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Molecular beam epitaxy growth of monolayer niobium diselenide flakes

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Monolayer niobium diselenide ($NbSe_2$) is prepared through molecular beam epitaxy with hexagonal boron nitride (hBN) as substrates. Atomic force microscopy and the Raman spectroscopy have shown that the monolayer $NbSe_2$ grown on the hBN possesses triangular or truncated triangular shape whose lateral size amounts up to several hundreds of nanometers. We have found that the precisely controlled supply rate and ultraflat surface of hBN plays an important role in the growth of the monolayer $NbSe_2$. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4963178]

The recent studies on two-dimensional (2D) metals, in particular, the metallic transition metal dichalcogenides (TMDs), have shown that 2D metals are essentially different from bulk metals, leading to discoveries of interesting phenomena arising from the low dimensionality. For example, interesting collective electronic properties, including the emergence of the Bose metal phase, the enhanced charge-density-wave (CDW) order, the coexistence of CDW order and superconductivity, and the Ising pairing protected by spin-momentum locking in superconductivity, have been demonstrated in 2D metallic TMDs.[1–5] In addition, the Fermi level, namely, the density of states (DOS), of 2D metallic layers can easily be tuned via electrostatically gating samples, which in turn modifies the interaction between carriers and between carriers and ions. The tunability of the Fermi level can lead to further discovery of electronic phases in 2D, meaning that 2D metallic layers are rich sources of physics.

The bottleneck in the research on 2D metals is the difficulty in preparation of samples. Although the mechanical exfoliation, a top down technique, has been applied to prepare 2D semiconductors (semiconducting TMDs and black phosphorus, for example),[6–8] the strong inter-layer interaction arising from the metallic bond has made the application of the top-down method to metallic layers difficult. Even though a few papers report on the exfoliation-based preparation of 2D metals,[1–3] a different approach, a bottom-up method, is a prerequisite to prompt the exploration of the full potential of rich physics in 2D metals.

The purpose of this work is to develop a bottom-up method for the growth of 2D metallic layers. For this purpose, we have focused on the molecular beam epitaxy (MBE) technique. MBE is a bottom-up method for thin film growth, where sources are supplied as a molecular beam to a growth substrate in high-vacuum condition. In MBE growths, the precise controllability in thickness, the fine tuning of dopant concentration, and the capability in abrupt change in composition (which leads to formation of heterostructures) are available, and these characteristics have made MBE a versatile tool for the preparation of high-quality semiconducting quantum wells.[9,10] The MBE growth of 2D metallic layers and identification of the monolayer structure with microscopy have been reported,[5] but it is still few, and domain sizes have been limited to several tens of nanometers. Another bottom-up method, chemical vapor deposition (CVD), is also a versatile tool for the preparation of thin films, but the application of CVD to the growth of 2D metallic layers is limited.[11,12] In order to explore basic physics of 2D metals, further development of the growth technique is needed to achieve controllable growth of larger crystals of 2D metals.

Here, we have focused on the MBE growth of the monolayer niobium diselenide ($NbSe_2$) with hexagonal boron nitride (hBN) as substrates. 2H-$NbSe_2$ is a layered metallic TMD, where Nb atoms are sandwiched by two layers of selenide atoms with trigonal prismatic coordination geometry. In-plane bonding between selenide and niobium atoms is covalent, whereas no direct bondings between adjacent layers are present. Superconductivity and charge-density-wave (CDW) phase have been found in bulk crystal of this material and have recently been found also in the monolayer ~ultrathin $NbSe_2$.[1,13–16] One of the prime reasons why we used hBN as growth substrates is that hBN provides an atomically flat surface without dangling bonds, which minimize the strain energy and facilitate diffusion of the sources to grow ultrathin $NbSe_2$ flakes via the Frank-van der Merwe mode.[17] In addition to the advantage in growth, hBN has an advantage in characterization of physical properties. Because hBN is an insulator with a large bandgap (~6 eV), hBN substrates do not hinder the observations of the optical and electronic properties of 2D materials. In addition, extrinsic scattering from substrates is suppressed in 2D materials on hBN, which leads to the observation of their intrinsic properties.[18,19] The MBE growth of ultrathin $NbSe_2$ has been reported in 1980s–1990s, where the $NbSe_2$ crystals were grown on the layered MoS_2 or surface-terminated GaAs.[20,21] These pioneering works indicate that a substrate without dangling bonds, such as hBN, is well suited for the growth of $NbSe_2$.

