J Mater Sci (2008) 43:525–529
DOI 10.1007/s10853-007-1854-9

5TH BRAZILIAN MRS MEETING

Optical and structural properties of PbI_2 thin films

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Received: 29 December 2006 / Accepted: 15 May 2007 / Published online: 20 July 2007

Abstract Lead iodide thin films were fabricated using the spray pyrolysis technique. Milli-Q water and N.N-dimethylformamide were used as solvents under varying deposition conditions. Films as thick as 60 μm were obtained. The optical and structural properties of the samples were investigated using Photoluminescence, Raman scattering, X-ray diffraction, and Scanning electron microscopy. In addition, the study included also the electronic properties which were investigated by measuring the dark conductivity as a function of temperature. The deposition technique seems to be promising for the development of thick films to be used in medical imaging.

Introduction

Due to its high atomic number ($Z_{Pb} = 82$, $Z_I = 53$) and intrinsic band gap of about 2.4 eV, lead iodide (PbI_2) is a very promising semiconductor for applications in ionizing radiation detectors that operate at room temperature. For instance, the study of this material has been focused for the development of X-ray detectors for digital radiography in medical applications [1]. Lead iodide is an anisotropic semiconductor that consists of hexagonal layers (I–Pb–I) where the bonding between layers is weak (van der Waals). Contrary to mercury iodide, the material presents a lack of a destructive phase transition between the room temperature and its melting point [2].

Previous extensive studies on the influence of the purity of starting PbI_2 powder on single crystal growth (bulk) have been reported by several authors that obtained samples with good crystalline properties. Thus, improvements in performance of PbI_2 based devices could be possible with increasing purification [3]. Therefore, there are few works related to the study of these materials as polycrystalline thin films, a form that is desired for applications in large area devices in medical diagnosis. Other authors have produced prototypes using thin films of PbI_2 produced by thermal evaporation and their experiments present high resolution and sensitivity both for static and dynamic imaging [1].

In this work the spray pyrolysis (SP) deposition technique was used as an alternative way for the fabrication of PbI_2 polycrystalline thin films with potential applications in X-ray detectors. This method has been applied to deposit a wide variety of materials aimed for applications such as solar cells, sensors and biosensors [4, 5]. This method is interesting because of its simplicity and relatively low cost once that it does not require expensive equipments, and because it can be easily expanded for large areas [6]. The main advantages and limitations of the deposition technique comparing three starting powders with the inclusion of extra iodine in the deposition atmosphere were already discussed [7].

When using SP, Milli-Q water can be used to dissolve the powder of PbI_2 as long as the substrate deposition temperature is greater than 100 °C. Nevertheless, one of the drawbacks of this solvent is the small deposition rate of

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1 μm/h. In this work, N.N-dymetilformamide (DMF) organic solvent was used for dissolution of the PbI_2, presenting a higher deposition efficiency.

We therefore give special attention in this paper to the optical and structural properties of PbI_2 thin films produced with DMF solvent (PbI_2–DMF) with a comprehensive study of the effects of substrate temperature during deposition. The characterization of the electrical properties is also included.

Experiments

Commercially available PbI_2 with nominal purity of 99.999% from Aldrich was used as starting powder. The home-made apparatus used in this work, as well as details of the method were previously described [6]. The thin films were deposited on corning glass substrates sitting in the range from 175 °C up to 250 °C. The maximum deposition time was 3.0 h, and the distance between the spray nozzle and substrate was maintained at 20 cm. The rate of consumption of the precursor solution was 0.16 cm^3/min and the nitrogen atmosphere into the chamber was operated at a flow rate of 8×10^3 cm^3/min.

The crystal quality was verified by X-ray diffraction experiments (XRD) using Cu K_α radiation from a Siemens D5005 (40 kV/40 mA) diffraction system. The scattering angle (2θ) scanning was performed from 5° up to 65° with a step of 0.02°. Photoluminescence (PL) spectra were obtained at 15 K in the range from 485 nm up to 690 nm using a HeCd laser in 325 nm (3.80 eV) as excitation source. We performed Raman scattering experiments from 50 cm^{-1} up to 350 cm^{-1}, at room temperature with a resolution of 4 cm^{-1} using a Jobin Yvon U1000 double spectrometer with illumination at 514.5 nm Ar^+ laser (Coherent INNOVA 90-6), with photomultiplier detection (RCA C31034-A02 at –20 °C). The dark current was recorded as a function of temperature in the range from 270 K to 370 K, and the measurements were performed with a constant temperature rate of 3 °C/min while the sample was kept in vacuum. Graphite coplanar electrodes were deposited on the surface of the samples because it makes ohmic metal-semiconductor contact with PbI_2 [8]. Palladium and graphite have been used as electrode materials with similar results for PbI_2. The electrodes lines were 1 mm wide, 5 mm long, and presented a gap of 2 mm. An external dc voltage of 50 V was applied to the sample.

