Directional X-ray response of mercuric bromide films

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$HgBr_2$ was synthesized from HgO, HNO_3 and NaBr in aqueous solution. The material was then purified by two sublimations at 220 ºC and with an initial pressure of 4 x 10^{-3} Pa. $HgBr_2$ films were grown by the Physical Vapor Deposition (PVD) method onto 1" x 1" glass substrates. Growth conditions were a source temperature of 120-220 ºC and a growth temperature of 50-140 ºC; growth time was between 2 and 16 hours at an initial pressure of 4 x 10^{-3} Pa. The thickness of the films was between 100 and 1500 μm. For studying the anisotropic X-ray response of the films, growth conditions of no-adhesion between film and substrate were used: a source temperature of 190 ºC, a growth temperature of 80 ºC and a growth time of 2 hours. Films of 1500 μm in thickness were obtained, and were characterized by SEM and AFM. Detectors were then constructed in order to check the response of the films along and perpendicular to the substrate plane, by palladium thermal deposition, palladium wire attachment with aquadag and acrilic encapsulation. Whatever the considered direction, the electrodes were ohmic. Resistivities in the order of 10^{11} Ω.cm for both directions were obtained when dark current was measured perpendicular or parallel to the substrate. When irradiated with ^{241}Am source, films gave the same signal to noise relations of 1.5 at 50 V for both, perpendicular and parallel conduction respectively. Detectors are not sensitive to light, therefore they do not need light shielding when used as X-ray sensors. Resistivity and X-ray response results show similar values for both, perpendicular and parallel conduction. This result does not agree with the expected anisotropy that may be attributed to a layer compound. However, the lack of orientation of the film microcrystals, confirmed by SEM images, may be responsible for this result.

Keywords: Lead bromide, anisotropy, X-ray detection

1. INTRODUCTION

The search for materials useful for ionizing radiation detectors has steadily increased during the last decades. New and wider applications of ionizing radiation push continuously the detector development, asking for better performances, but also for new devices. These needs have determined the improvement of the methods for obtaining high pure materials, and for growing single crystals and crystalline films appropriate for the task.

Mainly, two methods are used for X and gamma radiation detection. The indirect method consists of using an intermediate material, for instance a photographic film or a scintillator. When X-rays are absorbed, produce chemical (photographic films) or physical processes (scintillator, light emission) in it, which, with a further process (reveled for photographic films or light collection by a photomultiplier tube or a photodiode for scintillators), give a signal proportional to the X-ray energy, dose, or both. This method is applied for single counting or spectrometry, using scintillators, thermoluminescent materials, etc, and also for X-ray imaging, using radiographic films, and any kind of phosphor screens, such as scintillators, photoestimulable materials, etc. Scintillators, for example, absorb X-rays whose energy is converted into visible light.

Then photons are collected by a photomultiplier tube, by a photodiode, or, for imaging, by position sensitive photomultiplier tubes (PSPMTs), arrays of compact PMTs, PIN photodiode arrays, thin film transistors (TFT) or charged coupled devices (CCD). The direct method consists of the use of single crystals (for single counters and spectrometers) or pixelliated single crystals or crystalline films (for imaging) of semiconductors. When X-rays are absorbed, electron-hole pairs are produced in the semiconductor, and the applied field directs the charge carriers towards the correspondent electrode, or the imaging array (TFT).

Whatever the method of detection, the material must have the highest possible atomic absorption coefficient. Therefore, those compounds with higher density and atomic number of their elements, and then with a higher atomic absorption coefficient for X-rays, are in advantage. Within this framework, halides had played an important role in radiation detector development, and iodides, for example, have been used for both, direct and indirect applications, depending on their physical properties. If attention is paid to the energy band gap of the compounds, chlorides and fluorides are clearly insulators, whereas bromides and iodides may be insulators or semiconductors, depending on the cation [1].

From the point of view of detectors, the energy band gap will determine if the material may be used with the indirect method (as scintillator) or with the direct method (as semiconductor detector), or both. Single crystals of materials such as cesium iodide or sodium iodide, unactivated, or activated with thallium or sodium, are used as scintillators, whether for single counting or for spectrometry systems [2].

Mercuric, lead and bismuth iodides are being developed as semiconductor detectors, whether as single crystals for counting and spectrometry systems or as crystalline films for X-ray digital imaging [3-8]. The bromide family, with energy band gaps a bit wider than the iodide family ones, might be used as scintillators or semiconductors as well, depending on the cation. Thallium bromide, with an energy band gap of 2.7 eV, has been the most studied bromide, and its single crystals have been checked for detection as scintillators and semiconductors [9-11], with acceptable results. Polycrystalline films of thallium bromide have been also reported as direct and indirect detectors [12,13]. The growth of lead bromide films have been recently [14] reported.

