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Optical Characterization of PbI_2 Crystals Grown by Chemical Vapor Transport

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Abstract

This paper presents the growth and optical properties of lead iodide (PbI_2), which was grown by chemical vapor transport (CVT) method. The composition has been checked by energy-dispersive X-ray spectroscopy (EDS), the crystal structure has been verified by X-Ray diffraction (XRD) and the surface morphology has been examined by scanning electron microscope (SEM). We have performed absorption and photoluminescence (PL) measurements at the temperature range between 20 and 300 K. The band gap energies of PbI_2 are found at 2.36 and 2.507 eV at 300 and 20K, respectively, which are extracted from the temperature-dependent absorption spectra. The Direct band gap energy at 2.42 eV was verified by PL measurement at room temperature. On measuring the few-layer PbI_2 PL spectrum, we found that the band gap energy shifts toward high energy when the thickness of PbI_2 decreases. Moreover, we measure the temperature-dependent photoconductivity (PC) spectra of PbI_2 in the wavelength between 400 and 650 nm at a bias voltage of 5 V, and the temperature changes from 300 to 20K. The PC peak shifts from 520 to 490 nm as the temperature decreases from 300 to 20 K.

1. Introduction

In recent years, layer-structured semiconductors, such as graphene and transition-metal dichalcogenides (TMDCs), have attracted extensive research attention due to their remarkable characteristics such as mechanical flexibility, suitable band gap and high mobility [1]. PbI_2 is composed of covalently bonded I-Pb-I layer structure with a weak van der Waals forces existing between its neighbor layers, which has also attracted much attention due to the optical and electrical properties. PbI_2 is a wide band gap semiconductor with band gap energy at 2.36 eV at 300 K. It has been studied in the applications of solar cells, nuclear radiation detector, X-ray detector and other optoelectronic devices [2].

There are several kinds of method to grow PbI_2 crystals, such as chemical vapor deposition (CVD), chemical vapor transport (CVT), and physical vapor deposition (PVD). In this study, we grow PbI_2 crystals by using CVT method. In our synthesis, high purity lead and iodide elements were sealed into a quartz ampoule in a high vacuum condition. Then putting the ampoule into a two zone furnace and heating the ampoule at 750°C on the high temperature zone and 650°C on the low temperature zone for 14 days.

2. Results and discussions

Figure 1(a) shows the XRD pattern of PbI_2 crystals. Four strong and sharp diffraction peaks represent the (001), (002), (003), and (004) Miller planes indicating the as-grown PbI_2 is single crystal with two-dimensional sheets. The SEM image of PbI_2 flakes and energy-dispersive X-ray spectroscopy (EDS) result is shown in Figure 1(b and c). As shown in the SEM and EDS results, the smooth surface of PbI_2 with obvious layer structures and uniform distribution of lead and iodide elements indicate the good quality of PbI_2 crystals.

To probe the optical and electric properties of PbI_2, we measure the current-voltage (I-V) curves under the illumination of solar simulator (100 $mWcm^{-2}$) and dark conditions. As shown in Figure 2(a), the current is 3.3 and 0.3 nA at a bias voltage of 5V for the illuminated and dark conditions, respectively. It means about ten times increased currents has been observed under illumination. Figure 2(b) shows the temperature-dependent photoconductivity spectra of PbI_2 measured in the wavelength between 400 and 650 nm. The photocurrent reaches the maximum values at the wavelength of 520 nm at 300 K [3], and the peak shifts to 494 nm at 20K. The temperature dependence of the band gap energy is shown in Figure 2(c) with a linear line. In order to verify the response/recovery time of PbI_2, we measure the rise time and decay time by using a 405 nm laser operated at 100 Hz. As shown in Figure 2(d), the rise time (from 10% to 90% of maximum photocurrent) and decay time (from 90% to 10% of maximum photocurrent) of PbI_2 is estimated to be 700 and 500 us, respectively.

Figure 3(a-b) show the temperature-dependent absorption spectroscopy of PbI_2 flakes. According to the Kubelka-Nunk (K-M) conversion (as indicated in eq. (1)) of UV-vis absorption spectrum, the band gap energies at various temperatures can be verified. As shown in Figure 3(a) the band gap is 2.36 and 2.507 eV at 300 and 50 K, respectively [4]. The temperature dependence of the band gap energies is indicated in Figure 3(c) with a linear line. In order to investigate the band gap energies of bulk and few layer PbI_2, we fabricated few-layer PbI_2 flakes by mechanical exfoliation process from the bulk crystals [5]. Figure 3(d) shows the result of thickness-dependent photoluminescence (PL) for PbI_2 flakes excited by a 488 nm laser at room temperature. The bulk PbI_2 PL peak is located at 512 nm (≈ 2.42 eV), the peak intensity of PL becomes weak as the thickness decreasing. The thinnest PbI_2 flake emission peak becomes very weak at 502 nm (≈ 2.47eV) [6]. This result implies that the bulk PbI_2 is a direct band gap material and the thin layer PbI_2 may become an indirect band gap material. Moreover, for the PbI_2 bulk there is an emission peak at 522 nm which refers to the band gap observed in the absorption spectrum.

