Research Article
Photoluminescence Enhancement Effect of the Layered MoS$_2$ Film Grown by CVD

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The layered MoS$_2$ films have been prepared by the chemical vapor deposition (CVD) method, which shows numerous MoS$_2$ convex flakes (i.e., MoS$_2$ nanosheets) on SiO$_2$/Si substrates. The convex flake islands form a uniform layered film and the single flake corresponds to one small piece of monolayer MoS$_2$ film; they show a strong photoluminescence (PL) radiation as a whole. The thickness of the layered MoS$_2$ films increases with the increases of growth time, the effect of diverse growth time on the properties of layered MoS$_2$ films has been discussed, and the PL enhancement effect is due to the PL intensity accumulation from each of the convex flakes. The strong PL radiation has been found by annealing the samples and the reason has been analyzed. The layered MoS$_2$ films could provide more photon energy than both the monolayer MoS$_2$ film and the bulk MoS$_2$. This work provides a fundamental study about the device fabrication based on layered MoS$_2$ films. The optoelectronic devices based on this study will be more energy efficient.

1. Introduction

Recently, transition metal dichalcogenides (TMDs), MX$_2$ (M = Mo, W; X = S, Se, and Te) have attracted extensive attention for their great potential in the fields of catalyst [1–4], nanoelectronic, and optoelectronic devices [2–15]. The transistors fabricated with the molybdenum disulfide (MoS$_2$) films demonstrate good on/off current ratio and high carrier mobility [7–10, 16–19], which make them very suitable for next generation transistors devices. Substantial works have been devoted to prepare MoS$_2$ films [10, 20], including mechanical exfoliation [21], liquid exfoliation [22, 23], physical vapor deposition (PVD), and CVD [2, 3, 11, 12]. However, synthesis of large-size MoS$_2$ single crystal films is still challenging. The thin MoS$_2$ film prepared by the mechanical exfoliation method based on scotch-tape can control the thickness, but the output is very low which makes it not suitable for electronic applications. The liquid exfoliation can generate large quantities of monolayer dispersions, but relatively small flakes limit their use in electronics or photonics applications. The approach of PVD is hard to achieve because of the high sublimation temperature (1100$^\circ$C) and low oxidizing temperature of MoS$_2$. Compared with other methods, CVD is one of the most effective strategies for synthesizing large-area, high quality MoS$_2$ films [18, 19]. It was employed in a broad range of applications, such as FETs, LEDs, energy storage devices, and sensors, and MoS$_2$-based logic circuits have great potential for commercial applications in the future.

It is well known that, in bulk MoS$_2$, the energy band is 1.29 eV, while, in monolayer MoS$_2$ film, the energy band is 1.85 eV. Due to the change of band gap from bulk MoS$_2$ to monolayer MoS$_2$ film, the PL radiation appears. This phenomenon has been reported a lot [24–26], but the obvious PL radiation appeared in the layered MoS$_2$ films composed of convex flakes, and the strong PL radiation produced during the annealing process has not been reported before. In this work, the layered MoS$_2$ films is composed of many small convex flakes and exhibits relative uniformity film as a whole, so it shows a multilayer MoS$_2$ Raman characteristic and a monolayer MoS$_2$ PL characteristic simultaneously. In the layered MoS$_2$ films, the PL enhancement effects were observed and the reasons were analyzed.
2. Experiments and Results

The MoS$_2$ films were grown with MoO$_3$ (99.95%, Sigma-Aldrich) and S (99.98%, Sigma-Aldrich) powders as precursors. MoO$_3$ and S powders were put in different temperature districts separately due to their different sublimation temperatures. The amount ratio between MoO$_3$ and S was 1:10, in which MoO$_3$ was 0.01 g and S was the 0.1 g, and the sulfur powder is completely overdosed. The size of the SiO$_2$/Si substrate was 10 mm × 10 mm with 300 nm thickness of SiO$_2$ on Si. The substrate was upside down above MoO$_3$ and N$_2$ was used as the protection gas. The N$_2$ flow velocity was 50 sccm mainly decided by the diameter of the quartz tube. Figure 1(a) shows a schematic of CVD setup for MoS$_2$ films growth. The furnace includes three temperature districts. S powder was put in the first temperature district near the N$_2$ entrance port and MoO$_3$ powder was put in the third temperature district near the N$_2$ exit port. The second temperature district was as a temperature transition zone. The S powder, the second temperature district, and the MoO$_3$ powder were raised up to 250°C, 500°C, and 730°C in 47 min, respectively, and kept at the temperature for 5 min, which aims to make sure the two precursors can be sublimation and start reaction at the same time. Then the furnace cooled down to room temperature naturally. Figure 1(b) shows the temperature variation curves for both precursors which illustrates a whole growing process of MoS$_2$ films by CVD method, and the growth time (chemical reaction time) of MoS$_2$ is 5 min. The 730°C growth temperature is the relatively low temperature for MoO$_3$ sublimation [27, 28], which aims to ensure the film does not grow to be too thick. The growth time is chemical reaction time of MoO$_3$ and S which plays a very important role for the synthesizing MoS$_2$ films. The layered MoS$_2$ films with diverse growth time (5, 10, 15, and 20 min, resp.) are synthesized, and diverse growth time leads to different growth results which will be discussed in Figure 1.

