Stoichiometry, Surface and Structural Characterization of Lead Iodide thin Films

J. F. Condeles*, R. C. Z. Lofrano†, J. M. Rosolen†, and M. Mulato*
*Departamento de Física e Matemática, FFCLRP, Universidade de São Paulo – USP and
†Departamento de Química, FFCLRP, Universidade de São Paulo – USP, Av. Bandeirantes 3900, Ribeirão Preto - SP, Brazil

Received on 4 April, 2005

In this work we present the structural properties and stoichiometry analysis of thin films of lead iodide (PbI_2). This material is a very promising semiconductor material for the development of X-ray detectors in digital medical imaging. An alternative deposition method called Spray Pyrolysis was used. We discuss the main advantages and limitations of the deposition process comparing three different starting material powders. Extra iodine atmosphere during deposition and the effect of post-deposition thermal treatment is also discussed. The structural properties were studied by X-ray diffraction, Atomic Force Microscopy (AFM), Scanning Electronic Microscopy (SEM) and stoichiometry analysis were performed using Energy Dispersive Spectroscopy (EDS).

Keywords: Thin films; Lead iodide (PbI_2); Spray Pyrolysis

I. INTRODUCTION

Digital medical imaging is evolving fast in the past decades. Some X-ray digital imagers have even come to the market already. But, for these applications a phosphor must be used on top of the a-Si:H pixelated active matrix imager [1,2,3]. The phosphor is responsible for the conversion of the X-ray photons into photons with wavelength in the visible range, which in turn are absorbed by the p-i-n a-Si:H photodetector. This method is called indirect. On the other hand, for the idealized direct method [4], a photoconductor would be used to directly convert the X-ray photons into electric charge. The charge would in turn be stored in a capacitor in each pixel. A single microcrystalline silicon thin film transistor is also used for the addressing of each pixel [5]. In this case, the electric signal response is proportional to the amount of incident radiation on each pixel. The direct detection method is better because a lower dose would be used to obtain the same quality of the final image, as compared to the indirect method. There is no system in the market based on the direct method yet, mainly due to problems in the development of the photoconductors as thin films. A compromise between high atomic number semiconductor materials, thin film deposition technique and final photoelectric properties must be optimized [6].

The spray pyrolysis was used as alternative technique for the deposition of thin films. The main advantages of this method are: i) the reduced deposition time, and ii) the fact that it can be easily expanded for large areas, leading to the development of radiation detectors desired for the industrial fabrication of medical imagers. According to the present authors knowledge, this method has never been used by any research group in the past for the fabrication of lead iodide (PbI_2). Among the many material candidates for the direct detection system, lead iodide is a very promising candidate [7]. The bulk crystalline phase has a melting point at 408^{o}C, a dielectric constant equal to 21, a mass density of 6.2 g/cm^3 and forbidden band gap of 2.34 eV. Its atomic number is Z_{Pb}= 82 and Z_I= 53 [8].

II. MATERIALS AND METHODS

The experimental method was discussed in detail in another work [9]. The temperature controlled substrates (corning glass) are introduced into a chamber, which is vacuum pumped. The pumps are stopped and a flow of carrying gas (nitrogen) is further established due to a positive pressure inside the chamber.

Three different starting powders were used:
i) a powder produced at our labs using $Pb(NO_3)_2$ + 2KI $\rightarrow$ PbI_2+ 2KNO_3 (*main results when nothing mentioned*);
ii) a powder produced by High Purity Chemical (Japan, 99.99%) and
iii) a powder produced by Aldrich Chem. (EUA, 99.999%).

The powder is dissolved in DI water at 100^{o}C, and the solution is then cooled down and filtered for the removal of the excess salt. Water can be used as a solvent as long as the substrate deposition temperature is above 100^{o}C. The solution is carried by the nitrogen gas towards the heated substrates as a spray: water is eliminated and the PbI_2 film is grown.

The structural properties of the original powder and the obtained thin films are here presented and discussed. The effect of post-deposition thermal treatment as well as the influence of an iodide atmosphere during deposition is also discussed. The structural properties were studied by X-ray diffraction (XRD) (copper k_α radiation of 1,5406 Å from a Siemens D5005 diffractometer) and both scanning electron microscopy (SEM) and atomic force microscopy (AFM) as well. Energy dispersive spectroscopy (EDS) is also used for the analysis of stoichiometry.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the X-ray diffractogram of the original powder and a typical thin film of PbI_2. The bottom curve corresponds to the home-fabricated powder, while the top curve corresponds to a film deposited at 225^{o}C. According to the Joint Committee on Powder Diffraction Standards (JCPDS),

reference number 07-0235, the main diffraction peaks are identified as (001) at 12.80 degrees, (101) at 25.60 degrees, (003) at 38.70 degrees and (202) at 52.50 degrees. Nevertheless, even though the different salt materials present different purity, the diffraction peaks look pretty much the same as the ones in Figure 1. Note that the powders and the films look yellowish.

