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Heteroepitaxy of Layered III-VI Semiconductor GaSe on Hydrogen-Terminated Si(111) Surfaces

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Layered III-VI semiconductor GaSe films have been grown heteroepitaxially on HF-treated Si(111) surfaces. Active dangling bonds on the Si(111) surface are regulary terminated by hydrogen atoms. The GaSe film grows through weak van der Waals interaction with the substrate, relaxing the lattice-matching condition drastically. Single crystalline GaSe films can be grown from the initial stage in spite of the large difference in their crystal structures. High resolution electron energy loss spectroscopy reveals a good quality of the grown GaSe films.

§1. Introduction

Heteroepitaxy is becoming one of the most important technologies in realizing new electronic devices. But so far good heteroepitaxial growth has been possible between limited number of materials, because good lattice matching is needed between them to bind dangling bonds on the substrate surface coherently with the atoms in the overgrown material.

The lattice matching condition, however, can be drastically relaxed when the heteroepitaxial growth proceeds with van der Waals interaction on such dangling-bond-free surfaces as cleaved faces of layered materials. This type of epitaxy was successfully applied to the heteroepitaxial growth between many kinds of layered materials, and called "van der Waals epitaxy".[1-6]

Here we report a new extension of van der Waals epitaxy. We tried to grow a layered material on technologically important Si surfaces. Recently it has been reported by many research groups that surface dangling bonds on a Si(111) surface can be regularly terminated with hydrogen atoms by aqueous HF treatment.[7-11] In the case of dilute HF treatment, there mainly exist trihydrides (-SiH_3) on the flat part of the Si(111) surface (Fig. 1(a)).[9] In contrast, the surface treated by *p*H modified buffered HF is covered only with monohydrides (≡SiH) (Fig. 1(b)).[10,11] The hydrogen terminated Si(111) surface results in very inert one with quasi van der Waals nature. Then it is expected that a layered material grows on that surface with the van der Waals interaction.

Among many layered materials we have chosen III-VI compound semiconductor GaSe, because it can be grown at rather low substrate temperature.[6] As is shown in Fig. 2, a unit layer of GaSe includes four atomic layers of Se-Ga-Ga-Se, and the Se-Se length in the top layer is 0.3755 nm. The Si-Si length in the top layer of Si(111) substrate is 0.384 nm. Thus the lattice mismatch between the substrate and the overgrown film is about 2%.

§2. Experimental

Substrates were n-type Si(111) wafers. They were first cleaned by conventional RCA method and boiled in $HCl:H_2O_2:H_2O$ (1:1:4) solution for 10 min to make a thin oxidized layer.

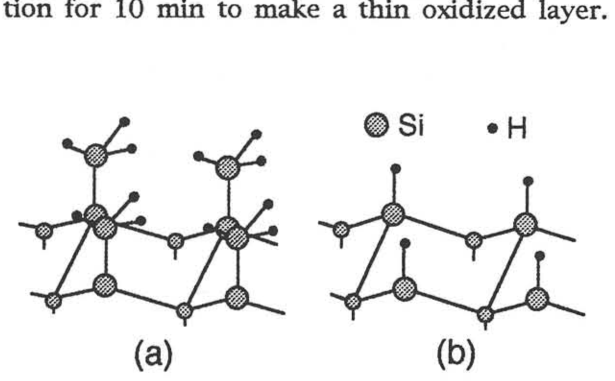

Fig. 1 Schematic views of hydrogen terminated Si(111) surfaces: (a) terminated by -SiH_3 radicals, (b) terminated by hydrogen atoms.

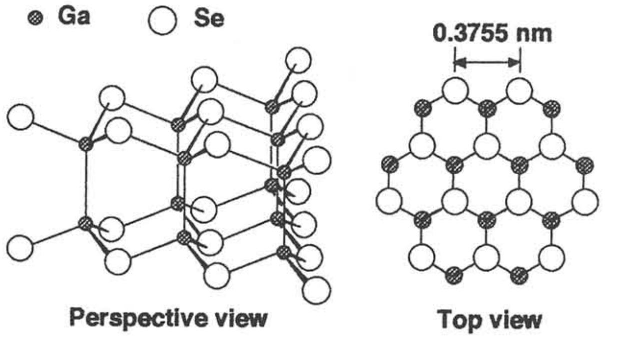

Fig.2 Perspective and top views of a unit layer of GaSe.

