Extended Abstracts of the 15th Conference on Solid State Devices and Materials, Tokyo, 1983, pp. 309-312

B-6-7

Heteroepitaxy onto Surfaces with No Dangling Bonds
—Heteroepitaxy of Selenium on Cleaved Faces of Tellurium—

Nahomi Aoto, Kazumasa Sunouchi and Atsushi Koma

Institute of Materials Science, University of Tsukuba

Sakura-mura, Ibaraki 305, Japan

Thin selenium films have been epitaxially grown on clean cleaved faces of tellurium by molecular beam epitxy. The surfaces of tellurium substrates and epitxially grown selenium films have been characterized *in situ* by RHEED, AES and LEELS. Quite good quality of heteroepitaxial films have been prepared, even though lattice constant along c-axis of selenium is smaller than that of tellurium by about 20 %. This large mismatch in lattice constants has been proved to be overcome because there exist no dangling bonds at the interface and because growth mechanism is van der Waals type.

§1. Introduction

Recently heterostructures with atomic order dimensions have been successfully fabricated and they have made it posssible to realize such new electronic devices as superlattice devices and heterojunction bipolar transistors etc.. There exist, however, a few problems to be solved in the preparation of qood qualities of heterostructures. One is the lattice matching between materials forming hetrostructures, which limits the combination of materials. The other is the interface electronic states which affects the device performance seriously. Those difficulties seem to be overcome, if one chooses materials with no dangling bonds on their surfaces as those for heterostructures.

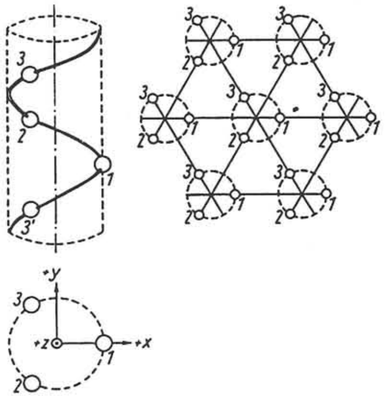

Fig. 1 Crystal structure of selenium and tellurium.

Here we will report on the heteroepitaxy of selenium onto cleaved faces of tellurium by means of molecular beam epitaxy. Selenium and tellurium are semiconducting elements from column VIb of the Peiodic Table and have peculiar crystal structures consisting of atoms arranged in spiral chains as is shown in Fig. 1. The atoms in a chain are bound with covalent bond, whereas the bond between chains are purely van der Waals type. The crystals can be cleaved easily along the chains and it is expected that no dangling bonds appear on their cleaved faces. Therefore selenium on tellurium seems to be the simplest heterostructure having no dangling bond at the interface and is suitable to see the growth feature of this kind. There are a few reports on heteroepitaxy of selenium onto tellurium[1-3], but non of them has dealt with it from the point of heteloepitxy onto the surface with no dangling bond. In the present work both the substrate and the epitaxial layer have been characterized *in situ* by reflection high energy electron diffraction (RHEED), Auger electron spectroscopy (AES) and low-energy electron energy loss spectroscopy (LEELS). It has been proved that very good quality of selenium films can be epitaxially grown on cleaved faces of tellurium in spite of large mismatch in the lattice constants of those materials.

§2. Characterization of Cleaved Faces of Tellurium

Tellurium substrate was prepared by cleaving a single crystal in the air just before loading it into UHV system shown in Fig. 2. The surface of the substrate was checked with AES and proved to be clean except slight carbon contamination even before cleaning treatment. Heating at 200 °C under pressure less than 4 x 10^{-8} Pa made the surface clean completely, as is seen in Fig. 3, which shows AES spectrum of tellurium substrate after cleaning. This surface has been found to be very inactive and kept clean even after exposure to 1 atmosphere oxygen, indicating its nature having no dangling bonds on its surface. This nature has been more clearly checked by LEELS.

Fig. 4 shows LEELS spectra of a clean cleaved face of tellurium for various primary electron energies taken with constant energy resolution using a double pass cylindrical mirror analyser. As is seen in the figure, essentialy the same loss peaks appear in all the spectra, and no new peak relating to intrinsic surface states due to dangling bond appears in the spectra for lower primary electron energies. This is quite contrast to the case for clean surfaces of such typical semiconductors as Si, Ge and GaAs, in which loss peaks relating to dangling bonds appear in LEELS spectra for primary electron energy of less than 100 eV. This is a strong experimental evidence that there exists no dangling bond on the cleaved face of tellurium.

