BiI_3 nucleation and coalescence onto amorphous substrates

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BiI_3 nucleation and coalescence was performed onto glass substrates. Further film growth onto the best nucleated layers were then made, with the objective of using these films as detectors for digital imaging. BiI_3 was synthesized from $Bi_2O_3CO_2$.H2O y KI, and then treated with HI to avoid the formation of BiOI by hydrolysis. The material was purified by zone melting followed by two sublimations. Nucleations were performed by physical vapor deposition (PVD) on 2"x2" glass substrates with an initial pressure of 4×10^{-3} Pa. Source and substrate were electrically heated, with temperatures ranging from 150-180 ºC and 50-150 ºC for source and substrate respectively, in order to study supersaturation influence on nucleation. The obtained nuclei were between 0.2 to 0.03 μm in size. Annealing was performed seeking for nuclei coalescence, heating them at 80-110 ºC during 5 days. Coalescence was only observed when annealing the smallest nuclei (sizes between 0.03 and 0.05 μm). Optical microscopy shows that nuclei coalescence giving rounded and highly oriented microcrystals, about 100 times larger in size than the original nuclei. Nuclei coalescence was found to increase with annealing time and temperature. Further growth of BiI_3 films was performed onto the best nucleated and coalesced layers. These films were characterized by optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Results are very promising; however, microcrystals do not have a preferred orientation as is desirable for using them for the final application they are intended for. Future work will be conducted to improve nucleation and coalescence seeking for uniformity as far as the best orientation for such final application, that means, for ionizing radiation digital imaging.
Keywords: BiI_3, nucleation, coalescence

1. INTRODUCTION

Nowadays, X-ray imaging is applied in many fields, such as medicine, industry, science, cargo inspection, and astronomical observation [1-5]. Photographic films, phosphor screens and amorphous silicon arrays have been used as imaging detectors for many years, but all these devices are indirect detectors, with low efficiency and poor spatial resolution. For that reason, crystalline films of high atomic number and high radiation absorption coefficient semiconductors are being studied, because they absorb the X-rays and convert them directly into electrical charges, which can be read, for example, by a thin film transistor (TFT) [6]. For that purpose, layers of appropriate semiconductors are grown onto imaging devices as such TFTs. When radiation is absorbed, electron-hole pairs are produced in the semiconductor, and the applied electric field directs them towards the imaging array. Materials with high atomic absorption coefficient, wide energy band gap but low energy necessary for the creation of an electron-hole pair, high mobility - life-time product, high purity and good stoichiometry, have to be used for such layers. Also, layers with the appropriate orientation and structure have to be grown: the maximum radiation absorption will take place when the film microcrystals are oriented parallel to the substrate, that means, perpendicular to the radiation beam. Besides, a better charge transport will occur for a texturized, or the best, for an epitaxial film. Finally, the better charge collection will take place for plain electrodes, such as the ones which may be deposited on the surface of a texturized or epitaxial film.

Bismuth tri-iodide, like mercuric and lead iodides, is a layered compound whose crystal lattice built from three layer packages (I-Hg-I; I-Pb-I; I-Bi-I) with weak Van der Waals bonding between adjacent planes of iodine atoms and perpendicular to the *c* axis [7–9]. Other analogies between bismuth tri-iodide and lead iodide are the metal ion outer electron configuration (5d 6s), and the melting point close to 408 ºC, depending on material purity.
BiI_3 presents good values of the properties important for X-ray detection, as can be seen in Table I.

Material	Z	d (g/cm^3)	μ (cm^2/g)	ΔE (eV)
a-Se	34	4.3	48.2	2.3
CdTe	48/52	6.2	21.4	1.4
TlBr	81/35	7.6	74.9	2.7
HgI_2	80/53	6.4	50.1	2.1
PbI_2	82/53	6.2	52.8	2.5
BiI_3	83/53	5.8	48.1	1.7
Reference		[10]	[11]	[10]

Table I - Comparison of the properties of BiI_3 with the ones of the other semiconductors used for growing films intended for X-ray imaging. Z: atomic number; d: density; μ: photon atomic absorption coefficient at 20 keV ; ΔE: energy band gap at room temperature

