Characterization and Simulation of PbS Photoconductors Prepared by Chemical Bath Deposition.

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Abstract — **The present work deals with the characterization and simulation of lead sulfide (PbS) photoconductors infrared detectors growth by Chemical Bath Deposition (CBD) method. Three different solutions bath are used in order to explore the doping effect and oxidant agent on detection capabilities. Photoelectrical characterization indicates that detectors performances depend strongly on oxidant and doping agents. A simulation study with surface state model is also presented. The physical parameters are deduced and are found to be in agreement with those published in the literature**.

Keywords- Chemical Bath Deposition; photoconductors; infrared detectors; surface state model; PbS.

I.   INTRODUCTION

Thin film lead sulfide detectors have been widely used over the past years for radiation sensing in 1 to 3µm spectral region. They are mainly very useful in academic, commercial and military applications. In military application, PbS detectors are used for both tactical and strategic systems, with a very strong emphasis towards an increasing requirement for large area multiple element arrays.

Unlike most other semiconductors IR detectors, lead sulfide materials are used in the form of polycrystalline films approximately 1µm thick and with individual crystallites ranging in size from approximately 0.1µm to1 µm. They are usually prepared by chemical bath deposition (CBD), which generally yields better uniformity of response and more stable results than the evaporate methods [1]-[5].

As-deposited PbS films exhibit very low photoconductivity, however, a post deposition process are used to achieve final sensitization. To obtain high performance detectors, lead chalcogenide films need to be sensitized by oxidation. This oxidation may be carried out using additives in the deposition bath, post-deposition heat treatment in the presence of oxygen, or chemical oxidation of the films.

Others impurities added to the chemical–deposition solution for PbS have a considerable effect on photosensitivity films characteristics [5]-[9]. They may increase the photosensitivity by some order of magnitude more than films prepared without these impurities [8] [9].

This work deals with characterization and simulation of PbS photoconductors infrared detectors prepared by CBD. The effect of oxidant agent and Bismuth Nitrate additives on the performances of PbS detectors is also examined. Finally, a simulation study with surface state model proposed in [10] [11] is also presented. This paper is organized as follows: Section I presents the particularities associated with PbS infrared photo- detectors development. Section II details the experimental procedure for devices fabrication and characterization. After analysis of surface morphology and film structure in subsection III.A, we performed optical measurements (III.B) in order to understand the effect of additives of oxidation and doping on structural and optical properties of deposited PbS films. Based on surface state model reviewed in subsection III.C, a comparison between photoelectrical measurements of developed PbS photoconductors and theoretical prediction is proposed in subsection III.D. The conclusions and perspectives are described in Section IV.

II.   EXPERIMENTAL DETAILS

The setup deposition of *E. Pentia et all* [9] was used for growing the PbS films over three bath solutions, summarized in Table I. The bath 1 contain the basic precursors which are Lead Nitrate $Pb(NO_3)_2$, Sodium Hydroxide (NaOH) and Thiourea $SC(NH_2)_2$, the bath 2 contain in addition an oxidant agent, named Hydroxylamine Hydrochloride (NH_2OH-HCl), and the bath 3 contain in addition to bath 2, the Bismuth Nitrate $Bi(NO_3)_3$ as doping agent.

Aqueous solution of 0.069 M lead nitrate, 0.69 M NaOH and 0.24 M thiourea were used. In order to prepare PbS films, the following procedure was adopted: 20 ml of lead nitrate solution was mixed with 20 ml of NaOH with constant stirring. The initial color solution was milky, after it became transparent, 20 ml of thiourea solution was gradually added followed by addition of oxidant with 20 ml of 0.086 M Hydroxylamine Hydrochloride (NH_2OH.HCL), again with constant stirring, the global solution was diluted with 20 ml of water. Finally, a small quantity of Bismuth nitrate with 1.5 ml of $2.06 10^{-4}$ M was added to some reactions. The PbS films were deposited on microscope glass substrate cleaned, for about 48 h, in a mixture of (HNO_3, ($K_2Cr_2O_7$: H_2SO_4; 1:10), 1% EDTA followed by rinsing in distilled water.