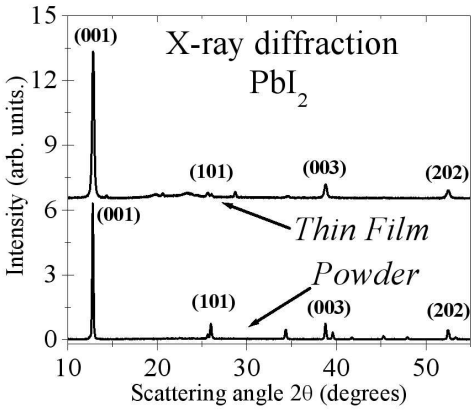

FIG. 1: X-ray diffractogram for lead iodide. The bottom curve corresponds to the home-made powder, and the top curve corresponds to a film deposited at 225^{o}C for 2.5 hours, using a spray-substrate distance of 16.5cm.

As already mentioned, the substrate temperature can be controlled. We made films with substrate temperatures from 150 up to 270^{o}C. As already published [9] the crystal size for a film deposited at about 225^{0}C are about 30 nm, and it depends linearly on deposition temperature with a rate of 0.12 nm/^{o}C.

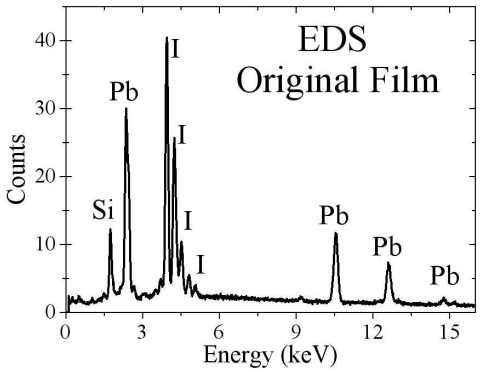

FIG. 2: Energy Dispersive Spectroscopy for original PbI_2 thin film.

The stoichiometry of the obtained films were investigated by EDS, as presented in Figure 2. Note that the spectrum presents well defined peaks of lead and iodine, besides revealing also the presence of silicon detected from the substrate. The analysis of Figure 2 leads to the conclusion that the material has smaller amount of iodine than expected: a PbI composition is suggested. That might be related either to the deposition process itself or the EDS technique (iodine could have been removed from the film during the measurement).

The Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) pictures of the original sample, which has a surface roughness of about 0.3 μm is presented in Figure 3. Sub-micrometer crystalline domains with size distribution are observed in Figure 3(a).

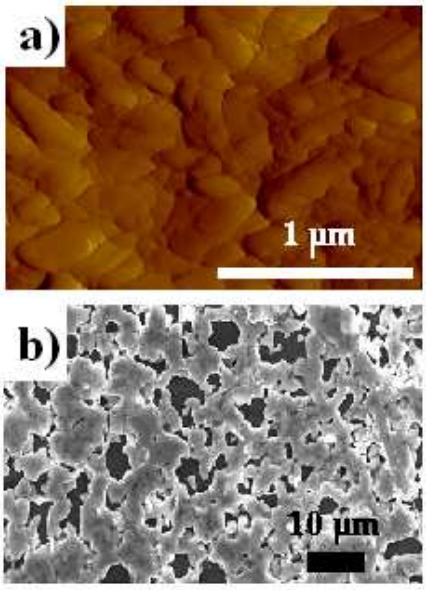

FIG. 3: a) Atomic Force Microscopy (AFM) and b) Scanning Electron Microscopy (SEM) for an original PbI_2 film deposited at 225^{o}C, for 2.5 hours using a spray-substrate distance of 16.5 cm. The dark regions in b) correspond to the uncovered substrate.

The dark spots in Figure 3(b) correspond to the uncovered glass substrate (SiO_2), as previously suggested by the lower energy EDS data in Figure 1. Note that no trace of oxygen was detected by EDS. The deposited film is only 3-μm thick. For further technological applications, a longer deposition time should be used in order to obtain a thicker and fully homogeneous film that covers the whole substrate.

