The Influence of Deposition Conditions on the Photoconductive Properties of Chemically Deposited Lead Sulphide

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The influence of the deposition time and the ratio of hydroxide to lead ion concentration in the precipitation solution on the photoconductive properties of chemically deposited PbS layers was investigated.

From measurements of time constant, noise and resistance, it could be shown how the deposition conditions control the number of trapping centres and carrier density. The trapping centres may be connected with excess lead atoms deposited in the PbS lattice under the conditions of preparation.

Introduction

One of the most interesting problems in connection with photoconductive films of the lead salt type is the substantial difference between the value of the relaxation time of photosensitive films and that of single crystals of the same material.

Most features of the behaviour of lead salt films can be explained by theories given by Petritz[1]. According to Petritz some centres in the crystallites act as traps for minority carriers. Their recombination with majority carriers is only possible after thermal excitation, this fact causing a considerable delay time.

With Petritz's theory as a basis, this paper presents a study of the influence of the ratio of the concentration of hydroxide ions to lead ions in the precipitation solution, in combination with the deposition time, on some photoconductive properties of chemically deposited PbS layers.

Experimental

The lead sulfide layers were chemically deposited[2] from aqueous solutions of lead nitrate, thiourea, aminoiminomethane-sulfinic acid and varying amounts of sodium hydroxide. The ratio of the concentrations of hydroxide and lead ions varied between 9.6 and 12.0. Another parameter was the time for which the substrates were exposed to deposition.

Blackbody radiation (500 °K) in the form of a train of pulses with slowly increasing frequency f was allowed to fall on such PbS-detectors. The frequency f_c was determined at which the ac-response is 0.707 times its low-frequency limit. The time constant τ is then calculated from f_c by the equation

$$\tau = 1/2\,\pi f_c\,, \tag{1}$$

f_c was measured by means of a test apparatus shown in Fig. 1.

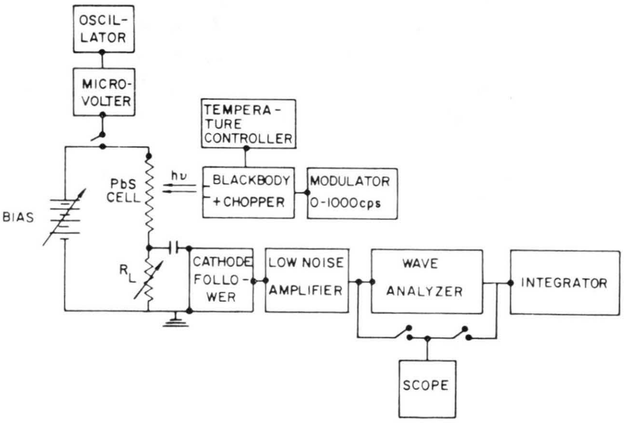

Fig. 1. Test apparatus for measurement of time constant, noise and resistance.

The load resistor R_L was matched to the resistance R_D of each detector. The bias current density was kept constant at 100 μA/cm. A change in the current density through a detector cell did not influence the measured time constant. Furthermore, the wavelength of the incident radiation has negligible influence on the time constants, as shown by the insertion of different low pass filters ($0.5-2.5\ \mu$ cut off) between the blackbody and detector.

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[1] R. L. Petritz and J. N. Humphrey, Phys. Rev. **105**, 1736 [1957].

[2] O. A. Kunze, O. G. Malan, P. A. Büger, and W. Fink, Z. Naturforsch., in print.

Noise measurements also were made by means of the apparatus shown in Fig. 1. The bandwidth Δf of the wave analyzer was 6 cycles and the generation-recombination noise was calculated as will be described in the discussion.

