Electrical Properties of Ba,Ho Doped PbI$_2$

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Abstract

Barium and Holmium have been introduced into polycrystalline lead iodide during solution growth of thin films. Electrical characterization (current vs. voltage measurements , resistivity, carrier concentration and mobilities as a function of the doping concentrations) clearly demonstrates that both dopants introduce donor level in the PbI$_2$ band gap and compensate for the native acceptor defects of lead iodide, Barium as a dopant having the greater influence.

Keywords: electerical properties of PbI$_2$

الخصائص الكهربائيه ليوديد الرصاص المشوب بالباريوم والهولوميوم

الــخــلاصــة

تم ادخال الباريوم والهولوميوم في يوديد الرصاص متعدد التبلور خلال عمليه انماء الاغشية الرقيقــة بطريقة المحلول ، ودراسه الخصائص الكهربائية (تيار مع فولتيه ، المقاومية ، تركيــز حــاملات الــشحنة والتحريكية كدالة لتغير وزن المادة المشوبه وقد وجد ان الشائبتين المدخلتين تعمل عمل مستويات مانحة في يوديد الرصاص في فجوة الطاقة وتعمل على اطفاء تاثير عيوب المستويات القابلة في يوديد الرصاص، وقد وجد ان تاثير الباريوم كان اكبر من الهولوميوم .

Introduction

Lead iodide (PbI$_2$) is a highly photoconductive wide band gap semiconductor (E$_g$ = 2.32eV) [1],and due to its basic properties [2] (high atomic number of its elements Z$_{Pb}$ = 82, Z$_I$ = 53) and mass absorption coefficient (only 7 μm of lead iodide is sufficient for 90% absorption of 6-KeV radiation and 1560 μm for 120 KeV) lead iodide which been considered as a very attractive material for room temperature radiation detection, especially for low energy X-ray spectrometer and its applications [3-7].

Using thin polycrystalline layer instead of single crystal wafer is an alternative approach to overcome the difficulties in growing large crystals of PbI$_2$ with good uniformity. Deposition of PbI$_2$ polycrystalline layers from solution is a very comfortable method and reliable technique [8-10], the basic principle consists in the controlled precipitation on substrate in order to form a film . Hence, the characterization of the electrical properties of such layers is there for a great concern both for improving their preparation and evaluating their ability to fulfill the requirements needed for the starting material in making detectors.

All detectors made from metal iodides are photoconductive detectors [11-15], in such type the performance is largely affected by the electrical properties especially the (S/N) ratio and (μ *τ) value [13, 14]. To have high value of (S/N) ratio we need a detector with very low dark current , and to do so the starting material

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should have high resistivity , while the (μ *τ) value needs higher value for both , and this means low scattering and recombination centers.

Many attempts have been made to determine the type and activation energies of the different metals in PbI$_2$. Silver, which is probably the main residual impurity in lead iodide, has been recognized as a shallow acceptor level [16] (about 0.1 eV above the valence band) and its influence on the resistivity has been reported by several authors. Copper, which belongs with the same group, has been associated to an acceptor energy level situated 0.32 eV above the valence band. The role of Cu$^+$ in the luminescence of PbI$_2$ has been demonstrated [17]. Other recognized acceptor dopants in lead iodide are sodium [18] and potassium. Increase in the conductivity of potassium doped PbI$_2$ has been shown [19]. Antimony (Sb^{3+}) was found to introduce two deep traps situated at 0.21 eV and 0.35 eV or 0.27 eV and 0.41 eV, depending on the direction of the field with respect to the c-axis [20]. The possibility of doping lead iodide with Mn, Ni and Fe has been demonstrated but only optical characterization has been performed so far [21,22]. The influence of Zn doping on the structural and optical properties has also been studied [23]. In the same way, the better effect and influence of rare earth metals on the purification and therefore on the resistivity has been recently shown [24].

Nevertheless, the main source of energy levels in PbI$_2$ seems to be intrinsic structural defects [25, 26], i.e. iodine vacancies which could be associated with two shallow donor levels and lead vacancies which introduce two acceptor levels. It can be noticed in addition that interstitial iodine was suggested to deteriorate the transport properties of nuclear radiation detectors [27]. Recently Ponpon has demonstrated the influence of Tin (Sn) as n-type dopent [28] .

In this work we make a comparative study between Barium (Ba) and Holmium (Ho) as a dopants .

