambient air. Conventional Si_3N_4 cantilevers were used for both the surface observation and the lithography. After the AFM lithography, the samples were returned to the same MBE chamber. C_{60} molecules were evaporated from a different Knudsen cell. After the growth of C_{60}, sample surfaces were observed again using an AFM.

Results and Discussion

As described above, samples were transferred between the MBE chamber and the AFM apparatus for the growth and the lithography. In order to observe the nanostructure of C_{60} after the growth, the position at which the GaSe mask has been removed must be located. In general, it is very difficult to locate a nanometer structure smaller than 10 nm using AFM without guiding marks. Fortunately, our samples had inherent marks which helped in locating drawn patterns smaller than 10 nm. Figure 2 shows AFM images of a monolayer GaSe film on a MoS_2 substrate. A wide area (35 μm × 35 μm) image is shown in Fig. 2. It is easy to fix this area on the MoS_2 substrate using an optical microscope equipped to the AFM system. The AFM image reveals the existence of many droplets on the surface. Excess Ga atoms seem to form liquid droplets on the MoS_2 surface and react with Se so that their surfaces become stable. The “map” of the arrangement of those droplets can be used as marks to determine the position of the drawn pattern.

Figure 2(b) indicates a flat area among these droplets. Two bright triangular islands are the second GaSe layer. Many twisting lines can be seen, and these are also used as marks to determine the exact position of the drawn pattern after the growth of C_{60}. Those lines are anti-phase boundaries among GaSe domains. There are two types of GaSe domains with different stacking sequences of Ga and Se atomic layers, which results in the anti-phase boundary. Details of the growth of GaSe on MoS_2 are described elsewhere.[12]

The removal of the masking GaSe layer was performed by scanning the AFM cantilever back and forth over the sample surface in the contact mode. The repulsive force between the cantilever and the surface was set to 0.089×10^{-9} N. Figure 3 shows the process of AFM lithography on the GaSe monolayer. The darker triangular hole in Fig. 3(a) is a bare MoS_2 region where the GaSe mask did not cover, and the brighter triangular island is the second layer GaSe domain. Both of these can be used as fine marks. The cantilever was vertically moved between these marks. At the initial stage of the lithography, a small hole appears on the surface (Fig. 3(b)), then it expands along the direction of scratching (Fig. 3(c)). Eventually, a long groove can be formed (Fig. 3(d)). The smallest groove width of the groove previously carved is 8 nm. The depth of the groove measured by the AFM is equal to the monolayer thickness of GaSe. The MoS_2 surface is not scratched by the AFM cantilever with the same repulsive force, thus the depth of holes or grooves can be made uniform, equal to the thickness of the GaSe monolayer. By repeating the formation of holes and grooves, more complicated patterns can be drawn.

C_{60} molecules were evaporated on the patterned substrate. Figure 4(a) shows an AFM image before the growth of C_{60}. As shown in the lower-right part of the figure, the letter “K” was drawn using AFM lithography. An enlarged image of the “K” is shown in Fig. 4(b). Here, triangular holes on the surface represent bare MoS_2 regions not covered by GaSe. A perfect masking GaSe film without those holes can be grown by optimizing the growth condition, as shown in Fig. 2(b).

Figure 4(c) shows an AFM image after the growth of C_{60} for 2 min at a substrate temperature of 180°C with a flux intensity of 4×10^{-6} Pa. Not only triangular MoS_2 regions, but also the “K” region are filled with C_{60} molecules. In the case shwon in Fig. 4(c), a slight excess of C_{60} was deposited, or the substrate temperature was lower than expected, and some molecules flowed onto

the GaSe regions, which is more clearly seen in the enlarged AFM image in Fig. 4(d). It is clear, however, that the nucleation of the C_{60} molecule occurred only on bare MoS_2 regions, because no C_{60} domain exists on GaSe where a hole or a cut pattern did not exist. It must be noted that we have already succeeded in growing 10-nm-wide C_{60} nanostructures with the exact same shape as that of the bare MoS_2 region between masking GaSe domains.[11] Thus, it will be possible to grow C_{60} nanostructures with the exact shape drawn by AFM lithography, as long as the appropriate growth conditions are used.

The size of the nanostructure will be decreased if STM is used for the lithography, because atomic-scale patterning on layered material substrates by STM has already been reported.[4, 15, 16] Furthermore, the selective growth of molecular crystals has been reported for other combinations of materials.[17] Thus, it seems possible to expand constituent materials to other molecular crystals such as metal-phthalocyanines, or to metal atoms which migrate freely on the layered material surface without the reaction.

