Epitaxial growth of transition metal dichalcogenides on cleaved faces of mica[a)]

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We have grown ultrathin films of layered transition metal dichalcogenides ($MoSe_2$,$NbSe_2$) heteroepitaxially on cleaved faces of mica (muscovite). This is the first success in the heteroepitaxial growth between highly heterogeneous layered materials having different crystal structures and lattice constants that differ by as much as 58%. The lattice matching condition is greatly loosened in those cases because the growth proceeds with weak van der Waals forces between the substrate and the grown layer. This opens a new way to fabricate a heterostructure composed of many kinds of layered materials having various physical and chemical properties.

I. INTRODUCTION

Recently, heterostructures with an atomic order thickness have been grown successfully and several new electronic devices have been realized. But in most cases heterostructures with an atomic order thickness have been limited to those between such semiconductors as GaAs and AlGaAs, having a lattice mismatch as small as 0.1%. There are dangling bonds on clean surfaces of usual semiconductors, with which strong bonds are formed between the substrate and the overgrown film. This introduces distortions and/or nucleates dislocations in the overlayer when lattice matching condition is not satisfied.

There are, however, a number of materials having no dangling bonds on their cleaved faces. The epitaxial growth on such faces proceeds with van der Waals forces, and we call this kind of epitaxy van der Waals epitaxy.[1-3] It has been proven that a good heterostructure having a very abrupt interface can be grown with the van der Waals epitaxy.[4] It has also been proven that the grown film has its own lattice constant even in the first layer at the interface.

So far, we have succeeded in the van der Waals epitaxy among such transition metal dichalcogenides (TX_2) as MoS_2, $MoSe_2$, and $NbSe_2$.[1-5] They have a layered crystal structure and their unit layers are bound to each other by weak van der Waals forces.[6] A unit layer of TX_2 has a X–T–X sandwich structure, and the top layer of X atoms has a sixfold symmetry in the plane (see Fig. 1). It is possible to grow epitaxial films of TX_2's having their bulk lattice constants even when there exists a lattice mismatch as large as 9% between the grown film and the substrate.[2]

In the present work, we have applied the van der Waals epitaxy to more heterogeneous systems. We have tried to grow epitaxial films of $MoSe_2$ and $NbSe_2$ on mica substrates. Mica [muscovite, $KAl_2(OH)_2(Si_3AlO_{10})$] also has a layered structure in which each layer is bound by van der Waals forces, and it is easily cleaved, forming no dangling bonds on its face. But the crystal structure of mica is considerably different from that of TX_2 as shown in Fig. 2. In the cleaved face of mica, unit triangles of three oxygen atoms are arranged to have sixfold symmetry, and the lattice constant of the *a* axis of mica is much larger than those of TX_2's. For example, muscovite has a larger lattice constant by 58% than $MoSe_2$. Therefore, it is interesting to know whether or not the van der Waals epitaxy really occurs in these highly heterogeneous systems. If that kind of epitaxy is realized, it becomes possible to use mica as a substrate for ultrathin heterostructures composed of various TX_2's. Mica has the following advantages as a substrate: It has enough hardness while it is easily cleaved, is transparent in the visible region, and is thermally stable up to 700 °C. Therefore, various physical properties of ultrathin TX_2 films may be investigated by using epitaxial films on mica substrates.

II. EXPERIMENTAL

TX_2 ($MoSe_2$ and $NbSe_2$) films were grown with a molecular beam epitaxy system having three UHV chambers.[7] The mica substrate was natural muscovite, cleaved in air just before loading into the fast-entry chamber. The growth of TX_2 films was carried out in the growth chamber, which has a base pressure of 8×10^{-9} Pa. Before loading selenium shots into a Knudsen cell, they were purified by melting under a vacuum to remove the oxidized portion. Pure molybdenum (3N5) or niobium (4N) was evaporated with electrostatic focusing electron beam evaporators, which minimize inter-

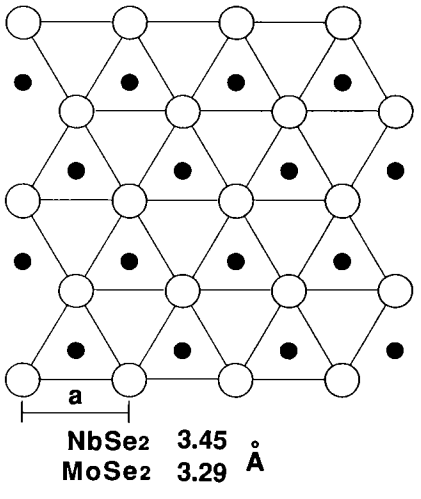

FIG. 1. Crystal structure of TX_2 (0001). (○) Selenium atoms at the topmost layer and (●) molybdenum or niobium atoms at the second layer.