Next the wafers were etched in 1% HF solution for 2 min, and rinsed in deionized water. Then the surface oxide was removed and the surface dangling bonds were terminated by hydrogen atoms. The properly hydrogen-terminated Si surface became hydrophobic. As described in the previous section the Si surface treated by this method is mainly covered with Si-trihydrides (-SiH_3), and in this report we discuss only the growth on that substrate. Treated substrates were then immediately introduced into the load-lock chamber.

GaSe films were grown by MBE method. The base pressure of the MBE chamber was 7×10^{-9} Pa. Elemental Ga and Se were evaporated from Knudsen cells and their flux intensities were monitored by a flux monitor of a nude ion gauge type. Reflection high electron energy diffraction (RHEED) was used to monitor the surface structure during growth. Grown samples were transferred to an analysis chamber without breaking a vacuum, and high resolution electron energy loss spectroscopy (HREELS) was used to know their crystallinity.

§3. Results and Discussions

To grow a GaSe film heteroepitaxially on the hydrogen-terminated Si(111) substrate, it was important to control the substrate temperature. We have already found that good GaSe films grew on GaAs(111)A, B surfaces at the substrate temperature of 400 °C.[6] However, no single domain GaSe film was obtained when the growth of GaSe was tried at the substrate temperature of 400 °C on a hydrogen-terminated Si(111) surface. Figure 3 shows RHEED patterns of the substrate (a, b), and of the GaSe film as thick as 300 nm grown at 400 °C (c, d). A same diffraction pattern was observed with any direction of the incident electron beam, indicating that the grown film has a fiber-texture structure. In other words, the grown film consists of many domains of GaSe. Each domain is single-crystalline layered GaSe and its *c*-axis is normal to the substrate. But the *a*-axis of each domain, which is distributed azimuthally, has random directions.

This may arise from the fact that the terminating hydrogen atoms desorbed from the Si(111) surface at 400 °C and active dangling bonds had appeared before the growth of GaSe. To control the desorption of hydrogen atoms, the growth of GaSe was examined at the substrate temperature of 300 °C at first, and it was raised to 400 °C just after a monolayer-equivalent amount of GaSe was deposited. Figures 3(e) and 3(f) show RHEED patterns of

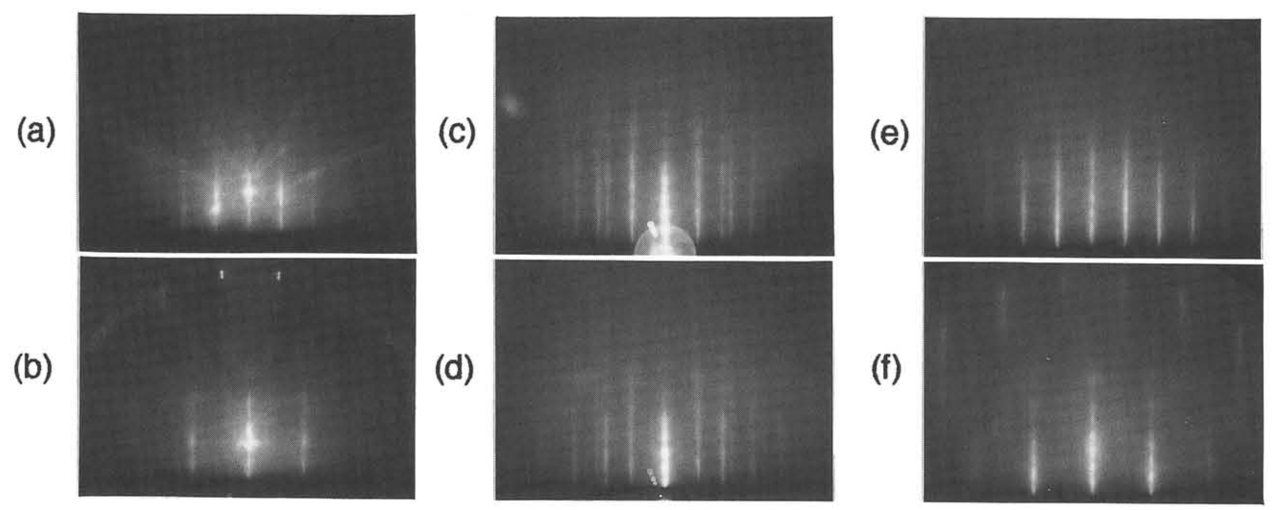

Fig. 3 RHEED patterns of a hydrogen terminated Si(111) substrate(a, b), a multi-domain GaSe film (c, d) and a single-domain GaSe film (e, f). The incident electron beam is parallel to the $[10\bar{1}]$ axis (a, c, e) and the $[11\bar{2}]$ axis (b, d, f) of the Si(111) substrate, respectively.

the GaSe film as thick as 300 nm grown by this method. Sharp bright streaks of the RHEED pattern prove the single-domain growth and the good crystallinity of the grown GaSe film. Thus it is concluded that a single domain GaSe film grows epitaxially on a Si(111) surface provided that active dangling bonds are regularly terminated by hydrogen atoms. The good crystallinity of the grown film was also checked by X-ray diffraction measurement.