Mercuric bromide has a high density (6.1 g/cm^3) and a high atomic coefficient (156 μm are necessary for absorbing 90% of 30 keV radiation [15]). It has a wide energy band gap of 3.6 eV, and its detectors may work at room temperature as well [16].

Taking into account the physical properties of $HgBr_2$, and the results obtained with films of other heavy metal iodides, and of lead bromide for digital imaging, we thought that films of $HgBr_2$ might be investigated as well for such purpose. On the other hand, $HgBr_2$ shares with the heavy metal iodides a high vapor pressure below the melting point. Therefore, we considered interesting to know if films of $HgBr_2$ could be grown by the Physical Vapor Deposition method. Finally, these halides are layered compounds and therefore they might exhibit anisotropic properties. In light of these antecedents, this paper reports the growth of $HgBr_2$ films, and the study of their anisotropic electrical properties and X- ray response.

2. METHODS

$HgBr_2$ was synthesized from mercuric nitrate and sodium bromide in solution, according to a modification performed on a reported technique [17]. Stoichiometric amounts of reactants were used for synthesizing the material, which was then purified by two sublimations with an initial pressure of 4 x 10^{-3} Pa. Neither purity nor stoichiometry of this material were investigated.

The growth of $HgBr_2$ films was performed by the Physical Vapor Deposition (PVD) method. Typical growth conditions were an initial pressure of 4 x 10^{-3} Pa, a source temperature of 120-220 ºC and a growth temperature of 50 – 140 ºC and a growth time between 2 and 16 hours.

Film thicknesses were measured by absorption of the ^{241}Am 59.5 keV radiation; the photopeak was selected with an EG&G Ortec Solid Scintillation NaI(Tl) spectrometry system. Films were characterized by optical microscopy using a Nikon Model EPIPHOT 300 microscope and by scanning electron microscopy (SEM) with a JEOL 5900 system with an EDS microprobe Vantage NORAN.

In order to check electrical and radiation anisotropic response properties of the films, detectors with electrodes parallel and perpendicular to the substrate were assembled by deposition of palladium onto them as front, lateral and rear electrodes. Palladium leads 0.001" in diameter were attached using "aquadag" (from Acheson Inc., Amsterdam, The Netherlands) and an encapsulation with protective coating ("Humiseal" from Chase Corp., Woodside, NY, USA) was then made. Room temperature measurements in both directions of dark current density through the films were performed by applying a negative bias voltage from a EG & DG Ortec (Model 556) DC high voltage power supply, to the top electrode (for studying dark current perpendicular to the substrate) or to the lateral electrode (for studying dark current parallel to the substrate). The current signal was registered with a Keithley electrometer (Model 614).

The response of the films was evaluated by the signal-to-dark ratio $[(I-I_0)]/I_0$ where I is the current density through the irradiated detector, and I_o the dark current density for both parallel and perpendicular to the substrate.

3. RESULTS AND DISCUSION

The best film growth conditions achieved of no adhesion between film and substrate were a source temperature of 190 ºC and a growth temperature of 80 ºC; a growth time of 2 hours, with an initial pressure of 4 x 10^{-3} Pa. Several runs have been performed and results have been reproducible.

Fig. 1 shows scanning electron microscopies of a representative film of $HgBr_2$. Films have thicknesses between 100 and 1500 μm (±5 %), appropriate for absorption of radiation for X-ray imaging.

