

# Annealing temperature effects on optical and photoelectric properties of sputtered indium-doped PbSe thin films

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Abstract Indium-doped PbSe thin films deposited on Si(111) by magnetron sputtering were annealed at different temperatures and characterized using the X-ray diffraction, Fourier transform infrared spectroscopy and physical properties measurement system. After the annealing treatment, an oxidation layer containing PbSe, PbO, SeO<sub>2</sub> and In<sub>2</sub>Se<sub>3</sub> is formed on the film surface. The optical band gap of the annealed samples increases to a maximum of 0.276 eV at 150 °C, and then decreases with the annealing temperature due to the position shift of the valence band maximum and the conduction band minimum. The photoelectric sensitivity of the annealed indium-doped PbSe thin films increases by 1.5-2 times, compared with the untreated samples. Moreover, the average value of the resistance change rate increases almost linearly with the annealing temperature due to the concentration of the dark charge carriers increases with the annealing temperature confirmed by the Hall effect measurements.

# 1 Introduction

Lead selenide (PbSe) thin films have been widely used as infrared detectors due to their high photoelectric sensitivity and stability at room temperature, when compared with other lead chalcogenides (PbS, PbTe, etc.) [1–7].

Generally, the photoelectric properties of the PbSe thin films are mainly affected by the film composition and structure, which can be modified by the doping elements and the preparation process (including post-treatment), respectively [8-11]. In the literature, the band structure, conductive mechanism, charge carrier concentration and mobility of the PbSe thin films can be modified by many doping elements, such as In, S, Sn, Te, etc. [12–16], which consequently improve the film photoelectric properties. Among these elements, In element shows unique effects, which can create deep energy states in the PbSe forbidden band, and consequently lead to the slow relaxation of the PbSe electronic system [1, 17, 18]. Besides, the Fermi level of the PbSe thin films can be stabilized by the doped In atoms, which is beneficial to obtain stable n-type (or p type) semiconductor materials. Within this research, the indium-doped PbSe thin films were chosen to be studied due to their potential applications in high quality infrared detectors.

Currently, the PbSe thin films can be prepared by many chemical, electrochemical and physical methods, such as chemical bath deposition [19], electrochemical deposition [20], thermal evaporation [21] and molecular beam epitaxy [22], etc. Compared with these methods, magnetron sputtering is a competitive way to prepare PbSe thin films due to the lower cost, easier handling and higher quality products. Within this research, the indium-doped PbSe thin films were prepared by the magnetron sputtering. According to the previous research results, the annealing treatment after the preparation is an essential method to improve the photoelectric properties of the PbSe thin films [23, 24]. However, the effects of the annealing treatment parameters, especially the annealing temperature, on the properties of the sputtered indium-doped PbSe thin films have not been studied in detail yet. Besides, the reasons related to

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the high photoelectric sensitivity are complicated, and it is beneficial to determine the dominating ones.

In this paper, the indium-doped PbSe thin films were prepared using magnetron sputtering and the obtained samples were annealed at 100, 150, 200, 250 and 300 °C five different temperatures, respectively. The effects of the annealing temperature on the photoelectric properties of the indium-doped PbSe thin films were studied using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and physical properties measurement system (PPMS). The results show that the photoelectric sensitivity of the sputtered indium-doped PbSe thin films increases almost linearly with the annealing temperature due to the dark charge carrier concentration decreases with the annealing temperature.

## 2 Experimental

#### 2.1 Deposition

The indium-doped PbSe thin films were deposited on the polished Si(111) substrates by using the PM500-S sputtering system equipped with the MF-5 K medium frequency sputtering power source. The PbSeIn  $(n_{Pb}:n_{Se}:n_{In} = 47.5:47.5:5)$  ternary alloy targets with the purity of 99.99 % were used. During the deposition process, the substrate temperature was kept at 250 °C for improving the crystallinity of the sputtered thin films. Besides, the deposition time was 60 min, and the sputtering power was 150 W.