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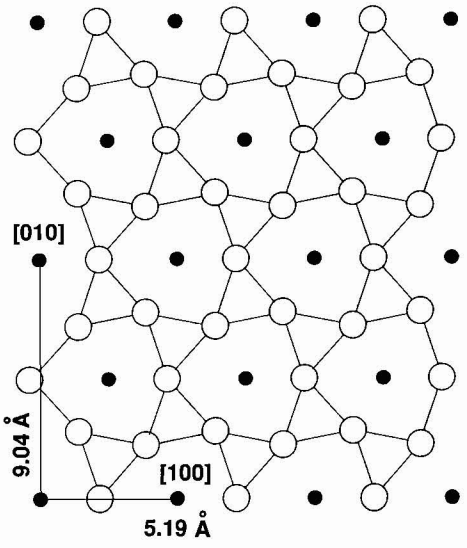

FIG. 2. Crystal structure of muscovite (001). (○) Oxygen atoms and (●) potassium atoms. Half of the potassium atom sites are unoccupied.

ference to the reflection high-energy electron diffraction (RHEED) measurement. Intensities of molecular beams were monitored by two quartz-crystal oscillators located near the substrate, and controlled so that the Se-rich atmosphere was achieved. A real-time monitoring of the surface of the substrate and the grown film was made by RHEED. The accurate film thickness was measured by a surface-roughness gauge after the growth.

The grown samples were transferred to the analysis chamber without breaking the vacuum. The chamber was equipped with a double-pass cylindrical mirror analyzer (PHI 15-255GAR) controlled by a microcomputer system. Auger spectra and electron energy-loss (EEL) spectra of substrates and grown films were measured to know the surface atomic composition and to characterize the electronic structure, respectively. The EEL spectroscopy was also used to make a nondestructive indepth profiling of the interface of the grown heterostructure.

III. RESULTS AND DISCUSSION

A. Evolution of RHEED patterns during the growth of $MoSe_2$ on a mica substrate

Figures 3(a)–3(e) show the change in RHEED patterns during the growth of a $MoSe_2$ film on a cleaved face of mica. The substrate temperature was 500 °C and the growth rate was ~0.2 nm/min. The incident electron beam was fixed along the [100] crystal orientation of the mica substrate (see Fig. 2).

Figure 3(a) shows the RHEED pattern of the mica substrate. Figures 3(b)–3(e) show RHEED patterns taken after the deposition of 1/5, 1/2, 1, and 2 unit layers of $MoSe_2$, respectively. Here, 1/5 unit layer means that a unit layer having 0.65 nm thickness covers 1/5 of the substrate face. As the deposit amount increased, the intensity of streaks from the mica substrate became weak. Instead, sharp streaks with a different line interval appeared clearly. This interval corresponds to the lattice constant of a bulk 2H–$MoSe_2$ crystal

