Real-time monitoring of 2D semiconductor film growth with optical spectroscopy

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Abstract
Real-time monitoring of the growth is essential for synthesizing high quality two dimensional (2D) transition-metal dichalcogenides with precisely controlled thickness. Here, we report the first real time in situ optical spectroscopic study on the molecular beam epitaxy of atomically thin molybdenum diselenide (MoSe2) films on sapphire substrates using differential reflectance spectroscopy. The characteristic optical spectrum of MoSe2 monolayer is clearly distinct from that of bilayer allowing a precise control of the film thickness during the growth. Furthermore, the evolution of the characteristic differential reflectance spectrum of the MoSe2 thin film as a function of the thickness sheds light on the details of the growth process. Our result demonstrates the importance and the great potential of the real time in situ optical spectroscopy for the realization of controlled growth of 2D semiconductor materials.

Keywords: two dimensional transition-metal dichalcogenides, molecular beam epitaxy, real-time monitoring, optical spectroscopy, molybdenum diselenide

(Some figures may appear in colour only in the online journal)

1. Introduction

Atomically thin structures of layered materials, such as graphene [1, 2], black phosphorus [3, 4] and transition-metal dichalcogenides (TMDs) [5–8], are currently of great interest in both fundamental research and the application of nano-scale devices due to their remarkable physical and chemical properties. In particular, the TMDs represent a large family of layered materials, many of them exhibit tunable band gaps that can undergo a transition from an indirect band gap in bulk crystals to a direct band gap in monolayer [5–8]. Consequently, in comparison with graphene, two dimensional (2D) TMDs exhibit many distinct and attractive properties and have emerged as a fascinating class of atomically thin semiconductors for a new generation of electronic and optoelectronic devices.

One of the most challenging requirements for the industrial application of the 2D-TMD materials is the synthesis of device relevant atomically thin films. A large amount of studies have been being carried out to grow large-area, high-quality, single-crystal 2D-TMDs. Among these efforts, the technologies compatible with the existing microelectronic processes, such as chemical vapor deposition [9, 10] and molecular beam epitaxy (MBE) [11–21], are receiving particular attention. On the other hand, real-time monitoring of the growth of 2D-TMD materials has seldom, if ever, been reported. This is rather surprising since it is well known that the in situ real time monitoring of the growth is essential regarding both the fundamental understanding of the process and the practical in-line control.

Although only atomically thin, TMD monolayers are excellent light absorbers in the visible range. The absorption spectra of MX2 (M = Mo, W and X = S, Se) exhibit
characteristic peaks associated to the excitonic resonances and the interband electronic transitions [5, 22–24]. The two lowest energy absorption peaks, labeled as A and B, are attributed to the excitonic transitions occurring at the K (K') point of the Brillouin zone. The pronounced absorption peak C at higher energies is associated to interband transitions occurring in the region near the Γ point of the Brillouin zone where the valance and conduction bands are nested [22, 24, 25]. These absorption features are characteristic of the 2D TMDs and depend sensitively on the number of layers, the dielectric environment, the defect density and the residual strain regarding the peak positions and spectral shape [5, 23, 26]. These factors make the optical spectroscopy one of the most powerful method for the characterization of 2D-TMD materials. Indeed, deep understandings on the unique electronic and optical properties of atomically thin TMD films have been achieved with the help of optical spectroscopy [5, 22–24]. In this work, we have monitored, in real time and in situ, the evolution of the optical reflectance during the MBE growth of atomically thin MoSe2 films using differential reflectance spectroscopy (DRS) [5, 22–24]. The extremely high sensitivity of DRS allows us to monitor the growth from the initial stage. Most importantly, based on the characteristic spectral line shape, the growth regime of MoSe2 monolayer can be well distinguished from the bilayer and thus allows a precise control of the number of the layers.

