The Spectral Response of PbS Films

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Two possible ways are reported of influencing the spectral response of PbS films prepared by chemical deposition. An increase in the ratio of hydroxyl to lead ions in the deposition solution causes a shift of the peak spectral response from 1.3 μ to 2.8 μ. The addition of a reducing agent (hydroxyl amine hydrochloride) also markedly influences the spectral response. The time constant, resistance and thickness of the films have been measured and an attempt is made to explain all the observations on the basis of a modified conduction model.

Introduction

According to the theory[1] which describes the mechanism of photoconductivity in an intrinsic photoconductor such as PbS, the spectral limit is set by the energy gap of the photoconductor. Thus, if the band gap energy is E_g, the photoconductive limit is given by

$$\lambda_c = 1.24/E_g \qquad (1)$$

where λ_c is in microns and E_g in eV. Values of E_g for PbS at 25 °C have been reported[2] to range between 0.30 eV and 0.40 eV corresponding to wavelength limits of 4.1 μ and 3.1 μ, respectively.

According to Humphrey[2], Avery[3], and Dalven[4] the spectral response may be changed as a result of oxidation of the film induced by baking. Heavy doping with oxides shifts the spectral response to longer wavelengths. No theoretical basis has been advanced to explain this change of spectral response in the case of PbS films.

This paper presents two further ways by which the spectral response of PbS films may be influenced and these are here discussed on the basis of a simple model.

Experimental

Preparation of films was done by chemical deposition[5]. The measurements of time constant and resistance were carried out by a test apparatus described in a previous paper[6]. In order to graphically present the change in relative spectral response as a function of various parameters it has proved convenient to express the spectral response in terms of a parameter p. This quantity is defined as the percentage of the 500 °K blackbody response which is transmitted by a low pass filter with a 50% cut off arbitrarily chosen at 2.6 μ. A low p value consequently implies a short wavelength response, and conversely for a large value of p.

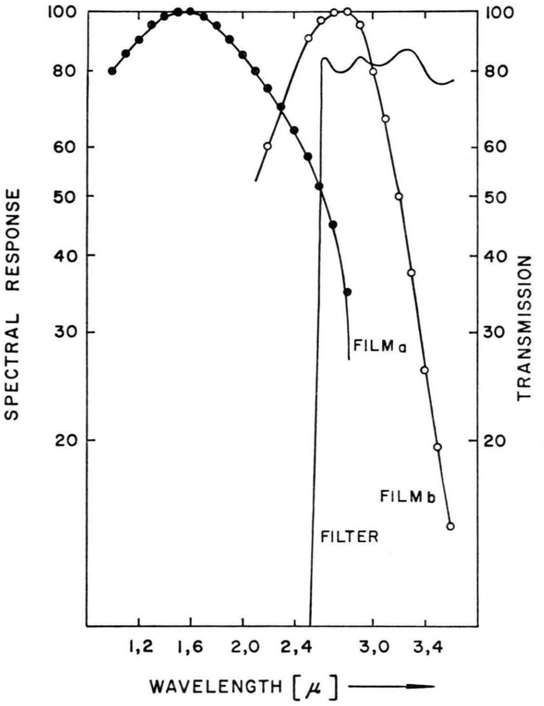

Fig. 1. Spectral response of two distinct films and characteristics of the filter used.
Film a: Deposition time: 15 min; ratio $K = 10.0$.
Film b: Deposition time: 30 min; ratio $K = 11.6$.

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The complete relative spectral response curves of two representative films (a) and (b), as measured on a 1 m-Jarrel-Ash scanning spectrometer, are shown in Fig. 1 as is also the transmission curve of the cut off filter. The thickness of the films was determined mechanically with a "Talystep" apparatus.

Results

Figures 2 (a) and (b) illustrate, respectively, the dependence of the spectral response parameter p and the time constant τ on the ratio K of hydroxyl to lead ions in the deposition solution. The dependence on deposition time is also shown. The present results show a wider range of K values than previously reported[6].

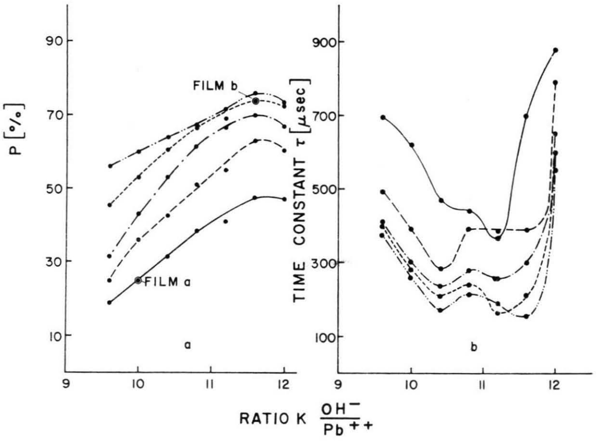

Fig. 2. Spectral response parameter p depending on the ratio K of hydroxyl to lead ions and on the deposition time. The relative spectral response of a and b is illustrated in Fig. 1. (b) Time constant depending on the ratio K and on the deposition time. ———— 15 minutes, — — — 20 minutes, —·— 25 minutes, - - - - - 30 minutes, —··— 35 minutes.

The spectral response of PbS films may also be changed in a marked way by the addition of a reducing agent to the chemical deposition bath. Figures 3 (a), (b), (c), and (d) show the way in which the spectral response parameter p, the film resistance R, the thickness d and the time constant τ vary for films which result on adding variable amounts of reducing agent (in this case hydroxylamine hydrochloride, $NH_2OH \cdot HCl$). As before, the dependence of each of these parameters on the deposition time is also shown. The deposition bath was adjusted to a constant hydroxyl to lead ion ratio of $K = 10.4$.