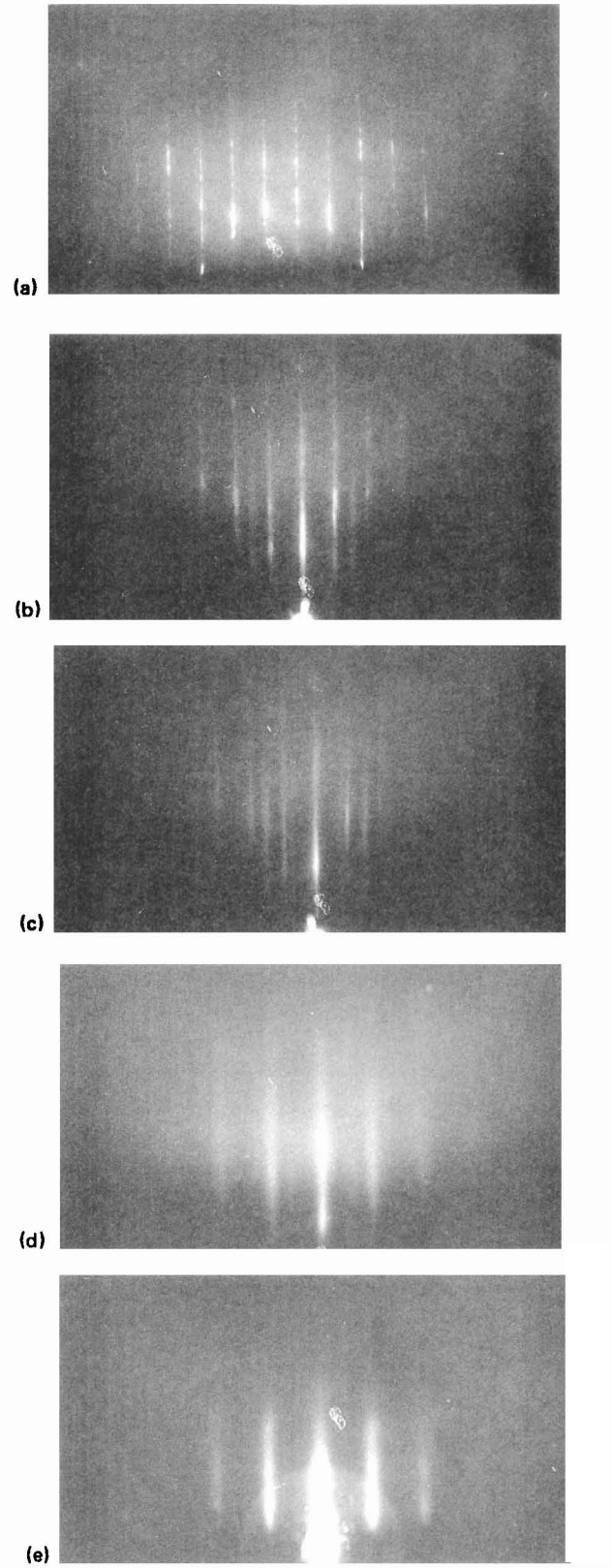

FIG. 3. Evolution of RHEED patterns of $MoSe_2$ grown on mica. The orientation of incident electron is parallel to the [100] azimuth of mica. (a) Mica substrate; (b) $\frac{1}{5}$ unit layer; (c) $\frac{1}{2}$ unit layer (d) 1 unit layer; (e) 2 unit layers. The arc pattern in (e) does not mean the existence of the polycrystalline part in the grown film. It does come from a halo of the direct electron beam, because that arc was seen even when no sample was placed.

within the experimental error of the RHEED measurement (~1%). After two unit layers of $MoSe_2$ were grown, the streak pattern of the mica completely disappeared. The

change of RHEED patterns indicates that a smooth and uniform $MoSe_2$ film with its own lattice constant epitaxially grows even from the initial state.

The observation of RHEED patterns with other incident directions of the electron beam shows that the heteroepitaxially grown film of $MoSe_2$ on a mica substrate also has a sixfold symmetry and its c axis is perpendicular to the surface. Figures 4(a)–4(d) show RHEED patterns of the mica substrate [Figs. 4(a) and 4(b)] and three unit layers of $MoSe_2$ grown on the substrate [Figs. 4(c) and 4(d)], with the incident electron beam orientation parallel to the [100] [Figs. 4(a) and 4(c)] and the [310] [Figs. 4(b) and 4(d)] orientation of the substrate. These two directions differ from each other by 30°. The streak interval of the RHEED pattern in Fig. 4(c) is equal to that of a bulk 2H–$MoSe_2$ crystal observed with the incident electron beam along its $[11\bar{2}0]$ orientation. On the other hand, the bright streak pattern in Fig. 4(d) coincides with that of a 2H–$MoSe_2$ crystal taken along the $[10\bar{1}0]$ orientation and its streak interval is $\sqrt{3}$ times as large as that of the $[11\bar{2}0]$ orientation. Thus, the relation between crystal orientations of the grown $MoSe_2$ film and the mica substrate is indicated as $MoSe_2[11\bar{2}0]$ ||mica[100] on $MoSe_2(0001)$||mica(001) or, in other words, $MoSe_2[10\bar{1}0]$|| mica[310]. It should be noted that the main axis of the grown layer aligns to that of the substrate in spite of the large difference in the crystal structure.

