

# Heteroepitaxial growth of layered transition metal dichalcogenides on sulfur-terminated GaAs{111} surfaces

Keiji Ueno, Toshihiro Shimada, Koichiro Saiki, and Atsushi Koma

Department of Chemistry, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan

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Layered transition metal dichalcogenides ( $\text{MoSe}_2$ ,  $\text{NbSe}_2$ ) have been heteroepitaxially grown on  $(\text{NH}_4)_2\text{S}_x$  ( $x \cong 2$ ) treated GaAs(111)Ga, GaAs( $\bar{1}\bar{1}\bar{1}$ )As surfaces in spite of the large difference in their crystal structures. The *in situ* observation of reflection high-energy electron diffraction has shown that the grown film has its own lattice constant even from the first layer. The lattice matching condition, which is severely restricting in the usual heteroepitaxial growth case, is greatly relaxed in the present system because only weak van der Waals forces exist between the grown film and the substrate. This results from the fact that sulfur atoms regularly terminate dangling bonds on the GaAs surface after the  $(\text{NH}_4)_2\text{S}_x$  treatment.

Recently heterostructures consisting of ultrathin layers with atomic order thicknesses have been successfully fabricated by molecular beam epitaxy and other epitaxial growth techniques. Exploitation of them has made it possible to construct such new electronic devices as superlattice devices and electron wave devices. But good heteroepitaxial growth was possible only for very limited combinations of materials, since the existence of dangling bonds requires almost exact lattice matching between the overgrown and substrate materials.

The lattice matching condition, however, has been found to be drastically relaxed when layered materials are used as the constituent materials.<sup>1-3</sup> Atoms existing in a unit layer of a layered material are bound through strong covalent bonds, whereas the layers are held together only via weak van der Waals forces. Thus they are easily cleaved parallel to the layers, and no dangling bonds appear on the cleaved surface. Therefore, it is expected that the growth of a layered material onto such surfaces proceeds via van der Waals forces, and that good heteroepitaxial growth occurs even with the existence of a large lattice mismatch.<sup>1-3</sup> We call such type of growth van der Waals epitaxy.<sup>1-3</sup> Through van der Waals epitaxy, the fabrication of various kinds of heterostructures using a variety of layered materials as constituents has become a distinct possibility. For example, among the layered transition metal dichalcogenides ( $\text{TX}_2$ 's) there are such insulator as  $\text{HfS}_2$ , such semiconductors as  $\text{MoS}_2$  and  $\text{MoSe}_2$ , and such superconducting metals as  $\text{NbS}_2$  and  $\text{NbSe}_2$ .

Previously we have shown that van der Waals epitaxy can be applied to the heteroepitaxial growth between layered materials.<sup>1-3</sup> In the present letter we report our extension of the van der Waals epitaxy method to the growth of layered materials on widely used three-dimensional material substrates. As mentioned above, the dangling bonds on a clean surface may prevent good heteroepitaxial growth of a layered material on it. But growth through van der Waals forces would become possible if regular termination of the surface dangling bonds is accomplished and kept stable even at the high temperatures required for good epitaxial growth. It has been reported recently that the dangling bonds on GaAs{111} surfaces can be regularly terminated with sulfur

atoms after  $(\text{NH}_4)_2\text{S}_x$  ( $x \cong 2$ ) treatment.<sup>4,5</sup> The termination is stable up to 500 °C, so such treatment is likely to be very suitable for our purpose. Here we report the epitaxial growth of  $\text{MoSe}_2$  and  $\text{NbSe}_2$  on  $(\text{NH}_4)_2\text{S}_x$ -treated GaAs{111} surfaces [hereafter, the treated surfaces are referred as "S-GaAs(111)Ga" or "S-GaAs( $\bar{1}\bar{1}\bar{1}$ )As" ].