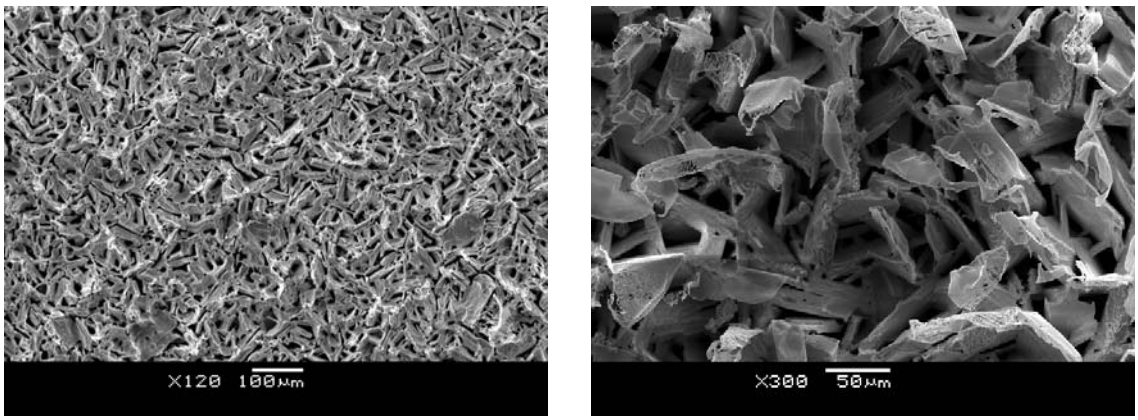


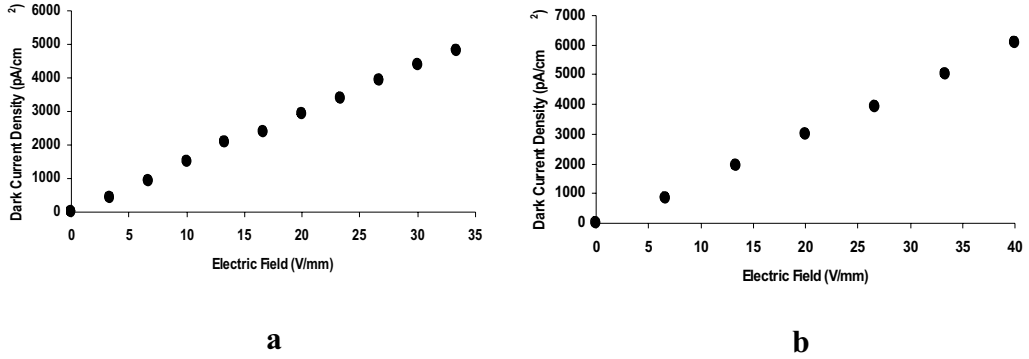
Fig. 1 Scanning Electron Microscopies of a representative film of $HgBr_2$, source temperature of 190 ºC and a growth temperature of 80 ºC; a growth time of 2 hours, with an initial pressure of 4 x 10^{-3} Pa

Film grain sizes are between (20 ± 10%) and (50 ± 10%) μm for $HgBr_2$ films, in the order of the pixellation needed for an acceptable spatial resolution for X-ray imaging.

Films of other layered compounds such as mercuric, lead, and bismuth iodides and lead bromide [18] have shown preferred growth orientations, with the *c* axis of their microcrystals perpendicular [19, 20] or parallel [21] to the substrate.

This fact leads us to think that $HgBr_2$ films may also grow with a preferred growth orientation. However, Fig.1 shows by far less evident orientation. Future efforts will be conducted to elucidate the crystallographic orientation of the film microcrystals.

Fig. 2 depicts the dark current density of a representative film as a function of the electric field applied to the detector using the electrodes in which electric field is perpendicular to the substrate (Fig. 2 a) and parallel (Fig. 2 b) to the substrate. The resistivities are 3.4 x 10^{11} Ω.cm and 3.3 x 10^{11} Ω.cm respectively. The dark current density is lower than 10 pA/mm^2 (the TFT maximum permissible value) for electric fields above 0.2 V/μm for both directions.

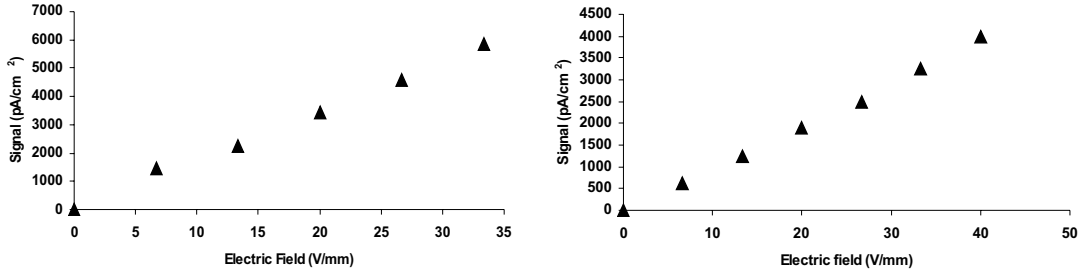


a **b**

Fig. 2. Dark current density of a representative film as a function of the electric field applied to the detector.

1. *For electric field perpendicular to the substrate*
2. *For electric field parallel to the substrate*

Fig. 3 shows the response of a representative film to a ^{241}Am source. The signal to dark responses of 1.5 at 35 V were obtained in both, for perpendicular and parallel conduction respectively.



a **b**

Fig. 3. Response of a representative films to a ^{241}Am source.

2. *Contacts perpendicular to the substrate*
3. *Contacts parallel to the substrate*

The detectors were also checked with visible and ultraviolet light, giving no response, therefore they do not need light shielding when used as X-ray sensors.

4. CONCLUSIONS

The anisotropical characterization of $HgBr_2$ layers for X-ray digital imaging is reported here for the first time. They have appropriate thickness and grain size for direct digital X-ray imaging. Comparing the resistivity values for both, perpendicular and parallel conduction, the obteined results do not agree with the expected anisotropy that may be attributed to a layered compound. This behaviour may be due to the lack of orientation of the film microcrystals, observed in SEM images and that must be confirmed by X- ray diffraction.

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