

PHOTOSENSITIZATION OF PbS FILMS BY THERMAL TREATMENT IN CONTROLLED ENVIRONMENT

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The paper presents a study regarding the increasing of photosensitivity of PbS thin films applying thermal treatment in controlled environment. Thermal treatments at temperatures ranged between 70 – 100 °C in dry air, dry air without CO₂ and oxygen enriched air medium were applied. Electrical and photoelectrical properties were investigated as a function of temperature and environment.

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1. Introduction

Lead sulphide (PbS) is an important semiconductor with a narrow band gap [1] that can be used as photodetector for IR radiation.

PbS films obtained by Chemical Bath Deposition (CBD) from aqueous [1-10] or methanolic solution [11] were studied in a series of recent papers.

If the films are obtained by CBD, they have photosensitivity as prepared. The photosensitivity that depends on various factors, such as: obtaining method, thickness, composition, structure and the morphology [12,13] of the film can be improved by introducing oxidants in the reaction environment [14-20], reducing agents [21-23], or by the application of thermal treatments in oxygen-containing environment [22-24].

During treatments p type PbS films with crystal defects are formed. The resultant junctions are responsible for the photosensitivity [13].

Kothiya et al [15], showed that annealing of the PbS films at 120°C under vacuum ($5 \cdot 10^{-2}$ Torr) for 4-5 h affects the electronic properties considerably but does not cause any appreciable change in the structure except in smoothing the grain boundaries to a certain extent.

In this work we studied the influence of thermal treatments on PbS films photosensitivity in controlled environments (dried air, air without CO₂, or oxygen enriched air) at low temperature (70-100 °C).

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2. Experimental

PbS thin films were obtained by CBD. Optical glass slides with dimensions of $6 \times 3.5 \times 0.8$ mm³ were used as substrates. The deposition solution had the following composition: $\text{Pb}(\text{NO}_3)_2$ – $1.4 \cdot 10^{-2}$ M; $(\text{NH}_2)_2\text{CS}$ – $5.7 \cdot 10^{-2}$ and NaOH – 0.158 M [24]. Two layers were deposited at 25 °C, for 30 minute each [25].

In order to apply thermal treatments to films in controlled environment, a glass precinct provided with glass stopcocks and a system for placing the samples provided with electrical contacts for measuring the electrical resistance during of after treatment was used. The treatment precinct has been placed into an electrical oven specially adapted in this purpose (fig. 1).

In the first stage of the research, PbS films have been treated in air. The optimal temperature of treatment has been found to be 90 °C [26] in order to improve photoelectrical properties.

In the second stage of the research the treatments have been made using dried air from which CO₂ have been removed. In this purpose, the air passes through a battery of absorbers, with controlled rate (40 bubbles/minutes) filled with NaOH granules, silica gel and P₂O₅ – in order to remove water, and filters with 0.2 μm pores, in order to remove solid impurities.

For the evaluation of the influence of the thermal treatment, photosensitivity S, was determined at 25 °C in order to select the samples with good initial photosensitivity and eliminate the samples without sensitivity. Then, the threshold flux was determined using the device presented in [24].

The photosensitivity S can be calculated with the relation:

$$S = \frac{\Delta R}{R_1} = \frac{R_D - R_1}{R_1} \quad (1)$$

where: R_D is the sheet electrical resistance in the dark; R_1 - the sheet electrical resistance measured under illumination with a tungsten lamp, under 100 W/m².

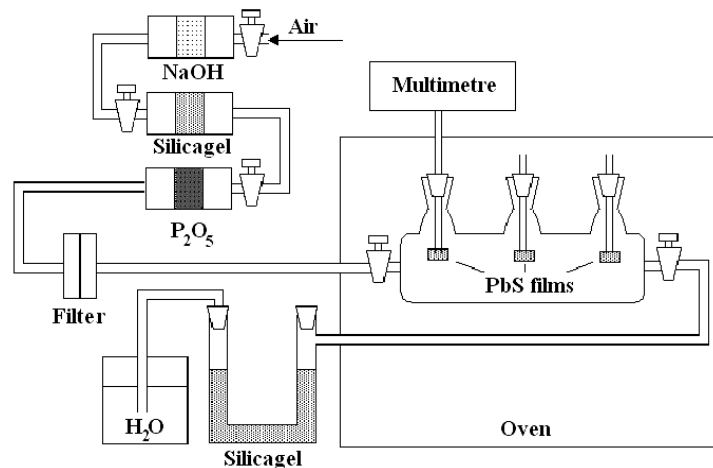


Fig. 1. Sensitizing precinct for thermal treatment in controlled environment

The threshold flux of the photo detector F^* was calculated with the relationship:

$$F^* = \frac{M_T \cdot A_{CN} \cdot A_{FR}}{\pi l^2 \sqrt{\Delta f} \cdot A_{FR}} \quad \left[\frac{W}{\text{cm} \sqrt{\text{Hz}}} \right] \quad (2)$$

where: M_T ($M_T=0.62 \text{ W/cm}^2$) was energy emittance of the black body at 573 K; A_{CN} – radiant area of the black body [cm^2]; A_{FR} – photosensitive film area [cm^2]; l – the distance from the black body to the photosensitive film [cm], Δf – wave frequency [Hz].