Results and discussions

Lead iodide was dissolved in milli-Q water at 100 °C up to the limit of solubility (4.2 g/L). After dissolution, the mixture was cooled down to room temperature. The precipitation of small crystallites occurs after the cooling, thus the excess material was filtered. The final concentration of the solution is 3.1 g/L. This concentration corresponds to the saturation of PbI_2 dissolved in H_2O at room temperature. The same concentration of PbI_2 in DMF was used to produce samples for comparison. Both samples will be identified as $PbI_2(H_2O)$ and PbI_2(DMF), respectively.

Figure 1 presents the results of XRD experiments for $PbI_2(H_2O)$ and PbI_2(DMF) thin films both deposited at 225 °C for 2.5 h. The data show that the relative crystallinity of PbI_2(DMF) is 37% greater than $PbI_2(H_2O)$. The main observed peaks are the (001), (101), (003) and (202). These were identified using the Joint Committee on Powder Diffraction Standards, reference number 07-0235. It should be noted that the results of the diffraction experiment are somehow comparable to the ones obtained before [6]. We used Scherrer's formula [9] to evaluate the size of the crystalline grains, and the obtained mean values are approximately 27 and 35 nm for $PbI_2(H_2O)$ and PbI_2(DMF) thin films respectively. The variation of the grain size is important for applications as radiation detectors and it is possibly related to the fact that temperature of vaporization of the two solvents is not the same.

The final thickness of the samples as a function of PbI_2 concentration in DMF is presented in Fig. 2. A total deposition time of 2.5 h and a substrate temperature of 225 °C were adopted. The thickness was estimated from cross-section SEM. For the same deposition time the final thickness increases linearly with concentration. Note that the thickness for PbI_2(DMF) deposited using 3.1 g/L is

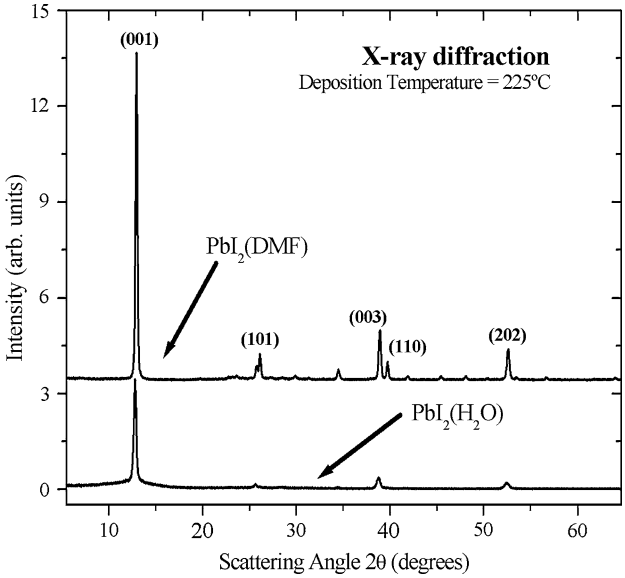

Fig. 1 X-ray diffraction data for PbI_2 thin films obtained using H_2O and DMF as solvents

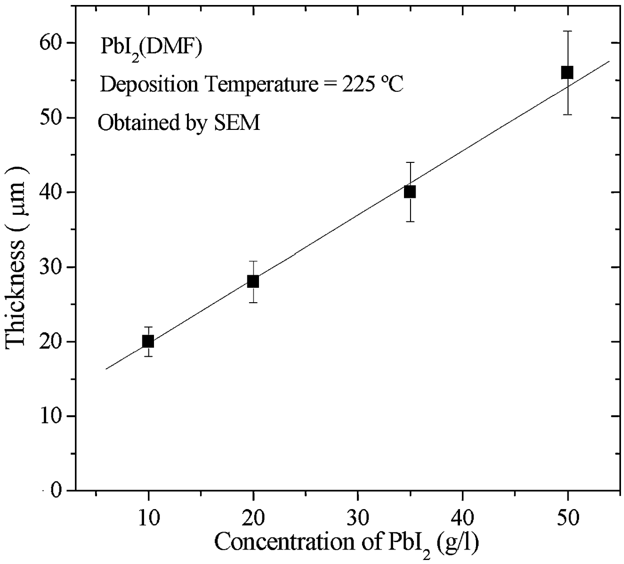

Fig. 2 The final thickness of samples produced with $PbI_2(DMF)$ as a function of concentration

approximately 5 times larger than the one for the film deposited using water as solvent. This result can be attributed to the distinct viscosities of the solvents and different solvent vaporization point, what may cause a variation of the droplet size, impact and vaporization effect on the surface of the substrates.