Figure 1 shows a schematic picture of MBE setup developed for the growth of $NbSe_2$. We supply niobium and selenide atoms by an electron-beam evaporator and a low-temperature Knudsen cell (K-cell), respectively, and their supply rates are measured *in situ* by a quartz-crystal oscillator thickness monitor; the supply rates of niobium and selenide in this study range from 0.00015 to 0.0026 and 0.0051

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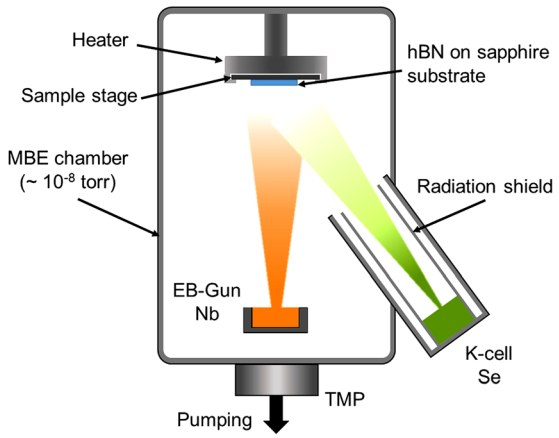

FIG. 1. A schematic presentation of the MBE setup for growth of $NbSe_2$.

to 0.0099 nm/s, respectively. In our MBE setup, a radiation shield is installed to avoid unintentional heating of the K-cell by the radiation during electron-beam evaporation of Nb. We use hBN flakes, whose lateral size varies from several to several tens of micrometers as growth substrates; hBN flakes were prepared by exfoliation from a single crystal of hBN, and the exfoliated flakes were put onto a c-plane sapphire or SiO_2/Si substrates. Raman spectra of hBN flakes show the sharp Raman band at 1366 cm^{-1} with a full-width-at-half-maxima (fwhm) of 8 cm^{-1}, which clearly demonstrates high crystallinity of the present hBN flakes. The hBN flakes deposited on a sapphire substrate are placed on the sample stage, which was heated up to 450–780 °C.

To confirm the growth of $NbSe_2$, we have performed atomic force microscopy (AFM) and Raman spectroscopy. Figure 2(a) shows a close-up AFM topographic image of the $NbSe_2$ crystals grown on hBN, where truncated triangular contrasts from the grown crystals are clearly seen. The MBE growth of this sample was performed at 780° for 60 min with

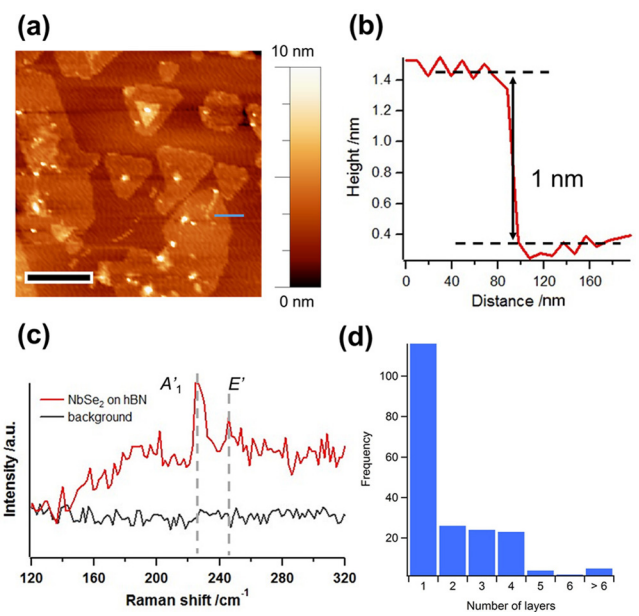

FIG. 2. (a) An AFM topographic image and (b) the corresponding height profile of the $NbSe_2$ grown on hBN. (c) A typical Raman spectrum and (d) a histogram of layer-number distribution. 533 nm excitation was used to measure the Raman spectrum. The scale bar in (a) corresponds to 250 nm.