2. Experiments

The MBE growth of MoSe2 thin films was carried out in a home-built ultra high vacuum (UHV) chamber with a base pressure below $1 \times 10^{-9}$ mbar. During growth, a rather high Se flux was used in order to maintain a Se rich environment. Consequently, the pressure in the chamber was increased to around $1 \times 10^{-3}$ mbar during deposition. The Se flux was generated from a Knudsen effusion cell, whereas the Mo beam was ejected from an e-beam evaporator. As the evaporation materials, Se powder and a 2 mm diameter Mo rod with purities of 99.999% and 99.95%, respectively, were used. The deposition rates at sample position were measured using a quartz crystal microbalance. For the results reported in this paper, the deposition rates of Se and Mo were set to be $2 \times 10^{-1}$ Å s$^{-1}$ and $1 \times 10^{-3}$ Å s$^{-1}$, respectively. One side epi ready α-Al2O3(0001) crystals (KJMT Corp.) were used as the substrates. The root-mean-square surface roughness of the polished surface was about 0.2 nm as characterized by AFM. The α-Al2O3(0001) substrates were first cleaned sequentially in a supersonic bath of acetone and methanol for 10 min each and then in deionized water for 60 min. Afterwards, the substrates were etched in a 15 mmol solution of HNO3 in an ultrasonic bath for 30 min, and subsequently rinsed thoroughly with deionized water. After being blow-dried with filtered dry N2 gas, the substrates were annealed at 1000 °C for 1 h in air and then naturally cooled down to room temperature. Finally, the substrates were introduced into the UHV chamber where they were heated up to 700 °C for 10 min in order to desorb the water and other contaminants from the surface. During depositions, the substrate temperature was maintained at 250 °C.

A differential reflectance (DR) spectrometer was attached to the UHV chamber in order to monitor the evolution of the optical reflectance in situ during the co-deposition of Se and Mo on the substrate surface (see figure 1). A light beam provided by a super-stable white light emitting diode is directed through a fused silica window onto the α-Al2O3(0001) substrate at close to normal incidence. The spectra of the reflected light beam was recorded using a spectrometer with a CCD array detector. An acquisition time of 2 s per spectrum was used to collect all the spectra used in this paper. The DR spectra are then obtained from [27]:

$$\frac{\Delta R}{R} = \frac{R(t) - R_0}{R_0},$$

where $R_0$ and $R(t)$ denote the reflectivity of the bare α-Al2O3(0001) substrate and the one after a deposition time of $t$, respectively. The DR signal $\frac{\Delta R}{R}$ thus reveals the change of the optical reflectivity with respect to the clean α-Al2O3(0001) surface as a function of the deposition time $t$ [27].

The ex situ Rutherford backscattering spectrometry (RBS) measurements were performed using the AN-700 van de Graaff accelerator at the department of atomic physics and surface science of the institute of experimental physics at JKU Linz. The experimental geometry is schematically exhibited in figure 2(d). The accelerator is capable of creating monoenergetic beams of H, D atomic and molecular ions and He$^+$ ions with energies in the range 30–700 keV and primary beam currents up to several μA. In the present study 600 keV He$^+$ ions were used. The samples were analyzed in a HV-chamber with a base-pressure of $1 \times 10^{-7}$ mbar. RB spectra were recorded using a liquid nitrogen cooled high-resolution
surface barrier (SSB) detector (detector resolution: 7 keV) and a standard SSB detector (detector resolution: 10 keV). The stoichiometric ratio and nominal thickness of the MoSe2 thin films were deduced using SIMNRA software [28] from the experimental RBS spectra. For the calculation, a density of 6.98 g cm$^{-3}$ and a molar mass of 253.68 g mol$^{-1}$ have been used for MoSe2 thin films.

The morphology of the MoSe2 thin films was investigated ex situ using atomic force microscopy (Bruker MultiMode) in the tapping mode. A soft cantilever (TipsNano) with a force constant of $\sim$2 N m$^{-1}$ and a resonant frequency of $\sim$87 kHz was employed. Raman spectra of the MoSe2 films were collected using a Renishaw inVia Raman microscope with an excitation wavelength of 532 nm. Measurements were performed in a confocal micro configuration using a $\times$100 microscope objective lens and a 2400 Grooves mm$^{-1}$ grating. The laser beam, at a power level of 2 mW, was focused on a spot with a diameter of $\sim$1 $\mu$m. All ex situ measurements were performed at room temperature. For DR measurements performed ex situ, an inverted microscope (Nikon Eclipse Ti) is used. A tungsten halogen white light source is reflected into a $\times$50 ultra-long working distance objective using a neutral density, achromatic beam splitter and then focused on the sample ($\sim$2 $\mu$m spot diameter). The reflected signals from the MoSe2 covered areas ($R_{\text{MoSe2}}$) and the bare substrate areas ($R_{\text{substrate}}$) were collected by the objective separately and sent back through the beam splitter into the spectrometer. The DR spectra $\Delta R/R$ were then calculated by $\Delta R/R = (R_{\text{MoSe2}} - R_{\text{substrate}}) / R_{\text{substrate}}$ [5].