#### 2.2 Annealing

The GSL-1800X vacuum tube furnace (Shenyang Kejing Auto-instrument Co., Ltd) was used to conduct the annealing treatments. Within this research, five different annealing treatments were performed based on the chosen temperature range: 25-100, 25-150, 25-200, 25-250 and 25–300 °C, respectively. During the annealing process, the temperature increased from 25 to 100, 150, 200, 250 and 300 °C with the rate of 5 °C/min, respectively, and then immediately decreased to 25 °C with the cooling rate of 5 °C/min, i.e., there is no heat preservation phase. The total time for these five annealing treatments is 30, 50, 70, 90 and 110 min, respectively. Moreover, during the whole process, the furnace tube was filled by oxygen with the flux of 40 ml min<sup>-1</sup>. In order to study the electrical properties, the resistances of the indium-doped PbSe thin films were real-timely measured during the whole annealing process using the Fluke 8808A digital multimeter.

#### 2.3 Characterization

The crystal structure of the sputtered indium-doped PbSe thin films was studied using the anode diffractometer (Dmax-RB 12 KW, Rigaku) with the Cu Ka radiation source,  $\lambda = 1.5406$  Å, and  $10^{\circ}$ – $100^{\circ}$  2 $\theta$  scan range with 8°/min scanning rate. In order to study the difference of the chemical states on and beneath the film surface, the XPS tests were performed using the AXIS ULTRA<sup>DLD</sup> (SHI-MADZU) X-ray photoelectron spectrometer after the film surface was etched for 120 s by  $Ar^+$  with the etching energy of 3000 eV. The differences between the dark and light resistance of the thin films were obtained using the Fluke 8808A digital multi-meter in a dark chamber equipped with a 275 W infrared light. The light resistance was recorded for 300 s in 20 s steps after the dark resistance remained invariable, and the dark resistance was recorded for the same time duration and steps after the illumination. The infrared transmittance spectra of the sputtered indium-doped PbSe thin films were obtained by the Excalibur 3100 Fourier transform infrared spectrometer (FTIR) from 7000 to 400 cm<sup>-1</sup> range with 2 cm<sup>-1</sup> resolution at room temperature. The Hall effect measurements were conducted just for the annealed indium-doped PbSe thin films using the PPMS with 5000 Gs magnetic field intensity, 20 µA current and 10 V voltage.

### **3** Results and discussion

#### 3.1 Electrical properties

Five annealing treatment temperature ranges (25 to 100, 150, 200, 250 and 300 °C, respectively) were chosen based on the annealing temperature effects on the PbSe thin films crystal structure [25]. The film resistance (or conductance) variation with the temperature is an important factor to estimate the electrical properties of the sputtered indium-doped PbSe thin films, which were real-timely measured during the annealing treatment process, as shown in Fig. 1. Here just the results for the 300 °C treated sample was shown, since the other four samples exhibited similar results, and just the temperature range was different.

The resistivity of the indium-doped PbSe thin film decreases from 0.89  $\Omega$  cm to 0.083  $\Omega$  cm as the temperature increases from room temperature to 300 °C, indicating typical characteristics of the extrinsic (impurity) semiconductor materials. It is interesting to note that the resistivity reaches a small maximum at about 105 °C, which is attributed to the charge carriers mobility decreases at this temperature, while the concentration remains constant due to the complete ionization of the impurities [1].



Fig. 1 Variation of the indium-doped PbSe thin films resistivity as the annealing temperature increases from room temperature to 300 °C. The *inset* shows the variation of the resistance difference ( $\Delta R$ ) with the annealing temperature

Generally, the resistance of the sputtered indium-doped PbSe thin films reaches a new value when the temperature is reduced to room temperature due to the irreversible microstructure changes. The difference between the new and the old resistance is an important parameter to estimate the stability of the thin films, which is represented as:

$$\Delta R = \frac{R_{new} - R_{old}}{R_{old}} \times 100\%$$
<sup>(1)</sup>

where  $R_{new}$  and  $R_{old}$  represent the indium-doped PbSe thin films resistance obtained after and before the annealing treatment. Both of these two values were collected at room temperature, and the results are shown in the Fig. 1 inset. When the annealing temperature is lower than 200 °C, the  $\Delta R$  values of the indium-doped PbSe thin films are similar, about 27 %. However, when the annealing temperature is higher than 250 °C, the  $\Delta R$  value increases dramatically, about 83 % at 300 °C, indicating that the microstructure of the indium-doped PbSe thin films changes within this high temperature range, which is confirmed by the XRD results (shown in Sect. 3.2).

