Optical and electrical properties of MoS₂ and Fe-doped MoS₂

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1. Introduction
Since the discovery of graphene, the study of two-dimensional semiconductor has become an important topic for science and applications. The family of transition-metal dichalcogenides (TMDCs) exists in bulk form as stacks of multilayers crystallized in a lattice with strong covalent bonds within a layer and piled up by weak van der waals attraction between interlayers. TMDCs are materials composed by the formula MX₂, where M is a transition metal element and X is a chalcogen, to form layered structures of the form X-M-X, the two chalcogen atom layers is separated by a plan of metal atoms. Recently, MoS₂ has attracted a lot of studying interest due to its unique physical properties and applications [1]. In this paper, single crystal MoS₂ and Fe-doped MoS₂ were grown by chemical vapor transport (CVT) method using iodine as a transporting agent. The intentional doping concentration of iron is 0.5%. The temperature gradient is controlled from 1050 to 935 °C to provide an optimal diffusion gradient for crystal growth. The growing period is set to be 720 h. After that the layered crystals are performed and shown in Fig. 1. Furthermore, the optical properties are studied by reflectance (R) and piezoreflectance (PzR) spectra at different temperatures between 20 and 300 K. Using photoconductivity measurements, their optical responses and carrier life time have been studied. Hall measurements were performed to study the carrier concentration and mobility. On the other hand, the electrical conductivity were measured at different temperatures ranging from 20 to 300 K. From the experimental results, the doping effect of iron and the activation energies are determined.

2. Results and discussion
The samples of MoS₂ and Fe-doped MoS₂ are presented in Fig. 1. It can be observed that the samples have flat surface and layered structure. Although, the samples are stacked up by many layers when they were grown. It is easy to be separated into thin specimen with smooth surface. Fig. 2 shows the reflectance spectra of MoS₂ and Fe-doped MoS₂ taken at temperature range between 20 and 300 K. Three main resonance features are presented in each spectrum. At 300 K the first peak locates at around 1.39 eV indicated as I feature, the second one indicated as A feature at 1.83 eV and third one indicated as B feature at 2.02 eV. The I feature is an indirect band gap transition. The values of features A and B are a little lower than that observed in the absorption peaks and PL peaks of atomically thin MoS₂ samples [2]. These two features arise from direct band gap transitions between the maxima of split valance bands (v1, and v2) and the minimum of the conduction band (c1). The splitting comes from the combined effect of the interlayer coupling and spinorbit coupling. They are shifted to 1.91 and 2.11 eV, respectively at 20 K. In the reflectance spectra of Fe -doped MoS₂, the two direct band gap transitions are very close to that of MoS₂. Thus, we know that the crystal structure has no obvious change due to dopan atoms. In addition, we also observed the indirect band gap at 1.39 eV.

In figure 3 the PzR spectra of MoS₂ and Fe-doped MoS₂ are present in different temperatures ranging from 20 to 300 K. The primary two direct gap and one indirect gap are observed at the photon energies corresponding to that observed in reflectance spectra. Furthermore, at low temperatures a small feature located on the right side of A feature has been observed. This feature has also observed in MoS₂ PzR spectra. This transition did not observed in one-layered MoS₂ absorption or PL measurements. We believe that it could result from the interlayer interaction.

In figure 4 the solid-triangle lines and solid-square lines are least-square fits of Lorentzian line-shape function to summarize the temperature dependent direct band gap transitions of A and B. The temperature dependence of the broadening parameters of A and B transitions will be given by fits fit to varshni equation [3] and the experical expression proposed by O’Donnel and Chen [4].

About the electric properties, we did the temperature dependent conductivity measurements. The results are presented in Fig. 5. The conductivity of undoped MoS₂ is obviously higher than that of Fe-doped. We believe that this reult leads to the deep trapping centers resulting from the Fe doping. The activation energy can be extracted from the temperature dependence of conductivity using the equation given by [5].

\[ \sigma = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \] (1),

where \(\Delta E\) is the activation energy for conduction, \(\sigma_0\) and is a pre-exponential factor. The inset in Fig. 5 present the enlarged Arrhenius plot where the straight solid lines are the fits with Eq. (1). From the slopes of these straight lines, the activation energies for MoS₂ and Fe-doped MoS₂ are obtained to be 80 and 133 meV, respectively.

The photoconductivity spectra are presented in Fig. 6 at 14 K. It is found that the absorption edge starts at around
1.45 eV and a sharp absorption happening at 1.93 eV. These results demonstrate that the A and B features observed in reflectance and piezorelectance spectra come from direct band gap transitions.

Fig. 1 Photos of MoS$_2$ (left) and Fe-doped MoS$_2$ (right).

Fig. 2 Reflectivity spectra of MoS$_2$ and Fe-doped MoS$_2$ at different temperatures.

Fig. 3 PzR spectra of MoS$_2$ and Fe-doped MoS$_2$ at different temperatures.

Fig. 4 Temperature dependent excitonic transition energies of MoS$_2$ and Fe-doped MoS$_2$.

Fig. 5 Conductivity spectra of MoS$_2$ and Fe-doped MoS$_2$ at different temperatures.

Fig. 6 Photoconductivity spectra of MoS$_2$ and Fe-doped MoS$_2$ at different frequencies.

Fig. 7 (a) Hall mobility of MoS$_2$ and Fe-doped MoS$_2$ at different temperature. (b) Carrier concentration of MoS$_2$ and Fe-doped MoS$_2$ at different temperatures.

3. Conclusions
We have grown MoS$_2$ and Fe-doped MoS$_2$ layered semiconductors and observed their indirect absorption edge I and direct absorption edges A and B by reflectance, PzR and PC spectra. From the optical spectra of the undoped and Fe-doped MoS$_2$, the indirect and the two direct band gap transitions are very close. Thus, we know that the crystal structure has no obvious change due to dopant atoms. We also present the doping effect in electrical properities by temperature dependence of resistance and Hall measurements. The doping atoms induce deep level trapping centers and increase the resistance and the activation energy.

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References