The Amorphization of Monolayer MoS$_2$ Induced by Strong Oxygen Plasma treatment

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By strong oxygen plasma treatment with 100 W on monolayer MoS$_2$, we observe the disappearance of the Raman modes of MoS$_2$. The phenomena of no MoO$_3$ formation shown by Raman spectra and the appearance of the Mo$^{4+}$ peak and decreased O concentration shown by X-ray photoelectron spectroscopy are attributed to that the state of MoS$_2$ translates from crystal to amorphous after strong oxygen plasma treatment. The amorphization of monolayer MoS$_2$ is further confirmed by the quenching of photoluminescence (PL) and the disappearance of two absorption peaks related to A, B exciton which demonstrates the disordered bandgap. Finally, we found that the amorphous MoS$_2$ can improve the absorption fraction at the visible light (500–750 nm) which is potential for future visible light photocatalysis.

Keywords: MoS$_2$, amorphization, oxygen plasma treatment.

1. INTRODUCTION

Recently, there is a great research interests in the two-dimensional (2D) material due to its adjustable properties. Molybdenum disulfide (MoS$_2$) among the two-dimensional semiconductors, offers a layer-dependent energy gap: an indirect gap of 1.2 eV for the bulk MoS$_2$ and a direct gap of 1.9 eV for the monolayer MoS$_2$, which has huge potential for optoelectronic applications [1, 2]. Tailoring the properties of MoS$_2$ can fulfill the requirements of novel applications. Strain engineering can be used to modulate electrical properties of MoS$_2$, which is a common method of modulating the material optical and electrical properties [3, 4, 5, 6]. For example, MoS$_2$ experienced a direct-to-indirect bandgap and semiconductor-to-metal transition by mechanical strains [7]. Defects engineering, especially ion bombardment, which is a controllable method of introducing defects can also be used to modulate the electrical and optical properties of MoS$_2$. The photoluminescence (PL) intensities can be enhanced by oxygen plasma irradiation on the MoS$_2$, which is due to the enhancement on the radiative recombination exciton caused by p doing on MoS$_2$ through oxygen adsorbed on the defects. [8-9]

However, quenching of the PL also is observed by oxygen plasma treatment on monolayer MoS$_2$ [10]. This phenomenon is explained by the reduction of the radiative recombination efficiency due to the MoO$_3$ formation which causes the direct bandgap evolves to the indirect bandgap. The electrical properties of MoS$_2$ can also be tuned from semiconductor to insulator by the oxygen plasma treatment due to the MoO$_3$ regions formation in the same way [11].

The mechanism of the different phenomenon is caused by the reaction between oxygen and monolayer MoS$_2$ under different oxygen plasma power (which means that the oxygen plasma is generated at different radio frequency (RF) power), the enhancing of PL is supposed to the mild plasma treatment which means the plasma power is about no more than 20 W while the quenching of PL is supposed to the strong plasma treatment which means the plasma power is no less than 100 W.

In this work, we present the strong oxygen plasma treatment with plasma power 100 W on monolayer MoS$_2$. The crystalline structure of MoS$_2$ involves to amorphization after stronger oxygen plasma treatment which is demonstrated by that the Raman spectrum shows no evidence of MoO$_3$ while the X-ray photoelectron spectroscopy (XPS) shows the evidence of Mo$^{4+}$ and the decreased oxygen concentration. The quenching of PL spectrum and the corresponding absorption spectrum also demonstrated that the bandgap lowered due to the amorphization. Also, we find that the amorphized MoS$_2$ can improve the absorption fraction in the visible light (500 nm–750 nm). Theoretical calculation and experimental work all found that the pristine MoS$_2$ is good candidate as photocatalytic due to its bandgap (~1.9 eV) which is within the visible light range [12, 13]. For example, the MoS$_2$ nanosheet-coated TiO$_2$ exhibits high hydrogen production [14]. Hence, our finding can be applied to the visible light photocatalysis.

2. EXPERIMENTAL DETAILS

2.1. Sample preparation

The pristine monolayer MoS$_2$ was grown on c-face sapphire via chemical vapor deposition (CVD) method, which has been reported elsewhere [15]. The oxygen
plasma was carried out using Plasma lab 80Plus. The oxygen plasma was operated with 100 sccm oxygen, 100 W power, 25 mtorr pressure and 3 s plasma exposure.

2.2. Characterization

The Raman spectra were measured by a micro-confocal laser Raman spectrometer (Renishaw-invia) (λ = 532 nm, power = ~2 mW, beam spot size = ~ 1 μm) with a 532 nm laser in ambient environment at room temperature. The XPS spectra were recorded out using a AIXSX photoelectron spectrometer (Kratos analytical Ltd, AlKαX-ray) operated at 15 kV and 10 mA and the beam spot size is = ~ 15 μm. PL measurements were carried out by fluorescence spectrometer (Horiba) with 50× objective. The absorption spectra were measured by UV-Visible Near-Infrared Spectrophotometer (Carry 5000).

3. RESULTS AND DISCUSSION

Fig. 1 shows the effect of strong oxygen plasma exposure on the Raman spectra of as-grown monolayer MoS2 on sapphire substrate. Except for the peaks of c-face sapphire substrate, two new peaks at 384 cm⁻¹ with a full width at half maximum (FWHM) of 6.31 cm⁻¹ and 403 cm⁻¹ with a FWHM of 6.27 cm⁻¹ are observed in the pristine MoS2 sample which are shown in Fig. 1.

