Invited

Van der Waals Epitaxy—A New Method to Prepare Ultrathin Heterostructures—

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Good quality of heterostructures with subnanometer thicknesses have been grown with newly developed van der Waals epitaxy. The van der Waals epitaxy can be realized in the materials having no dangling bonds on their clean surfaces, on which epitaxial growth proceeds by van der Waals forces. We have succeeded in growing an ultrathin selenium film on a cleaved face of tellurium and ultrathin NbSe₂ or MoSe₂ films on a cleaved face of 2H-MoS₂ by making full use of the van der Waals epitaxy. Although there exists lattice mismatch as large as 20 % between those constituent materials, the grown film has been proved to be good single-crystalline one having lattice constant of its own even in the first atomic layer at the interface.

Introduction

Recently ultrathin heterostructures with atomic order thicknesses have been grown successfully by molecular beam epitaxy (MBE) or metalorganic chemical vapor deposition (MOCVD) and they have made it possible to realize such new electronic devices as superlattice devices, quantum well lasers and heterostructure bipolar transistors. But SO far ultrathin heterostructures have been limited to those between semiconductor materials and good quality of ultrathin heterostructures have been fabricated predominantly with GaAs-AlAs system in which ideally small lattice mismatch of 0.1 % is Usually there appear dangling bonds on realized. the clean surfaces of semiconductors, and this makes it difficult to grow good heteroepitaxial film without good lattice match in the constituent materials.

There are, however, materials having no dangling bonds on their clean surfaces, on which epitaxial growth proceeds with van der Waals forces [1,2]. We call that kind of epitaxy as van der Waals epitaxy. It is expected that good heterostructures can be grown even between materials having large lattice mismatch in the van der Waals epitaxy. It is also expected in the van der Waals epitaxy that a very abrupt interface with small amounts of defects can be fabricated because of the nonexsistence of the dangling bonds. Thus the van der Waals epitaxy seems to be one of the most powerful technique to prepare a good quality of heterostructure with atomic order thickness. Here we will report on the fabrication of ultrathin heterostructures grown by the van der Waals epitaxy and *in situ* characterization by reflection high energy electron diffraction (RHEED), Auger electron spectroscopy (AES) and low-energy electron energy loss spectroscopy (LEELS).

 Growth of Ultrathin Selnium Films on Cleaved Faces of Tellurium

Selenium on tellurium is the simplest heterostructure which can be made with the van der Waals epitaxy [3]. Those materials have peculiar crystal



Fig. 1. Schematic diagram of experimental apparatus.

structures consisting of atoms in spiral chains. The atoms in a chain are bound to each other with strong covalent forces, whereas the chains are bound to each other only with weak van der Waals forces. Thus the crystal can be cleaved easily along the chains without producing dangling bonds on their surfaces.

Selenium film was grown on a cleaved face of tellurium by using a MBE system shown in Fig. 1. Tellurium substrate was prepared by cleaving a single crystal just before the loading into the UHV system. The surface was cleaned by heating at 200 °C under the vacuum of 3×10^{-8} Pa. The cleanness of the surface was checked with Auger electron spectroctscopy, and no trace of contamination was observed. The selenium film was grown at a rate of 0.1 nm/s under the substrate temperature



Fig. 2. RHEED patterns of Te substrate (a) and heteroepitaxially grown Se films with thicknesses of 0.4 nm (b) and 600 nm (c). of 80 °C. The thickness of the grown film was monitored with a quartz microbalance.

Crystal morphorogy was monitored by RHEED with the accelerating voltage of 25 kV. Fig. 2(a) shows a RHEED pattern of the tellurium substrate. The observed lattice constant agrees with that written in the literature within the experimental error and no reconstruction is seen. Fig. 2(b) shows a RHEED pattern observed after the growth of selenium film with 0.4 nm thickness, which is about that of a monolayer film. As is seen in the figure, fairly good streak pattern with a line interval corresponding to selenium crystal is observed even in the first grown layer at the interface, on which a streak pattern coming from the underlying tellurium substrate superposes. Clearer RHEED pattern of selenium was observed after 600 nm thick film was grown, as is shown in Fig. 2(c). The scales for Figs. 2(a) through 2(c) are the same, and those figures indicate a good ultrathin selenium film with its own lattice constant has been grown on tellurium substrate, of which lattice constants differ by about 20 % to each other. It must be noted here that the lattice constant of the heteroepiaxial film grown with the van der Waals epitaxy has its own value being different from that of the substrate. This feature is completely different from the case of the strainedlayer superlattice, in which the lattice constant of the heteroepitaxial film is forced to be the same as that of the substrate [4].

It has also been proved from the *in situ* AES and LEELS measurements that the heteroepitaxially grown selenium film has a good quality comparable to that of bulk single-crystalline selenium even though its thickness is as thin as 0.4 nm.