Experimental

The samples studied here were the thin polycrystalline film PbI$_2$ layers prepared by cooling to the room temperature of boiling saturated aqueous PbI$_2$ solution. The main residual impurity in the base material was (Ag < 4 ppm in weight). The polycrystalline layers were grown using a method similar to one proposed earlier [8] .First, lead iodide powder (0.5 gm) was dissolved in ionized water (250 ml) at 100 ^{o}C. Then the solution was slowly cooled down to20 ^{o}C. Owing to the fact that the solubility of PbI$_2$ in water decreases by a factor of approximately 10 when cooling down from 100 ^{o}C to 20 ^{o}C, precipitation of small crystallites occurred rapidly after evaporation of the excess water, thin layers (typically 3-15μm thick) were obtained on the glass substrates. For electrical measurements two graphite electrodes (parallel strips at 5 mm in width, separated by 5 mm) were deposited on the front surface, while for Hall measurements four equal inter distant graphite electrodes were deposited. Doped samples were deposited using the same procedure with adding of the following weight of both Ba and Ho (2, 5, 7 mg) to the aqueous PbI$_2$ solutions. All measurements were carried at room temperature.

Results

Figure (1 a, b) shows the influence of the dopant weight on the dark I-V values compared to the undoped. For higher

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doping weight ($\geq$ 5 mg) doping with (Ba) gives lower current values than (Ho). Table (1) summarizes the results of Hall characteristics, and for comparison the dark current of undoped samples is shown also. It is clear that the all samples doped with (Ho) and (Ba) show lower current measurements for both dopant impurities.

Figure (2a,b) shows the variations in the electrical resistivity as a function of the dopant weight, there is a steeper power law increasing and for higher dopant weight there is a clear change in the slope (resistivity per unit doping weight). Figure (3 a,b) shows the dependence of carrier concentration on doping weight where the two curves have different trends The carrier concentration appears to be saturated with higher doping weight in the case of (Ba) ,while in the case of (Ho) the concentration increase four times with increasing dopant weight. Figure (4a, b) shows the variation in mobility with doping weight ,it is clear that undoped samples have higher mobility and the (Ho) doped samples show a decrease in weight while (Ba) doped samples shows increasing trend with weight.

The carrier concentration (n) and mobility (μ) was calculated from the tow relation [29]:

$$n = B/qd * I/V_H \qquad \ldots\ldots\ldots(1)$$
$$\mu = \sigma nq \qquad \ldots\ldots..(2)$$

where:

n carrier concentration

B magnetic flux in Tesla

q electron charge

d sample thickness

I current, V_H Hall voltage

μ mobility

σ conductivity

Discussion

According to the hypothesis proposed by [28] the starting material contains two

acceptors levels situated at (0.1eV) and (0.3eV) with concentrations $N_1 = 3*10^{12}$cm^{-3} and $N_2 = 10^{14}$ cm^{-3} respectively. Our presumed explanation is the introduced impurities (Ba), (Ho) will compensate for these acceptor levels, and the compensation process begins with the low ionization energy level which needs lower doping weight to be compensated. The higher energy level due to its higher ionizations energy and concentration needs more doping weights than the first . Figures (1) and (2) confirmed strongly that the compensation with (Ba) is more effective than with (Ho), this result is very clear if we compare the ratio of ($\Delta \rho / \Delta$ w){the resistivity per unit doping weight}.For doping weight $\leq$ 2 mg for (Ba) is ($2.45 *10^{13}$) and for (Ho) is ($1.05*10^{12}$) For higher doping weight $\geq$ 5mg the difference increases and becomes ($7.385 * 10^{12}$) for (Ba) and ($1.5 * 10^{10}$) for (Ho). Since the doping weight for both salts is the same, and (Ho) has ionization energy {2.49eV, 2.43eV} according to [24] we think that (Ba) occupies lower ionization levels.The decrease in the carrier concentration with (Ba) weight is in parallel with the increasing trend in resistivity, while the increase in the carrier concentration with (Ho) weight could be attributed to the low solid solubility of (Ho),although these are preliminary results and need to be followed up with more detailed studies. The fact that the mobility decreases with (Ho) weight while it increase with (Ba) may be due to a real variation in material properties [perhaps an increase in the number of coherent domains in the case of (Ho)].