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right) \tag{1}$$

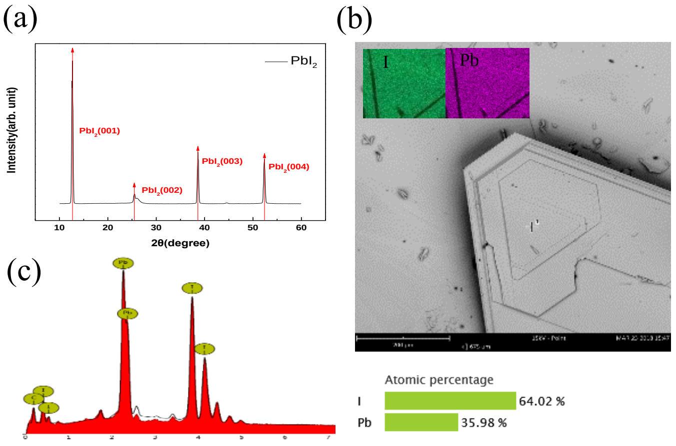

Figure 1 (a) shows the XRD pattern of the as-prepared PbI_2 flakes. (b) and (c) are SEM image and EDS spectrum of PbI_2 crystals.

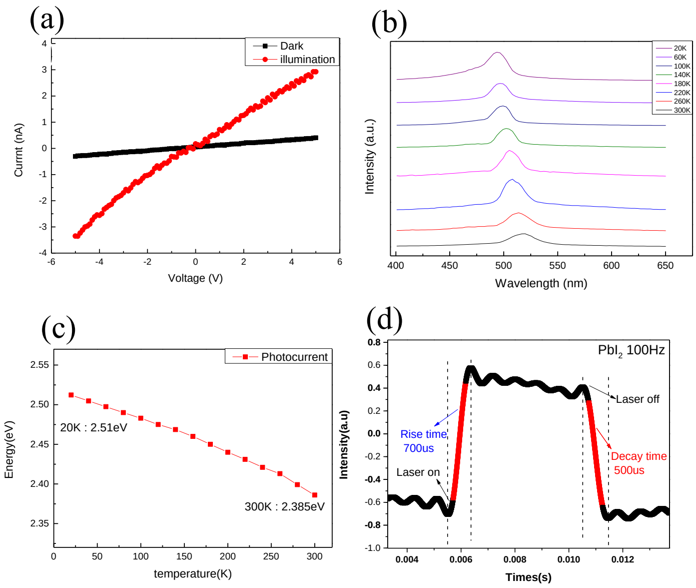

Figure 2 (a) I-V curves of PbI_2 flake with and without the illumination of solar simulator, and (b) Temperature-dependent photoconductivity spectrum at a bias of 5V. (c) The maximum of Photocurrent at the different temperature of 20K to 300K. (d) Response/recovery time of PbI_2 under a 405 nm laser.

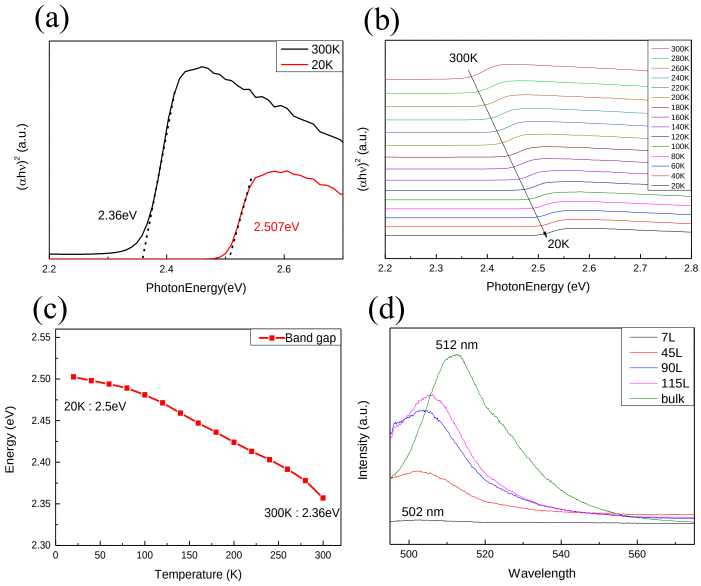

Figure 3 (a-c) shows the temperature-dependent PbI_2 absorption spectrum, and the band gap is considered to be 2.36eV to 2.5eV at the temperature of 300K to 20K. (d) PL spectrum excited by 488 nm laser at room temperature.

3. Conclusions

In conclusion, we have grown PbI_2 single crystals by using CVT method. The results of XRD, SEM, and EDS show the PbI_2 crystals have good crystalline quality. Also, we conducted a series of measurements including the I-V measurement with and without illumination, temperature-dependent photocurrent and photocurrent rise/decay curves to study the optical properties. There is a high response at the wavelength of 520 nm and the rise time and decay time are 700 and 500 us, respectively. Moreover, we measure the temperature-dependent absorption spectrum and PL measurements. We verified the band gap energy at 2.36 eV at 300 K and it increases to 2.5 eV at 20K. Furthermore, the PbI_2 bulk is a direct band material and becomes an indirect band material when the thickness of PbI_2 decreases to a few layers. These results strongly indicate that PbI_2 has the potential of becoming optoelectronic devices.

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