§3. Van der Waals Epitaxy of Transition Metal Dichalcogenides

Transition metal dicalcogenides are the most suitable materials for the van der Waals epitaxy. They have layered crystal structuresres, which are formed of unit layeres consisting of transition metal atoms sandwitched by chalcogen atoms. The atoms in a layer are bound by strong covalent bonds, whereas the layers are weakly bound to each other by van der Waals forces. Thus the crystals can be easily cleaved along the layers, and no dngling bonds appear on their cleaved faces [5], onto which the van der Waals epitaxy is possible. Since there are various types of materials in the including insulatransition metal dicalcogenides superconducting tors, semiconductors and even many kinds of metals, it is possible to prepare heterostructures by the van der Waals epitaxy using those materials. Here we will describe on the heteroepitaxy of a metallic NbSe₂ film onto a semiconducting 2H-MoS₂ substrate as an example [6].

An ultrathin NbSe₂ film was grown on a cleaved face of natural molybdenite in the same MBE system A Knudsen cell was used for as shown in Fig. 1. selenium source and an electron beam evaporator was used for niobium source. The substrate surface was cleaned by heating at 300 °C under the vacuum of 3 x 10⁻⁸ Pa. The heteroepitaxial film was grown with the arrival ratio of Nb/Se of about 1/5 under the substrate temperture of 700 °C. The growing rate was 0.01 nm/s. Fig. 3(a) shows a RHEED pattern of the 2H-MoS₂ substrate. The observed lattice constant agrees with that written in the literature within the experimental error. The RHEED pattern observed after growth of NbSe2 film with 0.6 nm thickness is shown in Fig. 3(b). That thickness is about that of a unit layer of NbSe2. A streak pattern with line intervals cor-



Fig. 3. RHEED pattern of a 2H-MoS₂ substrate (a) and a NbSe₂ film grown on a cleaved face of 2H-MoS₂ (b).

responding to the lattice constant of $NbSe_2$ is seen, which indicates that a smooth single-crystallin monolayer film of $NbSe_2$ with its own lattice spacing has been grown on the cleaved face of 2H-MoS₂ regardless of the exsistence of a lattice mismatch as large as 9 % between those materials. Although the lattice constant of the grown film is different from that of the substrate, their a-axes have been proved to be aligned to each other.

Fig. 4 shows the Auger electron spectra of $2H-MoS_2$ substrate, heteroepitaxially grown $NbSe_2$ film and a clean cleaved face of single-crystalline $2H-NbSe_2$. Although small signals coming from the underlying MoS_2 substrate are also seen because of very thin thickness of the prepared film, the AES specrum of the grown film is very close to that of the single-crystalline $NbSe_2$, indicating the right composition of the prepared film.

The LEELS spectra of the above-mentioned monolayer NbSe₂ film in the valence electron excitation region is shown in Fig. 5 together with those of 2H-MoS₂ substrate and a clean cleaved face of single-crystalline NbSe2. Since the probing depth of LEELS is shorter than AES [7], only the signal coming from the top layer is seen in the LEELS Actually it is seen in Fig. 7 that the spectrum. spectrum of the monolayer NbSe2 is just the same as that of single-crystalline one. This is a strong evdence that an ideally good ultrathin NbSe₂ film is grown on the MoS₂ substrate without



Fig. 4. AES spectra of 2H-MoS₂ substrate, heteroepitaxially grown NbSe2 film and a cleaved face of a single crystal of NbSe₂.



Fig. 5. LEELS spectra of 2H-MoS₂ substrate, heteroepitaxially grown NbSe₂ film and a cleaved face of a single crystal of NbSe₂.

forming the island structure or mixed cystal.

We have shown in Fig. 4 that the signal from the underlying MoS₂ substrate superposes to that of the top NbSe2 film. It has been estimated from the signal ratio that the thickness of the NbSe₂ film is about 6.5 A in agreement with the estimation by the guartz microbalance. We have also checked the uniformity in the thickness of the grown ultrathin film by observing the strength of the substrate singnal superposed to the AES spectrum for various parts of the specimen. Fig. 6 shows the AES spectra of the various part of the 5 mm x 5 mm area of the specimen. As is seen in the figure, almost the same AES spectrum has been obtained for every part, indicating the extreme uniformity in the thickness of the grown film.

We have also succeeded in growing a good quality of ultrathin $MoSe_2$ film on a cleaved face of 2H-MoS₂ in the same manner, which implies the universal usefulness of the van der Waals epitaxy for the fabrication of an ultrathin heterostructure formed of any combination of transition metal dichalcogenides.

§ 4. Conclusion

In conclusion we have succeeded in fabricating good quality of ultrthin heterostructures by van der Waals epitaxy. The present technique has



Fig. 6. AES spectra of various part of 5 mm x 5 mm area of ultrathin NbSe₂ film grown on a cleaved face of 2H-MoS₂.

opened a new way to prepare many kinds of heterostructures consisting of metal, semiconductor or insulator films with any thickness from subnanometer by using various transition metal dichalcogenide materials. The present system seems to be one of the most hopeful candidate one to realize the excitonic superconductivity in the ultrathin metal-semiconductor heterostructure proposed bv Allender, Bray and Bardeen [8]. Another interesting field to which the van der Waals can be applied is the fabrication of a Josephson junction formed solely of single-crystalline materials.

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