3. Results and discussions

Figure 2(a) shows the DR spectra recorded in situ during the co-deposition of molybdenum and selenium. The DR intensity increases in a broad region and a peak is formed around 2.6 eV. Based on the energetic position, this peak can be attributed to the absorption peak C due to the excitonic transition of MoSe2 [22, 24, 25]. This is a clear sign of the nucleation and the growth of the MoSe2 thin film. Compared to the spectral line shape measured at room temperature [22, 24, 25], the peak C plotted in figure 2(b) is relatively broader. This observation can be attributed to the fact that the current spectra were recorded at an elevated substrate temperature of 250 °C. The absence of the excitonic absorption
peaks A and B in figure 2(b) can be explained by the same reason. Actually, it has been demonstrated that the intensity of the absorption peaks A and B decrease dramatically with increasing the sample temperature [29]. Indeed, our ex situ DR spectrum measured at room temperature show well resolved absorption peaks of A, B and C (see figure 5(a)). Furthermore, a red shift of peak C can be recognized with increasing the deposition time. This effect can be revealed even clearly by inspecting figure 2(b) where the ΔR/R spectra recorded at deposition times of 3800 and 6600 s, respectively, are plotted. This observation is in conformity with the tendency of the red shift for the peak positions of A, B and C with increasing the number of layers for MX2 semiconductors [23, 26, 29]. Actually, it will become clear that the ΔR/R spectra recorded at 3800 and 6600 s are dominated by the characteristics of the MoSe2 monolayer and bilayer, respectively.

In order to have a closer inspection of the details of the growth, the evolution of the DR signal at 2.67 eV is plotted as a function of the deposition time in figure 2(c). It becomes clear that the increase of the DR intensity at 2.67 eV is not linear. Actually, the rising of the DR intensity is very slow at the initial stage of the growth and becomes faster gradually with the deposition time. The incremental variation of the DR signal between sequent spectra can be recognized from figure 2(d), in which the derivative of the DR transient at 2.67 eV is presented. Based on the behavior of the derivative of the DR intensity, the growth can be divided into two regimes: the rising speed of the DR signal increases almost linearly in the first growth regime and this acceleration stops in the second one. Based on the deposition rate determined using RBS (figure 3(c)), the nominal thickness of the MoSe2 thin film deposited after the first regime was ∼0.65 nm, which coincided nicely with the monolayer thickness of MoSe2 [13]. This allows us to assign the first regime to the growth of the monolayer MoSe2. The red shift of the peak position evidenced in figure 2(b) supports also this assignment.

In order to determine the elemental composition and the film thickness of the MoSe2 thin films, RBS measurements were carried out on MoSe2 thin films grown on α-Al2O3(0001) surfaces with various deposition times. The 600 keV +He+ RBS spectra recorded from two samples with deposition times of 45 min and 120 min, respectively, are plotted in figures 3(a) and (b). The backscattering peaks associated to Mo and Se atoms are well resolved and the areas under each peaks can be precisely determined. Since channeling of the He ions in the α-Al2O3(0001) single crystalline substrate cannot be excluded at the normal incidence of the ion beam in the current experiment setup (figure 3(d)), the spectrum of the substrate is not a reliable choice to set the number of projectiles in the SIMNRA simulation [28]. Instead, all MoSe2 thin film samples were measured relative to a Au reference sample for 4 × 3 min. The spectrum of Au was then used to calibrate the number of projectiles, in which the count rates of the low resolution detector were saved during the measurements. This procedure allows us to calculate the correct number of projectiles for the individual spectra from the relative Au/MoSe2 measurement. From the
The ratio of the atomic density of Se and Mo (Se:Mo) were determined to be (2.28 ± 0.02):1 and (2.24 ± 0.02):1 for the thin films with deposition times of 45 min and 120 min, respectively. These numbers are reasonably close to the stoichiometric ratio of MoSe$_2$ crystal verifying the formation of MoSe$_2$ thin films. Furthermore, the positions of the out-of-plane $A_{1g}$, and in-plane $E_{2g}$ Raman active modes confirm the formation of the 2D MoSe$_2$ layers. Most importantly, the almost complete absence of the $B_{2g}$ mode at 353 cm$^{-1}$ for the sample with a thickness of 0.41 nm verifies the film is dominated by monolayer MoSe$_2$. For the 1.27 nm thick sample, on the other hand, $B_{2g}$ peak with very low intensity becomes visible indicating the formation of the bilayer. Furthermore, the $A_{1g}$ peaks locate at 241 and 242 cm$^{-1}$ for 0.41 nm and 1.27 nm thick films (see figure 4(b)), respectively. These positions fit excellently with the ones measured from the mechanically exfoliated monolayer and bilayer MoSe$_2$ [30] and verify again the thickness determined by in situ DRS and the ex situ RBS measurements. The corresponding full width of half maximum (FWHMs) of the $A_{1g}$ peaks are 5.19 and 4.65 cm$^{-1}$ for the MoSe$_2$ films with thicknesses of 0.41 nm and 1.27 nm, respectively. Comparing with the FWHM of the $A_{1g}$ peak measured from the mechanically exfoliated 2D MoSe$_2$ layer, which is around 1 cm$^{-1}$ [30], these numbers are relative larger. This observation suggests the formation of defect rich 2D MoSe$_2$ layers with relative small grain size [20].