The substrates used were Si-doped *n*-type GaAs(111)Ga and ( $\bar{1}\bar{1}\bar{1}$ )As wafers. The (111)Ga wafer was etched in a  $\text{H}_2\text{SO}_4\text{:HCl:H}_2\text{O}$  (2:2:5) solution at 50 °C for 20 min and rinsed in de-ionized (DI) water. The ( $\bar{1}\bar{1}\bar{1}$ )As wafer, on the other hand, was etched first in a  $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$  (5:1:1) solution at 60 °C for 1 min, followed by a (5:1:40) solution of the same compounds for 20 s at RT, then rinsed in DI water. The etched substrates were dried and dipped into a solution of  $(\text{NH}_4)_2\text{S}_x$  ( $x \cong 2$ ) for a day at room temperature.<sup>5</sup> The period of dipping was varied from several hours to several days, but no appreciable difference was observed. After the substrate was taken out, yellow droplets of the solution were blown off with dry  $\text{N}_2$  gas. The treated substrate was introduced to a vacuum chamber and heated to about 400 °C to remove excess sulfur prior to the growth of  $\text{TX}_2$ 's on it.

The epitaxial growth was carried out in a molecular beam epitaxy chamber with a base pressure of  $8 \times 10^{-9}$  Pa. Purified selenium was evaporated from a Knudsen cell. Electrostatic focusing electron beam evaporators were used for evaporation of molybdenum and niobium. Intensities of molecular beams were monitored by quartz crystal oscillators placed close to the substrate. A Se-rich atmosphere was attained during the growth. A reflection high-energy electron diffraction (RHEED) system was used for a real-time monitoring of surfaces of the substrates and the grown films. The substrates and the grown films were characterized by Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS). The EELS was also performed to make a nondestructive in-depth profiling of the interface of the grown samples.

The RHEED patterns of a S-GaAs(111)Ga substrate which was heated to 400 °C in the vacuum are shown in Figs. 1(a) and 1(b). The incident electron beam used to obtain the patterns shown in Figs. 1(a) and 1(b) was set to be parallel to the  $[10\bar{1}]$  and  $[11\bar{2}]$  crystal axes of the substrate,