§3. Growth and Charcterization of Selenium Films on Tellurium

Selenium film was grown on clean cleaved face of tellurium with molecular beam epitaxy using the system shown in Fig. 2. The substrate temperature was 80 °C and growing rate was 0.1nm/s. Fig. 5 (a) shows the RHEED pattern of tellurium substrate The observed lattice constant agrees with that shown in literature within the experimental error and no surface reconstruction is seen. That pattern disappeared just after opening the shutter for selenium beam and eventually RHEED pattern of selenium appeared. Fig. 5(b) shows the RHEED pattern taken after growth of 50 nm selenium film. The scales for Fig. 5(a) and (b) are the same, and those figures show a good single-crystalline selenium film has been epitaxially grown on tellurium,

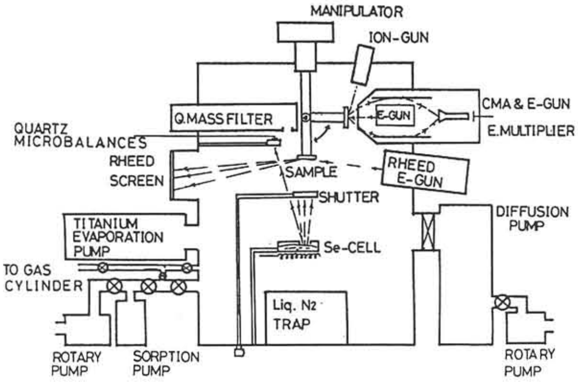

Fig. 2 Schematic diagram of MBE growth and characterization system.

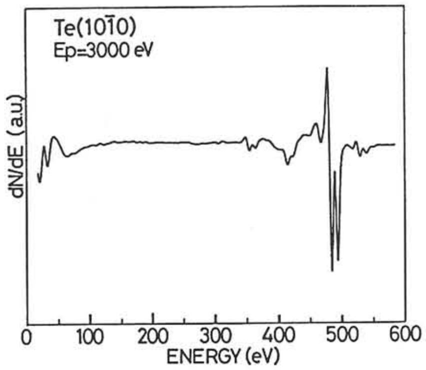

Fig. 3 AES spectrum of clean cleaved face of tellurium.

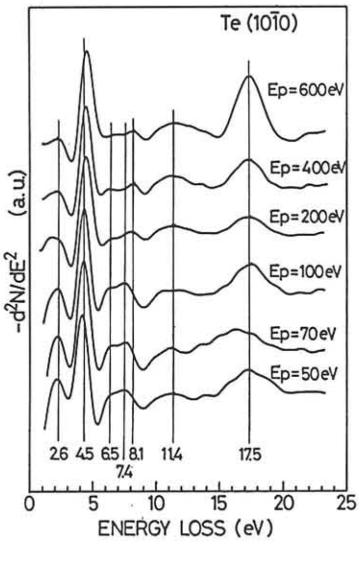

Fig. 4 LEELS spectra of clean cleaved face of tellurium.

of which lattice constants are different by about 20 % to each other.

Fig. 6 shows the AES spectrum of the selenium film thus prepared. The spectrum was measured in the same chamber for MBE, and with pulse count technique and numerical differentiation method to keep the primary electron current and thus its effect as small as possible. This was especially useful in the characterization of thin selenium film, which was easily damaged. For comparison AES spectrum of cleaved face of single-crystalline selenium grown with Bridgman method and that of amorphous selenium, which was prepared by rapid deposition on Si substratate at room temperature, are also shown in the same figure. As is seen in the figure selenium grown epitaxially on tellurium is very clean and no trace of impurities is seen in its spectrum. Moreover fine structures in the spectrum are resolved better than those of a cleaved face of single crystal or

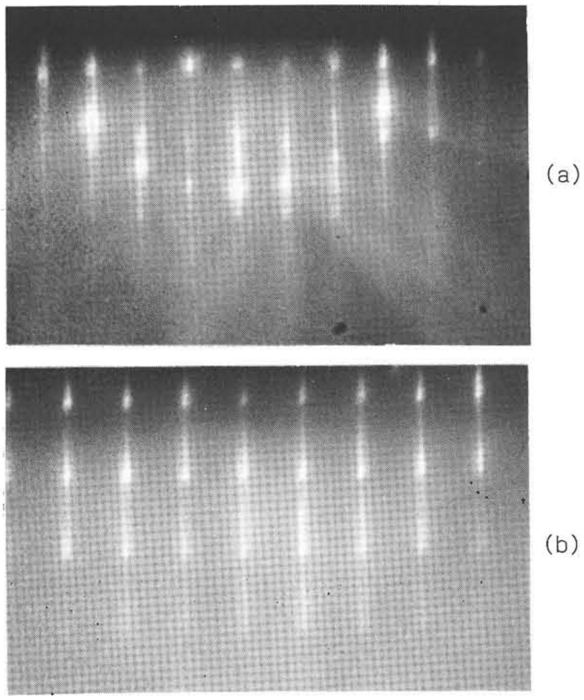

Fig. 5 RHEED patterns for Te substrate (a) and epitaxially grown Se (b).