3. Results and discussions

In a previous study we have shown that during long (0-40 hours) thermal treatments at 90 °C in air, the electrical resistances of the films attain maximum values after 20 hours, and then the values are decreasing [26]. In the same study we have shown that the photo-sensitivities increased significantly after a short treatment time, and remained almost constant during treatments of 4-24 hours, and then they decreased almost linearly.

In this study the treatment time varied between 38 to 155 minutes.

In Fig. 1, the electrical resistances of the films thermally threaded at 90°C in dried air are presented. As can be seen from Fig. 1, for all the samples, the resistances of the films have been increased. It was attained a maximum for 96 minutes thermal treatment, and then the resistance of the films decreased linearly. The increase of the resistance varied between 89.7 and 117.7 %. The lack of humidity from air leads to the reach of electrical resistance maximum after a shorter treatment than in the case of treatments applied in humid air (96 minutes comparing to 20 hours [26]).

Air humidity is another factor that strongly influences the electrical resistance of PbS films, as shown in [27], although adsorption equilibrium has been established after about 30-200 minutes, as a function of humidity, at room temperature [27].

The increasing of electrical resistance can be correlated to dehydration process, while the decreasing of electrical resistance when the thermal treatment period exceeds 96 minutes can be correlated both to the structural minor rearrangements of PbS particles during thermal treatment, rearrangements that takes places at the surface of the films even if the treatments are made in vacuum [15].

In Figure 2, the threshold flux of the films thermally threaded at 90°C in dried air is presented. The photo-sensitivities of the films improved for all treated samples (the photosensitivity of the films is higher when the threshold flux is smaller), the increase, ranging between 23.75 to 50 %. The best result was obtained for the sample treated for 155 minutes, the threshold flux decreased by 50 %.

In Figures 3 and 4, the results obtained after thermal treatment in air in the absence of CO_2 are presented.

When PbS films were treated at 90°C in air in the absence of CO_2 , the increase of electrical resistance varied between 81.25 (for 38 minutes thermal treatment time) to 312.94 % (for 138 thermal treatment time). After 138 minutes of thermal treatment, the resistance tends to stabilize.

It seems that the absence of CO_2 in annealing environment have an important effect leading to an important increase of electrical resistance during thermal treatment. Comparing fig. 2 and 4 one can noticed that the presence of CO_2 influence the photochemical properties. CO_2 is absorbed [28] on the surface of the film and forms PbCO_3 , increasing the resistance of the film, up to 800 $\text{k}\Omega/\text{sq}$. Increasing treatment time the amount of adsorbed CO_2 increased to, leading to the decreasing of threshold flux (fig. 2).

The threshold flux decreased for all the samples (fig. 4) when samples were annealed in air without CO_2 . The decrease of the threshold flux varies between 33.33 %, for the sample treated for 38 minutes to 59.13 % for the sample treated for 138 minutes in air in the absence of CO_2 . The final value obtained for threshold flux was almost the same for all the treatment time, even if the initial threshold flux was a little different.

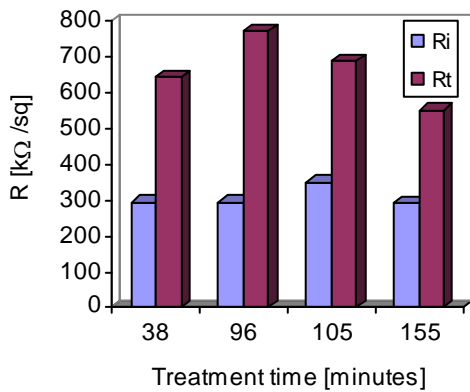


Fig. 1. The electrical resistances of the films thermally threaded at 90°C in dried air (R_i – initial resistance, R_t – the resistance after thermal treatment)

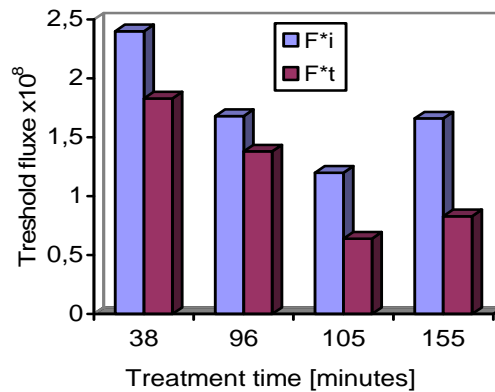


Fig. 2. The threshold flux of the films thermally threaded at 90°C in dried air (F^*i – initial threshold flux, F^*t – the threshold flux after thermal treatment)

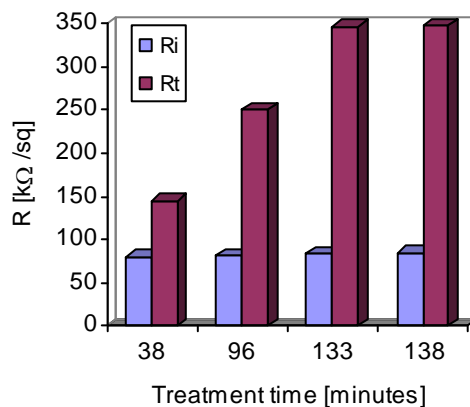


Fig. 3. The electrical resistances of the films thermally threaded at 90°C in air in the absence of CO_2 (R_i – initial resistance, R_t – the resistance after thermal treatment)