In figure 5(a), the DR spectra of MoSe$_2$ thin films with a thickness of 1.27 nm measured ex situ at room temperature is plotted. As a reference, the DR spectrum of the same sample but recorded in situ at an elevated temperature of 250 °C is also presented in the same graph. The general appearances of these two spectra are very similar showing the C peak at ∼2.67 eV with a broad tail in the low energy side. However, above this tail, the characteristic absorption peaks of A and B become resolved at room temperature [23, 24]. This observation confirms our argument that the absence of the peaks A and B for DR spectra recorded in situ during growth is due to the elevated substrate temperature. Indeed, it can be recognized in figure 5(a) that even peak C is partially smoothed out at 250 °C.

The corresponding morphology of the 1.27 nm thick MoSe$_2$ thin film can be revealed from the AFM image presented in figure 5(b). The surface is covered by an almost completed layer with some vacancy areas in between. More
detailed information regarding the morphology and the structure of the thin film can be obtained by inspecting the height profile exhibited in figure 5(c). Actually, the height profile reveals that the thin film contains a two-layer structure. The thickness of the top most layer is \(\sim 0.6\) nm which is very close to the MoSe\(_2\) monolayer thickness of 0.65 nm. Therefore, we can attribute it to the second monolayer (2nd ML) of MoSe\(_2\) which rests at the topmost of the film. The pits resolved in the next level through the vacancies of the 2nd ML show irregular profile with depths much smaller than a monolayer. We attribute these pits to the vacancies within the almost completed 1st ML of MoSe\(_2\). The thickness and the film structure determined from the morphology revealed by AFM is thus in fully agreement with that deduced from \textit{in situ} DRS as well as \textit{ex situ} RBS and Raman spectroscopy measurements. Furthermore, this AFM result is inline with the morphology of MBE MoSe\(_2\) layers grown on Al\(_2\)O\(_3\)(0001) [20] and other substrates [17, 21] revealed using aberration-corrected high-resolution transmission electron microscopy.

4. Conclusion

In conclusion, the MBE growth of atomically thin MoSe\(_2\) films on \(\alpha\)-Al\(_2\)O\(_3\)(0001) has been investigated by monitoring the optical reflectance in real time using DRS. The DR spectra with the characteristic line shape of MoSe\(_2\) are formed upon the simultaneous deposition of Se and Mo onto the \(\alpha\)-Al\(_2\)O\(_3\)(0001) surface. A closer inspection shows that the DR spectral line shape and the way of its evolution exhibit a pronounced dependence on the deposition time, i.e. the film thickness. Consequently, the growth of the 1st ML MoSe\(_2\) can be well distinguished from the following ones. Actually, monitoring the evolution of the DR intensity at a single selected energy allows a precise control of the film thickness during growth. The \textit{ex situ} characterizations using RBS, AFM, Raman spectroscopy and DR spectroscopy corroborate the conclusion deduced from the real time \textit{in situ} DRS measurements regarding the film thickness, the elemental composition, the vibration modes and the optical absorption. The result highlights the importance and the great potential of the real time \textit{in situ} optical spectroscopy in realizing well controlled growth of 2D semiconductor materials.

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