Photoconductive properties of lead iodide films prepared by electron beam evaporation*

Zhu Xinghua(朱兴华)[1,2,†], Yang Dingyu(杨定宇)[1], Wei Zhaorong(魏昭荣)[1], Sun Hui(孙辉)[1], Wang Zhiguo(王治国)[2], and Zu Xiaotao(祖小涛)[2]

(1 School of Optoelectronic Technology, Chengdu University of Information Technology, Chengdu 610025, China)
(2 Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, China)

Abstract: Lead iodide (PbI_2) films have been prepared by the electron beam evaporation technique, and their photoconductive response to visible light was investigated under different deposition and illumination conditions. It is found that the films' photoconductive response speed increases and the relative sensitivity decreases with the increase of substrate temperature due to the opposite requests for photo-carrier lifetime. Further, appropriately increasing the film's thickness and rising substrate temperature simultaneously can effectively balance the opposite demands. Under optimized conditions of a substrate temperature of 200 ℃, a source–substrate distance of 30 cm and a deposition time of 10 min, the prepared films exhibit the best response properties. In addition, the response to illumination with different wavelengths was also measured, revealing that the decline of response performance with increasing wavelength is due to the lower photon energy of incident light.

Key words: PbI_2 films; photoconductive response performance; deposition conditions
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1. Introduction

PbI_2 is a wide band gap semiconductor ($E_g > 2.3$ eV) with high atomic weight ($Z_{Pb} = 82$, $Z_I = 53$) and a resistivity of about $10^{13}\Omega$·cm and is regarded as one of the most attractive materials for ionizing radiation detectors and X-ray imaging[1,2]. PbI_2 films act as the direct conversion layer of radiation detectors, and the response to radiation photons of different energies is very important for understanding the properties and improving the detection performance. The influence of γ-rays on the electrical properties of the films has been investigated by Dmitriev, and is valuable for studies of the detection of high energy photons[3].

However, the photoconductive response of PbI_2 films to visible light has not been thoroughly studied. Some preferable response properties of the films to visible photons are expected to be useful for photoelectric detectors besides ionizing detection. Meanwhile, the electron–hole pair generation and recombination process in PbI_2 films should be valuable to understand the interaction mechanism of X-ray or γ-ray photons with the films[4,5]. The aim of this work is to analyze the photoconductive characteristics of PbI_2 films that were prepared under different conditions, such as substrate temperature, source–substrate distance and deposition time. Using different representative visible lights generated by approximate monochromatic LED lamps, the photoconductive response of different samples was measured so as to acquire optimized deposition parameters of PbI_2 film with better photoconductive performance.

2. Experimental procedure

The PbI_2 films used in this work were deposited on borosilicate glass substrates by an electron beam evaporation technique. Al electrodes were then deposited on the films by a DC magnetron sputtering method. The substrate was heated by an array of tungsten–halogen lamps and the substrate temperature (T_S) was controlled between room temperature (RT) and 200 ℃. The source–substrate distance (d_{S-S}) was respectively set as 25 cm, 30 cm and 35 cm. As the starting material, PbI_2 powder (purity 99.995%) was placed in a graphite crucible. The evaporation electron beam and the excitation high voltage were fixed at 25 A and 6.5 kV separately. The deposition process was maintained for 10 to 30 min under a background vacuum of 4×10^{-3} Pa. The substrate was held to keep rotating to improve the films' uniformity. The samples were all *in-situ* deposited and measured without a further annealing process.

Before the photoconductivity measurement, the film with Al electrodes was placed into a light-tight vacuum chamber for 2 h. Four LED light sources had been set previously in the chamber, which could be switched in turn to irradiate the film for a period of time. The resistivity was measured using an EST-121 micro ammeter, and a computer was connected as a data processor. The light power of the LED lamps is 0.03 W. Their wavelengths are respectively blue (460–470 nm), green (515–520 nm), yellow (580–585 nm), and red (620–625 nm). The film's test area between the two Al contact electrodes is 10 $\times$ 55 mm^2, as shown in Fig. 1. The photoconductivity was calculated from the tested surface resistivity and the area between the electrodes according to the following formula.