Conclusions

The compensation effect of (Ba) and (Ho) in polycrystalline layers of lead iodide has been demonstrated. Introduction of both leads to a significant increase in the material resistivity which

can be accounted for by considering the donor behavior of these elements in PbI$_2$. The results explained depend on the hypothesis is that both introduce deep levels with different ionization energies in PbI$_2$.

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Table (1) The calculated parameters from Hall measurements

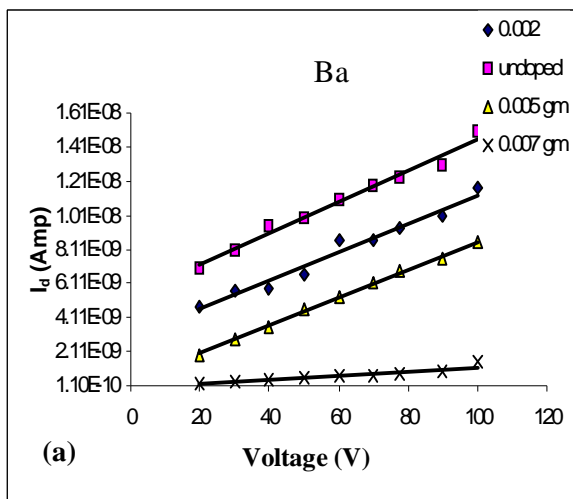| Deposition conditions	undoped	Weight of Ba			Weight of Ho		
Weight (mg)	0	2	5	7	2	5	7
Resistivity(W.cm) $*10^8$	0.25	49	52.3	200	2.08	2.17	2.49
Carrier concentration (cm^{-3}) $* 10^9$	3700	280	65	7.2	680	920	3420
Mobility(cm^2/V.sec) $* 10^{-2}$	6.5	0.46	1.86	4.3	4.4	3.1	0.73
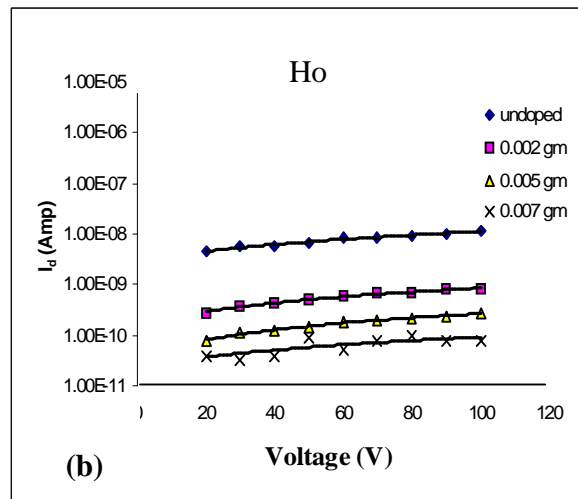
Figure (1 a ,b): Plot of the current vs. voltage characteristics of Ba ,Ho doped samples at 300K.
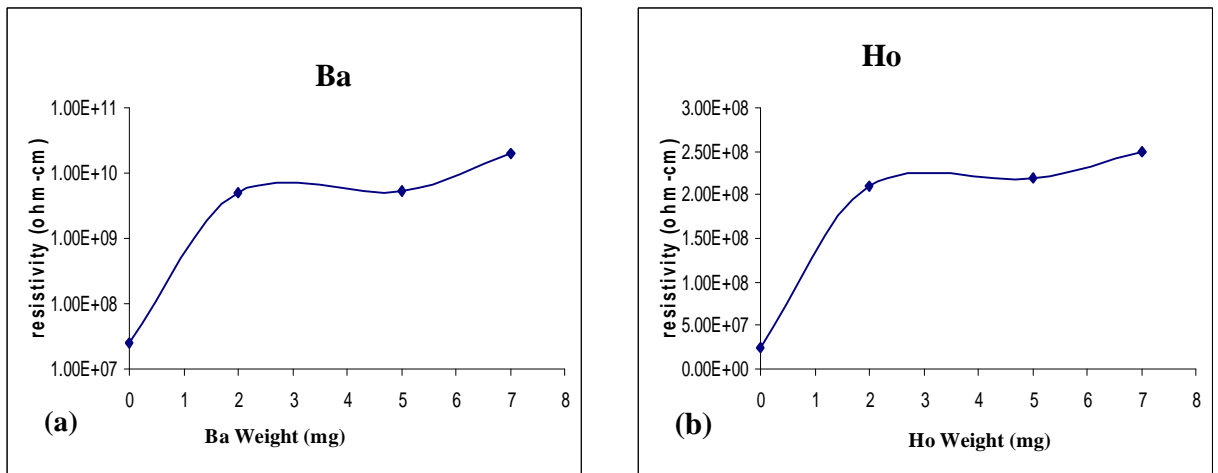
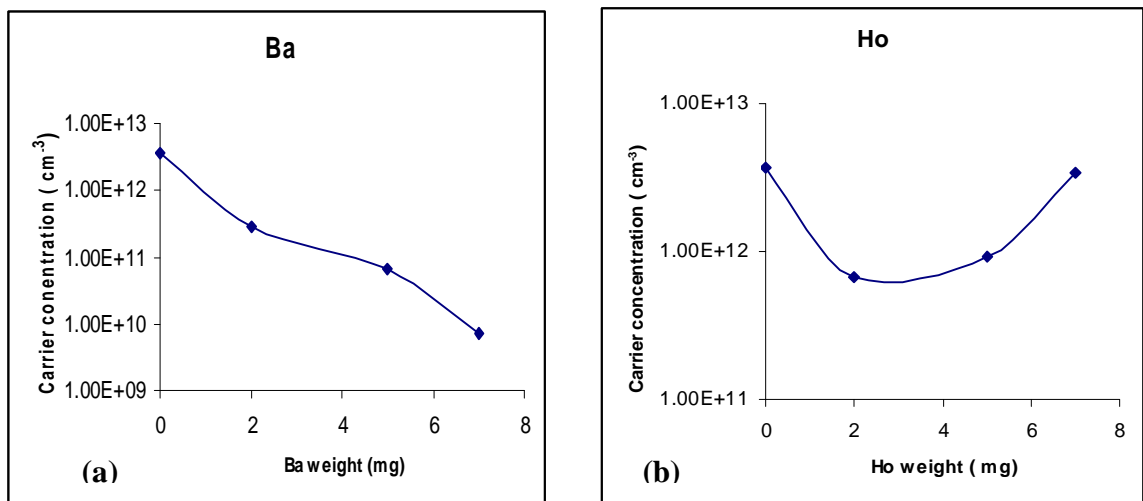**Figure (2a ,b): Variation of doped samples resistivity with doping weight**