In Figs. 4(c) and 4(d), however, there appear some weaker streaks between main bright streaks. A similar result was reported in the case of the epitaxial growth of Ag on Si(111) 7×7 surface,[8] which was called "texture structure." It means that most areas of the grown layer preferentially have an epitaxial orientation with the substrate, but parts of them are rotated around the c axis in the plane. The texture structure in the growth of $MoSe_2$ on a mica substrate seems to be caused by the presence of K atoms on the cleaved face of the mica.[9] They remain randomly on the face when the mica is cleaved. So some areas of grown $MoSe_2$ are prevented from aligning to the mica substrate. Nevertheless, most areas are well aligned in the same way as in other van der Waals epitaxy. The existence of the above-mentioned nonaligned area could be the origin of an increase in the widths of streaks in the RHEED pattern from Fig. 3(c) to Fig. 3(e).

B. Characterization of an ultrathin film of $MoSe_2$ by electron spectroscopies

Shown in Fig. 5 are Auger spectra of a mica substrate [Fig. 5(a)], a film of $MoSe_2$ [Fig. 5(b)] grown on a mica substrate, and a bulk 2H–$MoSe_2$ crystal [Fig 5(c)]. The thickness of the grown film was about one unit layer (0.65 nm). There appear both signals of Mo and Se from the grown $MoSe_2$ film in Fig. 5(b), and the peak intensity ratio between the signals is the same as that of the Auger spectrum of a bulk 2H–$MoSe_2$ crystal. This indicates that a stoichiometric $MoSe_2$ film was really grown on the mica substrate. In Fig. 5(b), there appear some signals from the substrate. The mean-free paths of the Auger electrons of potassium and oxygen are longer than the thickness of the grown film, so their signals could be detected through the overlayer of $MoSe_2$. There is a possibility that the grown $MoSe_2$ film does not cover up the substrate and the Auger signals from the substrate are directly seen. But the uniformity of the grown ultrathin film is confirmed by the EEL spectrum of the grown sample, as shown below.

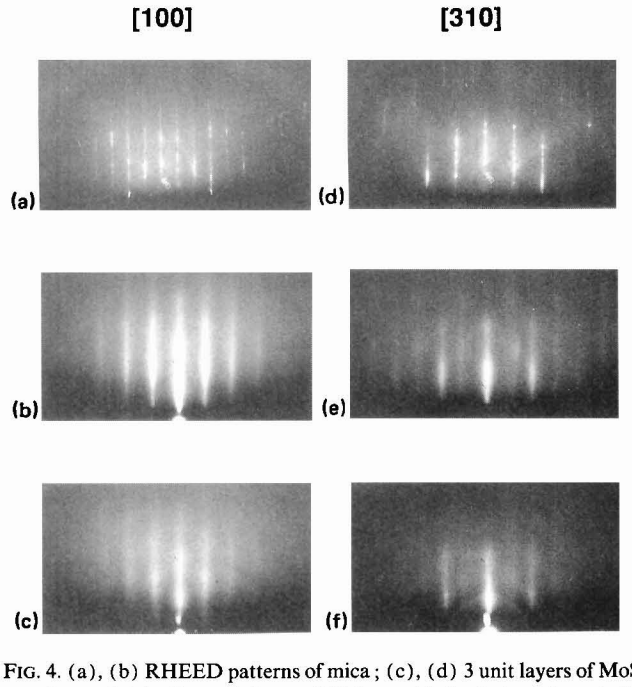

FIG. 4. (a), (b) RHEED patterns of mica; (c), (d) 3 unit layers of $MoSe_2$ on mica, and (e), (f) a unit layer of $NbSe_2$ on $MoSe_2$/mica substrate. The incident beam is parallel to the [100] (a), (c), (e) and the [310] (b), (d), (f) orientations of mica. The arc in (f) is a similar halo of the direct electron beam as mentioned in the caption of Fig. 3.