In order to observe the morphology of layered MoS$_2$ films, the Scanning Electron Microscope (SEM) images with diverse growth time have been shown in Figure 2. In Figure 2(a), the layered MoS$_2$ films were generated with 5 min growth time, a lot of convex flakes can be seen on the surface of the substrate, and they resemble standing vertically on the substrate. It should be noted that the film is actually composed of these loosed convex flakes and they form a relatively uniform film structure. Every piece convex flake corresponds to a monolayer film, and a number of convex flakes lead to strong PL radiation together. Figures 2(b) and 2(c) show the SEM images of the layered MoS$_2$ films with 10 and 15 min growth time, respectively. It is obvious to see the number of convex flakes less than the number generated in 5 min growth time; in 15 min growth time, the number of convex flakes is the least. It means most convex flakes accumulated into a thick film and deposited on the substrate led to the film becoming denser. Accompanied by thickening of the film, the PL intensity becomes weaker, which will be shown in Figure 2.
Figure 2: SEM images of morphology of layered MoS$_2$ films with (a) 5 min, (b) 10 min, and (c) 15 min growth time, respectively.

Figure 3: (a) Raman and (b) normalized PL spectra of layered MoS$_2$ films synthesized with diverse growth time. The samples are excited under 532 nm laser.

3. Analysis and Discussion

3.1. MoS$_2$ Synthesized with Diverse Growth Time. The Raman and PL spectra of layered MoS$_2$ films with diverse growth time have been measured and shown in Figures 3(a) and 3(b), respectively. There are two first-order Raman active modes (the in-of-plane vibration mode $E_{2g}^1$ and the out-of-plane vibration mode $A_{1g}$) that can be observed in Raman spectra, they are corresponding to the phonon modes of Raman scattering, and, more importantly, the two Raman active modes $E_{2g}^1$ and $A_{1g}$ are regularly varied with the thicknesses of thin MoS$_2$ film. The frequency of the characteristic peak of $E_{2g}^1$ and $A_{1g}$ mode decreases (red shift) and that of $A_{1g}$ increases (blue shift), the value of $\Delta$ is increased, and the number of layers increased. It is due to the fact that restoring force between interlayer S-S bonds in layered MoS$_2$ is increased, resulting in an increase in frequency of $E_{2g}^1$ mode.
to the convex flake structure, only the thickness of the thin sheets is investigated. Take Figure 4(a) as an example, the thickness of the film shown in the right figure is measured along the blue line in the left picture. Then the thickness is read by the height difference in the right figure. It just gives a relative thickness for fixed position, but it is still able to give an intuitive expression of the sample thickness. As we can see in Figure 4, with the extension of growth time, the film thickness increases, consistent with the results of Raman and PL spectra, and the number of layers is also consistent with results derived from the Raman spectra.

Bulk MoS\(_2\) is one kind of indirect bandgap material and the monolayer MoS\(_2\) is a direct bandgap material [32, 33]; it is a salient feature of MoS\(_2\). Bulk MoS\(_2\) shows negligible PL intensity, while monolayer MoS\(_2\) film exhibits the strongest PL intensity. It is due to the fact that when the indirect band gap changes to the direct band gap, monolayer MoS\(_2\) film leads to increment of radiation photon energy compared with the bulk MoS\(_2\), which means the quantum efficiency enhances and the PL radiation increases. So the PL intensity is inversely dependent on the thickness of MoS\(_2\) nanosheets. Normalized PL spectra of layered MoS\(_2\) films with diverse growth time has been shown in Figure 3(b), take the sample of 5 min growth time as an example, it has two emission wavelengths at 664 nm (A exciton) and 623 nm (B exciton) [28–31], respectively, arising from the direct excitonic transitions at the Brillouin zone K point, and the energy difference between these two peaks arises from the spin-orbital splitting of the valence band. According to previous researches, only monolayer or two layers MoS\(_2\) film can emit the PL radiation [17, 34–36]. However, through the preparation method described above, the multilayer MoS\(_2\) films still show a strong PL radiation (characterized by Raman spectra showed above). It is due to the fact that convex flakes structure contributes to the PL radiation accumulation, resulting in the PL enhancement effect. Every convex flake is approximate to one monolayer MoS\(_2\) film, a lot of convex flakes stacking on the substrate approximate to many monolayer MoS\(_2\) films, and they radiate PL together from the same small area on the substrate excited by 532 nm laser, leading to PL radiation enhancement. So the layered MoS\(_2\) films prepared by this way have a higher MoS\(_2\) content and provide a large number of monolayer MoS\(_2\) nanosheets simultaneously.