Figure 4 presents the XRD data for the region of the main peak only, for the case of original films fabricated using the three starting powders with different purities. In order to try to increase the iodine content in the film, extra experiments where also conducted: small iodine stones were placed on top of the heated substrate holder, close to the substrates, during the deposition of the thin films. The XRD data for these films are also presented in Figure 4, identified as "with iodine".

While the crystallinity of the original films is not influenced by the purity of the starting powder, the same is not the case for films deposited with extra iodine. Regardless of the purity of the starting powder, the presence of iodine stones lead to

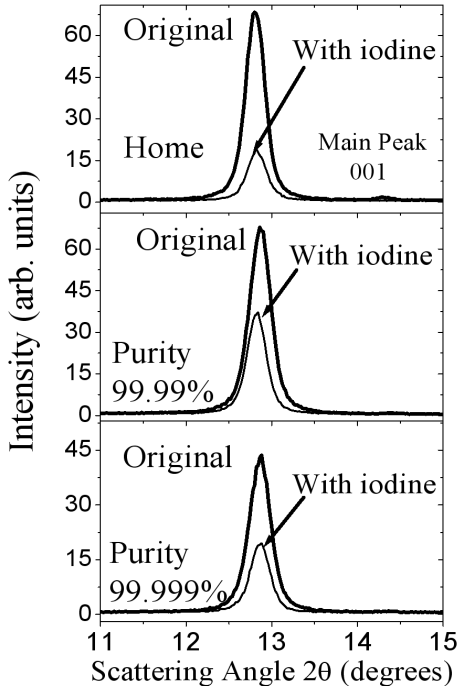

FIG. 4: XRD data for the main peak (001) only for original thin films and films deposited with extra iodine stones, for varying PbI_2 powder purities.

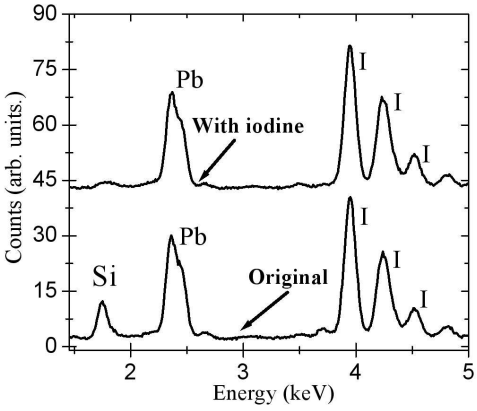

FIG. 5: Relative peak of the energy dispersive spectroscopy Experiment for original film and film deposited with iodine atmosphere.

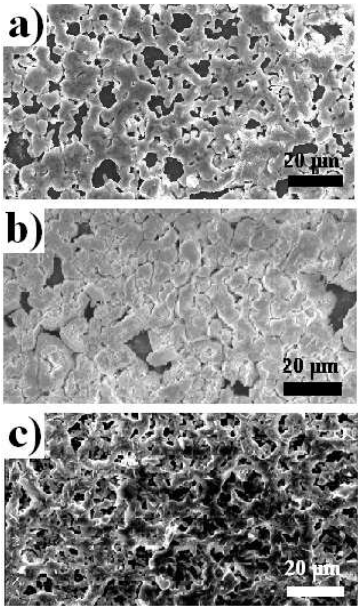

FIG. 6: Scanning electronic microscopy (SEM) for a) thin films deposited without iodine (original), b) thin film deposited with extra iodine stones and c) original film presented in (a) after post-deposition thermal treatment at 300 °C for 3h in nitrogen atmosphere.

lower intensity peaks that might be due either to lower crystallinity or smaller final thickness of the obtained film. Nevertheless, the influence of the iodine stones is smaller for higher purity powder. The ratio of the integrated areas varies from 3.2 to 2.1, from top to bottom in Figure 4.

The EDS data for original film and a film grown with iodine (home made PbI_2 starting powder) are compared in Figure 5. No variation is observed for stoichiometry, and the most important fact is the missing Si peak for the "with iodine" film. This suggests a better coverage of the substrate, and could indicate a lower thickness of the film (as previously suggested by the XRD data) given the fact that more material might be filling the observed dark spots in the SEM data of Figure 3. The EDS data for the other films discussed in Figure 4 cannot be shown here due to the lack of space, but neither a variation of stoichiometry nor the presence of impurities were ever observed.

Thus we are lead to conclude that the main influence of the iodine stones is the creation of an iodine atmosphere during growth. The extra iodine atoms in this atmosphere are important to increase the surface coverage of the substrate, possibly at the expense of a smaller final thickness. This is corroborated by the SEM data presented in Figure 6.

