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Effect of thermal annealing at a low temperature on exciton dynamics in semiconducting $MoTe_2$ crystals

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Abstract

We investigated the effect of low temperature annealing at 100℃ on exciton dynamics in semiconducting $MoTe_2$ crystals. For few layer $MoTe_2$ flakes on SiO_2, the thermal anneal dramatically reduced a PL intensity due to an increase in nonradiative recombination based on environmental degradation of $MoTe_2$ crystals. On the other hands, for a bulk $MoTe_2$ case the reduction of the PL intensity by thermal annealing was small compared with those for the few layer $MoTe_2$. Furthermore, it was demonstrated that hBN encapsulation can improve thermal stability of $MoTe_2$ crystals owing to suppression of interactions with surface impurities

1. Introduction

Two dimensional transition metal dichalcogenides (TMDs) have attracted great research interests owing to their unique properties such as band structure modification dependent on the layer number and exciton formation at room temperature based on large binding energy [1,2]. In particular, semiconducting molybdenum ditelluride (2H-$MoTe_2$) has a bandgap energy around 1 eV at room temperature, which is applicable to the light source for Si-based optical communications [3]. To fabricate the Si-based opto-electronic devices, thermal annealing at low temperature (100 – 300℃) is widely utilized in some processes of lithography and sintering after metal electrode formation. On the other hands, 2H-$MoTe_2$ has a drawback that it causes environmental degradation of crystal quality in an atmosphere over a short period of several days [4,5]. The interactions between intrinsic defects and molecules of oxygen and nitrogen strongly affect exciton dynamics due to formation of defect states within the optical bandgap. Thus, thermal annealing should accelerates the environmental degradation of 2H-$MoTe_2$ crystals. In this study, we investigate the effect of low temperature annealing in an atmosphere on exciton dynamics in few-layer 2H-$MoTe_2$. It is demonstrated that encapsulation by hexagonal boron nitride (hBN) is effective for improvement of thermal stability of the few-layer 2H-$MoTe_2$.

2. Sample fabrication

2H-$MoTe_2$ (supplier: 2D semiconductors) and hBN flakes are exfoliated from bulk crystals. Bulk hBN crystals are grown employing a temperature gradient method at high pressure and high temperature. Flakes of 2H-$MoTe_2$ and hBN are prepared onto a polydimethylsiloxane (PDMS) sheet. We fabricate two types of sample structures with a dry transfer technique using these flakes on the PDMS sheet as source materials. First samples comprise trilayer (3L) and pentalayer (5L) 2H-$MoTe_2$ deposited on a Si substrate with a 290-nm-thick SiO_2 film. A second sample structure comprises 3L 2H-$MoTe_2$ encapsulated by hBN. These sample structures are subsequently annealed at 100℃ for 1 hour in an atmosphere. We estimated the layer number of 2H-$MoTe_2$ from a photon energy of a maximum intensity in the steady-state photoluminescence (PL) spectrum [1].

3. Results and Discussions

Figures 1(a)-1(c) show PL spectra for 3L, 5L and bulk $MoTe_2$ on SiO_2 before and after thermal anneal, respectively. These spectra are normalized at a peak intensity obtained from the sample before thermal annealing, and are measured at low excitation power to avoid a change of the PL spectral shape based on many-body interactions such as an exciton-exciton annihilation and a heating effect by a laser irradiation [6,7]. For all samples, the PL intensity is seen to reduce by

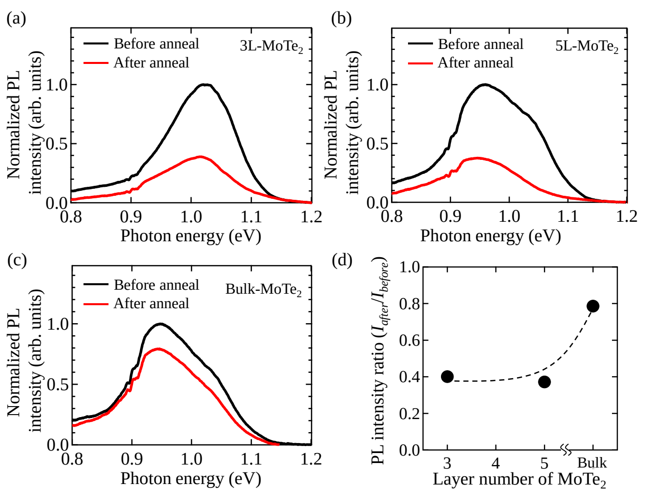

Fig. 1 PL spectra before and after thermal annealing for samples with (a) 3L-, (b) 5L-, and (c) bulk-$MoTe_2$ on SiO_2. (d) A ratio of integrated PL intensities between before and after thermal annealing plotted as a function of the layer number.