When the growth time is increased, the PL intensity decreased, which means the thickness of the layered MoS\(_2\) films increased. What is more, the peak wavelength shifts to red with the increasing of growth time (664 nm at 5 min, 668 nm at 10 min, 672 nm at 15 min, and 676 nm at 20 min). When the thickness of layered MoS\(_2\) films increased, the layered MoS\(_2\) films changed from direct bandgap to indirect bandgap gradually, the energy band gap decreased, so the wavelength had a red shift. The thickness of the layered MoS\(_2\) films increased with the growth time, which is consistent with Raman spectra. That is to say, when the growth time becomes longer, more MoS\(_2\) nanosheets are deposited on the substrate, the space among the convex flakes becomes smaller, the film becomes denser, and the PL radiation weakened. Different positions of the MoS\(_2\) domain were measured and similar results were obtained, indicating the continuity and stability of samples.

3.2. MoS\(_2\) Synthesized with Different Annealing Temperatures

Annealing process usually played a very important role in material preparation [19]. So the layered MoS\(_2\) films synthesized with different annealing temperatures have also been studied. The annealing temperature changed from 780°C to 840°C with 20°C temperature spaces, respectively, and MoS\(_2\) film without annealing was also measured for a comparison. The Raman spectra of layered MoS\(_2\) films at different annealing temperatures are shown in Figure 5(a). Without annealing, the difference of two Raman characteristic peaks is 21 cm\(^{-1}\), corresponding to the two atom layers. When the sample is annealed, the difference between the two Raman peaks increases as the annealing temperature increases, which means that the film becomes thicker. But the PL radiation does not become weaker correspondingly. The PL spectra are shown in Figure 5(b), and the PL intensity of annealing samples is much larger than the sample without annealing. At the beginning, with the increasing of the annealing temperature, the PL intensity increases and reaches the maximum value at 800°C, it has a great improvement compared with the MoS\(_2\) film without annealing. Then the PL intensity decreases with the further increasing of annealing temperature, but it is still higher than the PL intensity of MoS\(_2\) film without annealing. A stronger PL enhancement effect has been shown in the annealing samples because more defects were induced to the samples and more convex flakes were generated on the substrates. The layered MoS\(_2\) film has the strongest PL radiation at 800°C, the optimal annealing temperature means the best temperature for the convex flakes generation.

In order to further understand the mechanism behind the different growth conditions, the X-ray diffraction (XRD) spectra are measured for both samples with diverse growth time and different annealing temperatures. As we can see in Figure 6(a), with the increase in growth time, more crystal orientations appear, and the intensity of (002) peak increases, and the results proved that the samples transform from layered MoS\(_2\) to bulk MoS\(_2\), resulting in an enlargement of the difference value between the two Raman characteristic peaks, consistent with the Raman spectra shown in Figure 5(a), which means the film becomes thicker. In Figure 6(b), after the samples have been annealed, the (100) peak disappears and the (102) peak appears, and different crystalline orientations may cause the change in the PL intensity. When the annealing temperature increases, the full width at half maximum (FWHM) of (002) peak increases, indicating that the grain size becomes smaller. The intensity of (002) peak is proportional to degree of bulk material [37]. At 800°C annealing temperature, the intensity of (002) peak is weakest, and the PL intensity is strongest, which shows the highest degree for film formation, which is consistent with the PL spectra in Figure 5(b). More importantly, PL intensity of layered MoS\(_2\) is proportional to defect density and impurity concentration [38]. The introduction of more defects in the annealing process is also one reason for PL radiation enhancement.
Figure 4: AFM images of MoS$_2$ synthesized with (a) 5 min, (b) 10 min, (c) 15 min, and (d) 20 min growth time.
4. Conclusions

In this paper, the layered MoS$_2$ films on SiO$_2$/Si substrates have been prepared by CVD method. It is composed of lots of MoS$_2$ convex flakes, each convex flake corresponding to a monolayer MoS$_2$ film which has a PL radiation, and lots of convex flakes showed strong PL radiation as a whole. The effect of diverse growth time on the quality of the layered MoS$_2$ films has been discussed, and the strongest PL radiation has been observed on the layered MoS$_2$ films with 5 min growth time. A strong PL enhancement effect was found after the samples were annealed, and the strongest PL intensity has been obtained under the growth condition of 730°C and annealing at 800°C. It provides a foundation study for preparation of layered MoS$_2$ film by CVD. In the previous study, it usually could not observe so strong PL radiation when the difference between the two characteristic Raman peaks exceeded 20 cm$^{-1}$, but, due to the MoS$_2$ convex flakes structure, the monolayer and multilayer MoS$_2$ films coexist on the substrate, and the samples have a higher MoS$_2$ content and provided a monolayer component simultaneously. So it could provide more charge carriers and 2D component when it is used in optoelectronics devices. This work provides a new choice about the device fabrication based on the layered MoS$_2$ films generated by CVD method. It could provide more photon energy due to more charge carriers.
that emerged through the direct band transition. The opto-electronic devices based on this study will be more energy efficient and environmentally friendly and are of interest to the development of sustainable energy.

**Conflicts of Interest**

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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