TABLE I.   SOLUTIONS BATH

Bath 1	$Pb(NO_3)_2$	NaOH	$SC(NH_2)_2$		
Bath 2	$Pb(NO_3)_2$	NaOH	$SC(NH_2)_2$	$NH_2OH.HCl$	
Bath 3	$Pb(NO_3)_2$	NaOH	$SC(NH_2)_2$	$NH_2OH.HCl$	$Bi(NO_3)_3$

After drying, one facet of this substrate was stuck with an inert paste on a support having T format introduced vertically in the reaction bath containing the chemical mixture. After some time, the transparent color solution started to change to become completely black after one (01) hour.

The measured film thicknesses, using DEKTAK profilometer, were about 150 nm for both films elaborated with and without oxidant. Thicker films were obtained by repeated deposition. Gold electrodes were evaporated on the surface of PbS films for electric and photoelectric measurements in a coplanar configuration. The films characterizations were performed after annealing in air at 80° C for approximately 70 h.

Structural properties were evaluated by x-rays diffraction using a D5000 Siemens diffractometer. The scans were carried out at room temperature, in the conventional $\theta/2\theta$ mode using Cu-Kα radiation (0.1542 nm). The morphology was observed by scanning electron microscopy (SEM) using a JEOL 6400F microscope. The optical properties were studied with a CARY 5000 UV-Vis-NIR double beam spectrometer. The photoconductivity measurements were performed with a system constituted by a standard IR light source, an Oriel MS257 monochromator operated in the range 1-20 μm, a chopper fixed at 400 Hz and the acquisition equipment composed with spectrum analyzer, lock-in amplifier and oscilloscope.

III.   RESULTS AND DISCUSSIONS

A.   Surface morphology and films structures

Figures 1 and 2 show SEM micrographs of PbS films deposited with and without oxidant. It appears that the average grain size increases with the used oxidant. Concerning the films structural properties, Figures 3 and 4 show the effect of annealing treatment (T=80°C,for 72h) and Bismuth doping on the XRD (X Rays Diffraction) patterns of deposited PbS films. As can be seen, films deposited with hydroxylamine hydrochloride additive are less textured when compared to films prepared without this additive, which are (200) preferentially oriented, the grains become oriented quasi-equally with (200) and (111) crystallographic direction. The effect of annealing at 80°C for 72h and doping with bismuth nitrate, affects in opposite manner the XRD patterns. As seen, the annealing increases, while the doping decreases the films texture.
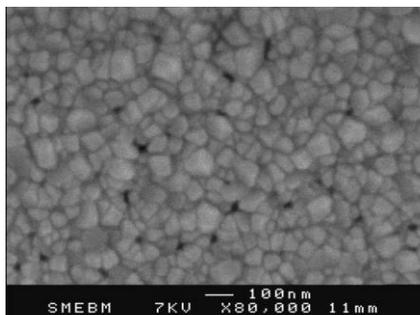

Figure 1. SEM image of PbS films prepared without oxidant agent
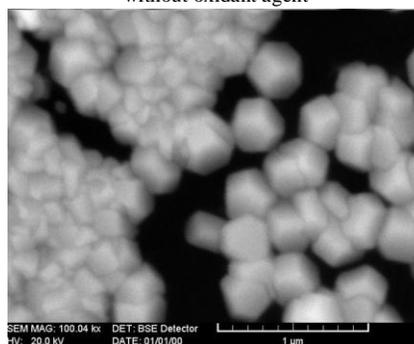

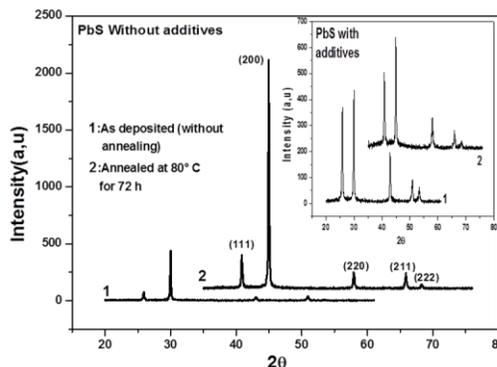Figure 2. SEM image of PbS films prepared with oxidant agent

