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Crystalline texture and mammography energy range detection studies of pyrolysed lead iodide films: Effects of solution concentration

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HIGHLIGHTS

- PbI_2 films were grown by spray pyrolysis deposition method.
- Variations in microstructure were studied using crystal texture calculations.
- The films were tested in the mammography X-ray energy range.
- The response is very linear with a slope of 13 μA/cm^2 R.

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ABSTRACT

Semiconductor lead iodide (PbI_2) films have been extensively studied due to their potential applications in room temperature ionizing radiation detectors. The influence of PbI_2 solution concentration on the final properties of the films grown by spray pyrolysis was investigated. The solution concentration was varied in the range of 10 g/l up to 50 g/l. Total deposition time of 2.5 h was used and average growth rate varying from 22 Å s^{-1} up to 62 Å s^{-1} was obtained as a function of solution concentration. X-ray diffraction was used to investigate the structural properties of the films. Variations in microstructure as a function of solution concentration were studied using crystal texture calculations. The smallest value of electrical resistivity was obtained for the largest solution concentration. Mammographic X-ray irradiation from 10 mR up to 1450 mR was carried out with equivalent photon energy at 14 keV and the sensor results are discussed.

1. Introduction

Room temperature ionizing radiation detectors have been extensively developed. Among the sensing materials, lead iodide (PbI_2) semiconductor films have been widely used [1–3]. PbI_2 presents a lamellar structure (I–Pb–I). The two simplest polytypes of PbI_2 are 2H–PbI_2 and 4H–PbI_2 which belong to the space groups D_{3d}^3 and C_{6v}^4, respectively [4]. PbI_2 presents large band-gap (Eg ~ 2.3 eV), high mass density (6.2 g/cm^3), high atomic number (Z_{Pb} = 82 & Z_I = 53), high X-ray photon absorption, γ-ray photon absorption, ionization and charge collection and low leakage current [5–8]. It is a very important material with a technological utility for the development of the active matrix flat panel imagers (AMFPIs) that can be used as detectors for X-ray digital radiography using the direct conversion method [9–13]. It can be applied in alpha particle detectors as well [14]. For digital radiography, thicknesses of the order of 100–500 μm are desired for the film to absorb a large fraction of the X-ray beam in the 20–80 keV range. Thick films shall provide an efficient collection of X-ray generated charge carriers once that X-ray absorption occurs throughout the material [15–18]. In order to maximize soft tissue image contrast the needed dose for a mammogram is high due to low equivalent photon energies. Thus, the administered dose to the patient could be smaller to obtain the same final image quality with the direct detection method, as compared to the indirect detection method [19].

The ultimate formation of the polycrystalline film depends on the deposition parameters used during the material growth [20,21]. In the present contribution, spray pyrolysis was the chosen technique for the deposition of PbI_2 films using N.N-

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dimethylformamide (DMF) as solvent for dissolution of the starting powder [22]. DMF presents a larger solubility limit for PbI_2 when compared to water. The main advantage of spray pyrolysis method might be attributed to its relative low cost and the fact that it also allows the deposition of films on top of large areas. The influence of solution rate and substrate temperature on the properties of lead iodide films deposited by spray pyrolysis using DMF as solvent was already previously reported [9]. A detailed study of the effects of PbI_2 solution concentration on the structural, electrical and X-ray irradiation properties of the final films is the focus of the present contribution. The use of the samples as sensing material for X-ray detection in the mammography energy region is also discussed.

2. Materials and methods

Polycrystalline PbI_2 films were grown from highly pure starting material (99.999% of purity) from Aldrich Co. The starting powder was dissolved in N.N-dimethylformamide (DMF) at room temperature. Spray pyrolysis deposition technique was described in other already published manuscripts [23]. In this work, an average solution rate of 0.16 cm^3/min was used. All films were grown on Corning 7059 glass substrates at 225 °C. A fixed distance of 20 cm between the substrate to spray-nozzle was used in all depositions. A nitrogen flow rate of 8.0×10^3 cm^3 min^{-1} was kept constant in order to standardize the inner atmosphere of the deposition chamber.

For the structural study, films were grown using several solution concentrations within the range of 10 g/l up to 50 g/l, for a fixed and continuous deposition time of 2.5 h. The temperature was kept constant during all growth period without significant deviation. Spray nozzle x-y movement was not used. In parallel, for exposition to X-ray irradiation in the mammography diagnosis region, some samples were deposited during 3.0 h with a fixed solution concentration of 40 g/l. The average growth rate as a function of solution concentration was investigated by cross-section scanning electron microscopy (SEM). X-ray Diffraction (XRD) from a Siemens D5005 diffractometer using Cu k_α radiation (1.5406 Å) was used for structural characterization of the samples. The 2θ angle was varied from 5 up to 60°.

