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Correlation between supersaturation and phase for the heterogeneous nucleation and coalescence of HgI_2 onto amorphous substrates

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HgI_2 99 % was purified by four evaporations at 300 ºC and with an initial pressure of 10^{-3} Pa. The heterogeneous nucleation of HgI_2 onto glass was studied by the physical vapor deposition (PVD) method, with and without argon atmosphere. Glass substrates 2"x2" in area, with and without palladium coating, were used for nucleation and coalescence. Nucleation conditions, specially supersaturation, strongly determined nuclei population and size but also determined the HgI_2 nucleation phase. A range of nucleation temperature between 30 ºC and 60 ºC for the substrate and the same temperature of the source for each set, and a range of initial Ar pressure between 1.3–2.6 x 10^4 Pa were found as appropriate for nucleation of the α (red) phase of HgI_2. Other nucleation condition, as a temperature gradient between the source and the substrate or an argon pressure higher than 4 x 10^4 Pa, determine nucleation of the β (yellow HgI_2) metastable phase.

Nucleation took place by the Volmer Weber mechanism, with islands 1-5 μm in size, for both, α and β phase. Coalescence was performed annealing the substrate at a temperature between 30 and 60 ºC and from 5 minutes to 24 hours, at an initial argon pressure of 10^4 Pa. Nuclei coalesce to form larger islands, which, in the case of β phase nuclei also transform to the α stable phase. From the experimental nucleation and coalescence conditions, correlations between supersaturation conditions and nuclei phase were established; theoretical considerations about the surface adhesion energy (γ_{hkl}) were made. Future efforts will be conducted to improve nucleation uniformity, to better study nuclei properties and to search for coalescence and further growth better conditions.

Keywords: HgI_2, phase transition, nucleation, coalescence

1.INTRODUCTION

Crystalline compound semiconductors films are very important because of their technological applications, such as solar cells and imaging adquisition systems.

Crystalline films can be classified taking into account their microcrystals orientation, in pollycrystalline (ramdomly oriented crystallites), oriented (in one or two axis) or epitaxial (single crystal orientation)[1]. The texture of the film is very important because it will determine some properties of the final devices made with it. Theoretical studies indicate that an epitaxial film will have better properties - for example optical, electrical and carriers transport - than a polycrystalline one. This may be attributed to a better transport though a perfectly ordered structure but also to the electrode uniformity and consequently to the electric field uniformity, when an electric field must be applied.

The family of the heavy metal halides has been being studied as X – ray detectors for imaging systems for more than ten years [2-10]. Mercuric iodide has the best properties for such application: high atomic number, high density, adequate band gap at room temperature and high radiation absorption coefficient. It has many polimorphic forms: red α-HgI_2, yellow β-HgI_2 and metastable orange phases. The α phase is tetragonal and stable up to 127 ºC, then it transforms into the yellow orthorrombic β-HgI_2 [11].

The variety of structural modifications has to be taken into account in the cristalization process of HgI_2. For instance, the concurrent appearance of red and yellow microcrystals is the main difficulty during the nucleation of HgI_2 from the vapor phase.

Until now oriented α-HgI_2 films were grown by several methods, mainly by the Physical Vapor Deposition (PVD) method. The signal to noise of these films are the highest reported for films of this compound; this let us to think that if the epitaxy of the film is succeed, even better properties would be obtained [12]. For this purpose a meticulous study of the first growth stages of the film growth (nucleation and coalescence) turned out indispensable. Nucleation is the first stage in any phase transition including crystallization. It can take place by three mechanisms, Frank-van der Merwe (by layers), Volmer Weber (in islands) and Stranski Krastanov (first layer by layer and then in islands), as a function of the surface adhesion energy (γ_{hkl}). A continuous monolayer can be obtained from island nucleation by further coalescence.

In light of these antecedents, we report here for the first time the correlation between supersaturation and phase for the heterogeneous nucleation and coalescence of HgI_2 onto amorphous substrates.

2. METHODS

Mercuric iodide Aldrich 99 % purified by four sublimations, at 300 ºC and an initial pressure of 10^{-3} Pa was used as starting material for nucleation experiments.

Nucleations were performed by the Physical Vapor Deposition method (PVD) onto 2" x 2" glass substrates with and without Pd coating. 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 material and nucleation temperature and time.

Parameters were varied to obtain the best nucleation conditions. A source temperature between 20 and 100 ºC, a nucleation temperature between 20 and 100 ºC, and an initial pressure from 10^{-3} to 4×10^4 Pa were used.