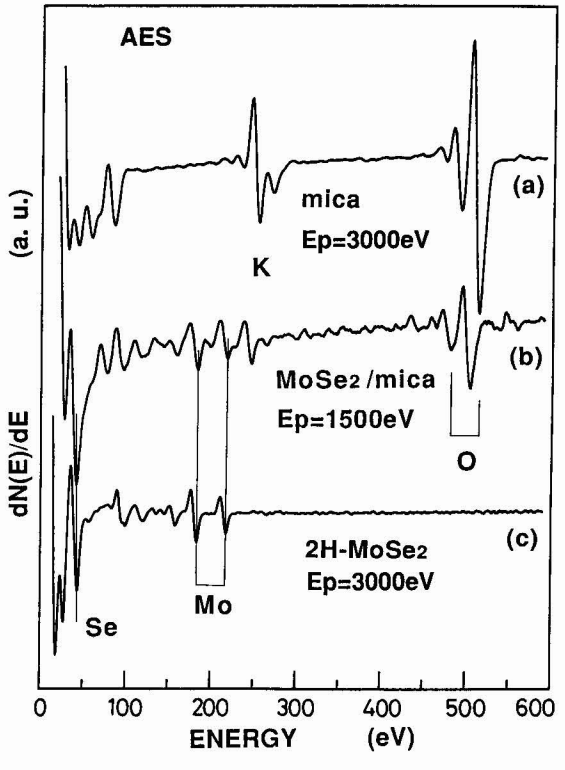

FIG. 5. (a) Auger electron spectra of mica, (b) an ultrathin film of $MoSe_2$ on mica, and (c) a bulk 2H-$MoSe_2$.

EEL spectra of the same ultrathin film of $MoSe_2$ on a mica substrate are shown in Fig. 6. For comparison, EEL spectra of the mica substrate and a bulk 2H–$MoSe_2$ crystal are shown in Figs. 6(a) and 6(d), respectively. It is possible to make a nondestructive indepth profiling of the electronic structure of an ultrathin film with EEL spectroscopy, in which the probing depth can be changed by changing the primary electron energy.[10] Figures 6(b) and 6(c) show the EEL spectra taken at incident electron energies of 1600 and 150 eV, in which cases the probing depth were 1.1 and 0.3 nm,[4,10] respectively. The EEL spectrum of the ultrathin film taken with the primary electron energy of 150 eV, whose probing depth is less than the thickness of the grown $MoSe_2$ film, is similar to that of a bulk 2H–$MoSe_2$ crystal and shows no signal coming from the mica substrate. This indicates that the ultrathin film of $MoSe_2$ covers uniformly over the mica substrate, and has a good quality similar to a bulk single crystal of $MoSe_2$. In the spectrum taken with the primary electron energy of 1600 eV, there appear some peaks at the same loss energies with the peaks in the EEL spectrum of a mica substrate, in addition to the signals from the grown $MoSe_2$ film, because the probing depth of the primary electron energy of 1600 eV is larger than the thickness of the grown film. For example, the peaks at 27.5 and 34 eV of loss energy in the spectrum of the mica [Fig. 6(a)] clearly appear in Fig. 6(b).

We have also succeeded in growing an ultrathin film of $NbSe_2$ of good quality on a mica substrate, and almost the same results were obtained as the growth of $MoSe_2$ on mica.[7]

C. $NbSe_2/MoSe_2$/mica heterostructure

In Sec. III B above, it is shown that TX_2 can be grown heteroepitaxially on a mica substrate. Here we will discuss the epitaxial growth of a different kind of TX_2 on a pregrown TX_2 on a mica substrate.

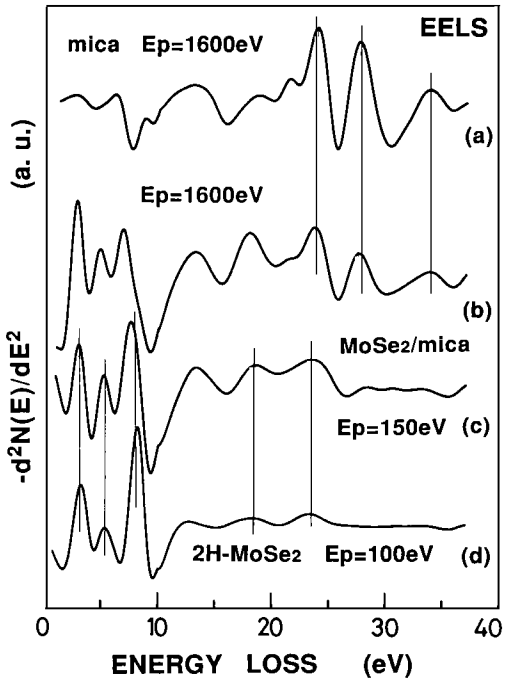

FIG. 6. (a) Electron energy-loss spectra of mica, (b) an ultrathin film of $MoSe_2$ on mica taken at 1600 eV and (c) 150 eV, and (d) a bulk 2H–$MoSe_2$.