Figure 3. Effect of annealing on the XRD patterns of PbS films
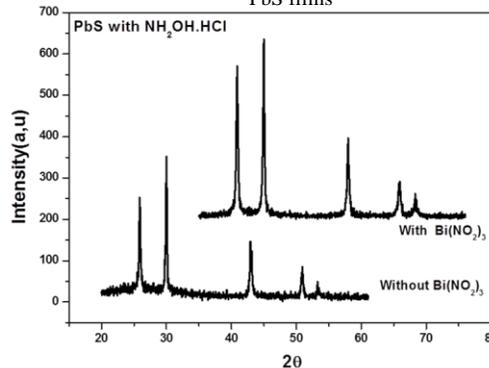

Figure 4. Effect of doping with $Bi(NO_2)_3$ on the XRD patterns of PbS films

B. Optical properties

Figures 5 and 6 show the transmittances (T$_{corr}$) and ($\alpha h \nu$)^2 plots of PbS films prepared with different baths and annealed at 80° C for 72 h respectively. The inset shows the absorption coefficient of these films. As shown, oxidant and doping affect the optical properties. The optical band gap was calculated from the spectral absorption near the fundamental absorption edge. The direct band gap of all synthesized PbS films was estimated using the Tauc relation given as follow

$$\alpha h \nu = A\left(h\nu - E_g\right)^{\frac{1}{2}} \qquad (1)$$

where 'A' is the parameter which depends on the transition probability. For direct transition in the fundamental absorption, ($\alpha h \nu$)^2 have linear dependence on the photon energy (hν). The intercept on energy axis gives the direct band gap energy. Based on the optical transmission measurements, we have obtained the direct band gap energy for PbS films grown by different baths, which is 0.42 eV for films prepared without additive (referred as 1), it becomes 0.5 eV for films prepared with oxidant (referred as 2) and 0.56 eV for films prepared with doping agent (referred as 3).
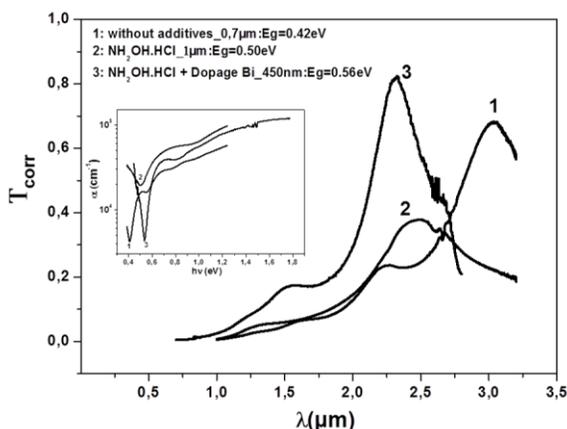

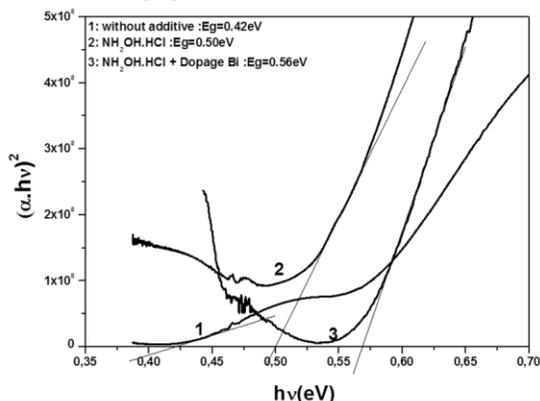Figure 5. Transmittances of PbS thin films prepared with different bath solution

Figure 6. Plot of ($\alpha h \nu$)^2 for PbS thin films prepared with different bath solution
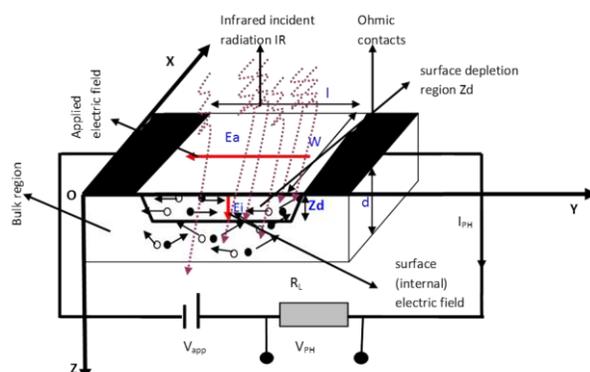