Attempts have been made for growing bismuth tri-iodide single crystal platelets by open flow sublimation and recrystallization [12], bulk monocrystals by PVD [8] and also by the vertical Bridgman method [7,9,13]. Bismuth tri-iodide films were grown years ago onto a monocrystalline substrate (lead iodide) and had thicknesses between 0.01 and 0.1 μm [14].
During the last years, our group has been studying the growth of BiI_3 films [15, 16] and platelets [17,18], and its application as X-ray detectors [15]. We have obtained oriented layers, and we have confirmed an improvement in orientation with the increase of the growth temperature [16]. Taking all these facts into account, we have changed the growth conditions up to a limit (higher growth temperature gives lack of adhesion of the film) and we have obtained oriented films but not epitaxial ones. Seeking for the epitaxy (for improving the charge transport and having a plain electrode), we considered that we had to improve the first stages of growth. For this reason, we study nucleation and coalescence of BiI_3 on glass substrates. As the final application requires to grow a film onto a TFT, which consists of several materials deposited on glass substrates, we studied nucleation, coalescence and further growth of BiI_3 onto glass substrates.

2. METHODS

Bismuth tri-iodide was synthesized from bismuth subcarbonate and potassium iodide and then treated with HI to avoid the formation of BiOI by hydrolisis. The material was purified by zone melting followed by two sublimations.
Nucleation and coalescence experiments were performed in quartz ampoules 11 cm in diameter and 16 cm in length, cleaned with aqua regia for 12 hours, rinsed with distilled water and outgassed for 12 hours at 800 ºC and 4 x 10^{-3} mmHg. Nucleations were performed by physical vapor deposition (PVD) in 2”x2” glass substrates with an initial pressure of 4 x 10^{-3} Pa. The system used was specially designed and constructed for getting a close control of the nucleation parameters, such as the geometrical disposition of the starting materials and nucleation temperature and time. Source and substrate were electrically heated, with temperatures in the range 150-180 ºC for the source and 50-150 ºC for the substrate, in order to study supersaturation influence on nucleation.

Annealing was performed seeking for nuclei coalescence, electrically heating them at temperatures between 80 and 110 ºC during 5 days, and in some cases at a pressure of argon of 27 KPa.

Grain size and microcrystal morphology of the resultant layers were observed 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.

Films of BiI_3 were further grown onto the best nucleated layers, using conditions appropriated for growing highly oriented films, as was reported elsewhere [16]. These films were characterized by optical microscopy, scanning electron microscopy and atomic force microscopy (AFM) using a Digital Instruments model Multimode Nanoscope 3A.

3. RESULTS AND DISCUSION

Nucleation

When nucleation was performed, varied nuclei sizes were observed, depending on growth temperature. Table 2 shows the average nuclei size for some representative growth temperatures.

Source Temp. (ºC)	Substrate Temp. (ºC)	Nucleation Time (s)	Nuclei size (μm)	Coalescence
180-160	100-150	30	0.2	Not observed
150	50	30	0.03-0.05	Observed
150	150	30	Nucleation was not observed	-
180	50-100	30	0.5-0.1	Not observed

Table 2-Representative nucleation conditions used for BiI_3 nucleation and coalescence and obtained grain sizes

The best conditions for nucleation were 150 ºC and 50 ºC for source and substrate respectively; nuclei of 0.03 μm in size were obtained. This fact correlates with previous experiments, and confirms that when the substrate temperature decreases the microcrystals grain size also decreases.

Annealing

The best annealing conditions were 110 ºC with a pressure of argon of 27 KPa. When annealing was performed to the best nucleations, coalescence was only observed for the smallest nuclei (sizes between 0.03 and 0.05 μm). After the annealing larger and rounded nuclei were observed, as can be seen in Figure 1.This is the first time that coalescence of BiI_3 nuclei has been observed. This type of coalescence corresponds to Ostwald ripening, where there is mass transport from the smaller nuclei to the larger ones; this occurs when nuclei tend to minimize the surface free energy of their structure. As showed in Figure 1, the coalesced nuclei are about 100 times larger in size than the original ones, and show a preferred orientation with their surface parallel to the substrate. As a result, coalescence determines that the larger nuclei grow at expenses of the smaller ones.