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† Corresponding author. Email: zxh@cuit.edu.cn
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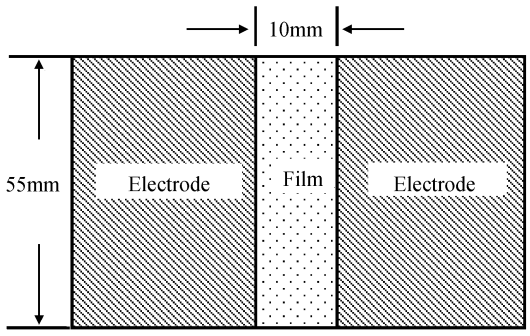

Fig. 1. Schematic diagram of a PbI_2 film with Al electrodes.

$$\sigma = l/wdR, \tag{1}$$

where l = 10 mm is the spacing between the two Al electrodes, w = 55 mm is the width across the film, d is the thickness of the prepared films, and R is the resistivity acquired by ETS-121.

A self-designed procedure for photoconductivity measurement developed in our experiment was employed. When the film was placed into the light-tight chamber, a DC voltage of 50 V was applied to it for 600 s. At the same time, the lamp was turned on to irradiate the film for 300 s and then turned off. The resistivity with a time step of 0.5 s was recorded during the illumination time of 300 s and the following decay time of 300 s. All the test procedures were executed at RT, and the data were recorded and processed automatically.

3. Results and discussion

The dependence of the films'photoconductivity on substrate temperature and illumination time is presented in Fig.2. These samples were deposited under the conditions of d_{S-S} = 30 cm at different T_S (RT, 80 ℃, 120 ℃, 160 ℃, 200 ℃) for 10–30 min. The blue LED lamp (460–470 nm) was used to irradiate the samples. Owing to different substrate temperatures and deposition times, there are some differences in the sample's thickness. From Fig. 2, the photoconductivity sharply increases immediately at the beginning of illumination, and then reaches a saturated value in about 50 s. Once illumination ends at the time of 300 s, the photoconductivity drastically declines and then gently falls towards certain stable dark-conductive values. This so-called tailing phenomenon is probably caused by the common persistent photoconductive effect due to defect trapped carriers[6].

To analyze the influence of substrate temperature on the film's response performance, two important parameters, photoconductive relative sensitivity and relaxation time[7, 8], were calculated. The parameters represent the film's response sensitivity and speed with respect to illumination time and deposition conditions. According to the semiconductor theory, photoconductive relative sensitivity can be expressed as:

$$S = (\sigma_i - \sigma_d)/\sigma_d = \Delta\sigma/\sigma_d, \tag{2}$$

where S is relative sensitivity, σ_i is photoconductivity, and σ_d is dark conductivity. As for the calculation of S, σ_i is taken to be the maximum value σ_S (saturation photoconductivity). Furthermore, at the time of switch on and off, the increase and decrease of photoconductivity should require the relaxation process. The dependences of photoconductivity variation on time during the increase and decrease processes are denoted as follows:

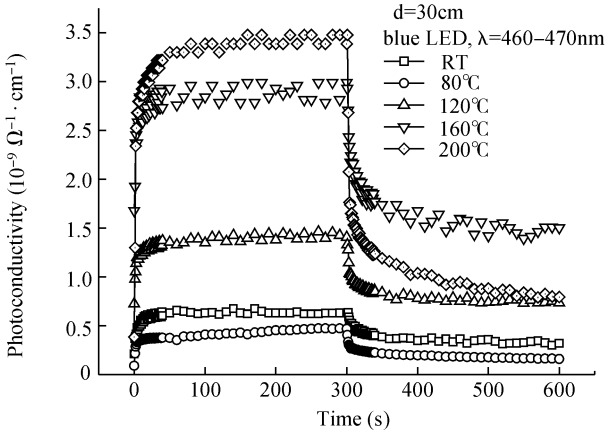

Fig. 2. Dependence of PbI_2 film's photoconductivity on substrate temperature.

Table 1. Response parameters of PbI_2 films prepared at different substrate temperatures (d_{s-s} = 30 cm).

T_S (℃)	τ_{rise} (s)	$\tau_{descend}$ (s)	S	Thickness (nm)
RT	7.98	55.24	2.16	2286
80	5.34	32.25	4.37	4048
120	6.12	7.01	1.01	823
160	5.18	12.70	0.67	633
200	1.43	12.52	7.96	1413

$$\Delta\sigma = \Delta\sigma_s\left(1 - e^{-\frac{t}{\tau_{rise}}}\right), \tag{3}$$

$$\Delta\sigma = \Delta\sigma_s e^{-\frac{t}{\tau_{descend}}}, \tag{4}$$

where $\Delta\sigma = \sigma_i - \sigma_d$, $\Delta\sigma_s = \sigma_S - \sigma_d$, and τ_{rise} and $\tau_{descend}$ represent rising relaxation time and descending relaxation time separately.