Figure 7. Schematic structure of surface state model [10]

C. Surface state model

Photoconductivity in PbS films can be explained by two models depending upon whether the semiconductor is single-crystalline or polycrystalline, which are recombination and barrier models respectively. The recombination model assumes that change in conductivity on illumination results from the change in the number of conducting electrons or holes per unit volume. In the barriers model, it is assumed that illumination produces little or no change in the density of charge carriers but an increase in their effective mobility. A large number of surface defects are produced along the crystalline boundaries. These surface defects capture electrons from the interior of the single-crystalline and produce space charge barriers. Illumination reduces the number of electrons in the surface defects and thereby lowers the barrier height. In real polycrystalline material, the observed photoconductivity may be due to a combination of both recombination and barrier processes. One of these combination models is the surface state model proposed by [10] [11] (figure 7).

This model treats the free surface with different manner of precedent model [12] [13]. It was characterized by surface state density (N_t), unique energy level (E_t) associated with defect localized in the forbidden gap and effective cross section (σ) rather than the surface recombination velocity. In this model, the barrier height at the semiconductor free surface is modified under photonic excitation. It was suggested that recombination influence directly the quantum efficiency of detector. All models accept that, the role of oxidant is assumed to introduce a trapping state that inhibits recombination; these traps capture the minority carriers and thereby extending the life time of material. As mentioned above, without the sensitization step, lead sulfide has very short life time and a low response.

The concentration of excess carriers density; the key parameter of this model, allows us to explore all the theoretical equations of detectors figure of merit. This parameter is calculated with a self-consistent way, taking into account the resolution of continuity equation of majority and minority carriers in the depletion and neutral (Bulk) region of material, given by [10][11];

$$\Delta n(z) = B_n \exp\left[-\left(\frac{z - z_d}{L_n}\right)\right] +$$

$$\frac{L_n}{2D_n}\int_{z_d}^{z} G(z')\left\{\exp\frac{-|z - z_d|}{L_n} - \exp\left[\frac{-(z + z' + 2z_d)}{L_n}\right]\right\}dz' \quad (2)$$

Where B_n is the concentration of excess carriers density at free surface (z=0), which is determined by the appropriate conditions of limits [14], Z_d, L_n, D_n and $G(z)$ are width of depletion region, diffusion length, diffusion coefficient and generation rate respectively. Detailed calculation of the surface analysis, optical generation and photoconductor performances (Signal, Spectral response or responsivity and specific detectivity) is presented respectively in the appendix.

D. Photo-detection performances measurement and simulation

In order to investigate the influence of oxidant and doping on detection and capabilities of PbS films, three photoconductive detectors prepared with and without additives (table I) have been analyzed. To avoid the Flicker noise, manifested at low frequency, the chopping frequency at 400 Hz and the total polarization voltage at 50 V have been fixed. The test set used provides radiant flux in a very narrow spectral band centered about any desired wavelength (λ). There are three functional controls on the monochromator:

- The centered λ of the exciting beam;
- The width of the spectral interval centered at λ;
- The amount of flux passing through the monochromator.

A constant flux per unit λ interval should be maintained for any selected λ center in the interval of [1-4 μm]. According to application data sheet of the infrared source, the power of infrared radiation is calculated manually by assuming the IR source as a blackbody at 1230° C (the IR source is a Silicon Carbide SiC emitted in the range of 0.7-28μm, the irradiance of this source is nearly the same of blackbody heated at 1230°C, particularly in 0.7-3μm spectral range) [15].

It is interesting to notice, here, that the noise is measured in the absence of light, with lock-in amplifier and spectrum analyzer under equivalent noise band width of Δf=50, the effective value of noise is done by $V_n/(\Delta f)^{1/2}$ [16]. The values of Vn (noise voltage in rms) for photoconductors prepared with three baths are 55.15, 86.3 and 63.6 μV respectively.

This measurement of noise is crucial in the calculating of spectral specific detectivity, which depends of the ratio of spectral response and noise.