Results

The results of our investigations are summarised in Figs. 2 to 5. The following facts could be observed:

1. *Dependence of τ on the detector resistance R_D.* A higher value of resistance is related to longer time constants as can be seen from Fig. 2.
2. *The generation-recombination noise* as a function of the factor $R\tau^{1/2}$ and the ratio K between the concentration of hydroxide and lead ions is given in Fig. 3.
3. *Dependence of τ on the detector temperature.* A rising detector temperature causes a decrease of the time constant. Experimental values observed by us are similar to those of MAHLMAN[3].
4. *Dependence of τ on the concentration ratio K.* The time constant τ, according to Fig. 4, decreases with an increase of K. Longer deposition times result in smaller time constants.
5. *Dependence of τ on the radiation intensity.* The time constant decreases, particularly for small values of the ratio K, with an increase of the irradiance, as can be seen from Fig. 5.

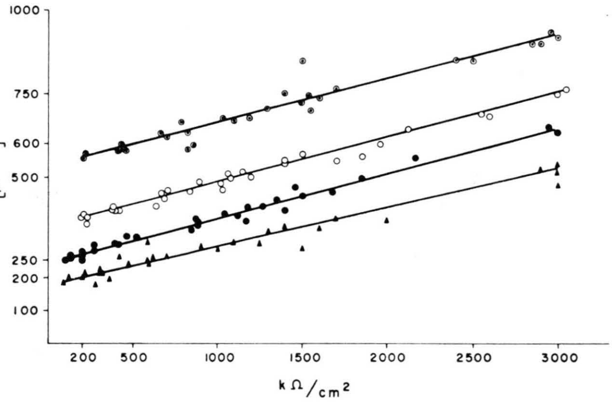

Fig. 2. Change of time constants in dependence of the resistance at different values of K, the ratio between the concentration of hydroxide and lead ions.
⊙=9.6, ○=10.0, ●=10.4, △=10.8.

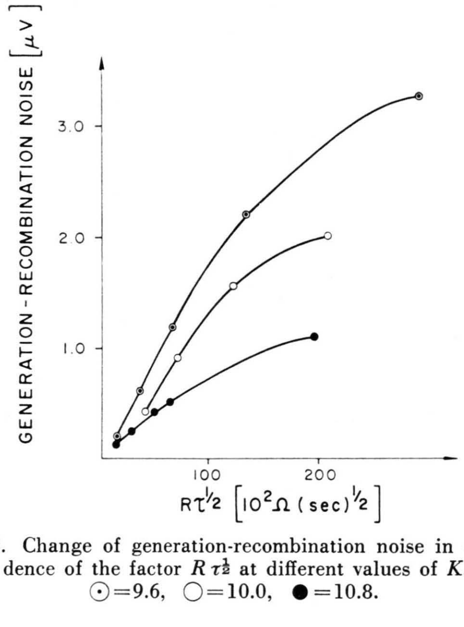

Fig. 3. Change of generation-recombination noise in dependence of the factor $R\,\tau^{\frac{1}{2}}$ at different values of K.
⊙=9.6, ○=10.0, ●=10.8.

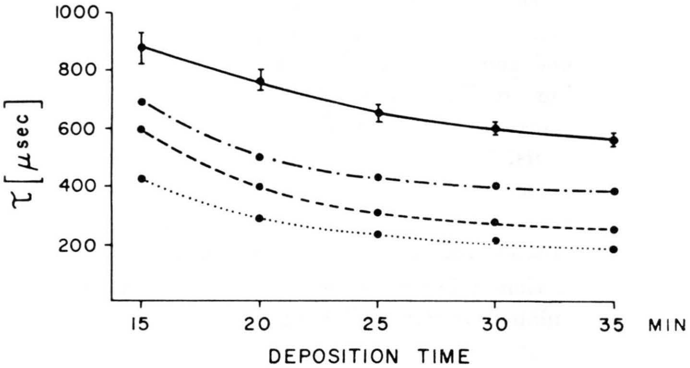

Fig. 4. Time constants in dependence of the deposition time and the ratio K (the first curve shows the deviation of the average value).
—— 9.6, —·— 10.0, — — 10.4, ···· 10.8.

Discussion

These results may be explained by some considerations about conduction and trapping mechanisms in photoconductive layers.