High resolution electron energy loss spectrum (HREELS) of the grown GaSe film is shown in Fig. 4. The energy loss peak at 30.0 meV comes from the excitation of a surface LO phonon (Fuchs-Kliever mode).[12] Multiple scattering of the FK phonon produces loss peaks at 30.0 x n (n=2,3,4,...) meV, and an energy gain peak is also observed on the left side of the primary peak. The energy-loss (or energy-gain) value of 30.0 meV agrees well with that calculated from the dielectric constants and the optical absorption data of a bulk GaSe crystal. This also indicates the good quality of the grown GaSe film.

Since it has been already proved that a variety of layered materials ranging from an insulator to a superconductor can be epitaxially grown on GaSe, the present success has opened a new way to grow various kinds of layered materials on the silicon surface by putting a GaSe layer as intermediating one.

§4. Conclusions

We have heteroepitaxially grown layered III-VI compound semiconductor GaSe on a hydrogen terminated Si(111) surface. The regular passivation of active dangling bonds and the control of the substrate temperature during the growth made it possible to grow a single-domain GaSe film with a good crystallinity.

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References

1) A. Koma, K. Sunouchi and T. Miyajima: J. Vac. Sci. & Technol. B3 (1985) 724.
2) A. Koma and K. Yoshimura: Surf. Sci. 174 (1986) 556.
3) K. Ueno, K. Saiki, T. Shimada and A. Koma: J. Vac. Sci. & Technol. A8 (1990) 68.
4) K. Ueno, T. Shimada, K. Saiki and A. Koma: Appl. Phys. Lett. 56 (1990) 327.
5) A. Koma, K. Ueno and K. Saiki: J. Crystal Growth 111 (1991) 1029.
6) K. Ueno, H. Abe, K. Saiki and A. Koma: Jpn. J. Appl. Phys. 30 (1991) L1352.
7) V. A. Burrows, Y. J. Chabal, G. S. Higashi, K. Raghavachari and S. B. Christman: Appl. Phys. Lett. 53 (1988) 998.
8) Y. J. Chabal, G. S. Higashi, K. Raghavachari and V. A. Burrows: J. Vac. Sci. & Technol. A7 (1989) 2104.
9) Y. Morita, K. Miki and H. Tokumoto: Appl. Phys. Lett. 59 (1991) 1347.
10) G. S. Higashi, Y. J. Chabal, G. W. Trucks and K. Raghavachari: Appl. Phys. Lett. 56 (1990) 656.
11) R. S. Becker, G. S. Higashi, Y. J. Chabal and A. J. Becker: Phys. Rev. Lett. 65 (1990) 1917.
12) R. Fuchs and K. L. Kliewer: Phys. Rev. 140 (1965) A2076.

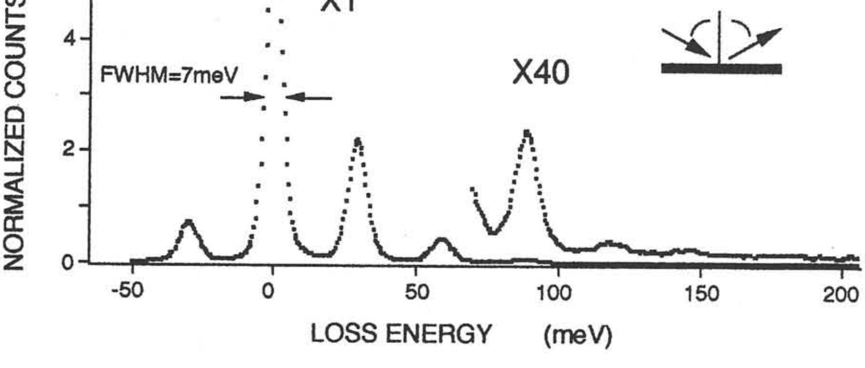

Fig. 4 HREELS of a GaSe film grown on a hydrogen-terminated Si(111) substrate.