As $(\Delta\sigma_s - \Delta\sigma)/\Delta\sigma_s = 1/e$, the corresponding t in Eq. (3) is equal to τ_{rise}, and as $\Delta\sigma/\Delta\sigma_s = 1/e$, the corresponding t in Eq. (4) is just equal to $\tau_{descend}$. So, a series of τ_{rise}, $\tau_{descend}$, S values of PbI_2 films deposited at different substrate temperatures were calculated, as shown in Table 1. The films' thickness, described elsewhere, is also listed in this table.

It can be seen from Table 1 that the film's τ_{rise} value non-monotonically descends from 7.98 to 1.43 s except 6.12 s at 120 ℃ with increasing substrate temperature. Simultaneously, the $\tau_{descend}$ value first decreases from 55.24 to 7.10 s and then increases to 12.70 s. At a substrate temperature of 120 ℃, the response speed depicted by both τ_{rise} and $\tau_{descend}$ comparatively better, but this sample only presents a relative sensitivity of 1.01. Furthermore, the relative sensitivity at different T_S is approximately proportional to the thickness of the films. The lowest S value of 0.67 corresponds to the smallest thickness of 633 nm.

This result can be ascribed to the conflicting demands of response speed and relative sensitivity for photo-carrier lifetime. At the beginning of illumination, because of trap centers in the

films, numerous carriers are captured by impurity and defect energy levels. This delays the rising of photoconductivity to some extent, and leads to the increasing of relaxation time. At the end of illumination, electrons and holes captured on trap levels can not directly combine but through thermal excitation. Because of the relatively smaller excitation rate, the release process of captured carriers is much slower than the capture process, especially for release from the deep energy level. So, the τ_{rise} value is smaller than $\tau_{descend}$ for the same sample, as shown in Table 1.

In semiconductor physics, photoconductivity is expressed as follows:

$$\Delta\sigma = q\alpha\beta I\mu\tau, \tag{5}$$

where q is electron charge, α is absorption coefficient, β is excitation quantum efficiency, I is light intensity, μ is mobility, and τ is carrier lifetime.

Considering Eqs. (2) and (5), to improve the film's response sensitivity, the saturation photoconductivity should be raised by increasing the photo-carrier lifetime. In contrast, to improve response speed, the photo-carrier lifetime should be shortened to reduce relaxation time. So, reduction of relaxation time and improvement of response sensitivity are interdependent to some extent: the former demands shortening the photo-carrier lifetime to enhance recombination efficiency, while the latter needs a longer photo-carrier lifetime to reduce recombination rate. Nevertheless, practical photoelectric detection requires heightening the film's photoconductive sensitivity and response speed simultaneously. So, the above factors should be considered systematically.

According to the inter-dependence of relative sensitivity and response speed on substrate temperature and thickness, it is expected that appropriately increasing the film's thickness and raising the substrate temperature can effectively balance the opposite demands. By increasing substrate temperature, the integrity of the film's crystal grain can be improved to reduce defects. The reduction of trapping probability of photo-carriers caused by lower defect levels should effectively shorten the photoconductive relaxation time. At the same time, by appropriately increasing thickness, the film's absorption efficiency for incident photons can be increased to improve the photoconductive sensitivity.

Thus, to validate the above expectation, the films were prepared at the same T_S of 200 ℃ but different thicknesses were used to measure the photoconductive response. These samples were simultaneously deposited at different d_{S-S} (20 cm, 25 cm, 30 cm) for 10 min, which leads to different thicknesses. The blue LED lamp (460–470 nm) was still used to irradiate the samples. The dependence of the film's photoconductivity on illumination time and source–substrate distance is shown in Fig. 3, and the photoconductive response parameters of these samples are listed in Table 2.