Short deposition times result in rather thin films having a high resistance (ca. 2.5 MΩ/sq). The resistance of a photoconductive film is defined as

$$R = L/q\,n\mu'\,w\,d\,, \qquad (2)$$

where L = length of the film, n = mean density of majority carriers in the crystallites, μ' = reduced mobility, which makes provision for the possibility of barriers[4], w = width, and d = thickness of the film.

[3] G. W. MAHLMAN, Phys. Rev. **103**, 1619 [1956].

[4] J. C. SLATER, Phys. Rev. **103**, 1631 [1956].

It could be shown by means of microscope interferometry that the thickness of films increases by only a factor 3 between the shortest deposition time used (15 min) and the longest one (35 min).

The resistance, as shown in Fig. 2, changes by a factor of ca. 25. This means that (with L and w constant) longer deposition times result in a significant increase of the factor $n\,\mu'$. Also the responsivity, which strongly depends on this factor $n\,\mu'$, increases with longer deposition times. By still lengthening the deposition time the resistance becomes very small, the time constants are nearly unchanged, but the responsivity drops due to a high dark conductivity.

The concentration ratio K in combination with the deposition time have a distinct influence on the detector noise characteristics. PbS detectors are mainly subject to frequency-dependent $(1/f)$ noise and generation-recombination noise (N_{gr}). According to HUMPHREY[5] the generation-recombination noise can be resolved from all other noise components. Figure 3 shows the generation-recombination noise, calculated in this way from measurement results, as a function of the factor $R\,\tau^{1/2}$ (which decreases with increasing deposition time) and K.

Generation-recombination noise is usually calculated using the following equation[6]:

$$(N_{\mathrm{gr}})^2 = \frac{2\,\tau\,R^2\,i^2\,\Delta f}{n(1+4\,\pi\,f^2\,\tau^2)} \qquad (3)$$

where $N_{\mathrm{gr}} \sim R\,\sqrt{\tau/n}$ represents the value for an intrinsic semiconductor. In the presence of a trapping mechanism, Eq. (3) will change to Eq. (4),

$$(N_{\mathrm{gr}})^2 = (N_{\mathrm{gr}})^2_{\mathrm{instrinsic}} \cdot \frac{a\,n+n\,p}{n\,p} \qquad (4)$$

where the constant a is dependent on the number of traps and p = density of minority carriers. This means that the increase of the generation-recombination noise which results from changes in the concentration ratio K and the deposition time is connected with an increase of the number of trapping centres. With PbS, the nature of these centres is that of minority carrier traps[1, 7]. Transitions between majority carriers and traps can be neglected.

There are therefore two points to be considered in discussing the time constant: Firstly there is a distinct increase of the factor $n\,\mu'$ upon increasing the deposition time and secondly there is a decrease in the number of trapping centres upon increasing the ratio K and probably upon increasing the deposition time.

The time constant of a PbS-photoconductor can be expressed by the following equation[8]:

$$\tau = \frac{N}{n_1}\,\frac{1}{C\,p_{\mathrm{e}}} = \frac{N}{n_1}\,\tau_{\mathrm{R}}\,, \qquad (5)$$

where N = number of trapping centres, n_1 = concentration of electrons in the conduction band, the Fermi level being at the centre energy, C = transition probability per second, p_{e} = concentration of holes in the valence band (equilibrium value), and τ_{R} = life time due to direct recombination.

The value of τ_{R} as found in the literature[7, 9] is approximately 10 – 20 μsec. This is considerably lower than the experimental value found in PbS (Figs. 2 and 4). There must therefore be a strong influence on the time constant of the number of trapping centres, N, and (or) the concentration of electrons in the conduction band, n_1. The latter value is also dependent on the temperature of the detector as well as on the energy of the bands and the trapping centres as shown in the following equation:

$$n_1 = \tfrac{1}{2}(\pi\,m_{\mathrm{e}} \cdot k\,T/h^2)^{3/2} \cdot \exp[(E_3 - E_1)/k\,T], \qquad (6)$$

where E_1 is the energy of the conduction band and E_3 the Fermi level, where the traps are also supposed[7] to be (Fig. 6).

