

3 - 22 Raman and Photoluminescence Spectrum of Single-layer MoS₂ irradiated by Swift Heavy Ion

Guo Hang, Sun Youmei, Liu Jie, Yao Huijun, Zeng Jian, Zhai Pengfei and Hou Mingdong

Two-dimensional (2D) materials have attracted great research interests due to their unique properties. 2D MoS₂, unlike its bulk form which widely used as solid lubricant and catalyst, is of brilliant application prospect in nanoelectronics and optoelectronics. The electronic devices work in kinds of radiation environment. To evaluate the ion radiation effects on material properties and stability of device, the swift heavy ion radiation effect on single-layer MoS₂ was studied in this work^[1–2].

Single-layer MoS₂ (presented as 1 L MoS₂ in the following paragraphs) was exfoliated from a single crystal bulk MoS₂ (SPI Supplies) onto 5 mm×5 mm silicon substrates covered with 270-nm-thick SiO₂. Optical microscopy (Olympus BX51) and confocal micro-Raman spectrometer (LabRAM HR800, Jobin Yvon Co.) were used to identify the layer thickness.

Irradiation experiments were performed at heavy ion research facility in Lanzhou (HIRFL). The samples were irradiated by ²⁰⁹Bi ions with an initial kinetic energy of 9.5 MeV/u. All irradiations were performed in vacuum at room temperature under normal incidence to the fluence ranging from 1×10^{10} to 1×10^{12} ions/cm². Aluminum foil degraders of different thicknesses were placed in front of the samples in order to adjust the ion energy and thereby the stopping power of the projectiles. The experiment parameter is the 450 MeV ²⁰⁹Bi ions with the electronic energy loss of 33.46 keV/nm.

The Raman and photoluminescence (PL) spectrum of the irradiated samples were tested by the same Raman spectrometer (LabRAM HR800, Jobin Yvon Co.). A 532 nm excitation laser line and a 50× long working distance microscope objective lens was chosen. In order to avoid heating samples, an optical filter was used to keep the laser power well below 0.5 mW. The resolution of Raman spectra was kept 0.5 cm^{-1} .

The Raman spectrum of pristine and MoS₂ irradiated by 450 MeV ²⁰⁹Bi ions are shown in Fig. 1. As shown in Fig. 1(a), the A_{1g} peak of the irradiated 1 L MoS₂ shifting toward high frequency (blueshift phenomenon) was observed with increasing fluence, while the peak position of E_{2g}^1 mode barely changes. For clarity, the evolution of the peak position for A_{1g} peak with fluence is shown in Fig. 1 (b), which clearly indicates the blueshift of A_{1g} peak with increasing fluence. The blueshift of A_{1g} peak is caused by a p type doping of MoS₂. The as-exfoliated MoS₂ is intrinsically n type doping with extra electrons in it^[1–3]. Air molecules absorb on the radiation introduced defects such as vacancies and drain electrons in MoS₂. In this way, p type doping occurs in irradiated MoS₂, which results in the blueshift of A_{1g} mode. Based on density functional theory (DFT) calculations and using group theoretical arguments, it has been explained that the A_{1g} mode specifically exhibits a stronger sensitivity to electron doping than E_{2g}^1 mode^[4]. A strong electron-phonon interaction for A_{1g} mode can have significant effects on phonon frequencies^[4–6]. So frequency of A_{1g} mode is more strongly affected than E_{2g}^1 mode.

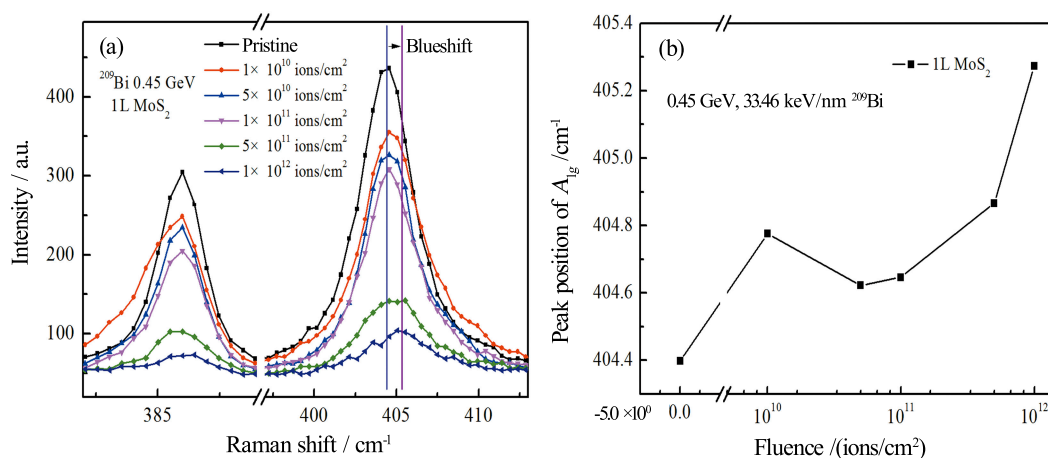


Fig. 1 (color online) (a) Raman spectra of pristine and 1 L MoS₂ irradiated by 450 MeV ²⁰⁹Bi ions. The blueshift of A_{1g} peak occurs with increasing fluence. (b) The peak position of A_{1g} for 1 L MoS₂ at a series of fluence, which shows the trend of the blueshift with increasing fluence.

