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Heteroepitaxy of $MoSe_2$ on GaSe-terminated Si(111)

Atomically-thin films of transition-metal dichalcogenides (TMDs) are of great interest because they show a variety of unique electrical, optical, and chemical properties that are strikingly different from their bulk counterparts. Molecular-beam epitaxy (MBE) is one of the most promising methods to synthesize thin TMD films: MBE enables us to epitaxially grow highly-oriented TMD thin films on arbitrary crystalline substrates, which is referred to as van der Waals (vdW) epitaxy. Here, we report on a systematic study of the MBE growth of $MoSe_2$ on the Si(111) substrate. To promote the vdW epitaxy of $MoSe_2$, the initial Si(111) surface was terminated with a GaSe bilayer prior to the growth. The GaSe-terminated Si(111) is highly passivated [1], making it suitable for the subsequent vdW epitaxy of TMD films. We show that the passivation of the Si(111) surface with the GaSe bilayer is effective in promoting the planar growth of $MoSe_2$ films [2].

The experiments were carried out using a multichamber ultra-high vacuum system consisting of MBE chambers. Clean Si(111)-(7x7) surfaces were prepared by radiatively heating in the MBE chamber and were confirmed by scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and reflection high-energy electron diffraction (RHEED). The Si(111) surfaces were terminated with the GaSe bilayer by simultaneously supplying Ga and Se molecular beams. The $MoSe_2$ films were grown using an electron-beam evaporator and the conventional Knudsen cell for Mo and Se beams, respectively. The beam-equivalent pressure (BEP) of Mo was controlled at $1x10^{-10}$ Torr, and that for Se was varied in the range of $1x10^{-9}$ Torr ~ $4x10^{-9}$ Torr. The typical growth rate was approximately 0.010–0.015 ML per minute. After the growth of $MoSe_2$ (25–150min), the samples were annealed at 420˚C under the Se molecular beam.

Figures 1(a) and 1(b) shows RHEED patterns of Si(111) taken along the <110> and <211> azimuths. Shown in Figs. 1(c) and 1(d) are RHEED patterns taken after the surface was terminated with the GaSe bilayer: the spacings of streaks are exactly the same as those of Si(111) substrates [Figs. 1(c) and 1(d)], indicating that the GaSe bilayer was pseudomorphically grown on Si(111). The $MoSe_2$ films were grown by exposing the GaSe/Si(111) substrate to the Mo and Se molecular beams at 200˚C, and were annealed at 420˚C. As shown in Figs. 1(e) and 1(f), the sample grown for 100 min shows sharp streaks: the streak spacings are 16% larger than those of Si(111) in both directions [Figs. 2(a) and 2(b)], which correspond to the in-plane lattice constant of 3.29 Å. Thus, the present results clearly show that highly oriented $MoSe_2$ films were epitaxially grown with the relationship of (0001)$MoSe_2$ // (111)Si and [1120]$MoSe_2$ // [110]Si.

Figure 2 shows a typical STM image of the $MoSe_2$ film grown for 100 min (nominal film thickness = 1.25 ML). The $MoSe_2$ films are not continuous and are composed of small domains (islands) with an irregular shape. It is also seen that the second-layer $MoSe_2$ islands are partially formed.

Figure 3(a) shows a high-resolution Mo 3d spectrum measured from the $MoSe_2$ film on the GaSe-terminated Si(111) substrate. For comparison, the data from the samples grown on the As-passivated Si(111) [3] (b), and Si(111)-(7x7) (c) substrates are also shown. Spectrum (a) shows the Mo 3d 5/2 and 3d 3/2 peaks at 228.8 eV and 230.3 eV, respectively: these values coincidence with those of bulk 2H-$MoSe_2$ [4] and monolayer $MoSe_2$ [5]. On the other hand, in the spectrum (b), there exists an additional component at binding energies lowered by ~1 eV. The position of the additional component agrees well with those of $MoSi_2$ [6]. Previous studies have shown that the deposition of Mo on the Si(111) substrate leads to the formation of amorphous $MoSi_2$ layers even at temperatures lower than 100˚C [7]. The sample grown on the clean Si(111)–(7x7) surface shows only the $MoSi_2$ component, indicating that the $MoSe_2$ phase is hardly formed. Thus, the As termination has little effect, if any, on the suppression of the Mo-Si reaction.