Equations (5) and (6) clearly explain our result 3: With increasing temperature the number of electrons in the conduction band is increased, thus causing the time constant to diminish. It is also possible to explain the results 1 and 4.

An increase of the carrier density causes a decrease of the time constant according to Eq. (5). This increase can be achieved by an increase of the deposition time. A decrease of the number of trapping centres also causes a decrease of the time constant. An increase in K, the ratio between hydroxide

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[5] J. N. HUMPHREY, Appl. Opt. **4**, 665 [1965].

[6] R. A. SMITH, F. E. JONES, and R. P. CHASMAR, The Detection and Measurement of Infrared Radiation, Clarendon Press, Oxford 1968, p. 208.

[7] F. M. KLAASEN, J. BLOK, H. C. BOOY, and F. J. DE HOOG, Physica **26**, 623 [1960].

[8] F. M. KLAASEN, K. M. VAN VLIET, and J. BLOK, Physica **26**, 605 [1960].

[9] W. W. SCANLON, Phys. Rev. **106**, 718 [1957].

[10] D. G. BELL, D. M. HUM, L. PINCHERLE, D. W. SCIAMA, and W. M. WOODWARD, Proc. Roy. Soc. London **217** A, 71 [1953].

and lead ion concentration, seems to result in a significant decrease in the number of trapping centres. Considering that such an increase in the precipitation solution favours the precipitation of lead sulfide and suppresses the precipitation of metallic lead [2, 11], there is a strong possibility that this metallic lead acts as trapping centres.

The strong dependence of τ on the number of trapping centres is also evident in Fig. 5, where τ is plotted as a function of the irradiance. While at low radiation intensities the time constants of detectors made with different ratios K differ quite appreciably, this difference decreases with increasing irradiance. At higher irradiation intensities more electrons are freed from the traps. The decrease in time constant is more distinct in detectors with a greater number of trapping centres.

Conclusion

The number of trapping centres for minority carriers and the factor $n\,\mu'$, in photoconductive PbS films, can be controlled during precipitation by changing the concentration ratio of hydroxide and lead ions and by varying the deposition time. In order to get a high responsivity, small noise and short time constant, the number of trapping centres in the crystallites should be kept to a minimum by selecting the optimum concentration ratio and deposition time, thereby probably influencing the amount of excess lead atoms in the PbS lattice.

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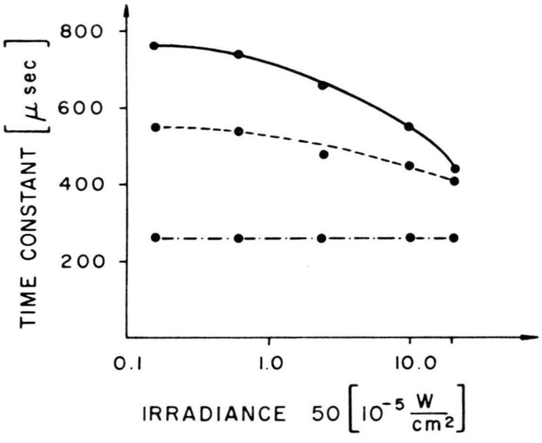

Fig. 5. Change of time constants with irradiance at different values of K.
—— 9.6, --- 10.0. —·— 11.2.

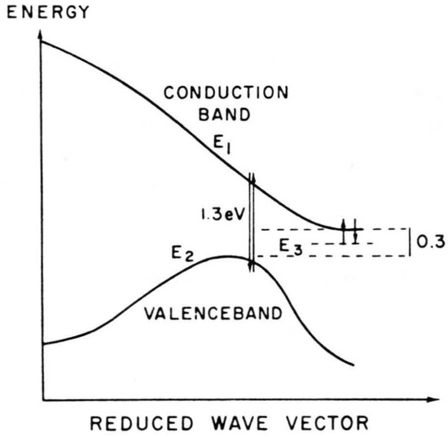

Fig. 6. Energy level diagram and transition rates in PbS-films (according to Bell [10]).

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[11] H. Basset and R. G. Durrant, J. Chem. Soc. **1927, 1401.**