#### 3.2 Surface chemistry and structure

The photoelectric properties of the sputtered indium-doped PbSe thin films are mainly affected by the film composition (especially the surface chemistry) and structure (especially the crystal size and the lattice constant). Generally, the surface oxidation layer acts as a passivation layer, which can inhibit the surface recombination of the charge carriers, and consequently improves the photoelectric sensitivity of the PbSe thin films. While the crystal size and the lattice constant can affect the band structure of the indium-doped PbSe thin films, which also consequently change the photoelectric properties of the thin films [26]. Within this research, the XPS and XRD measurements were performed to study the elements chemical states and the crystal structure of the sputtered indium-doped PbSe thin films, as shown in Figs. 2 and 3.

The XPS results of the indium-doped PbSe thin films treated at 100, 150, 200 and 250  $^\circ$ C not shown in this



Fig. 2 XPS spectra of the sputtered indium-doped PbSe thin films: a Pb element; b Se element; c In element

(a)

FLOTU

(b)<sub>2400</sub>





Fig. 3 Morphology and structure of the indium-doped PbSe thin films: a FE-SEM images; b XRD diffraction patterns. The *inset* in (a) shows the cross-section morphology of the sputtered thin film

paper, are similar to the sample treated at 300 °C. The Pb element has just PbSe one chemical state with the binding energy of 137.67 eV (Pb4f7/2) and 142.57 eV (Pb4f5/2) in the untreated PbSe thin films, while another PbO chemical state with the binding energy of 138.52 eV (Pb4 $f_{7/2}$ ) and 142.97 eV (Pb4f<sub>5/2</sub>) was created during the annealing treatment, as seen in Fig. 2a. The Se element has a similar situation to the Pb element, i.e., just PbSe one chemical state with the binding energy of 53.52 eV (Se3d<sub>5/2</sub>) and 54.37 eV (Se3d<sub>3/2</sub>) exists in the untreated PbSe thin films, while  $SeO_2$  with the binding energy of 58.67 eV was detected after the annealing treatment, as seen in Fig. 2b. The In element has just In<sub>2</sub>Se<sub>3</sub> one chemical state with the binding energy of 444.52 eV (In3d<sub>5/2</sub>) and 452.12 eV  $(In3d_{3/2})$  before and after the annealing treatment, as seen in Fig. 2c. Apparently, an oxidation layer contained PbSe, PbO, SeO<sub>2</sub> and In<sub>2</sub>Se<sub>3</sub> was formed after the annealing treatment.

According to the FE-SEM images in Fig. 3a, the surface of the sputtered indium-doped PbSe thin films is quite smooth, and there are no cracks, holes and inclusions. The stripes shown in the cross-section image originate from the cutting process before the FE-SEM tests, and they are not the crystal defects. In addition, the thickness of the sputtered indium-doped PbSe thin film is about 370 nm when the deposition time is 60 min.

The sputtered indium-doped PbSe thin films have the rock salt crystal structure, and the diffraction peaks at  $29^{\circ}$ ,  $60^{\circ}$  and  $97^{\circ}$  are attributed to PbSe (200), (400) and (600) reflections, respectively, according to the XRD patterns in Fig. 3b. In addition, no peaks belonging to other phases (such as PbO, SeO<sub>2</sub> and In<sub>2</sub>Se<sub>3</sub>) are observed, which may be attributed to their low content or poor crystallinity.

