

Fabrication of C₆₀ Nanostructures by Selective Growth on GaSe/MoS₂ and InSe/MoS₂ Heterostructure Substrates

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Abstract

C₆₀ molecules were deposited on a submonolayer InSe film which was grown on a MoS₂ substrate. In the previous experiment on the growth of a C₆₀ thin film on a GaSe/MoS₂ heterostructure, C₆₀ grew only on exposed MoS₂ regions and never nucleated on GaSe domains at substrate temperature above 180°C. In the present case, however, C₆₀ molecules grow only on InSe domains and do not nucleate on the exposed MoS₂ when the substrate temperature is higher than 80°C. Using this method, C₆₀ domains whose dimension is smaller than 100 nm could be fabricated on each InSe domain. The selectivity of the C₆₀ growth is supposed to originate not from the surface morphology of those heterostructures, but from the difference in adsorption energy and surface diffusion energy of C₆₀ molecules on the surfaces of three different layered materials and a C₆₀ film.

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InSe, C₆₀, Atomic force microscope

1. Introduction

Fabrication of atomic or molecular scale structures is one of the ultimate goal of material preparation. Owing to recent progress in ultra-thin film growth and sub-micrometer scale lithography of inorganic semiconductors, the fabrication of structures which show optic or electronic quantum size effects has been turned into reality [1]. Furthermore, advances in scanning tunneling microscope (STM) or atomic force microscope (AFM) have enabled atomic-scale fabrication on solid surfaces [2-7].

On the other hand, many organic molecular crystals including C_{60} have attracted much attention in these 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. Thin film growth techniques of molecular crystals have been studied by many groups, and now single-crystalline monolayer films can be heteroepitaxially grown on many kinds of solid substrates. But to realize ultrahigh-density organic devices, formation of designed nanoscopic patterns of those molecules will be further required. It seems difficult, however, to apply the current photolithography technique to organic materials, even though it has been successfully used for the fabrication of nanostructures of inorganic semiconductors. Usually organic molecules are bound together by weak forces so that the masking or the lift-off process in the photolithography easily causes damages in them. Thus a new method has been urgently needed to fabricate the nanostructure of the organic molecular crystal.

Until now our group has been studying the heteroepitaxial growth of many kinds of organic molecular crystals. In the course of experiments we have found out the “selective growth” phenomenon of them [8-10]. An example of the selective growth is as follows [9]. First, a sub-monolayer epitaxial film of GaSe was grown on a MoS_2 substrate, whose surface consists of uncovered MoS_2 regions and overgrown GaSe domains. Then C_{60} molecules were deposited on it at various substrate temperatures. Atomic force microscope (AFM) observations revealed that C_{60} molecules adsorb only on MoS_2 but not on GaSe at substrate temperature higher than $180^\circ C$. As a result nanoscale structures of C_{60} as small as 20 nm

were fabricated on exposed areas of MoS₂ surrounded by monolayer GaSe. Furthermore, we have succeeded in fabricating designed nanostructures of C₆₀ [10]. A monolayer film of GaSe was uniformly grown on a MoS₂ substrate, and it was scratched with an AFM cantilever to expose nanoscale areas of MoS₂. The AFM observation indicated that C₆₀ molecules selectively nucleate on carved MoS₂ regions and designed nano-patterns of C₆₀ can be created.

In this paper we mainly report the selective growth of C₆₀ on InSe/MoS₂ heterostructure substrates. A unit layer of InSe has the same crystal structure as GaSe, but lattice constants, stacking of each unit layer and electronic properties are different from those of GaSe [11]. On a surface of each unit layer, no dangling bond appears in a similar way as such layered materials as MoS₂ and GaSe, and unit layers are bound together by the van der Waals-type weak force. Then it is possible to grow a single-crystalline heteroepitaxial film of InSe on another layered material substrate in spite of large differences in lattice constants or crystal structures. We named this type of heteroepitaxy “van der Waals epitaxy” [12], and many combinations of layered materials have been proved to be possible [13-19]. After the growth of InSe on MoS₂, C₆₀ molecules were deposited on it and the growth feature was observed by AFM. One of our purposes of the present experiment is to obtain basic data which will make clear the origin of the selective growth of molecular crystals. Another is to find a combination of materials of the heterostructure substrate, by which it becomes possible to form smaller nanostructures of molecular crystals.

