
Yangzhou Zhao¹**Hiroki Yokota², Haruna Ichikawa², Kazuyuki Takai^{1,2}**¹ Graduate School of Science and Engineering, Hosei University, Tokyo 184-8584, Japan² Dept. of Chemical Science and Technology, Hosei University, Tokyo 184-8584, Japantakai@hosei.ac.jp

Effects of defect formation in monolayer MoS₂ by low energy Ar⁺ ion beam irradiation

MoS₂ is a kind of promising material in the application of electronic devices using two-dimensional (2D) materials, but the structural defects of MoS₂ always exist in either way of samples CVD-grown or exfoliated from natural mineral. The defects' presence has a great influence on the structure, and electronic properties of MoS₂ due to its 2D nature. Meanwhile, the existence of defects has an impact on the electronic conductivity and molecular adsorption, where defect sites act as a carrier scattering source and major adsorption sites, respectively. In this study, in view of verifying the influence by defects on the structure and electronic properties, the monolayer MoS₂ is irradiated with low energy Ar⁺ ion beam in order to introduce defects under a well-controlled condition and then evaluated by Raman spectroscopy and photoluminescence (PL).

Monolayer MoS₂ was prepared by the mechanical exfoliation from bulk crystals of MoS₂ and then transferred to the surface of SiO₂ (285 nm)/Si substrate. Raman spectroscopy and photoluminescence (PL) was performed with an excitation wavelength of 532nm on a stage with controllable temperature.

The Raman spectra before, after ("0 sec") annealing and at each Ar⁺ ion irradiation time of monolayer MoS₂ are shown in Fig.1. In all samples, peaks corresponding to E_{2g} (in-plane vibration mode) and A_{1g} (out-of-plane vibration mode) are the characteristic Raman peaks of MoS₂, which appear around 390 cm⁻¹, 408 cm⁻¹, respectively. After Ar⁺ ion irradiation, both of the line widths of E_{2g} and A_{1g} peaks are increase and become broad as the increase of irradiation time. In previous study, the defects of MoS₂ introduced by ion beam irradiation is clarified into three sites; including S vacancy site, Mo vacancy site and MoS₆ cluster vacancy defects. Local phonon modes derived from the local vibration around the defects generate the satellite peaks on the low wave number side of E_{2g} peak and high wave number side of A_{1g} peak [1]. The observed increase of the line width is considered mainly because of the increase of the satellite peaks' contribution caused by the introduction of defects. Interestingly, the effect of the irradiation is more significant for E_{2g} in spite of less influence of charge transfer by molecular adsorption, where A_{1g} peak is much more sensitive due to its large electron-phonon coupling [2]. The presence of S vacancy weakens bond strength between the adjacent Mo atoms, resulting in more significant reduction for in plane vibration energy than that for out of plane. When the number of layers of MoS₂ increases, the effects on Raman spectra becomes moderate upon the same irradiation time.

Fig. 2 shows the PL spectra of monolayer MoS₂ at each Ar⁺ ion irradiation time. In all samples, A (1.84 to 1.88 eV) and B (2.02 eV) peaks corresponding to emission between two spin-split sub-bands, as the characteristic peaks of MoS₂, appear. After Ar⁺ ion irradiation, with the increase of irradiation time, the intensity of the A peak decreases significantly with the emerging of a tail at the lower energy side. Interestingly, the peak around 1.35 eV assigned to the emission related to impurity levels also rapidly decreases upon ion beam irradiation. It is explained as following. When defects are introduced into MoS₂, new defect states with various energy eigenvalues are generated just below the conduction band in the gap, and radiative relaxation of the excitons from various states causes observed tail over a wide energy range in A peak. However, non-radiative relaxation paths are also given by defect states introduced by the ion beam irradiation. Thus, the emission from deep impurity levels in the gap becomes suppressed as well as the main emission from the conduction band minimum at the K point.

References

- [1] Soungmin Bae et al, Phys. Rev. App., 7, 024001(2017).
- [2] B. Chakraborty et al., Phys. Rev. B, 85, 161403 (2012).

Figures

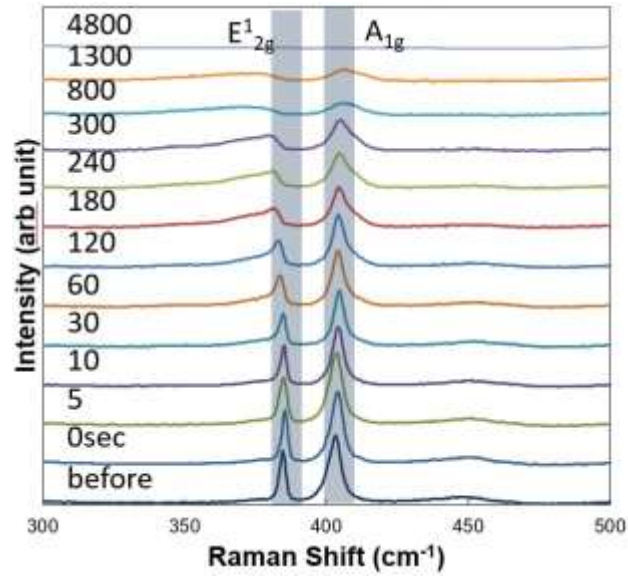


Figure 1: Raman spectra for monolayer MoS₂ irradiated Ar⁺ ion beam for 0-4800 sec and before annealing

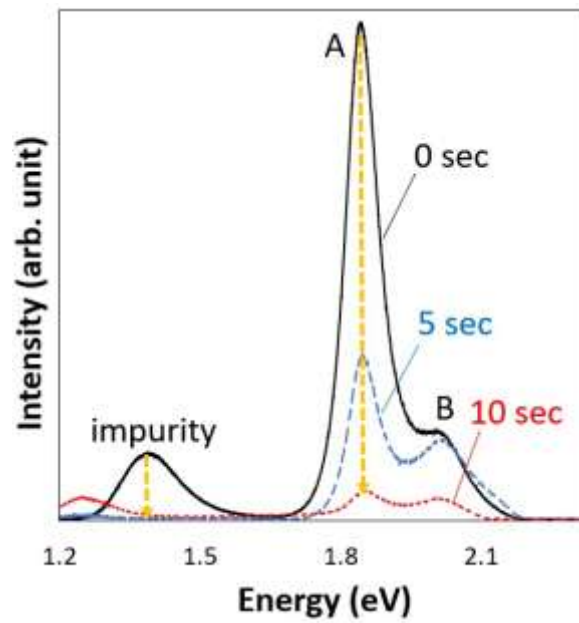


Figure 2: Photoluminescence spectra for monolayer MoS₂ irradiated with Ar⁺ ion beam for 0 sec, 5 sec, and 10 sec