The average crystal size, D, was estimated by the Debye–Scherrer equation [27]:

$$D = \frac{0.9\lambda}{B \cdot \cos\theta} \tag{2}$$

where  $\lambda$  denotes the wavelength of the X-ray radiation ( $\lambda = 1.5406$  Å), *B* represents the full width at half maximum (FWHM) and  $\theta$  is angle of the diffraction peaks.

The lattice constant, *a*, for the cubic structure was calculated as:

$$a = d\sqrt{h^2 + k^2 + l^2} \tag{3}$$

where *d* denotes the distance between the atomic lattice planes, and (*hkl*) are the Miller indices. It is interesting to note that the annealing treatment can dramatically change the average crystal size and lattice constant of the indium-doped PbSe thin films, as seen in Fig. 3 and Table 1. Compared with the untreated samples, the average crystal size of the annealed samples is much larger, and a maximum of 85.1 nm is obtained at 200 °C. This may be attributed to the recovery and recrystallization process in the indium-doped PbSe thin films [25]. When the annealing temperature is less than 200 °C, the integration of the grain boundaries leads to the crystal size growth, while the recrystallization proceed at higher temperature (>250 °C) can refine the crystal structure of the indium-doped PbSe thin films and create smaller crystal grains.

## 3.3 Optical properties

The FT-IR transmittance spectra of the sputtered indiumdoped PbSe thin films were recorded in 7000–400 cm<sup>-1</sup> (~1.4–25  $\mu$ m) wavenumber range at room temperature, as shown in Fig. 4a. The absorption edge of the sputtered indium-doped PbSe thin films is located between 2280 and 2670 cm<sup>-1</sup>. Moreover, compared with the untreated samples, the absorption edge of the annealed samples shows a clearly red shift. This indicates that the annealing treatment can dramatically change the band structure of the indiumdoped PbSe thin films. **Table 1** Average crystal size (*D*), lattice constant (*a*), experimental ( $E_g$ ) and calculated ( $E'_g$ ) band gap values of the indium-doped PbSe thin films

Sample	Sensitizing temperature, °C	D, nm	<i>a</i> , Å	$E_g$ , eV	$E'_g$ , eV
1	Untreated	28.3	6.1298	0.283	_
2	100	79	6.1482	0.265	0.0748
3	150	80.6	6.1453	0.276	0.0759
4	200	85.1	6.1462	0.274	0.0755
5	250	62.9	6.1492	0.265	0.0743
6	300	59.8	6.1515	0.261	0.0726

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Fig. 4 Optical properties of the sputtered indium-doped PbSe thin films: **a** FT-IR transmittance spectra; **b** relationship between the incident beam energy hv and  $(\alpha hv)^2$ . The *inset* in **b** shows the enlarged view of the band gap values

The photon-generated charge carriers obey the direct transition in the PbSe materials, so the optical band gap,  $E_g$ , of the sputtered indium-doped PbSe thin films can be derived from their transmittance spectra using the Tauc relation [28]:

$$(\alpha hv)^2 = B(hv - E_g) \tag{4}$$

where  $\alpha$  represents the absorption coefficient, which can be calculated from the transmittance results, *h* is the Planck's constant, *v* is the incident beam frequency and *B* is a constant. As shown in Fig. 4b and Table 1, the  $E_g$  value of the untreated sample is larger than the annealed samples, which may be attributed to the remarkable quantum confinement effect in the untreated thin films or the impurity levels created by the oxides and doped indium elements in the annealed samples [29]. Moreover, the  $E_g$  value of the annealed samples increases to a maximum of 0.276 eV when the annealing temperature is 150 °C, and then decreases with the temperature, which is attributed to the structure (especially the lattice constant) changes with the annealing temperature confirmed by the theoretical calculation shown in Fig. 5.

Within this research, the band structure and density of state (DOS) of the annealed indium-doped PbSe thin films were calculated by the first principles to further verify the



Fig. 5 Variation of the experimental  $(E_g)$  and calculated  $(E'_g)$  band gaps of the annealed indium-doped PbSe thin films with the annealing temperature

 $E_g$  variation with the annealing temperature. Since the film composition had almost no change due to the low annealing temperature confirmed by the XPS and XRD results. Just the film structure (mainly the lattice constant) was chosen as the band gap influencing factor to be studied in this paper. Five Pb7Se7InO supercells with the lattice constants listed in Table 1 were created and simulated based on the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional formalism [30].