2. Experimental

InSe films were grown by molecular beam epitaxy (MBE). The growth was performed in an ultrahigh vacuum (UHV) chamber with base pressure of 1×10^{-7} Pa. MoS₂ substrates with sizes of about $10 \times 5 \times 0.2$ mm³ were cut from natural molybdenite specimens. They were cleaved in air just before loading into the MBE chamber, and

thermally cleaned under UHV by heating at 500°C for 30 min. Elemental indium (6N) and selenium (6N) were evaporated from separate Knudsen cells, and the intensity of flux was monitored by a nude ion gauge locatable at the sample position. During the growth, the sample surface was monitored by reflection high energy electron diffraction (RHEED) to check crystallinity and coverage of the grown film. Details of the growth method and the growth mechanism of a GaSe film on MoS₂ are described elsewhere [19].

After the growth of the InSe or GaSe film, C₆₀ molecules were deposited on it in the same MBE chamber with a Knudsen cell charged with 99.8% C₆₀ powder. Then samples were taken out of the MBE chamber and observed by AFM (Seiko Instrument SPI-3800 and SPA-300 system) in air. Images were taken in a contact mode with a conventional Si₃N₄ cantilever at room temperature. In all AFM measurements the repulsive force between samples and the cantilever was set to 0.089×10^{-9} N.

3. Results and discussion

Figs. 1a and 1b show AFM images of InSe films grown on MoS₂ at a substrate temperature of 400°C with different coverage. Intensity of In and Se flux was set to 1.0×10^{-6} Pa and 4.0×10^{-5} Pa, respectively. It was confirmed by the RHEED observation that a single-crystalline InSe film grows heteroepitaxially on MoS₂. As shown in AFM images, InSe islands have a hexagonal or triangular shape, and coalesce into larger domains as the growth proceeds. At this substrate temperature, the coverage of the initial InSe layer can be controlled by the growth time. At lower substrate temperature, growth of the second layer starts before the initial layer completely covers the surface. Thus the substrate temperature was set to 400°C to form InSe domains with a desired coverage.

Figs. 2a - 2d are AFM images observed after the growth of C₆₀ on InSe/MoS₂ heterostructure substrates at 105°C (a, b), 80°C (c) and 55°C (d), respectively. The flux intensity of C₆₀ was set to 1×10^{-6} Pa. The growth was finished when streaks from the

grown C_{60} film were clearly observed in the RHEED pattern. At substrate temperature higher than 80°C , as shown in Figs. 2a - 2c, the nucleation of C_{60} molecules seems to occur at step edges of InSe domains. Then C_{60} domains mainly spread onto InSe surfaces with further deposition of C_{60} , while far smaller projections of C_{60} exist onto MoS_2 regions. Almost no isolate C_{60} domain, however, grows on MoS_2 . At substrate temperature lower than 55°C , C_{60} molecules nucleate on both InSe and MoS_2 regions as shown in Fig. 2d. Although Figs. 2a - 2c show the successful selective growth of C_{60} on the samples with 0.6 - 0.9 monolayer (ML) coverage of InSe films, the selective growth of C_{60} was also confirmed with smaller coverage of InSe as low as 0.1 ML. In such low-coverage case, the size of InSe domains could be as small as 100 nm. C_{60} nanostructures smaller than 100 nm can be fabricated selectively on those small InSe domains.

RHEED images taken after the growth of C_{60} show streaks with a much narrower interval than either that of MoS_2 or InSe. The streak interval and the symmetry of RHEED patterns well agree with those of an epitaxial film of C_{60} on a clean MoS_2 substrate [20]. This result suggests that an epitaxial C_{60} film with a closed-packed hexagonal structure grows also on InSe.