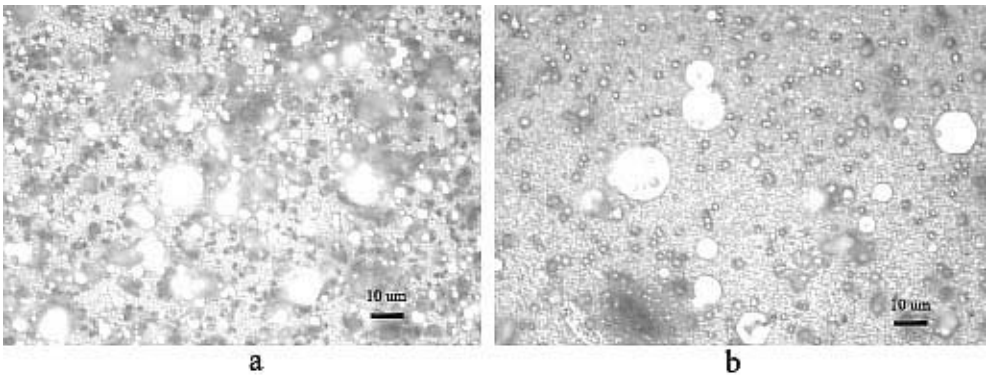

Figure 1 –Optical Microscopies, (a)Nucleation performed in the best conditions, (b)Previous nucleation after annealing.

However, we can distinguish in Fig 1.b other small nuclei that have not coalesced yet. Because of the size of these nuclei, they can not be studied by optical microscopy, and were observed by atomic force microscopy.

Further film growth

Films were grown onto the best annealed nucleations, for testing the influence of the first layer on their further growth. The film deposition conditions were 150-170 ºC and 300 ºC for substrate and source respectively. Unfortunately, we did not obtain a highly oriented film. Although the microcrystals in the coalesced layers have the desired orientation, there are very few and separated nuclei and possibly, only some microcrystals of the resultant film grow parallel to the substrate at the end, a polycrystalline film is obtained. Figure 2 shows an optical microscopy of a film grown onto a coalesced layer.

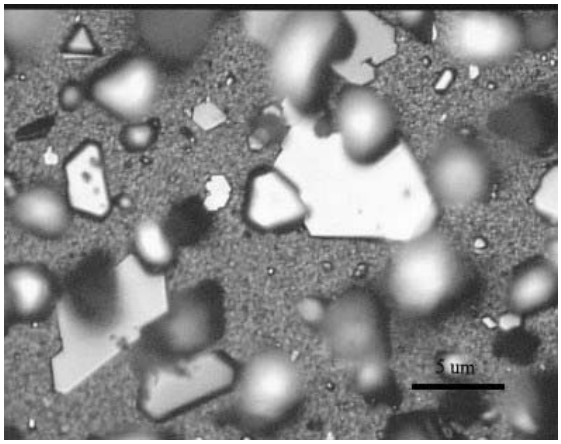

Figure 2 –Optical Microscopy of a representative film

Figure 3 shows an atomic force microscopy of the rear layer of smaller microcrystals, which can not be clearly seen in the optical microscopy.

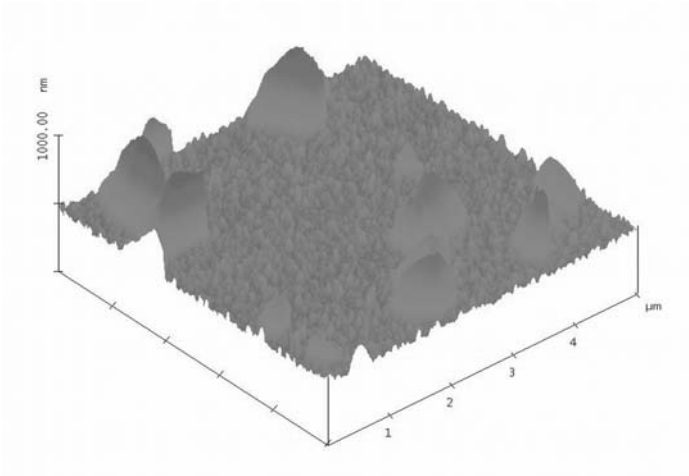

Figure 3 –Atomic Force Microscopy of a BiI_3 film

Although we have not obtained an epitaxial or highly oriented BiI_3 film yet, our results are very promising, because we have identified the conditions for nucleation and coalescence of this material onto an amorphous substrate.
Future work will be oriented to improve the conditions for BiI_3 nucleation and coalescence, seeking for a first layer homogeneous and oriented, for using it for further growth of an epitaxial film.

4. CONCLUSIONS

BiI_3 nucleation and coalescence were observed for the first time. It was possible to identify the coalescence of BiI_3 as Ostwald ripening. Orientation of the nuclei after annealing was also observed, and BiI_3 films were grown onto coalesced layers. Although these films have not yet the preferred orientation parallel to the substrate, results are very promising and led us to study more carefully the appropriate conditions for nucleation, coalescence and further film growth.

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