The calculated band structure of the five annealed indium-doped PbSe thin films are similar, and just the result of the 100 °C annealed sample is shown in Fig. 6a. Both the valence band maximum and the conduction band minimum of the indium-doped PbSe materials are located at M (0.5, 0.5, 0.0) symmetry points, indicating the direct transition of the charge carriers near the absorption edge. Moreover, the calculated band gap values,  $E'_g$ , of these five samples vary with the annealing temperature, and the trend is similar to the experimental results, as shown in Table 1 and Fig. 5. The deviation between the calculated and experimental band gap values is attributed to the underestimation effect of the GGA + PBE functional formalism, however, the varying trend is reliable [31].

As shown in Fig. 6b, the DOS near the valence band maximum shifts to the lower energy position when the annealing temperature increases from 100 to 150 °C, and then shifts almost linearly to higher energy position with the annealing temperature. Conversely, the DOS near the conduction band minimum shifts to the higher energy position when the annealing temperature increases from 100 to 150 °C, and then shifts almost linearly to lower energy position with the annealing temperature. Interestingly enough, the distance variations between the valence band maximum and the conduction band minimum with the annealing temperature are in agreement with the calculated band gap variations. This indicates that changing the annealing temperature can modify the micro-structure (mainly lattice constant) of the indium-doped PbSe thin films, leading to the position shift of the valence band maximum and the conduction band minimum, which consequently affect the optical and photoelectric properties of the thin films.

> (a) 5.0 2.5 2.5 -2.5 -5.0 ZA M G Z R X G

**Fig. 6** Calculation results of the annealed indium-doped PbSe thin films: **a** band structure; **b** DOS. Z (0, 0, 0.5), A (0.5, 0.5, 0.5), M (0.5, 0.5, 0.0), G (0, 0, 0), R (0.0, 0.5, 0.5) and X (0.0, 0.5, 0.0) shown in

Generally, the concentration of the photo-generated carriers in the extrinsic semiconductors is mainly affected by the band structure and the scattering mechanism, by changing the amount and lifetime of the photo-generated carriers [1]. The surface states of the indium-doped PbSe thin films treated at different temperatures are similar to each other (shown in Sect. 3.2). Besides, the same composition of the indium-doped PbSe thin films leads to similar scattering effects to the charge carriers, and consequently the concentration of the photo-generated carriers is dominated by the band structure of the indium-doped PbSe thin films. The concentration of the photo-generated carriers roughly decreases as the optical band gap increases [1]. Hence, the concentration of the photo-generated carriers in the sputtered indium-doped PbSe thin films treated at different temperatures decreases to a minimum and then increases as the annealing temperature increases from 100 to 300 °C, according to Fig. 5 and Table 1.

### 3.4 Photoelectric properties

Testing the difference between the dark and light resistance is a simple and effective way to evaluate the photoelectric sensitivity of the infrared detector materials [32].

As shown in Fig. 7a inset, the resistance of the thin films approximately remains constant in the dark (0–300 s), and then decreases dramatically when the light turns on (300–600 s). Finally it slowly returns to the original value when the light turns off (600–900 s). In fact, the dark resistance can't return to the original value in 300 s duration, indicating the time-consuming recombination process of the charge carriers in the polycrystalline indium-doped PbSe thin films [18].