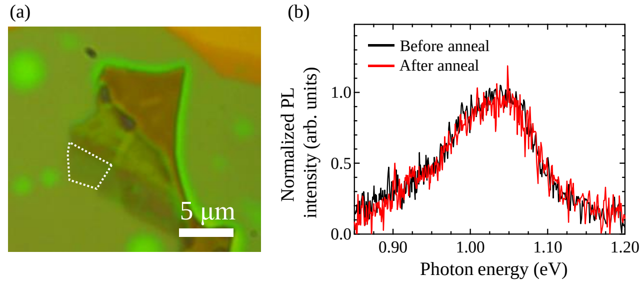

Fig. 2 (a) An optical microscope image and (b) PL spectra before and after thermal annealing for a 3L 2H-$MoTe_2$ encapsulated by hBN.

thermal annealing. The reduction of the PL intensity should be caused by an increase in nonradiative recombination based on crystal imperfections such as defects, impurities, and/or surface states. Figure 1(d) shows a ratio of integrated PL intensities between before and after thermal annealing (I_{after}/I_{before}) plotted as a function of the layer number of $MoTe_2$. The intensity ratios around 0.4 are obtained for the 3L and 5L $MoTe_2$. On the other hands, it is found that the intensity ratio of the bulk $MoTe_2$ is much larger than those of the few layer $MoTe_2$. The smaller intensity ratio (I_{after}/I_{before}) indicates a predominant nonradiative recombination due to formation of crystal imperfections by thermal annealing. It is therefore demonstrated that thermal stability of bulk $MoTe_2$ crystals is higher than those of the few layer $MoTe_2$. Since some vacancies are not formed in $MoTe_2$ crystals at a low temperature of 100℃, an increase in the nonradiative recombination by the thermal annealing should be attributed to interactions of photoexcited excitons in $MoTe_2$ crystals with oxygen and nitrogen molecules adsorbed on the surface. For bulk crystals, the photoexcited excitons generated at a deeper region in $MoTe_2$ might not nonradiatively recombined due to a separation between the excited excitons and surface impurities.

To avoid the interactions of 2H-$MoTe_2$ crystals with the surface impurities, we fabricated a heterostructure, which comprises 3L 2H-$MoTe_2$ encapsulated by hBN. Figure 2(a) shows an optical microscope image of the heterostructure. Bubbles cannot be seen in a $MoTe_2$ region surrounded by a white dashed line. Figure 2(b) shows normalized PL spectra for a sample before and after thermal annealing. The PL spectral shape is not largely changed even after thermal anneal, showing a large intensity ratio (I_{after}/I_{before}) of 0.95. It is demonstrated that interactions with surface impurities can be suppressed by hBN-encapsulation of 2H-$MoTe_2$. Although the PL intensity may be seen to be small even before thermal annealing because of a large intensity of a signal noise, it should be caused by not a dominant nonradiative recombination based on intrinsic crystal defects but low light outcoupling in the hBN-encapsulated 2H-$MoTe_2$. It could be concluded that the hBN-encapsulation can make it possible to improve thermal stability of $MoTe_2$ crystals.

4. Conclusions

We investigated the effect of thermal annealing on exciton dynamics in semiconducting $MoTe_2$ crystals. For few layer $MoTe_2$ flakes on SiO_2, the thermal anneal around 100℃ drastically reduced a PL intensity due to an increase in nonradiative recombination based on environmental degradation of $MoTe_2$ crystal. In contrast, for bulk $MoTe_2$ on SiO_2, the decrease of the PL intensity by thermal annealing was small compared with those of the few layer $MoTe_2$. Furthermore, we fabricated the 3L $MoTe_2$ encapsulated by hBN to avoid the effect of surface impurities adsorbed on the surface. It was demonstrated that hBN encapsulation can improve thermal stability of $MoTe_2$ crystals.

References

[1] C. Ruppert et al., Nano Lett. **14**, 6231 (2014).
[2] I.G. Lezama et al., Nano Lett. **15**, 2336 (2015).
[3] Y.-Q. Bie et al., Nat. Nanotech. **12**, 1124 (2017).
[4] B. Chen et al., ACS nano **9**, 5326 (2015).
[5] S. Larentis et al., ACS nano **11**, 4832 (2017).
[6] C. Robert et al., Phys. Rev. B **94**, 155425 (2016).
[7] C. Ruppert et al., Nano Lett. **17**, 644 (2017).