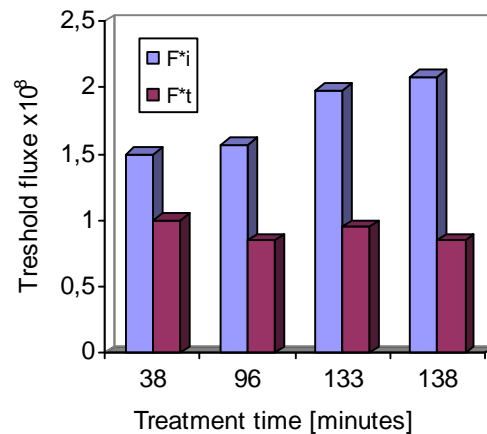


Fig. 4. The threshold flux of the films thermally threaded at 90°C in air in the absence of CO_2 (F^*i – initial threshold flux, F^*t – the threshold flux after thermal treatment)

A series of samples were treated in oxygen-enriched air. The oxygen has been prepared in the laboratory by the thermal decomposition of potassium permanganate ($KMnO_4$).



After a series of experimental tests similar to the one presented above, the optimal temperature for the treatment in oxygen-enriched air has been found to be 90°C, and the treatment time 130 minutes. In Figures 5 and 6 a series of samples treated as mentioned above are presented.

The electrical resistance increased between 242 to 900 %, while the threshold flux decreased between 800 and 940 %.

In Table 1, the ratio F^*i / F^*t , for the samples presented in Fig. 6 is presented.

Table 1. The ratio F^*i/F^*t , for the samples thermally threaded at 90°C in oxygen enriched air (F_i – initial flux, F_t – the flux after thermal treatment)

Sample	1	2	3	4	5
F_i/F_t	8.19	5.00	15.72	10.79	5.51

The photosensitivity of the films after treatment in oxygen enriched atmosphere increased from 5.51 to 15.72 times.

The excess oxygen from the air leads to an important improvement of photoelectrical properties of PbS improving the threshold flux.

C. C. Abarbanel [29] shown that oxygen diffusion in PbS films during annealing at various temperatures in the range of $250\text{--}400^\circ\text{C}$ for a fixed period of 1 hour determined the increasing of photoconductivity of PbS films.

The variation of film electrical and electrical properties as a function of annealing time at 90°C can't be explained only taking into consideration the adsorption / desorption of water. Other processes are involved. Chemical reaction took places during annealing and the reactions depend on the composition of environment.

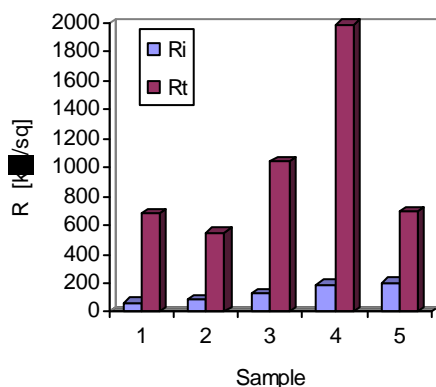


Fig. 5. The electrical resistances of the films thermally threaded at 90°C in oxygen-enriched air (R_i – initial resistance, R_t – the resistance after thermal treatment)

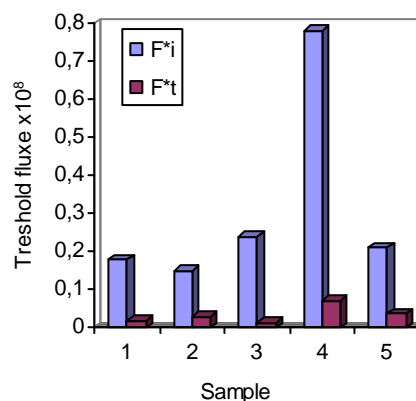


Fig. 6. The threshold flux of the films thermally threaded in in oxygen-enriched air (F^*i – initial threshold flux, F^*t – the threshold flux after thermal treatment)

PbS films can contain small amounts of other compounds formed during film formation, such as lead hydroxide [30] and a series of lead thiourea and hydroxide complexes. Lead sulphate can also be formed during thermal treatment at elevated temperatures.

Seghaier et al [30] studied the effect of thermal treatments of PbS films under nitrogen during 1 h at 200°C , showing that an increase of the disorder in the layer have been produced so the film becomes amorphous and/or a decrease of thin layer thickness after annealing took places. They made no studies related to photosensitive properties of PbS.

4. Conclusions

The paper presents a study related to thermal treatment of PbS thin films in controlled environment. The treatments in dried air or in air without CO_2 do not lead to important improvements of photosensitivity. When the samples were treated in oxygen-enriched air at 90°C for 130 minutes, the photosensitivity of the films increased from 5.51 to 15.72 times.

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