supply rates of 0.00032 and 0.0099 nm/s for Nb and Se, respectively. The formation of the truncated triangular crystals is a direct evidence of the growth of $NbSe_2$. This is because that the truncated triangular shape originates from the preferential appearance of zig-zag edges of niobium or selenide during the growth, being consistent with previous reports on CVD growth of semiconducting TMDs.[22,23] The particles seen on $NbSe_2$ crystals might be nuclei at the beginning of the growth, being also observed in CVD growth of TMD in previous reports.[24] The height profile of a grown crystal (Fig. 2(b)) provides the small deviation in height from the geometrically expected value, which arises presumably from adsorption of oxygen, water, or amorphous contaminants; the average height from 9 ultrathin $NbSe_2$ flakes is 1.14 (13) nm. We found that the height changes even in an identical flake where no step is visible, and this indicates the existence of the adsorbed molecules on $NbSe_2$ flakes. The lateral size of the $NbSe_2$ is about 200 nm, which is larger than that of $NbSe_2$ grown with MBE in a previous report.[5] Figure 2(c) shows a typical Raman spectrum of the $NbSe_2$, where two Raman bands characteristic to $NbSe_2$ at 224 and 248 cm^{-1} (A'_1, E') are seen.[25,26] There is no photoluminescence peak observed in the visible region, which is also consistent with the metallic nature of the $NbSe_2$ fabricated. Figure 2(d) is a height histogram of the grown $NbSe_2$, where more than 50 crystals were included in the data. As clearly seen, monolayers are the dominant in this sample, which is contrasted with the CVD growth of metallic TMDs; the typical thickness of metallic TMD grown by the CVD method is about trilayer ~20 nm NbS_2.[11,12] This clearly shows the advantage of the MBE method in the growth of 2D metals. The precisely controlled supply of niobium and selenide in MBE growth should be one of the keys to realize ultrathin 2D metals, the monolayer $NbSe_2$.

Figures 3(a) and 3(b) show low-magnification AFM topographic and the SEM images of $NbSe_2$ crystals grown on hBN. As clearly seen in the AFM and SEM images, there are only two crystal orientations in the grown $NbSe_2$, where 60° rotation of one orientation corresponds to the other. This should be caused by the interaction between the $NbSe_2$ grown and an underlayer hBN, and the three-fold symmetry of both crystals is the origin of the observed crystal orientation. The observed restriction in crystal orientation clearly indicates that the interface between $NbSe_2$ and hBN is clean, which is realized by the high-vacuum direct MBE growth of $NbSe_2$ onto a clean hBN (Figure 3(c)).

Figure 4 shows a typical AFM image of the $NbSe_2$ grown on the c-plane sapphire; the growth condition for this sample is exactly the same as the one used in the growth of $NbSe_2$ shown in Fig. 2. As shown in the figure, there is no formation of triangular crystals on the sapphire substrate. Thickness of the product ranges from 1 to 6 nm, which is much larger than those of the $NbSe_2$ grown on hBN. The lateral size of the product is quite small, typically less than 100 nm, which is also contrasted with the $NbSe_2$ grown on hBN. Even though a sapphire substrate is a crystalline substrate and possesses a flat surface after proper pretreatment (typical RMS surface roughness of sapphire substrates used in this experiment is 0.15 nm), the energy barrier for surface diffusion of sources, niobium and selenide atoms, should be larger on sapphire