Coalescence was performed annealing the nuclei at a temperature between 20 and 60 ºC and from 5 minutes to 24 hours at an initial Ar pressure of 10^4 Pa.

Nucleations and coalescences were characterized by optical microscopy using a Nikon Model EPIPHOT 300 microscope. Grain size was measured fron optical microscopy.

3. RESULTS AND DISCUSSION

The conditions for nucleation of α-HgI_2 (red) were: a temperature between 30ºC and 60ºC for the substrate and the same source temperature for each set (supersaturation equal zero), and a range of initial pressure between 10^{-4} Pa and 1.3–2.6 x 10^4 Pa of Argon. Other nucleation conditions, such as a temperature gradient between source and the substrate or an argon pressure higher than 4×10^4 Pa, determine nucleation of the β (yellow) metaestable phase.

The best nucleation condition in order to obtain the red phase (stable at room temperature) with appropriate grain size and nuclei density were a source temperature of 60 ºC, a substrate temperature of 60 º C and an initial pressure of 1.3 x 10^4 Pa of Ar. Table I summarizes the results obtained with different conditions.

Table I: HgI_2 phases obtained as a function of supersaturation and initial pressure for nucleation on glass substrates.

Supersaturation	**Source temperature (ºC)**	**Substrate temperature (ºC)**	**Initial Pressure (Pa)**	**Obtained Mercuric iodide phase**
> 0	40 - 100	30 - 80	$10^{-4} – 10^{4}$	β - HgI_2 (yellow)
0	30 - 60	30 - 60	10^{-4}	α - HgI_2 (red)
	60	60	1.3×10^{4}	α - HgI_2 (red)
			2.6×10^{4}	α - HgI_2 (red) β - HgI_2 (yellow)
			3.9×10^{4}	β - HgI_2 (yellow)
< 0	30 - 40	35-50	10^{-4}	No nucleation was observed

Correlation between nucleation, supersaturation and phase

No nucleation was observed with negative supersaturation as was expected, whereas adequate nuclei density of red HgI_2 was obtained with supersaturation equal to zero and low initial pressure. This behavior is supported by theoretical thermodynamical studies of the free Gibbs energy [13]. For heterogeneous nucleation the free Gibbs energy has two components, one directly proportional to supersaturation and the other directly proportional to the free energy of adhesion. The energy of adhesion makes negative the free Gibbs energy at zero supersaturation allowing the nucleation in such condition.

Thermodynamics also predicts that the further growth at zero supersaturation is not possible, this was experimentally observed by increasing the nucleation time with no change in nuclei size and density.

Although the yellow phase is stable above 127 ºC, β-HgI_2 nuclei were obtained at lower temperatures and positive supersaturation, as can be seen in Table I. This phenomenon was also observed and reported elsewhere [14].

Correlation between nucleation and vapour pressure

The vapour pressure of a condensed phase increases with the total applied pressure with the following equation $\ln\frac{\pi}{\pi_e} = \frac{V_S P_T}{RT}$, where π_e represents the equilibrium vapour pressure, and π the vapour pressure under a total pressure of P_T. As a consequence of this, the vapour pressure of HgI_2 at 60 ºC increases 14 % with the addition of 100 mmHg of Ar. Therefore, HgI_2 nuclei density increases with the argon pressure, giving the best condition of nucleation. However, Ar pressure can not be increased indefinitely. At about 2.6×10^4 Pa of argon pressure yellow nuclei start to growth. This behaviour can be attributed to the consequent increment in the HgI_2 vapour pressure, which could determine a change in the nuclei deposition kinetics.

Nucleation mechanisms

Fig 1 shows nucleations in both phases (a- red and b-yellow).