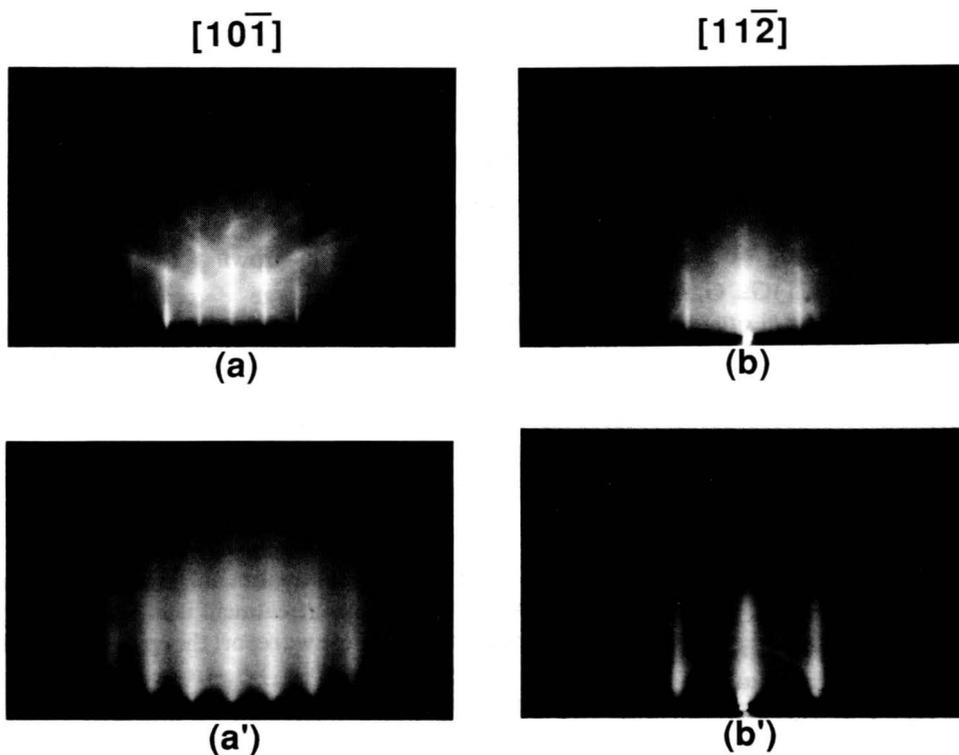


FIG. 1. RHEED patterns of (a) (b) S-GaAs(111)Ga substrate and (a') (b') ten unit layers of MoSe<sub>2</sub> grown on the substrate. The incident electron beam is parallel to (a, a') the [10 $\bar{1}$ ] axis and (b, b') the [11 $\bar{2}$ ] axis crystal orientations of the substrate, respectively.

respectively. Both patterns show good streaks having sixfold symmetry around the axis normal to the surface with no reconstruction being observed. The existence of sulfur atoms on the surface was also proved by the AES measurement. It is therefore conceivable that each dangling bond is regularly terminated by a single sulfur atom, resulting in the surface having sixfold symmetry.

A MoSe<sub>2</sub> film was grown on such surfaces at 400 °C. The growth rate was about 0.05 nm/min. After the growth of a 1/2 unit layer of MoSe<sub>2</sub>, a streak pattern of the grown film appeared in addition to that of the substrate. Here, "1/2 unit layer" means that a unit layer of MoSe<sub>2</sub> having 0.65 nm thickness covers half of the substrate surface. The lattice constant calculated from the streak intervals of that pattern was consistent with that of a bulk 2H-MoSe<sub>2</sub> crystal. The streaks originating from the substrate completely disappeared after the growth of two unit layers.

The streaks from the grown film, however, became broad when the growth was continued at the above-mentioned temperature. A higher growth temperature would be desirable for better crystallinity of the film, but it could not be raised above 550 °C in the present case, since sulfur atoms terminating the dangling bonds are desorbed.<sup>5</sup> In order to overcome this difficulty, the growth temperature was raised from 400 to 650 °C after growth of the first unit layer of MoSe<sub>2</sub>, and the growth was continued at 650 °C. This procedure led to a sharp streak pattern, which reveals improved crystallinity of the grown film. The RHEED patterns after growth of about ten unit layers of MoSe<sub>2</sub> are shown in Figs. 1(a') and 1(b'). It was found that the RHEED patterns

from the grown MoSe<sub>2</sub> film along [10 $\bar{1}$ ] and [11 $\bar{2}$ ] directions of the GaAs substrate were identical to those from a bulk 2H-MoSe<sub>2</sub> crystal along its [11 $\bar{2}$ 0] and [10 $\bar{1}$ 0] directions, respectively. It should be noted that the main axes of the grown film align exactly with the axes of the GaAs substrate in spite of the large difference in their crystal structures.

The growth of MoSe<sub>2</sub> was also attempted on S-GaAs(111)As surfaces with the same method. RHEED patterns from the S-GaAs(111)As surface also showed sixfold symmetry without any reconstruction. The MoSe<sub>2</sub> film grown on this surface had similar quality in terms of the crystallinity to that on the S-GaAs(111)Ga surface. Moreover, the growth of NbSe<sub>2</sub> films was attempted on S-GaAs{111} substrates and similar results were obtained, indicating the versatility of the present method.