Figure 3 presents the PL spectra for the same samples cited in Fig. 1. The experimental data for $PbI_2(H_2O)$ and $PbI_2(DMF)$ thin films are presented in Fig. 3a, b respectively. The experimental data are represented as the topmost curves, while the others underneath represent the numerical fitting of four Gaussians. The results show a line with a peak position near 2.50 eV (E_F) which is attributed to free excitons, while the line with peak position at 2.43 eV (E_B) is attributed to bound excitons. The E_F bands, which is more intense for $PbI_2(H_2O)$, is due to recombination of the free excitons with band-to-band transition. The intensity of this band is directly related to a better crystal quality. The E_B band is probably due to an intrinsic defect of the material such as dangling bonds from the grain boundary or surface roughness defects (both cause deep and shallow states).

The spectrum of lead iodide thin films exhibits similar properties to those of nano-particles [10] and bulk crystals [11]. Note that the curves exhibit two broad bands below the exciton edge. The third line with peak position at 2.41 eV (D) band is related to donors-acceptor pairs [12] and the increase of the D band is associated to impurities present in the bulk [13]. The broad line at 2.19 eV (G band) arises from the recombination of a trapped carrier with a free carrier, probably due to an intrinsic defect of intrinsic material, as well as E_B band. The E_B and G bands were

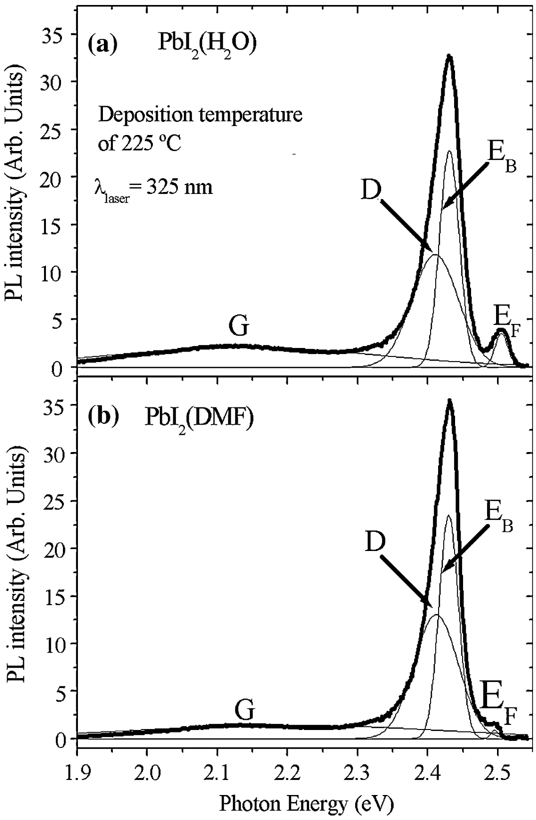

Fig. 3 The Photoluminescence (PL) characteristics of lead iodide thin films grown by SP using (**a**) H_2O and (**b**) DMF as solvents

discussed [13] and it was shown that they are linked to surface defects. It is interpreted as a radiative electron-hole recombination in a process of dissociation of bound exciton associated with the Pb^+ ions (positive fluctuations of the potential) created under band-to-band irradiation.

The vibration modes of the polycrystalline thin films have been investigated by Raman scattering. Figure 4

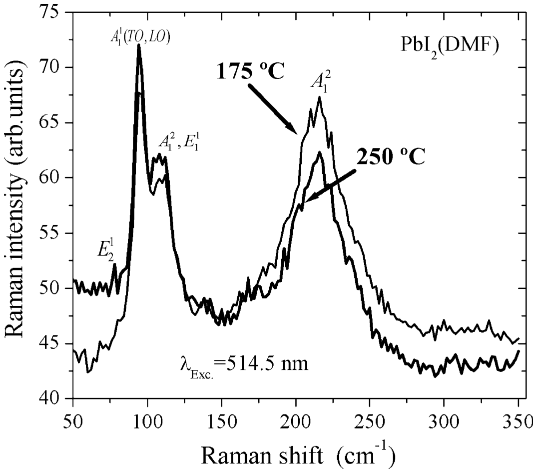

Fig. 4 The Raman scattering of the lead iodide samples deposited at 175 °C and 250 °C during 3 h using DMF as solvent (40 g/L)