As we have already reported [9], C_{60} molecules grow only on MoS_2 regions on a GaSe/ MoS_2 heterostructure substrate, showing the selectivity opposite to the InSe/ MoS_2 case. A typical AFM image of a C_{60} /GaSe/ MoS_2 heterostructure is shown in Fig. 3a, and schematic views of the selective growth of C_{60} on InSe/ MoS_2 and GaSe/ MoS_2 are shown in Fig. 3b. From those results, it is concluded that the selectivity does not come from the surface roughness of heterostructure substrates. If the roughness is the origin of the selective growth, GaSe and InSe domains would act as the same type mask against the growth of C_{60} , and the selective growth should occur in the same manner. Therefore the selectivity is thought to originate from the difference in the nucleation process of C_{60} molecules on three substrate materials and the grown C_{60} film.

After impinging on the substrate, C_{60} molecules freely migrate on inactive surfaces of

those materials if appropriate substrate temperature is given. For example, the migration length of a C_{60} molecule is known to reach tens of micrometers on a step-free clean MoS_2 substrate at a substrate temperature about $200^\circ C$ [21]. On such a surface the supersaturating condition of C_{60} molecules is easily achieved, and when the density of molecules becomes over the critical nucleation density, two-dimensional (2D) nucleation occurs and the growth starts. But if the substrate temperature is too high, C_{60} molecules desorb into the vacuum before the nucleation. Contrary if the substrate temperature is too low, C_{60} molecules cannot long migrate because of insufficient thermal energy, and they nucleate at once. In the followings, we will try to explain the selective growth feature on each heterostructure substrate by assuming different adsorption energy and surface diffusion energy of C_{60} on each substrate material.

(1) Growth on GaSe/ MoS_2

In the case of the GaSe/ MoS_2 heterostructure substrate, the selective growth of C_{60} occurs above $180^\circ C$. At this temperature, the size of bare MoS_2 regions seems to be smaller than the migration length of C_{60} due to the large adsorption energy and the small surface diffusion energy of C_{60} on MoS_2 . Then most of C_{60} molecules on MoS_2 can reach step edges of GaSe. Although many of C_{60} molecules continue migrating back to MoS_2 regions or onto GaSe domains, some lose their energy and nucleate there due to exposed dangling bonds at step edges. C_{60} molecules impinging on GaSe domains or coming from MoS_2 regions, however, will have a far shorter residence time if the adsorption energy on GaSe is small, and they will desorb before the nucleation. C_{60} molecules successively impinging on MoS_2 will migrate and be incorporated into C_{60} domains already formed around step edges. Thus, C_{60} molecules will fill up only exposed MoS_2 surfaces. The residence time of a C_{60} molecule on a C_{60} film surface is supposed to be long enough to nucleate and to form subsequent layers. As a result the third or the fourth layer of C_{60} can grow without spilling over onto GaSe regions, as shown in Fig. 3a.

(2) Growth on InSe/MoS₂

On the other hand, growth features of C₆₀ on the InSe/MoS₂ heterostructure substrate must be quite different, because the selective growth occurs at substrate temperature as low as 80°C. At this substrate temperature, C₆₀ molecules completely condense on a clean MoS₂ surface [20, 21]. Thus, the desorption of C₆₀ molecules from MoS₂ regions cannot be expected as the origin of the selective growth, and a different mechanism that gathers C₆₀ molecules from MoS₂ regions onto InSe domains must exist. We suppose that the migration length of C₆₀ on the InSe surface is much shorter than the size of InSe domains due to large surface diffusion energy, while that on MoS₂ is still longer than the size of MoS₂ regions even at 80°C.