Conclusions

A new method of fabricating nanostructures of organic materials on layered material surfaces using AFM lithography and selective growth has been developed. A monolayer GaSe film was grown epitaxially on a cleaved face of MoS_2, and nanosize patterns were drawn by scratching the grown GaSe film using AFM. It has been found that deposited C_{60} molecules nucleate only on the bare MoS_2 surface and fill up the carved nanostructures. This method presents a new way to fabricate complicated nanostructures of many kinds of organic molecular crystals in any desired shape.

Acknowledgement

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Figure captions

Fig. 1 A schematic view of the selective growth of C_{60} molecules on a nanoscale pattern formed on a GaSe/MoS_2 heterostructure using AFM lithography.

Fig. 2 AFM images of the masking GaSe monolayer on the MoS_2 substrate. (a): 35 μm × 35 μm image, (b): 3000 nm × 3000 nm image.

Fig. 3 AFM images showing the process of the nanoscale groove formation on masking GaSe using AFM lithography. (a): before lithography, (b): after 1000 scans of the cantilever, (c): after 2000 scans, (d): after 3000 scans. Horizontal fine lines in the images are noise caused by the horizontal scanning of the AFM measurement.

Fig. 4 AFM images before and after the growth of C_{60} on the nanosize pattern created on the GaSe/MoS_2 substrate. (a): before the growth of C_{60}, (b): enlarged image of "K" in (a) carved by the cantilever, (c): after the growth of C_{60}, (d): enlarged image of "K" in (c).