As mentioned above, the difference between the dark and light resistance is useful to evaluate the photoelectric





(a) 70 60 50 40 % 30 ≦R, 3x10 300 °C C 20 250 °C stace, 2x10 200 °C 10 150 °C 100 °C 600 90 0 Time. s Untreated 0 50 100 150 200 250 300 Illumination time, s

**Fig. 7** Photoelectric properties of the sputtered indium-doped PbSe thin films: **a** resistance change rate  $(\Delta \tilde{R}_t)$  under illumination as a function of the illumination time; **b** effect of the annealing

sensitivity of the sputtered indium-doped PbSe thin films. Within this research, the resistance change rate,  $\Delta \tilde{R}_t$ , at certain illumination time, *t*, was calculated using the following equation:

$$\Delta \tilde{R}_t = \frac{\bar{R}_D - R_{L,t}}{\bar{R}_D} \times 100\%$$
(5)

where  $\bar{R}_D$  represents the average value of the dark resistance recorded before the illumination treatment and  $R_{L,t}$  is the value of the light resistance at a certain illumination time *t*, as shown in Fig. 7a. Compared with the untreated samples ( $\Delta \tilde{R}_t \approx 32\%$ ), the photoelectric sensitivity of the annealed indium-doped PbSe thin films ( $\Delta \tilde{R}_t \approx 49-65\%$ ) increases by 1.5–2 times. It is interesting to note that the average value of the resistance change rate during the 300 s illumination, which was calculated as  $\overline{\Delta \tilde{R}} = \frac{\Delta \tilde{R}_0 + \Delta \tilde{R}_{20} + \Delta \tilde{R}_{40} + \cdots + \Delta \tilde{R}_{300}}{16}$ , increases almost linearly with the annealing temperature, as seen in Fig. 7b. This indicates that increasing the annealing temperature is an effective way to improve the photoelectric sensitivity of the sputtered indium-doped PbSe thin films in 100–300 °C range based on the current research.

Generally, the electrical resistance, *R*, of the sputtered indium-doped PbSe thin films can roughly be calculated as  $R = \rho \frac{L}{S}$ , where  $\rho$  is the resistivity, *L* represents the length between the testing electrodes and *S* denotes the sectional area of the thin film samples. Hence, according to Eq. (5),  $\Delta \tilde{R}_t$  can be represented as follows:

$$\Delta \tilde{R}_t = \frac{\rho_D \frac{L}{S} - \rho_{L,t} \frac{L}{S}}{\rho_D \frac{L}{S}} \times 100\%$$
(6)

where  $\rho_D$  and  $\rho_{L,t}$  represent the resistivity of the sputtered



temperature on the average resistance change rate  $(\Delta \tilde{R})$ . The *inset* in (a) shows the variation of the resistance in the dark and under certain illumination

indium-doped PbSe samples in the dark and under illumination *t*, respectively. Moreover,  $\rho_D = 1/n_D e \mu_D$ ,  $\rho_{L,t} = 1/n_{L,t} e \mu_{L,t}$ , where  $n_D(n_{L,t})$  and  $\mu_D(\mu_{L,t})$  represent the concentration and the mobility of the charge carriers in the dark (under illumination *t*), respectively, while *e* denotes the elementary charge. Thus, Eq. (6) can be represented as:

$$\Delta \tilde{R}_{t} = \frac{\frac{1}{n_{D}e\mu_{D}} - \frac{1}{n_{L,e}\mu_{L,t}}}{\frac{1}{n_{D}e\mu_{D}}} \times 100\%$$
(7)

For certain sputtered indium-doped PbSe samples, the mobility of the charge carriers is hardly varied before and during the illumination treatment if the variations of the structure and composition in the PbSe thin films are neglected, i.e.,  $\mu_D \approx \mu_{L,t}$ . Thus,  $\Delta \tilde{R}_t$  can simply be represented as:

$$\Delta \tilde{R}_t = \left(1 - \frac{n_D}{n_{L,t}}\right) \times 100\%$$
(8)

Apparently, the  $\Delta \hat{R}_t$  value is mainly affected by the ratio  $n_D/n_{L,t}$ , i.e., the ratio between the concentration of the charge carriers in the dark and under illumination *t*. The lower carrier concentration in the dark and higher carrier concentration under illumination are required to obtain the sputtered indium-doped PbSe thin films with higher photoelectric sensitivity.

In order to clarify the dominating factor for the high photoelectric sensitivity of the sputtered indium-doped PbSe thin films, the Hall effect measurements were conducted just for the annealed samples, as shown in Fig. 8.