When the substrate temperature is lower than 55°C, the migration length of C₆₀ seems to be shorter than the size of MoS₂ regions, and the nucleation of C₆₀ occurs both on InSe and MoS₂ as shown in Fig. 2d. Above 80°C, however, C₆₀ molecules impinging on the MoS₂ surface can migrate longer and go up to InSe domains. But on InSe domains, it is supposed that C₆₀ molecules easily lose their migration energy and nucleate. Then the density of C₆₀ molecules becomes the highest near the step edge on the InSe domain, because C₆₀ molecules are supplied also from neighboring MoS₂ regions. Thus, in the early stage of the growth, the nucleation of C₆₀ occurs around step edges of InSe domains, and the following growth occurs at step edges of C₆₀ islands faced to the InSe surface where the surface diffusion energy is highest. C₆₀ molecules successively impinging on MoS₂ can migrate onto C₆₀ islands or InSe domains, and they are incorporated into C₆₀ islands before returning to MoS₂ regions.

In addition to the nucleation around the step edge of InSe, 2D-nucleation of C₆₀ also occurs on plain InSe surfaces, as clearly shown in an enlarged AFM image in Fig. 2b. The existence of many small islands of C₆₀ also means that the migration length of C₆₀ molecules on the InSe surface is far shorter than the size of the InSe domain.

C_{60} molecules continue growing on the surface of InSe domains in such manner as explained above, but it becomes difficult for successively impinging C_{60} molecules to find the most stable nucleation position after they almost cover the InSe surface. Then it is supposed that the growth of C_{60} domains occurs on MoS_2 regions in addition to the growth on C_{60} domains. Fig. 4 shows an AFM image of a $C_{60}/InSe/MoS_2$ sample surface after excess amounts of C_{60} were deposited to cover InSe domains. Here the surfaces of InSe are almost covered with the initial layer of C_{60} , and subsequent islands of C_{60} grow on it. Furthermore, MoS_2 regions among InSe domains are also filled with small islands of C_{60} . It seems difficult to grow a thick C_{60} nanostructure selectively on InSe domains on the MoS_2 substrate, while it is possible to form C_{60} nanostructures thicker than 2 ML selectively on MoS_2 regions in the GaSe/ MoS_2 heterostructure .

As described above, the selective growth can be explained by considering the difference in the adsorption energy and the surface diffusion energy among substrate materials, but those energies have not been quantitatively measured yet. It is supposed that a C_{60} molecule on the substrate which has a larger adsorption energy suffers a larger distortion of charge balance in the molecule, and the break of vibrational symmetry may occur. Therefore we are planning to reveal it using high resolution electron energy loss spectroscopy (HREELS), which is known to be sensitive to the break of the vibrational symmetry in a molecule [22]. As for the determination of the surface diffusion energy, it is required to elucidate the effects of the substrate temperature and the dose of C_{60} molecules on the number of grown C_{60} islands for every substrate material [23].

4. Conclusions

Submonolayer domains of InSe were heteroepitaxially grown on a MoS_2 substrate, and C_{60} molecules were deposited on that InSe/ MoS_2 heterostructure. In contrast to our former

experiments on the growth of C_{60} on GaSe/MoS₂ heterostructures, C_{60} molecules cover only the overgrown InSe domains, and do not nucleate on the exposed MoS₂ surface at substrate temperature above 80°C. The selectivity of the C_{60} growth is thought to originate from the difference in both the adsorption and the surface diffusion energy of C_{60} molecules on each material (GaSe, InSe, MoS₂ or C_{60}) surface. C_{60} nanostructures smaller than 100 nm can be fabricated selectively on InSe domains in the present case, but the GaSe film seems to be a more adequate than InSe for fabricating smaller and as-designed nanostructures of C_{60} on the MoS₂ substrate.

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Figure Captions

Fig. 1 AFM images of InSe submonolayer films grown on MoS₂ substrates with different amounts of coverage, (a): 0.5 ML, (b): 0.9 ML.