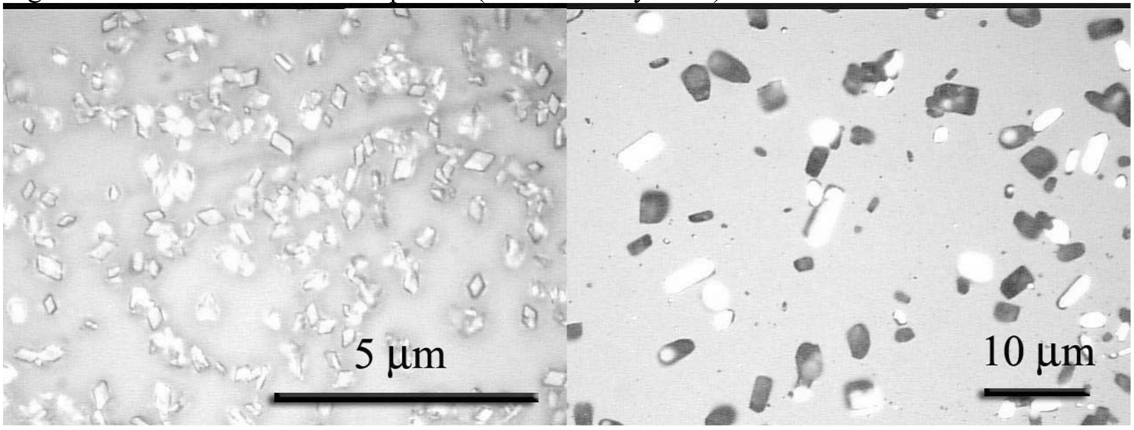

Fig. 1. a- Red(orthorrombic) α-HgI_2 nucleation. b-Yellow (tetragonal) β-HgI_2 nucleation

Nucleation took place by the Volmer Weber mechanism, with islands 1-5 μm in size, for both, α and β phase. This may be attributed to the low adhesion energy between the crystallites and the amorphous substrate.

Coalescence

Coalescence was performed annealing the substrate at a temperature between 30 and 60 ºC and from 5 minutes to 24 hours, at an initial argon pressure of 10^4 Pa. Fig 2 shows a coalescence of red nuclei obtained by annealing the substrate at 40 º C for 24 hours.

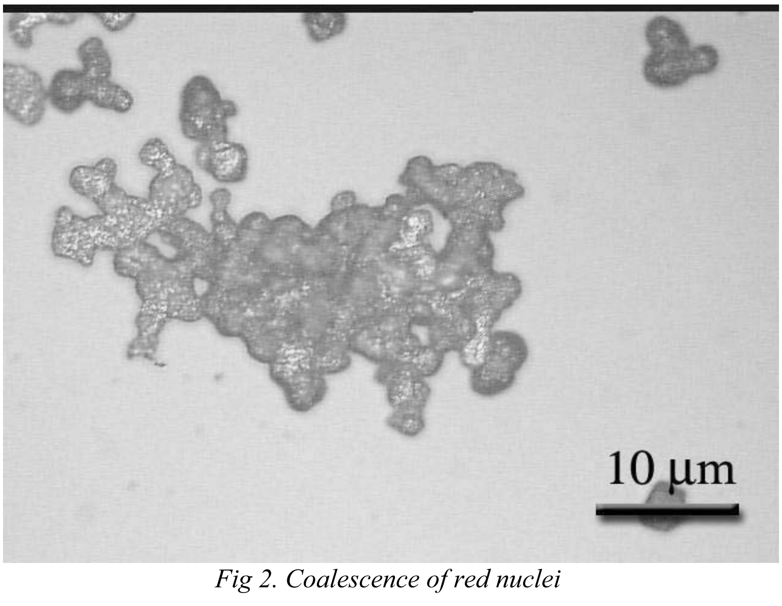

Fig 2. Coalescence of red nuclei

Fig. 3 shows a coalescence of yellow nuclei obtained by annealing the substrate at 40 º C for 24 hours

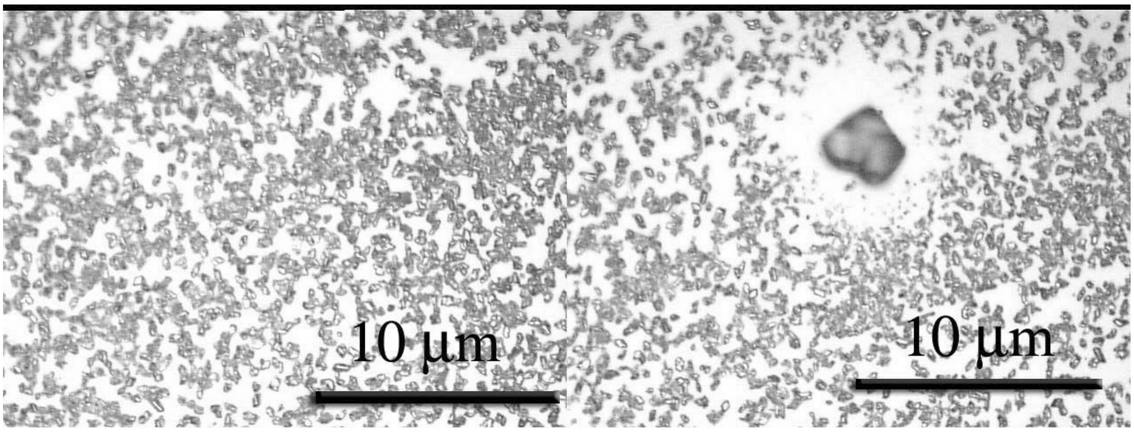

Fig 3. Coalescence of yellow nuclei

As the vapour pressure of a material is a function of the particle size, the small ones tend to shrink and the larger ones to growth because the vapour pressure above the small particles is greater than the vapour pressure above the large ones. As a consequence nuclei coalesce to form larger islands, which, in the case of β phase nuclei also transform to the α stable phase.