shows the results for as-grown films for two samples deposited at 175 °C and 250 °C with concentration of 40 g/L during 3 h, using DMF as solvent only. There were four bands observed in the 50–350 cm^{-1} region and they are at 75, 95, 110, and 215 cm^{-1}. Similar peaks were observed for PbI_2 platelets [13] and vapor grown PbI_2 [14]. The shear deformation mode (75 cm^{-1}) is unresolved at room temperature for both samples and the breathing deformation mode (95 cm^{-1}) remains a Raman singlet. According to the literature the line at about 110 cm^{-1} should consist of two peaks [15], but in our case they cannot be resolved. The fourth line at 215 cm^{-1} is considered to be the second order band corresponding to 2LO mode. It is conclusive that using a higher deposition temperature leads to a material that presents better characteristics and is probably thermodynamically more stable.

Figure 5 shows the dark current as a function of the inverse temperature of as-grown films for two sample deposited at 175 °C and 250 °C. Both samples exhibit semiconductor behavior where the dark current of the films increased with increasing temperature. For the sample deposited at 175 °C, an activation energy (E_a) of about 0.45 eV was measured for the whole temperature range (see Fig 5a), what indicates that a single transport mechanism dominates. The fact that E_a is smaller than half the band-gap of the material reveals that a strong non-intentional doping might have occurred, besides the intrinsic defects of the sample such as dangling and distorted bonds. On the other hand, for the sample deposited at 250 °C, two main transport mechanisms can be observed. While in the low temperature region, bellow room temperature, the activation energy is 0.31 eV, for temperatures above 50 °C, a value of 1.13 eV was obtained (see Fig. 5b). For the low temperature region, localized hopping and/or transitions due to donor and acceptor levels of impurities might be the dominating mechanism, while for the temperature region above 50°C band to band transitions seems to be the main contribution. The discussion above is corroborated by the PL data (see Fig. 3), where the bands with smaller energies are associated to defects as already discussed. A detailed analysis of the data in Fig. 3 shows that an intensity ratio of E_B/G and D/G bands about 50% larger is obtained for the case of the sample deposited at 250 °C when compared to the one at 175 °C. Also, the G band for the sample at 175 °C is centered at lower energies. In this sense, higher deposition temperatures would lead to a final material with less defects inside the gap, and thus with better transport properties. There are reported values of activation energies that vary from 0.1 eV to 1.0 eV when the film is silver doped with concentrations of about 5,000 and 2,800 ppm, respectively [16]. Additional studies obtained activation energies of 1.7 eV when the films were heated up to 200 °C [8]. Nevertheless, for a temperature range similar to our work, E_a stayed at about 0.3 eV only [8].

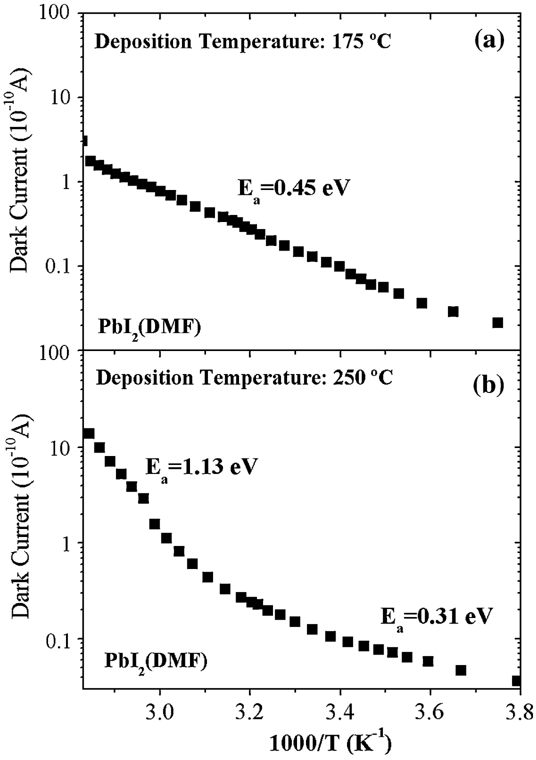

Fig. 5 Dark current as a function of temperature for thin film of PbI_2 deposited using DMF as solvent during 3 h at (**a**) 175 °C and (**b**) 250 °C. Concentration of 40 g/L

The electronic properties of the boundary between two adjacent grains depend primarily on the relative orientation of the crystalline domains. The significance for the transport is that it is expected that localized states be associated also with imperfect contacts between grain boundaries. The surfaces of the samples were investigated by SEM and the pictures corresponding to the samples discussed in Figs. 3–5 are presented in Fig. 6. Due to increasing deposition temperature the film morphology is changed towards lower porosity. The sample changed from a highly porous (Fig. 6a) to a denser structure (Fig. 6b). Note the existence of grains in both samples and that the amount of surface defects seem to be smaller for the sample deposited at higher temperature because of better surface coverage.