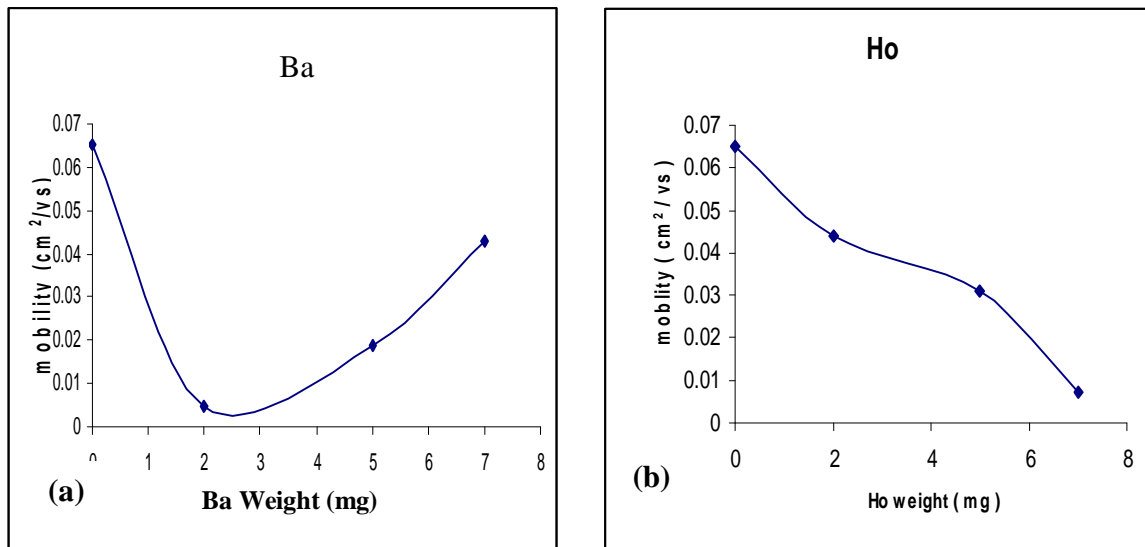**Figure (3 a , b) : charge carriers concentration curves vs. doping weight.**

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Figure (4 a , b) Mobility's curves plotted as a function of doping weight .