It can be observed the phase transition from yellow to red phase during the annealing process.

Future efforts will be conducted to improve nucleation uniformity, to better study nuclei properties and to search for coalescence and further growth better conditions.

4- CONCLUSIONS

Nucleation conditions, specially supersaturation, strongly determined nuclei population and size but also determined the HgI_2 nucleation phase. Zero supersaturation determine nucleation in the red phase. This condition only determines the nuclei formation, but not the further growth. Nuclei coalescence nuclei was reached, so the first steps of film growth of α-HgI_2 were achieved. Future effort will include the search of uniform first monolayers and further film growth.

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1. E. I. GIVANGIZOV, Oriented crystallization on amorphous substrates, 1st Edition, New York, Plenum Press, (1991)
2. J.S. IWANCZYK, B.E. PATT, C.R. TULL, L.R. MAC DONALD, N. SKINNER, E.J. HOFFMAN AND L. FORNARO, HgI_2 Polycrystalline Films for Digital X-ray Imagers, Trans. Nucl. Sci, 49, 160-164, (2001).
3. L. FORNARO, E. SAUCEDO, L. MUSSIO AND A. GANCHAROV, Towards epitaxial lead iodide films for X-ray digital imaging, Trans. Nucl. Sci., 49, 2274-2278, (2002).
4. G. ZENTAI, L. PARTAIN, R. PAVLYUCHKOVA, C. PROANO, G. VIRSHUP, L. MELEKHOV, A. ZUCK, B. BREEN, O. DAGAN, A. VILENSKY, M. SCHIEBER, H. GILBOA, P. BENNET, K. SHAH, Y. DMITRIYEV, J. THOMAS, M. YAFFE AND D. HUNTER, in Proc. SPIE, 5030, 77-91, (2003).
5. L. FORNARO, E. SAUCEDO, L. MUSSIO AND A. GANCHAROV, Comparison between sublimation and evaporation as processes for growing lead iodide Polycrystalline films, in Proc. SPIE vol. 4507, 99-107, (2001).
6. L. FORNARO, E. SAUCEDO, L. MUSSIO, A. GANCHAROV AND A. CUÑA, Bismuth tri-iodide polycrystalline films for digital X-ray radiography applications, Trans. Nucl. Sci., 51/1, 96-100, (2004).
7. A.CUÑA, I. AGUIAR, A. GANCHAROV, M. PÉREZ, L. FORNARO, Correlation between growth orientation and growth temperature for bismuth tri-iodide films, Crystal Research and Technology, 39/10, 899-905,(2004).
8. L. FORNARO, H. ESPINOSA, A. CUÑA, I. AGUIAR, A. NOGUERA, M. PÉREZ, Feasibility of HgBrI as photoconductor for direct X-ray imaging, IEEE Trans. Nucl. Sci, 52/6, 3103-3106, (2006).
9. L. FORNARO, H. CHEN, K. CHATTOPADHYAY, K.–T. CHEN, A. BURGER, Optical, electrical and surface characterization of mercuric iodide platelets grown in the HgI2-HI-H2O system, in Proc. Mat. Res. Soc. Sym., 487, 339-344, (1998)
10. M. GILES, A.CUÑA, N. SASEN, M. LLORENTE, L. FORNARO, Growth of lead bromide polycrystalline films, Crystal Research and Technology, 39, 10, 906-911, (2004).
11. M. PIECHOTKA, Mercuric iodide for room temperature radiation detectors. Synthesis, purification, crystal growth and defect formation, Material science and engineering, R18, 1-2, 1-98, (1997).
12. L. FORNARO, A. CUÑA, A. NOGUERA, I. AGUIAR, M. PÉREZ, L. MUSSIO, A. GANCHAROV, Low dark current *(0 0 l)* Mercuric Iodide thick film for X- Ray direct and digital imager, IEEE Transactions on Nuclear Science, 52/6, 3107-3110, (2006).
13. A.A.CHERNOV, Modern Crystallography III Crystal Growth, Springer-Verlag, Berlin Heidelberg, New York – Tokyo, (1984).
14. J.B. NEWKIRK, Acta Metall., 4, 316 (1956).