Figures 8, 9 and 10 show the signal, spectral response and specific detectivity of these photoconductive detectors fitted with surface state model [10] [11]. The oxidant enhances the capabilities of detection comparatively to detectors prepared without oxidant. The doping increases again these capabilities and decreases the peak wavelength.

The best adjustments are obtained with the data reported in Table II. It should be noted that, the confrontation between experimental and calculated data of signal is excellent, but a small discrepancy in spectral response and specific detectivity for the first point of measurement is observed. It is probably due to high fluctuation of signal at low wavelength. Also, the parameters issued with this simulation are in agreement with the published ones in the literature [17] [18].
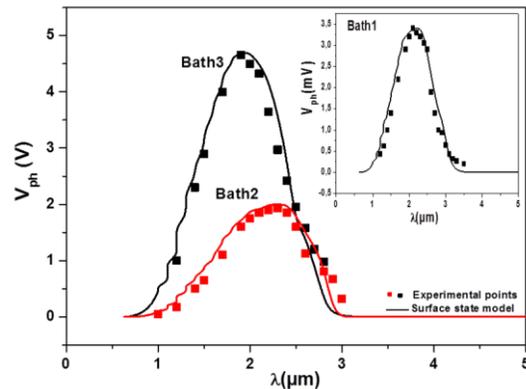

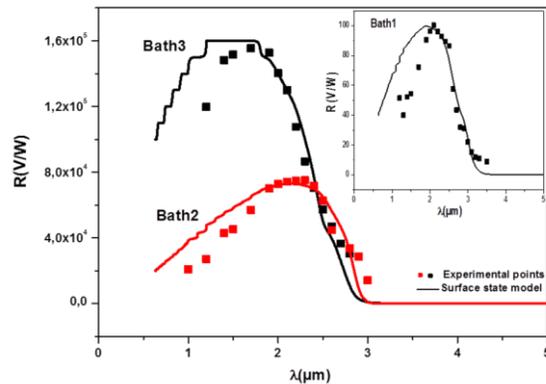Figure 8. Simulation of signal with surface state model

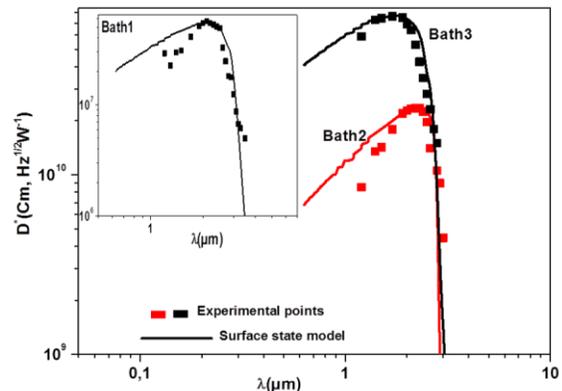Figure 9. Simulation of spectral response with surface state model

Figure 10. Simulation of spectral detectivity with surface state model

TABLE II. SIMULATION RESULTS

Detector	Bath 1	Bath 2	Bath 3
Simulated parameters			
E_g **(eV)**	0.43	0.43	0.48
L_p **(μm)**	500	500	400
Z_d **(nm)**	30	10	10
N_a **(cm^{-3})**	$5 10^{17}$	$5 10^{17}$	$5 10^{17}$
E_t **(eV)**	0.42	0.42	0.47
σ **(cm^2)**	$2.55 10^{-14}$	$3.4 10^{-16}$	$2.45 10^{-17}$
N_t **(cm^{-2})**	$1.5 10^{12}$	$5 10^{11}$	$5 10^{11}$
Introduced parameters			
d**(μm)**	0.7	1	0.45
A_d **(cm^2)**	0.4	0.3	0.4
R_L**(MΩ)**	0.1	0.1	0.25

IV. CONCLUSION

In the present work, detectors based on sensitized thin films, growth by chemical bath deposition are studied. The photoelectrical characterization allowed that, detectors developed without oxidant has approximately very low performances (Signal, Responsivity and Specific Detectivity) compared with those developed with oxidant. The use of doping agent increases again these performances along with decreasing the peak position wavelength of detector.

A simulation study of proposed IR photoconductors, using surface state model, has been also presented. The plots show the ability of this model to adjust their performance behavior.