According to the positive Hall coefficients of the sputtered indium-doped PbSe thin films, p type conductive mechanism is obtained within these films, i.e., the electrons and holes are the minority and majority carriers, respectively. As shown in Fig. 8, the charge carriers mobility increases to a maximum of about  $4.8 \text{ cm}^2 \cdot \text{V}^{-1} \text{s}^{-1}$ , and then decreases with the annealing temperature. It is interesting to note that the mobility of the charge carriers in the sputtered indium-doped PbSe thin films is much lower than that in the single crystal PbSe material, which is attributed to the strong scattering effect of the grain boundaries and the surface to the charge carriers [26, 33], confirmed by the XRD and XPS results.

The charge carriers concentration (in the dark) in the sputtered indium-doped PbSe thin films decreases almost linearly from  $3.4 \times 10^{18}$  to  $0.75 \times 10^{18}$  cm<sup>-3</sup> as the annealing temperature increases from 100 to 300 °C, which changes inversely with the  $\overline{\Delta R}$  value during the 300 s illumination. Combined with Fig. 7b, it is easy to conclude that the photoelectric sensitivity of the sputtered indium-doped PbSe thin films treated at different temperatures is dominated by the charge carriers concentration in the dark, instead of the mobility, which is in agreement with the above discussions of Eqs. (7) and (8).

Generally, the concentration of the photo-generated charge carriers is mainly affected by the band structure, especially the band gap of the semiconductor materials [1]. If other effects are neglected, the larger of the band gap, the fewer of the photo-generated carriers. According to the optical band gap values of the sputtered indium-doped PbSe thin films shown in Fig. 4 and Table 1, the concentration of the photo-generated charge carriers decreases as the annealing temperature increases from 100 to 150 °C, and then increases with the annealing temperature in the range of 200–300 °C. The variation of the photo-generated charge carriers concentration with the annealing temperature is not completely consistent with the variation of the average value of the resistance change rate,  $\overline{\Delta R}$ .



Fig. 8 Hall effect measurement results of the annealed indium-doped PbSe thin films: a charge carriers mobility; b charge carriers concentration

Based on the above results and discussions, the photoelectric sensitivity of the sputtered indium-doped PbSe thin films is mainly affected by the concentration of the charge carriers in the dark and under illumination, and moreover, the concentration of the charge carriers in the dark is the dominating factor.

## 4 Conclusions

Indium-doped PbSe thin films prepared by magnetron sputtering were annealing treated at five different temperature ranges (25 to 100, 150, 200, 250 and 300 °C, respectively), and the effects of the annealing treatment on the optical and photoelectric properties of the as-prepared thin films were studied in detail.

The resistance of the annealing treated samples increases sharply when the annealing temperature is higher than 250 °C due to the recrystallization process. After the annealing treatment, an oxidation layer containing PbSe, PbO, SeO<sub>2</sub> and In<sub>2</sub>Se<sub>3</sub> is formed, which can inhibit the surface recombination of the charge carriers.

The absorption edge of the sputtered indium-doped PbSe thin films is located between 2560 and 2200 cm<sup>-1</sup>, and a clear red shift of the absorption edge for the annealing treated samples is obtained compared with the untreated samples. Moreover, the optical band gap of the annealing treated indium-doped PbSe thin films increases to a maximum of about 0.276 eV at 150 °C, and then roughly decreases with the annealing temperature, which is attributed to the band structure variation, especially the position shift of the valence band maximum and conduction band minimum.

The photoelectric sensitivity of the annealed indiumdoped PbSe thin films increases by 1.5–2 times compared with the untreated samples. Moreover, the average value of the resistance change rate during the 300 s illumination increases almost linearly with the annealing temperature, indicating that increasing the annealing temperature is an effective way to improve the photoelectric sensitivity of the sputtered indium-doped PbSe thin films in 100–300 °C range. The photoelectric sensitivity of the sputtered indium-doped PbSe thin films is mainly affected by the charge carriers concentration in the dark and under illumination, and moreover, the first one is the dominating factor.

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