Fig. 2 AFM images of C₆₀ domains grown at various substrate temperatures on MoS₂ substrates covered with 0.6 - 0.9 ML InSe islands. (a): grown at 105°C, (b): an enlarged image of the same sample with (a), (c): grown at 80°C, (d): grown at 55°C.

Fig. 3 (a) A typical AFM image of the selective growth of C₆₀ on a GaSe/MoS₂ heterostructure substrate. (b) Schematic views of the selective growth of C₆₀ on InSe/MoS₂ and GaSe/MoS₂ substrates.

Fig. 4 An AFM image of the C₆₀/InSe/MoS₂ heterostructure in which excess amounts of C₆₀ were deposited at a substrate temperature of 105°C.

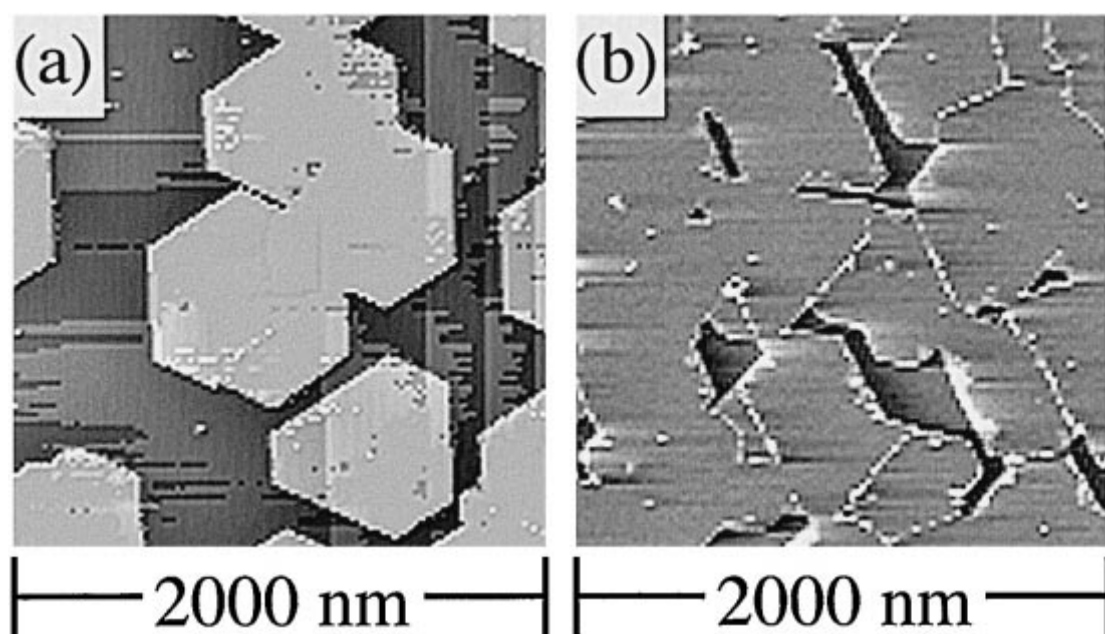


Fig. 1

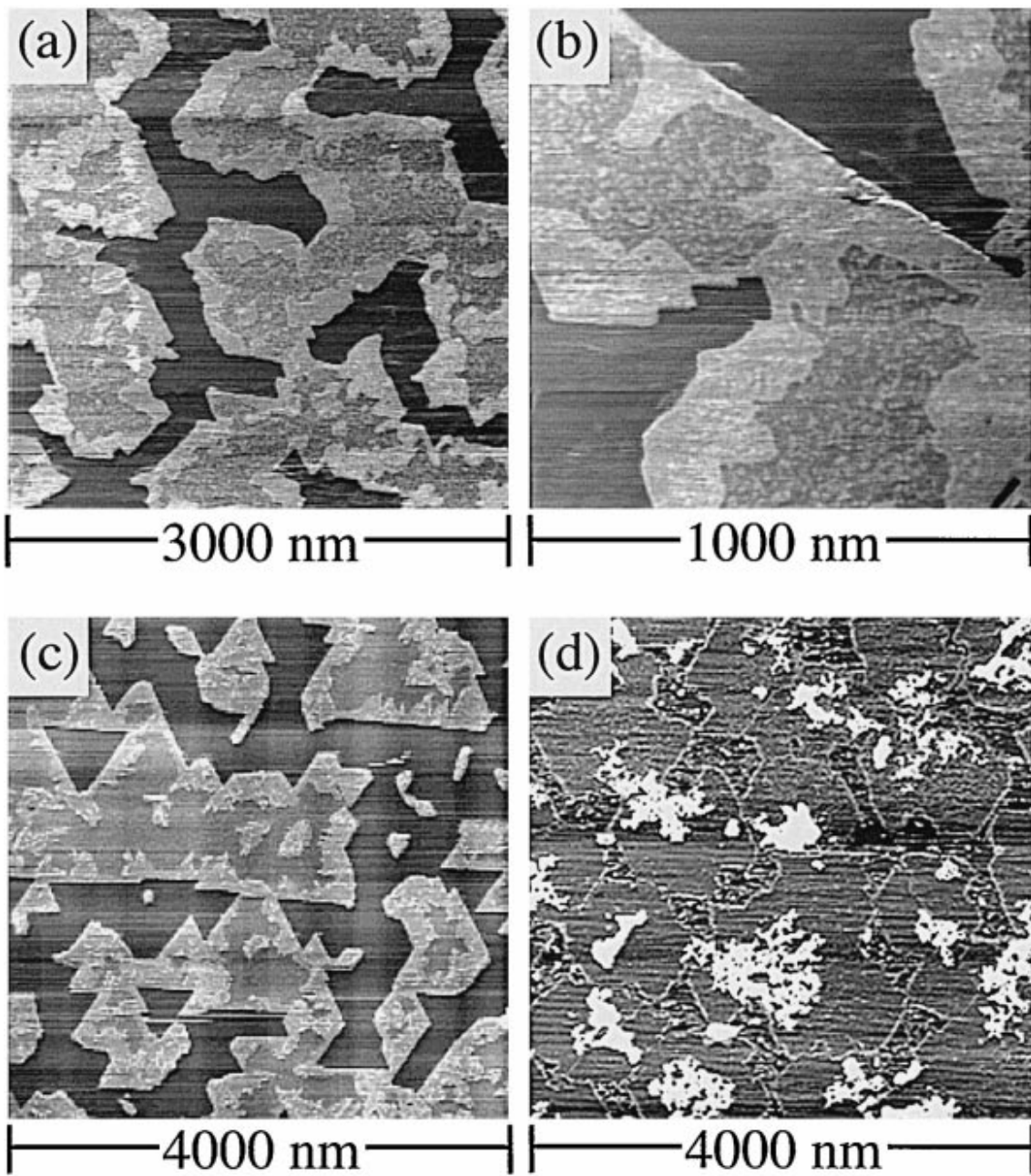


Fig. 2

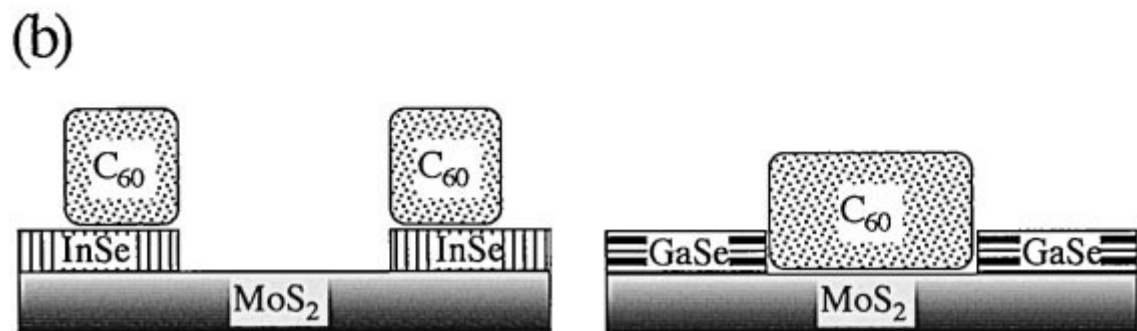
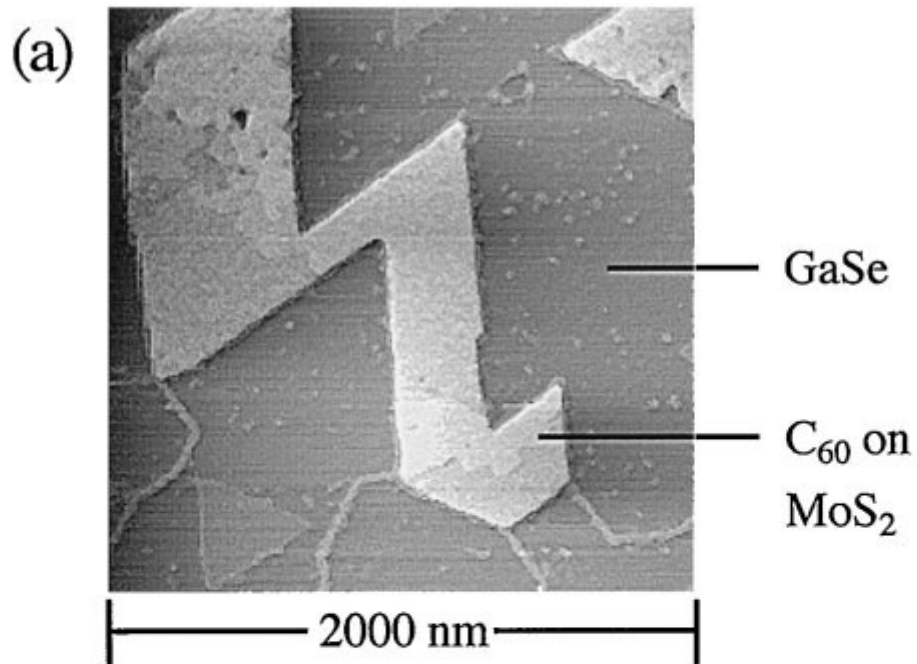


Fig. 3

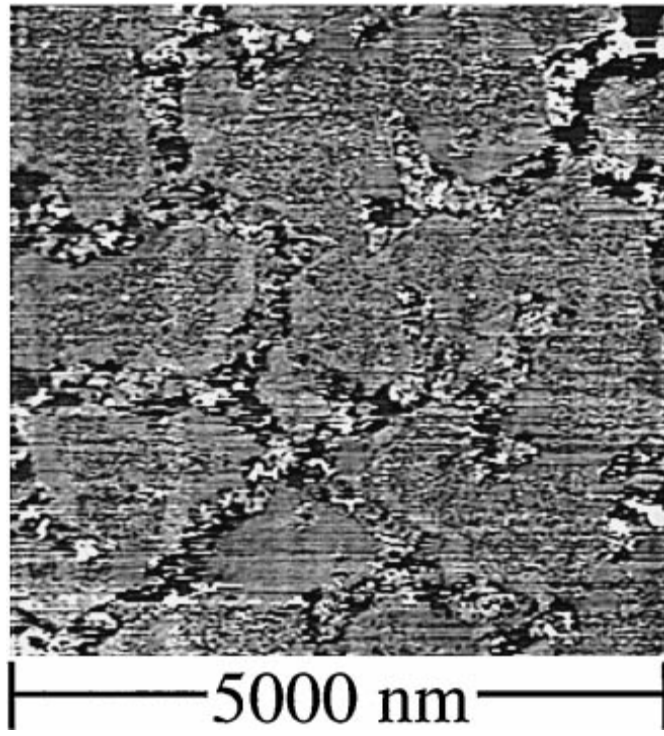


Fig. 4