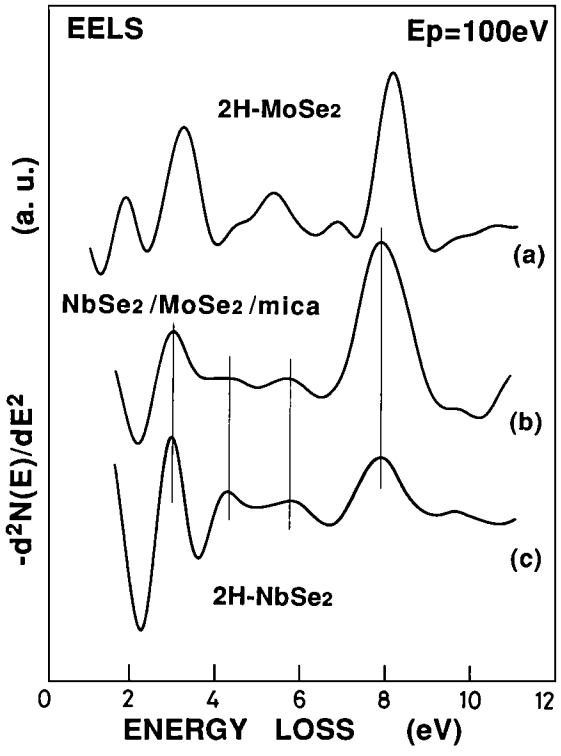

FIG. 7. (a) electron energy-loss spectra of a bulk 2H-$MoSe_2$ (b) ultrathin $NbSe_2$ film on a $MoSe_2$/mica substrate, and (c) a bulk 2H–$NbSe_2$.

Figures 4(e) and 4(f) show the RHEED patterns of a unit layer (0.63 nm) of $NbSe_2$ successively grown on an ultrathin film of $MoSe_2$ on a mica substrate. The thickness of the intervening $MoSe_2$ film is three unit layers (2 nm). The orientation of the incident electron was fixed through Figs. 4(a), 4(c), and 4(e) and through Figs. 4(b), 4(d), and 4(f). Figures 4(e) and 4(f) show similar streak patterns coming from sixfold rotational symmetry around the normal axis as the underlying $MoSe_2$ film. It is also proven that the *a* axis of the grown $NbSe_2$ film aligns to that of the underlying $MoSe_2$ film and the mica substrate. Furthermore, the streak interval of the RHEED pattern of the $NbSe_2$ film is smaller than that of underlying $MoSe_2$, reflecting the larger lattice constant of $NbSe_2$ by 4.8% than $MoSe_2$. Thus, it is concluded that an ultrathin film of $NbSe_2$ has grown heteroepitaxially on a $MoSe_2$/mica substrate in the same way as on a bulk single crystal of $MoSe_2$.

EEL spectra of 2H–$MoSe_2$ [Fig. 7(a)], the $NbSe_2/MoSe_2$/mica sample [Fig. 7(b)], and 2H–$NbSe_2$, [Fig. 7(c)], taken with a primary electron energy of 100 eV, are shown in Fig. 7. Peak locations of the EEL spectrum of the grown sample are almost identical with those of 2H–$NbSe_2$, but different from those of 2H–$MoSe_2$. This means that the ultrathin film of $NbSe_2$ almost covers up the $MoSe_2$/mica substrate and has an electronic structure similar to that of a bulk single crystal.

IV. CONCLUSIONS

We have grown transition metal dichalcogenides heteroepitaxially on mica substrates. The growth proceeds with van der Waals forces, and ultrathin films of $MoSe_2$ and

$NbSe_2$ epitaxially grow from the initial stage on the mica substrate in spite of large differences in their crystal structures. RHEED measurements show that the grown films of TX_2's on mica have the same lattice constants as bulk single crystals within its experimental error. Auger electron spectra and electron energy-loss spectra also indicate good quality of the grown films. We have also succeeded in growing a $NbSe_2/MoSe_2$ heterostructure on a mica substrate. This leads to a possibility to make various heterostructures using many kinds of TX_2's and to find remarkable properties in them. It has also opened a new way to apply the van der Waals epitaxy to the heteroepitaxial growth of such layered materials as graphite, CdI_2, GaS, etc., in addition to TX_2's.

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