Figure 6(a) corresponds to the SEM data of the original film (which EDS are presented as the bottom curve in Figure 5), while Figure 6(b) corresponds to the SEM data of a film grown with iodide stones (which EDS are presented as the top curve in Figure 5). As can be clearly seen a higher surface coverage is obtained for the "with iodine" (Fig. 6(b)) case.

The PbI_2 powder after being dissolved in DI water is also dissociated with the formation of lead and iodine ions. These ions recombined during the growth process, when the vaporization of the solvent occurs at the surface of the substrate. The rate of film growth is related to the capacity of these ions to recombine. Given the fact that no stoichiometry variation was observed, the whole of the extra iodine atoms seem to be

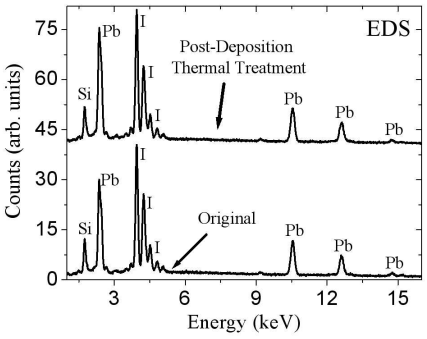

FIG. 7: EDS for original film (bottom) and the same film after post-deposition thermal treatment at 300°C, during 3 hours in nitrogen atmosphere.

the larger offer of possible recombination sites, leading to the final larger coverage of the surface of the substrate (Fig. 6(b)).

Figure 6(c) presents the SEM data for the original film in 6(a), after post-deposition thermal treatment at 300^{o}C, for 3 hours under nitrogen atmosphere. This experiment was performed in order to try to increase the surface coverage of the film, even after deposition. The data suggests a worsening in surface roughness, and a reduction in dark spot sizes, besides the more homogeneous distribution.

As shown by the EDS data of Figure 7, the thermal treatment does not lead to stoichiometry variation. Thus, the effect observed in Fig. 6(c) is only due to a structural reorganization of crystallites.

IV. CONCLUSIONS

This work presented the results of the fabrication of thin films of lead iodide using spray pyrolysis as the deposition technique. The films show an iodine loss, which cannot be compensated for, even with the use of extra iodine atmosphere during the growth. The extra iodine atoms lead to better recombination and covering of the surface of the substrate, without affecting the final crystalline structure of the samples. Post-deposition thermal treatment does not improve the quality of the film. Thus for technological applications, deposition times longer than 2.5 hours should be used and extra iodine should be incorporated into the film. Even in this case, the preliminary data shown in this contribution indicates that spray pyrolysis might be an interesting fabrication technique for the development of large area radiation detectors based on lead iodide.

Acknowledgements

We thank C.A. Brunello for experimental help, and the LNLS-Brazil for the EDS data. This work was supported by FAPESP (01/08221-9), CAPES and CNPq Brazilian agencies.

[1] R. Farrell, F. Olschner, K. Shah, and M.R. Squillante, Nuclear Instruments and Methods in Physics Research A **387**, 194 (1997).

[2] K.S. Shah, F. Olschner, L.P. Moy, P. Bennett, M. Misra, J. Zhang, M.R. Squilante, and J.C. Lund, Nuclear Instruments and methods in Physics Research A**380**, 266 (1996).

[3] F. Lemmi, M. Mulato, J. Ho, R. Lao, J. P. Lu, R. A. Street, and F. Palma, Applied Physics Letters, **78** (10), (2001).

[4] R. A. Street, R.B. Apte, T. Granberg, P. Mei, S.E. Ready, K.S. Shah, and R.L. Weisfield, Journal of Non-Crystalline Solids, **227-230**, 1306 (1998).

[5] M. Mulato, J. P. Lu, and R. A. Street, Journal of Applied Physics,**89** (1), 638 (2001).

[6] D. S. McGregor, H. Hermon, Nuclear Instruments and Methods in Physics Research A **395**, 101 (1997).

[7] Fornaro, E. Saucedo, L. Mussio, L. Yerman, X. Ma, and A. Burger, Nuclear Instruments and methods in Physics Research A **458**, (2001).

[8] M. Schieber, H. Hermon, A. Zuck, A. VilensKy, L. Melekhov, R. Shatunovsky, E. Meerson, Y. Saado, M. Lukach, E. Pinkhasy, S. E. Ready, and R. A. Street, Journal of Crystal Growth **225**, 118 (2001).

[9] J. F. Condeles, T. M. Martins, T. C. dos Santos, C. A. Brunello, M. Mulato, and J. M. Rosolen, Journal of Non-Crystalline Solids, **338-340,** 81 (2004).