It can be seen from Table 2 that the film deposited at d_{S-S} possesses the lowest τ_{rise} of 1.43 s and $\tau_{descend}$ of 12.52 s. Meanwhile, the S value (7.96) of the film with the largest thickness (1413 nm) is higher than the others. Because all the samples were prepared under the same conditions except for source–substrate distance, the difference in the response parameters can be attributed to the different thicknesses. Considering the results shown in Tables 1 and 2, the deposition parameters of PbI_2 film with optimized photoconductive performance can be confirmed: substrate temperature of 200 ℃, source–substrate distance of 30 cm and deposition time of 10 min. Under the conditions, the films present the fastest response speed and the highest sensitivity. This indicates that appropriately increasing the film's thickness and raising the substrate temperature can effectively balance the parameters' competing demands for photo-carrier lifetime so as to attain an optimized photoconductive performance.

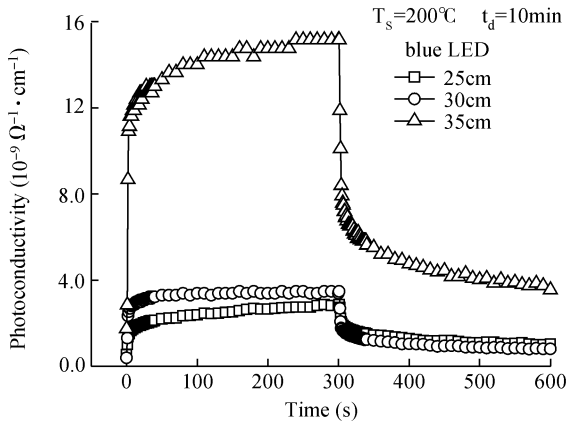

Fig. 3. Dependence of PbI_2 film's photoconductivity on source–substrate distance.

Table 2. Response parameters of PbI_2 films prepared at different d_{S-S} (T_S = 200 ℃).

d_{S-S} (cm)	τ_{rise} (s)	$\tau_{descend}$ (s)	S	Thickness (nm)
25	23.52	69.54	4.43	547
30	1.43	12.52	7.96	1413
35	3.53	15.26	7.74	333

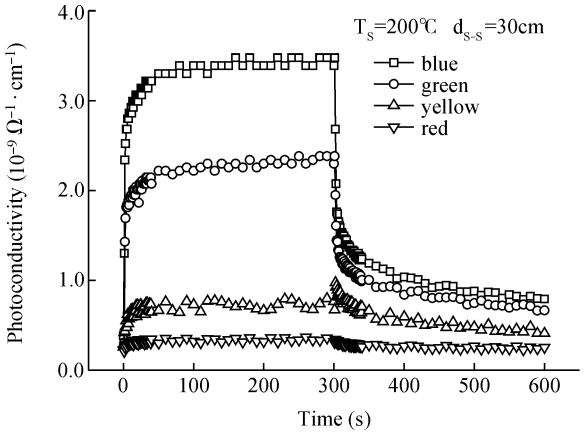

Fig. 4. Dependence of PbI_2 film's photoconductivity on source–substrate distance.

Additionally, the response of the film prepared at T_S of 200 ℃ and d_{S-S} of 30 cm to illumination at different wavelengths was measured, as shown in Fig. 4. The four LED lamps of blue (460–470 nm), green (515–520 nm), yellow (580–585 nm), and red (620–625 nm) were successively switched on to irradiate the sample. The photoconductivity of this sample shows a larger increase under the blue lamp than under the green one

and exhibits slight changes under the yellow and red lamps due to the different photon energies of incident light. When compared with the photon energy of blue (2.64–2.70 eV) or green (2.38–2.41 eV) light, that of yellow (2.12–2.14 eV) or red (1.98–2 eV) light is lower than the band gap ($E_g > 2.3$ eV) of PbI_2 film. The electron–hole (e–h) pairs excited by yellow and red light are too few to exhibit a photoconductive response. As is well known, the intrinsic excitation is the most important carrier excitation process in semiconductors, in which the productivity of e–h pairs is much higher than that in other processes. Moreover, photons with energy lower than the band gap can still generate a small number of e–h pairs, probably due to transitions arising from defect or impurity levels.

4. Conclusions

The photoconductive response of numerous PbI_2 films to visible illumination and deposition conditions were investigated. Two parameters, relative sensitivity and relaxation time, were used to describe the film's response performance. Appropriately increasing the film's thickness and raising the substrate temperature can effectively improve the response performance due to the balance between the two parameters' opposite requests for photo-carrier lifetime. As a result, under the conditions of a substrate temperature of 200 ℃, a source–substrate distance of 30 cm and a deposition time of 10 min, the films exhibit an optimized response performance. Finally, the decline of the film's response performance with increasing wavelength is attributed to the lower photon energy of incident light.

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