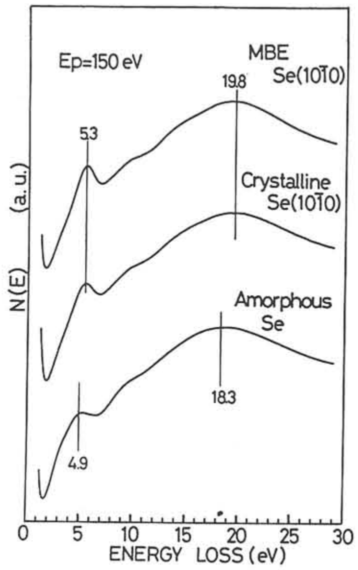

Fig. 7 Non-derivative LEELS spectra of various types of selenium.

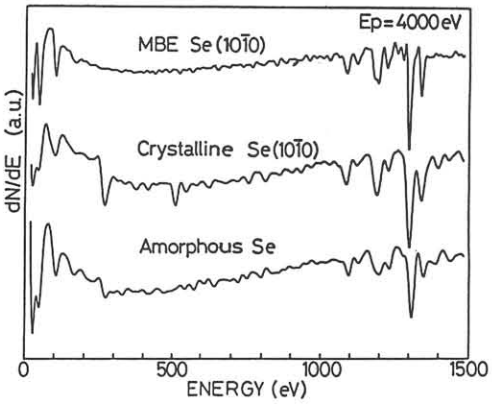

Fig. 6 AES spectra of various types of selenium.

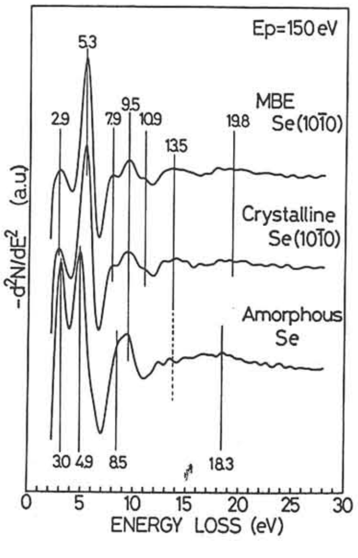

Fig. 8 Second deivative LEELS spectra of various types of selenium.

amorphous film, which indicates the perfection of the grown film.

LEELS spectra measured *in situ* are shown in Fig. 7 and Fig. 8 together with those of cleaved face of single-crystalline selenium and amorphous selenium. Fig. 7 shows non-derivative LEELS spectra. The upper and lower peaks in the figure arise from volume and partial plasmons, respectively. Energies for both plasmons in amorphous selenium are lower than those in epitaxially grown or single-crystalline selenium, reflecting lower density of amorphous selenium. Fig. 8 shows the second derivative LEELS spectra, which were obtained by numerical differentiation of the spectra in Fig. 7 to see the fine structures more clearly. Many peaks are seen in Fig. 8 in addition to plasmon excitation peaks, which come from transitions of valence electrons into conduction band. The spectrum for epitaxially grown film resembles very much that for single-crystalline selenium indicating that the electronic structure of the epitaxially grown film is quite similar to that of single crystal of selenium.

§4. Conclusion

In conclusion we have shown that good quality of selenium film can be epitaxially grown on cleaved face of tellurium, of which lattice constant is larger than that of seleinum by about 20 %. This large mismatch in lattice constant is overcome by non-existence of dangling bonds at the interface and by epitaxial growth solely with van der Waals force. This success has yielded possibility to prepare various type of heterostructures such as semiconductor-metal, semiconductor-insulator and insulator-metal hetrostructures, by using transition metal dichalcogenides. Those have layered crystal stuctures and form variety of materials from metal to insulator. Their layers are bound only by van der Waals force and thus good quality of hetrostructures are expected to be fabricated similarly regardless of lattice mismatch.

References

1) C. H. Griffiths and H. Sang: Appl. Phys. Lett. 11 (1967) 118.
2) M. Yabe: Jpn. Appl. Phys. 12 (1973) 1317.
3) M. El Azab, P.B. Sewell and C. H. Champness: J. Electronic Materials 5 (1976) 381.
4) A. Koma and K. Yoshimura: Jpn J. Appl. Phys. 22 (1983) L173.