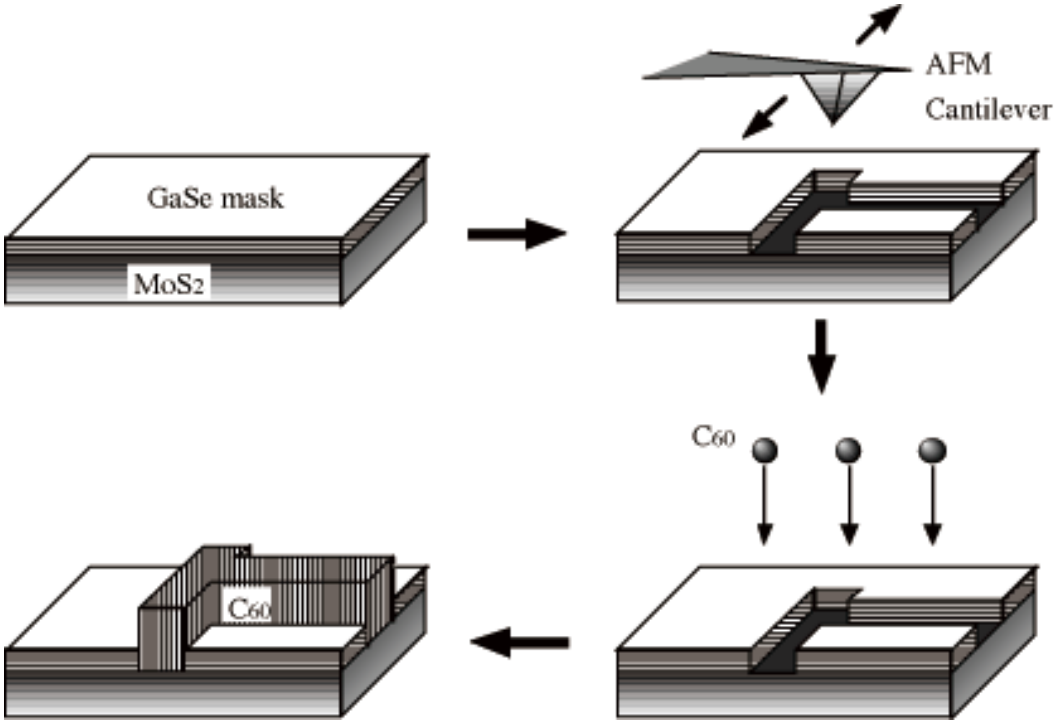

Fig. 1

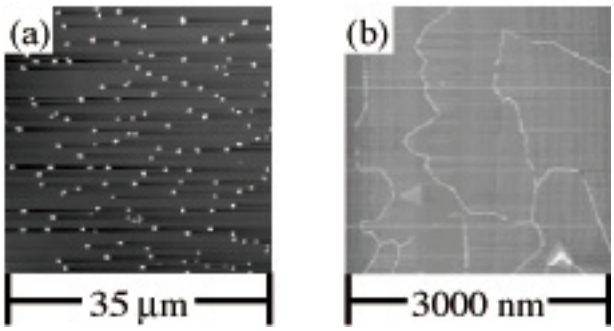

Fig. 2

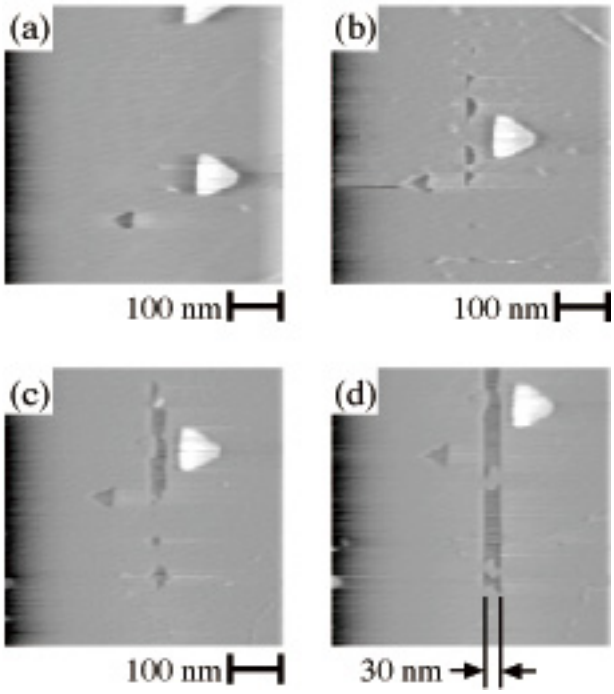

Fig. 3

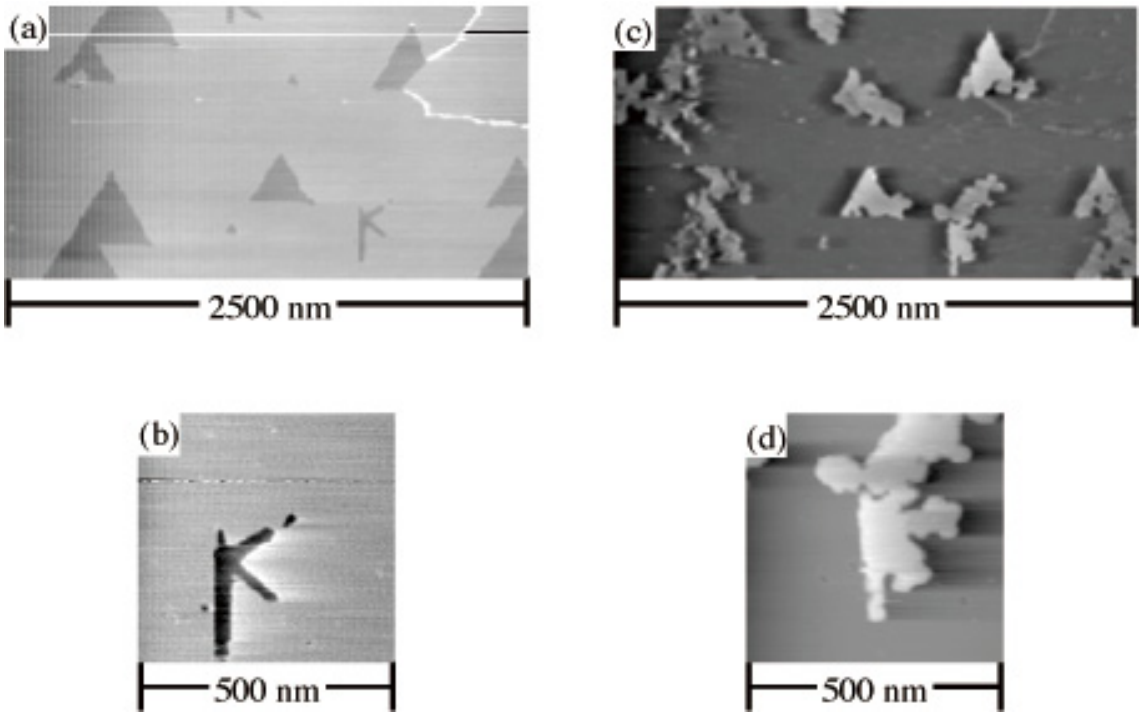

Fig. 4