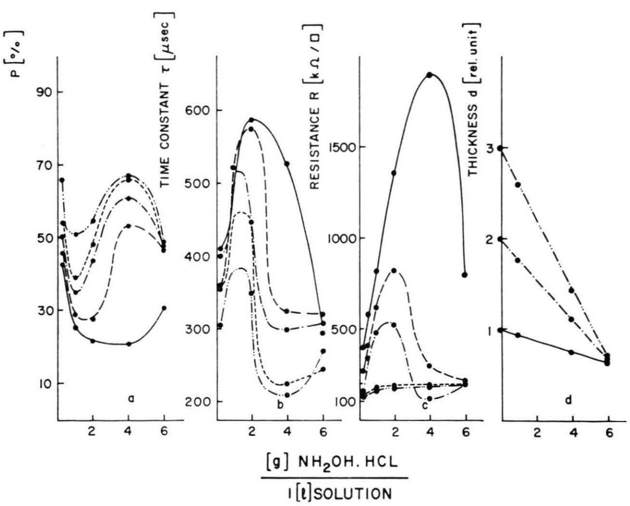

Fig. 3. Spectral response parameter p (a), time constant (b), film resistance (c) and thickness of the films (d) depending on the amount of added hydroxylamine hydrochloride and on the deposition time.

Discussion

1. Effect of Changing the Ratio K of Hydroxyl to Lead Ion Concentration

The dependence of the time constant on the deposition time and on the ratio K was discussed in a previous paper[6]. It was found that trapping centres and the factor $n\,\mu'$ (n = mean density of majority carriers; μ' = reduced mobility, which makes provision for the possibility of barriers) are mainly responsible for changes in the time constant. As reported previously, there is a distinct increase in this factor $n\,\mu'$ on increasing the deposition time. There is also a decrease in trapping centres on increasing K or when the deposition time is increased.

We may relate this dependence on K of the trapping centre density and the deposition time with a similar dependence of the time constant τ and the spectral response parameter p.

As is seen in Fig. 2, an increase in the ratio K and an increase in the deposition time both lead to a decrease in τ and an increase in p. An explanation of these features based on the following model is suggested.

In our model the conventional band gap energy E_g is modified to take into account the possibility that the wave function becomes localized near the extremities of the conduction and valence band. An

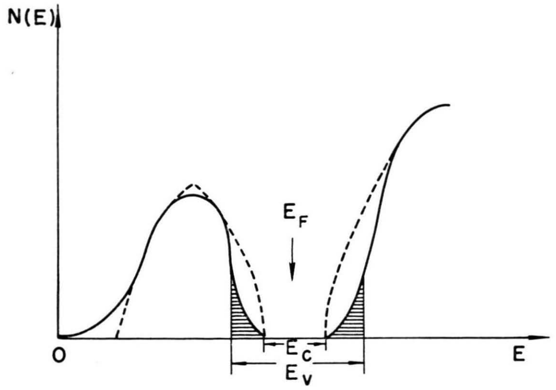

Fig. 4. Suggested band model for disordered PbS films. $N(E)$ = density of states; E_f = Fermi energy; – – – – crystalline; E_c = constant band gap energy; E_v = variable band gap energy.

electron in a localized state can be described as trapped and as such cannot move unless thermal energy frees it. In such a model (Fig. 4) the sharply defined value E_g is replaced for convenience by a constant energy value E_c and a variable energy E_v which takes into account the effect of the trapping sites and depends on the density of these sites. In general $E_v > E_c$ and in the limiting case of no trapping sites $E_c = E_v = E_g$.

The effect of the trapping sites, through capture of carriers, leads to a delay in recombination and consequently an increase of time constant. Since carriers of low energy are hindered, there will also be a consequent shift in the spectral response to shorter wavelength.

Increasing the ratio K and deposition time decreases the number of traps and increase the factor $n \mu'$. This causes a decrease of the band gap energy E_v, which in the ideal case approaches the band gap energy E_c. The model thus explains the observed longer wavelength response and shorter time constant.

2. The Effect of the Addition of Hydroxylamine Hydrochloride at a Constant Hydroxyl to Lead Ion Concentration

From a comparison of Figs. 3(c) and 3(d) it is immediately clear that the changes in resistance are unrelated to the thickness of the films and consequently mainly dependent on changes in the factor $n \mu'$ as discussed in Ref. [6].

As discussed above under Section 1, this factor also influences the spectral response and time constant. This is reflected in Figs. 3(a) and 3(b), which illustrate the dependence of the spectral response parameter p and the time constant τ on the amount of additive.

From Figs. 3(a), (b), (c), and (d) it can be seen that films prepared with the largest amount of additive (6 g/l) show values of p, τ, R, and d which are relatively independent of deposition time after 15 minutes. Hydroxylamine seems to accelerate the plumbite-thiourea reaction (see also Ref. [7]) so that it is quite possible that this acceleration causes a change in the order of the crystallites and/or an alteration in the size of the crystallites.

Changes in crystallite size will mainly affect the mobility of the carriers μ' and so change the resistance. A decrease in the degree of order, on the other hand, produces a high density of traps [8] in the films. Both these effects will strongly influence the band gap energy E_v in the suggested band model and would explain the features observed.

Conclusion

By increasing the ratio of the hydroxyl ion to the lead ion concentration in the deposition solution the peak spectral response of PbS films can be shifted from 1.3 to 2.8 μ. This shift is caused mainly by changing the number of trapping centres and the factor $n \mu'$. Addition of hydroxylamine hydrochloride produces films with small thickness, low resistance, short response time and a spectral response at fairly long wavelengths.

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