This work was supported by Innovative Science and Technology Initiative for Security, ATLA, Japan.

References

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Figures

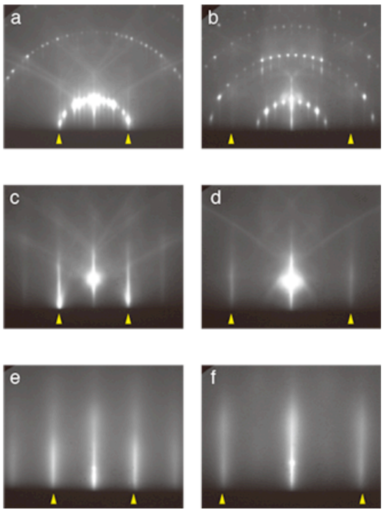

Figure 1: RHEED patterns of Si(111)-(7x7) [(a) and (b)], GaSe bilayer on Si(111) [(c) and (d)], and $MoSe_2$ on GaSe/Si(111) [(e) and (f)]. Arrow heads in RHEED patterns indicate the position of integer-order reflections. RHEED patterns were taken along the <110> [(a), (c), and (e)] and <211> [(b), (d), and (f)] directions of Si(111).

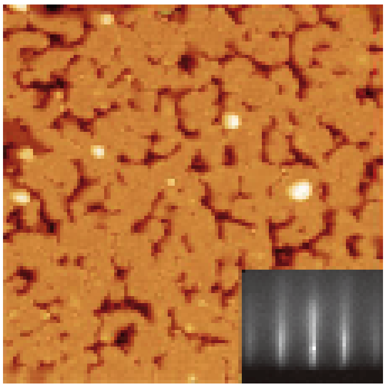

Figure 2: Typical filled-state STM image of the $MoSe_2$ film (nominal thickness = 1.25ML) on the GaSe/Si(111) substrate. Substrate temperature is 200˚C and the Se/Mo BEP ratio is ~10.

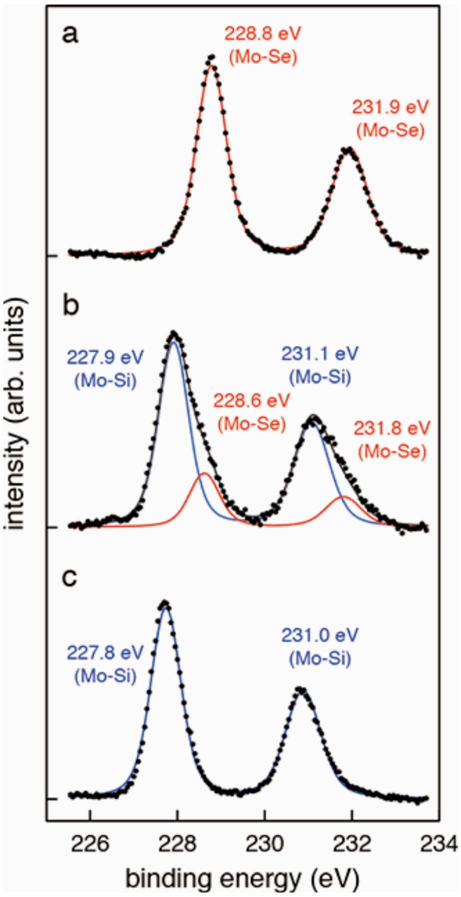

Figure 3: XPS spectrum of Mo 3d measured from $MoSe_2$ films grown on the GaSe-terminated Si(111) substrate (a). The spectra (b) and (c) were measured from the samples grown on the As-terminated Si(111)-(1x1) and Si(111)-(7x7) substrates, respectively.