Palladium (Pd) contacts in the coplanar configuration were previously evaporated on the surface of the substrates for electrical characterizations. Pd was used because it establishes ohmic contact with PbI_2 [19]. The current density was recorded in the dark and under X-ray exposure, as a function of electric field within the range from 25 V/cm to 250 V/cm. A Hewlett Packard (model 4140B) pA meter/dc voltage source was used.

Measurements under X-ray exposures were conducted at the Clinical Hospital of University of São Paulo (USP) in Ribeirão Preto-SP, Brazil. The photocurrent as a function of exposure was obtained using a X-ray source from General Electric Senographe 500T model within the range of mammography diagnosis region, with a molybdenum (Mo) anode with 0.5 mm Al filtration. This experiment was carried out using an ionization chamber 10 × 5–6 model and dosimeter 9015 model, both produced by Radcal Corporation. Equivalent photon energy of 14 keV was obtained using X-ray tube potential of 30 kVp. An electric field of 125 V/cm was applied to the PbI_2 films during irradiation and the distance of 45 cm between samples and X-ray source was kept constant. Electrical signal was recorded by a model 610C Keithley electrometer.

3. Results and discussions

Thickness was measured by cross-section SEM pictures as shown in Fig. 1. Average growth rate values were obtained within the range from 22 Å s^{-1} up to 62 Å s^{-1} as a function of solution concentration in the range of 10 g/l up to 50 g/l, as presented in Fig. 2. A linear increase with solution concentration was observed: there is direct proportionality between the amount of PbI_2 dissolved material that is dropped toward the substrates and the average growth rate. A final thickness limitation of 27 μm was already previously reported in the literature for PbI_2 films obtained by Physical Vapor Deposition (PVD) with deposition time of 3.0 h [24]. This limitation for maximum thickness was not observed for the present case.

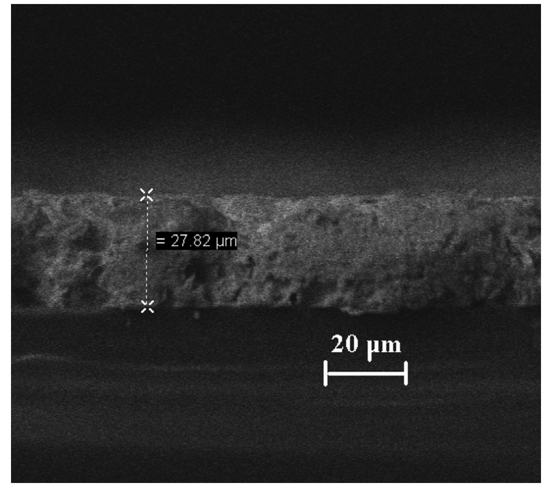

Fig. 1. Cross-section SEM picture for a film deposited using a solution concentration of 20 g/l.

The XRD pattern results are presented in Fig. 3. The XRD peaks for all samples were identified according to the Joint Committee on Powder Diffraction Standards, JCPDS, 07–0235. The most relevant diffraction peak observed in Fig. 3(a) is the (001), together with others less important such as (101), (102), (003), (110), (111), (103), (201) and (202), which are in agreement with the data base of the JCPDS. Note that the preferential direction of growth (001) presents much larger intensity than the other growth directions. Fig. 3(b) shows the details corresponding to a zoomed area from 20° to 55° for the film deposited at 35 g/l. A partial transformation of this material to the C_{6v}^4 4H form is indicated by the appearance of the ($\bar{1}$ 11) and ($\bar{1}$ 13) directions, which are exclusive for the 4H polytype [4].

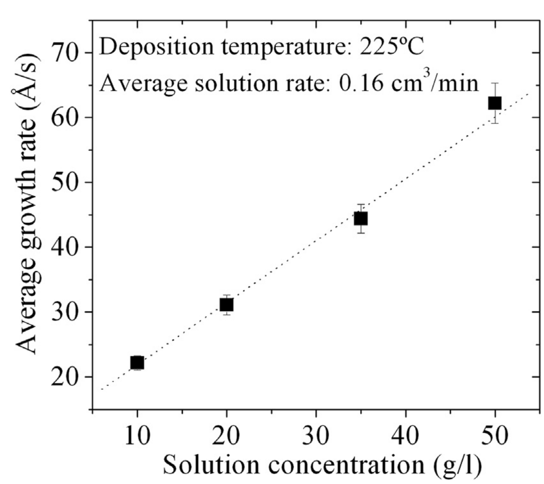

Fig. 2. Linear dependence of the average growth rate as a function of solution concentration. Total deposition time of 2.5 h at a substrate temperature of 225 °C, using a solution rate of 0.16 cm^3/min (PbI_2 in DMF).