In SP the substrate temperature is the main parameter that determines the morphology and structural properties of the films. An ideal deposition condition is when the droplet approaches the substrate with a small size. This ideal condition is changed because the droplet size can vary as a function of the temperature of the substrates. For a low temperature (175 °C in our case) the incoming droplets splashes onto the substrate and then the solvent vaporizes. At higher temperatures (250 °C in our case) the solvent partially evaporates even before the droplets reach the

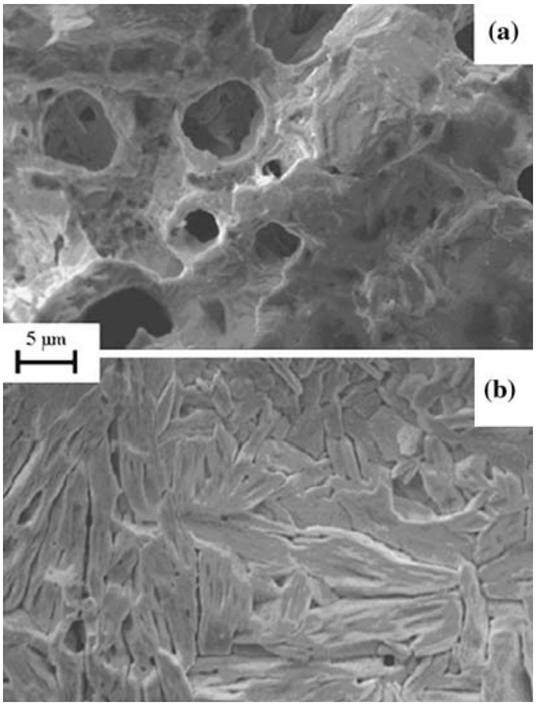

Fig. 6 SEM for lead iodide thin films deposited using DMF as solvent during 3 h at (**a**) 175 °C and (**b**) 250 °C. Concentration of 40 g/L

substrates. As a consequence, the final droplet size on top of the substrate is smaller than for lower temperatures. Also, the vaporization of the solvent occurs in a faster rate. The combination of these effects leads to a denser final structure. Some other parameters that could also influence the structure of the material are the distance between the spray nozzle and substrate, the rate of consumption of the precursor solution and the nitrogen flow rate. Nevertheless, in the case of the present investigation those were kept constant.

In summary, we believe that the mechanism of growth changes as a function of substrate temperature due to the final droplet size and due to the vaporization rate. In this sense, the films deposited at higher temperatures are structurally better. Vacuum evaporated films also show some sort of porous structure [17]. The authors present SEM pictures and report a final density that can vary from 3 g/cm^3 o about 5 g/cm^3, while the density of the bulk crystal is 6.2 g/cm^3 [17]. Note that their samples present the same preferred orientation of ours, given the fact that their dominant X-ray diffraction peak is also (001), and their SEM pictures show crystalline grains of about 2 μm. Our microscopy data in Fig. 6 show more elongated grains.

Conclusions

We have investigated the fabrication of lead iodide thin films by SP using H_2O and DMF as solvents. For the same concentration of PbI_2 in solution, and same deposition conditions, a deposition rate 5 times larger was obtained when DMF was used as solvent. The final sample is also more crystalline. This might be related to the difference between the vaporization point of water (100 °C) in relation to DMF (153 °C). Increasing the concentration of PbI_2 in DMF might lead to a final thickness of about 60 μm, for a total deposition time of 2.5 h. The variation of the substrate deposition temperature leads to variation of the final structural, optical and electric properties, with better results obtained for 250°C. Considering the deposition conditions and the final quality of the samples, the technique seems to be useful for the future development of films for radiation detection.

Acknowledgments This work was supported by CNPq (479316/2006-6), Capes and Fapesp (01/08221-9). We thank C. F. O. Graeff, C. A. Brunello, F. likawa and L. A. Montoro for experimental help.

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