As is mentioned above, the grown films of TX<sub>2</sub>'s have their own lattice constants even at the initial stage of growth. If chemical bonds exist at the interface, the grown film should be distorted and cannot have its own bulk lattice constant because of the lattice mismatch. Therefore, it can be considered that the heteroepitaxial growth of layered TX<sub>2</sub>'s on the passivated GaAs{111} substrate proceeds via van der Waals forces in a similar way as the van der Waals epitaxy between layered materials.<sup>1-3</sup>

A nondestructive in-depth profiling was attempted by EELS in order to examine the sharpness of the interface between the S-GaAs(111)Ga substrate and the grown MoSe<sub>2</sub> film. In EELS the profiling depth may be varied between 0.2 and 1.1 nm when the primary electron energy is varied from

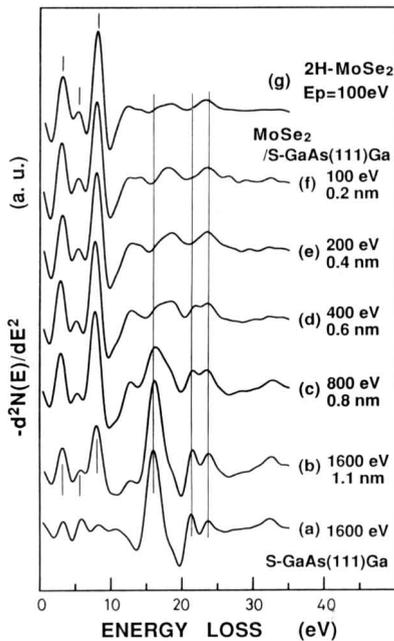


FIG. 2. Electron energy loss spectra of (a) a S-GaAs(111)Ga substrate, (b)–(f) a unit layer of MoSe<sub>2</sub> on this substrate taken at 1600–100 eV, and (g) a bulk 2H-MoSe<sub>2</sub> crystal. The profiling depth for each primary electron energy is as shown in the figure.

100 to 1600 eV.<sup>6</sup> Shown in Fig. 2 are the electron energy loss spectra of the MoSe<sub>2</sub> film with a thickness of a unit layer, 0.65 nm, which was grown on the S-GaAs(111)Ga substrate. Spectra of the substrate and a bulk 2H-MoSe<sub>2</sub> crystal are also shown for comparison. The spectra from the heterostructure are identical with that of a bulk 2H-MoSe<sub>2</sub> crystal when they are taken at primary electron energies of 100 and 200 eV. No signal from the substrate is seen at these primary energies. However, some signals from the substrate appear in the spectrum of 400 eV. Loss peaks at 16, 22, and 24 eV become prominent in the spectra taken at the primary energies of 800 and 1600 eV, the peak positions coinciding with similar peaks in the spectrum of the GaAs substrate. Considering the probing depth for these spectra, the abruptness of the interface between the substrate and the grown film may

be estimated to be as sharp as 0.1 nm. In addition, it is proved that the grown film has a quality comparable to that of a bulk single crystal of 2H-MoSe<sub>2</sub>, because the spectrum taken at the primary electron energy of 100 eV, which only probes the grown film, is identical with that of a bulk 2H-MoSe<sub>2</sub> crystal.

In conclusion, transition metal dichalcogenides (MoSe<sub>2</sub> and NbSe<sub>2</sub>) have been grown on (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>-treated GaAs(111)Ga and ( $\bar{1}\bar{1}\bar{1}$ )As surfaces. It has been proved for the first time that such layered materials can be epitaxially grown on an ordinary semiconductor that has dangling bonds on its clean surface. This results from the regular termination of the active dangling bonds by sulfur atoms, which enables van der Waals epitaxy to occur on the surface. The abruptness of the interface and the quality of the grown film were characterized by EELS. It has been found from these measurements that an epitaxial film of good quality with its own lattice constant can be grown on a three-dimensional substrate in the same way as van der Waals epitaxy between layered materials. This method opens a new way to join a layered material and an ordinary semiconductor and to make various heterostructures on a GaAs substrate using various kinds of TX<sub>2</sub>'s. This will make it possible to fabricate such complex integrated circuits as Josephson devices on GaAs-based devices.

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