The two prominent peaks correspond to the in-plane E₂g and out-of-plane A₁g vibrations of MoS2 respectively. The narrow position difference (~ 19 cm⁻¹) further confirms the monolayer thickness of MoS2[16]. Once the sample is treated by strong oxygen plasma with duration of 3 s, here, we called it 3 s oxygen plasma for simplicity, both E₂g and A₁g vibration modes disappear obviously which is shown in Fig. 1. The disappearance of the modes indicates that the MoS2 is damaged seriously.

The S atom is supposed to be removed by oxygen plasma firstly and then chemically bonded with O atoms. However, the MoS2 is not completely oxidized into MoO3 since the signature peaks (~ 225 cm⁻¹ and ~ 820 cm⁻¹) of MoO3 are not observed, marked by the grey area in Fig. 1 [11, 17]. To analyze the composition of the damaged MoS2, XPS spectra of the pristine MoS2 and 3 s oxygen plasma treated MoS2 on sapphire substrate are shown in Fig. 2. Fig. 2 a shows the survey XPS spectra of pristine as-grown monolayer MoS2 and 3 s oxygen plasma treated MoS2 exhibiting typical signals of sapphire overlaid with Mo⁶⁺ and S²⁻ signals. As shown in Fig. 2 b, in pristine MoS2 sample, a doublet Mo 3d₅/₂ and Mo 3d₇/₂ at ~ 233.0 eV and ~ 229.9 eV are observed, which has been reported elsewhere [18]. For the 3 s oxygen plasma treated MoS2, the binding energy of doublet Mo 3d₅/₂ and Mo 3d₇/₂ shift little and an additional peak at energy 235.7 eV is observed, corresponding to the higher oxidation state Mo⁶⁺ [11, 19, 20, 21]. However, the decreased instead increased oxygen concentration after 3 s oxygen plasma treatment shown in Fig. 2 d exclude the formation of MoO3. Since the signature peaks (~ 225 cm⁻¹ and ~ 820 cm⁻¹) of MoO3 are not observed, the data shows the possibility of the amorphization of monolayer MoS2 under strong oxygen plasma treatment [22].

To analyze the energy band of the strong oxygen plasma treated MoS2 and pristine MoS2, we take photoluminescence (PL) measurements and the PL spectra are shown in Figure 3. The sharp peaks at ~611nm, ~692nm and ~694nm appeared in PL spectra of both samples originated form the sapphire substrate. The strong peak centered at 676.5nm (1.83eV) for pristine MoS2 are not observed for simplicity. The phenomenon has been observed and is attributed to the formation of MoO3 [10]. MoO3 is an indirect bandgap (3.2eV) semiconductor and the radiative recombination must be assisted by electron-phonon scattering, therefore, leading the PL quenching.

Fig. 1. Raman spectra of as-grown monolayer MoS2 and MoS2 treated by oxygen plasma with duration of 3s on sapphire substrate

Fig. 2. a the survey XPS of the as-grown monolayer MoS2 and MoS2 treated by oxygen plasma with duration of 3 s on sapphire substrate and XPS spectra: b – Mo 3d; c – S 2p; d – O 1s levels of the pristine MoS2 and the 3s oxygen plasma treated MoS2 on sapphire substrate.
However, since the MoO$_3$ is not observed in our experiments, it is more likely attributed to the disordered band gap which is induced by the amorphization of crystalline structure.

![Graph](image)

**Fig. 3.** Photoluminescence spectra of pristine MoS$_2$ and 3 s oxygen plasma treated MoS$_2$

We also take absorption spectrum measurements of pristine MoS$_2$ and strong oxygen plasma treated MoS$_2$ on sapphire substrate to further understand the energy band. In Fig. 4, two prominent peaks located at $\sim$ 616 nm and $\sim$ 667 nm, corresponding to $\sim$ 2.0 eV and $\sim$ 1.86 eV are observed in the pristine MoS$_2$. It is known to arise from direct-gap transitions between the maxima of split valence bands and the minimum of the conduction band [1]. The lower absorption ($\sim$ 1.86 eV) peak of pristine MoS$_2$ matches the PL peak (1.83 eV) with 0.3 eV difference within the measurements error which is related to the A exciton. The higher absorption ($\sim$ 2.0 eV) peak of pristine MoS$_2$ is related to the B exciton though the PL peak is not observed due to the monolayer thickness [1]. However, the two peaks disappeared in strong oxygen plasma treated MoS$_2$ and it is attributed to the amorphization of crystalline structure which disordered the band gap. It is noted that the absorption of strong oxygen plasma treated MoS$_2$ on sapphire substrate is stronger than the pristine MoS$_2$ on substrate. It is also due to the disordered band gap which adsorbs the visible light (500 nm $\sim$ 700 nm) more widely. Therefore, it is potential for the application of visible light photocatalysis.

![Graph](image)

**Fig. 4.** Absorption spectra of pristine MoS$_2$ and 3 s oxygen plasma treated MoS$_2$

4. CONCLUSIONS

In conclusion, the missing of in-plane E$_{2g}$ and out-of-plane A$_{1g}$ vibrations of MoS$_2$ after strong oxygen plasma treatment with 100 W was observed. The Raman spectra of oxygen plasma treated MoS$_2$ with no MoO$_3$ peaks observed and XPS spectra with Mo$^{4+}$ peak observed are attributed to that the state of MoS$_2$ translates from crystal to amorphous after strong oxygen plasma treatment. The quenching of the PL and the disappearance of two prominent absorption peaks also demonstrate the amorphization of crystalline MoS$_2$ which causes the bandgap disordered. Also, our findings that the absorption fraction of strong oxygen plasma treated MoS$_2$ is higher than pristine MoS$_2$ provide a promising material candidate for future photocatalysis application.

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