The extracted physical parameters are in agreement with those published in literature.

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APPENDIX

A. Surface analysis

Assuming that Q is the absolute charge at the surface absorber material, then

$$Q = eZ_d N_a = eN_t(1-f)$$
$$\Downarrow$$
$$Z_d = \frac{N_t}{N_a}(1-f) \qquad (A1)$$

Where Z_d is the depletion region width and f the occupation probability of the donor energy level given by [10] [14]:

$$f = \frac{\Delta n(0) + n_0 + n_i \exp(\frac{E_t - E_i}{kT})}{\Delta n(0) + n_0 + \Delta p(0) + p_0 + 2n_i \cosh(\frac{E_i - E_t}{kT})} \qquad (A2)$$

Where $\Delta n(0)(\Delta p(0)), n_i$, E_t and N_t are the electron (holes) excess carriers concentrations at the surface, intrinsic carriers concentration, energy level of surface states and surface states density, respectively.
The electron (hole) concentration at the surface n_0 (p_0) is given by:

$$n_0 = \frac{n_i^2}{N_a} \exp(\frac{E_b}{kT}) \qquad (A3)$$

$$p_0 = N_a \exp(-\frac{E_b}{kT}) \qquad (A4)$$

The barriers height is given by:

$$E_b = \frac{eN_a}{2\varepsilon} Z_d^2 \qquad (A5)$$

B. Optical Generation

The optical generation rate is given by:

$$G_{ph}(z) = F_f \alpha \eta e^{-\alpha z} \qquad (A6)$$

Where F_f is the front surface flux modeled by Plank function, α is the absorption coefficient and the η is the quantum efficiency calculated by [19]:

$$\eta = \frac{(1-r).\left[1 - e^{-\alpha d}\right]}{1 - r.e^{-\alpha d}} \frac{\tau_{eff}}{\tau} \qquad (A7)$$

In which r is the reflection coefficient and τ_{eff} is the effective lifetime given by [19]:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau} + \frac{1}{\tau_s . Z_d} \qquad (A8)$$

With τ, and τ_s are the bulk and surface electron lifetime respectively.

C. Signal, Responsivity and Detectivity

The conductance of film (Figure 7) is given by:

$$\Delta g = \frac{Z\mu_n e}{l} \int_0^d \Delta n(z)dz \qquad (A9)$$

The signal in current and voltage is given by:

$$Iph = \Delta g.V$$
$$V_{ph} = I_{ph}.R_L \qquad (A10)$$

Where V is the bias voltage
The spectral response is given by:

$$R = \frac{R_0}{\sqrt{1 + (2\pi f \tau)^2}} \quad (V/W) \qquad (A11)$$

Where R_0:

$$R_0 = \frac{V_{ph}}{P_{inc}} (V/W) \qquad (A12)$$

f is the modulation frequency and τ the bulk carrier lifetime ($\tau = L_P^2/D_P$)

The specific detectivity is given by:

$$D^* = \frac{R_i \sqrt{A_d \Delta f}}{i_n} = \frac{R_V \sqrt{A_d \Delta f}}{V_n} \qquad (A13)$$

The total noise expression is done by

$$i_n^2 = i_{G-R}^2 + i_{1/f}^2 + i_{joh}^2 \qquad (A14)$$

$$i_n^2 = 4G^2 q(q\eta E_q A_d + qg_{th}d.A_d)\Delta f +$$
$$\frac{B_{1/f} \overline{i^2}}{f} \Delta f + \frac{4kT}{R_d} \Delta f \qquad (A15)$$

The $1/f$ noise is given by [20] where $B_{1/f} = \dfrac{C}{N_t A_d}$,

$C=0.1$, A_d is the detector area, N_t is the surface state density and Δf is the electrical bandwidth of detector.
At room temperature and high modulation frequency, the dominant compound of noise is the thermal generated-recombination part given by [21]:

$$i_n^2 = 4 q g i_0 \Delta f \qquad (A16)$$

Where i_0 is the dark current, Δf is the noise equivalent frequency bandwidth given by $1/(2t_{int})$ where t_{int} is electronic integration time and g is the gain of photoconduction.