The PL spectra of pristine and MoS₂ irradiated by 450 MeV ²⁰⁹Bi ions are shown in Fig. 2. The two characteristic

peaks of 1 L MoS₂ at ~ 1.84 eV and ~ 2.01 eV are known as the *A* and *B* excitons, corresponding to direct optical transitions from the highest spin-split valence bands to the lowest conduction bands. The PL spectra in Fig. 2 (a) show that as fluence increase to 5×10^{11} ions/cm², the blueshift of *A* exciton peak is observed. The peak becomes hard to be identified under 1×10^{12} ions/cm² fluence and the reason is unclear for now. For clarity, the evolution of the peak position for *A* exciton emission peak with fluence is shown in Fig. 2 (b). Exciton for as-prepared MoS₂ is X^- (eeh). After losing extra electrons to gas molecule absorbed on defects induced by ²⁰⁹Bi ion irradiation, the exciton will become X^0 (eh), which is of higher energy than X^- ^[5]. So the *A* exciton peak shows blueshift after irradiation. PL and Raman spectrum both illustrate that electron density in MoS₂ decrease with the increase of ion fluence.

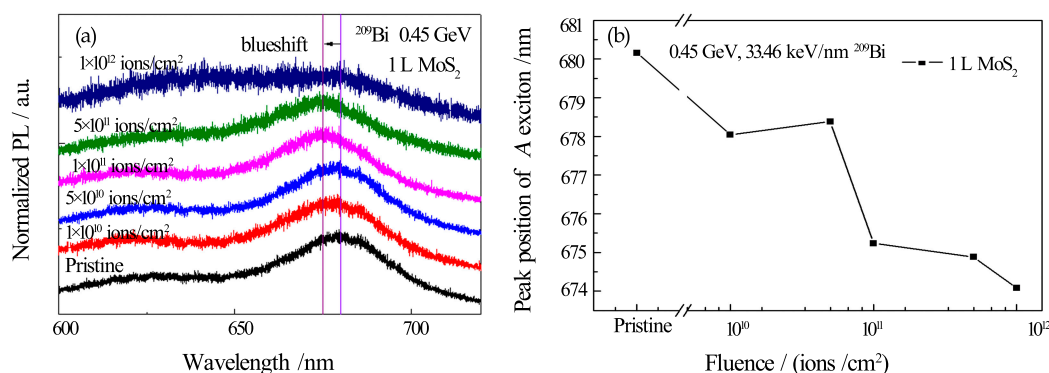


Fig. 2 (color online) (a) Normalized PL spectra of pristine and 0.45 GeV 1 L MoS₂ irradiated by 450 MeV ²⁰⁹Bi ions. The blueshift of *A* exciton emission peak occurs with increasing fluence. (b) The peak position of *A* exciton emission peak for 1 L MoS₂ at a series of fluence, which shows the trend of the blueshift with increasing fluence.

References

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3 - 23 Research Progress in Group of Energy Materials in 2014

Zhang Chonghong, Song Yin, Yang Yitao, Zhang Liqing,
Gou Jie, Chen Jiachao¹, J. Jang² and A. Kimura³

(¹Paul Scherrer Institute, Villigen PSI, Switzerland; ²Korea Atomic Energy
Research Institute, Daejeon, South Korea; ³Institute of Advanced
Energy, Kyoto University, Kyoto, Japan)

The progress of research going on in Group of Energy Materials (GEM), Material Research Center, in 2014 is in the following three aspects.

1. Facility development

In order to push forward our study on fusion reactor materials, we upgraded the irradiation terminal (128#) of the sector focused cyclotron (SFC) at HIRFL, by developing a new specimen stage specific for irradiation with low-fluence scattered ions. So far the terminal is capable of irradiation to both very low fluences (10^6 ions/cm²) and very high fluences (typically 10^{16} ions/cm²) for various materials. Specimen temperature can be readily controlled using the L-N₂ cooling stage or the the high-T stage (up to 600 °C). Our recent investigation with transmission electron microscopy (TEM) of the defects produced by high-energy Ne ions in steel specimens provides a clear evidence that defects were produced uniformly along the depth in the specimen, indicating that the energy degrader of the terminal works effectively to disperse the ion energy in a wide range. A photo of the terminal together with a SRIM estimate of depth profiles of damage in an 8% Cr reduced activation ferritic/martensitic steel (RAFMS) is shown in Fig. 1.