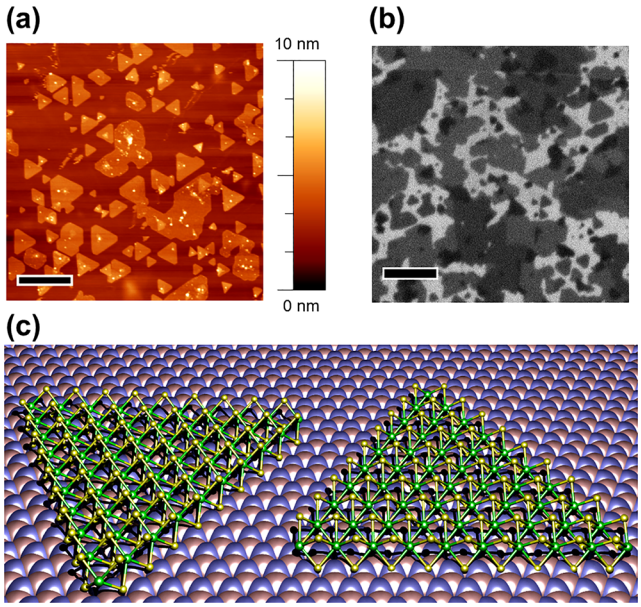

FIG. 3. (a) A typical AFM topographic image and (b) a SEM image of the grown $NbSe_2$. (c) Structure model of the monolayer $NbSe_2$ grown on hBN, where crystallographic orientation is limited. Scale bars in (a) and (b) correspond to 600 and 750 nm, respectively.

than those on hBN. This is because sapphire has dangling bonds at the surface whereas single domain hBN has virtually no dangling bonds at the surface; the difference in the surface properties of hBN and sapphire can be seen from the significant difference in the surface energy, 50 mJ/cm^2 and 1–2 J/cm^2 for hBN and sapphire, respectively.[27,28] In addition, hBN can provide several-micrometer scale flat surface without any steps whereas sapphire should have the step-terrace surface structure. These differences in surface characteristics should result in differences in the energy barrier for surface diffusion. When surface diffusion of sources is very slow due to the large energy barrier, deposited sources, in particular, niobium atoms, cannot diffuse before the growth reaction proceeds, leading to the formation of particle-like products with high nucleation density.

In conclusion, we have developed an MBE setup for the growth of 2D metallic layers. Using the developed MBE setup, the monolayer $NbSe_2$ has been grown on hBN substrates. The lateral size of the grown $NbSe_2$ amounts up to several hundreds of nanometers, which is significantly larger than those reported previously. The monolayer $NbSe_2$ grown

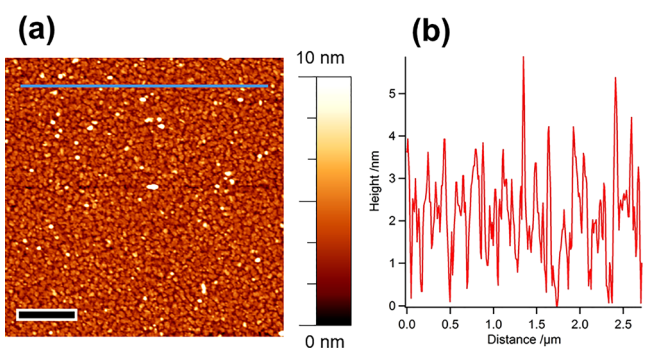

FIG. 4. (a) An AFM topographic image and (b) the corresponding height profile of the $NbSe_2$ grown on sapphire. The scale bar in (a) corresponds to 600 nm.

is the dominant product in the current MBE growth, which can be contrasted with the CVD growth of metallic TMDs. Precisely controlled supply rates of sources and atomically flat hBN substrates play important roles in the growth of the monolayer $NbSe_2$. The size of the grown $NbSe_2$ is compatible with device fabrication of the conventional lithography technique, and the same procedure can, in principle, be applied to other metallic TMDs. The present work shows that the MBE growth with hBN substrates can provide a platform to explore basic physics of 2D metals.

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