Sensitization of photoconductivity in tetragonal lead monoxide

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The thermal sensitization process for the enhancement of photoconductivity in tetragonal lead monoxide has been investigated. At a critical annealing temperature the photosensitivity has been found to have a maximum value ($\simeq 5 \times 10^2$) while the conductivity is observed to have a minimum value ($\simeq 10^{-10}\,\Omega$ cm). The transient response of the photocurrent exhibits an overshoot, the height of which is strongly dependent on the annealing temperature. These and other findings have been explained on the basis of sensitization due to the creation of two types of centres in the material.

1. Introduction

The photoconducting properties of lead monoxide (PbO) have recently drawn considerable attention since finding a number of applications in imaging devices such as television pick-up tubes (Plumbicon) [1, 2], electrophotography [3] and electroradiography [4]. In our recent investigations it has been found that the photoconductivity of yellow (orthorhombic) PbO could be considerably enhanced by thermal treatment [5]. The tetragonal form of PbO (red) has a much lower band gap (1.9 eV) as compared to the yellow variety (2.5 eV) and hence it is expected to have greater photosensitivity with a broader spectral response than the latter. Earlier studies reported for single crystals or thin films of red PbO indicate that they are highly photosensitive [6, 7]. However, these materials were mostly thermally annealed prior to investigations. In view of our earlier investigations it seems that thermal treatment may also play an important role for the sensitization of red PbO. Further, for the purpose of electrophotography, where use is made of mostly the powder-binder layer, it is necessary to investigate the material properties in powder form. The results of our investigations are described in this paper.

2. Experimental procedure

Red lead monoxide powder was prepared in the laboratory by Kwestroo and Huizing's method [8] using pure lead acetate and concentrated sodium hydroxide. The precipitated powder was thoroughly washed and dried for 24 h at 50° C. Its structure was determined using X-ray diffraction techniques and it was confirmed to be of pure tetragonal form. The fine powder was compressed into pellets at a pressure of 2 tonne cm^{-1} using a hydraulic press under ambient conditions. Silver electrodes were vacuum-deposited on the surface, 0.5 mm apart, in order to form a surface cell for studies on photoconductivity. The details of the measuring cell and the technique used were the same as reported before [5]. The light source was a tungsten-filament lamp equipped with interference filters (Carl Zeiss) having a 10 nm halfwidth and calibrated for intenstiy at different wavelengths using a standard photocell (NASA/ERDA Y-214). The photocurrent was detected by means of a Keithley 480 picoammeter. The transient response, being comparatively slow, was recorded on a fast $X-Y$ recorder (Riken Denshi 43CP) coupled to the picoammeter.

3. Results and discussion

In order to study the effect of annealing on the electrical and photoconducting properties of PbO, the samples were heated from room temperature to a temperature T_p and the current was monitored at a fixed bias voltage (300 V) in dark (I_D) as well under illuminated (I_L) conditions. The samples were then cooled thus completing one thermal cycle. This process was repeated a number of times with increase in T_p after each cycle. Fig. 1

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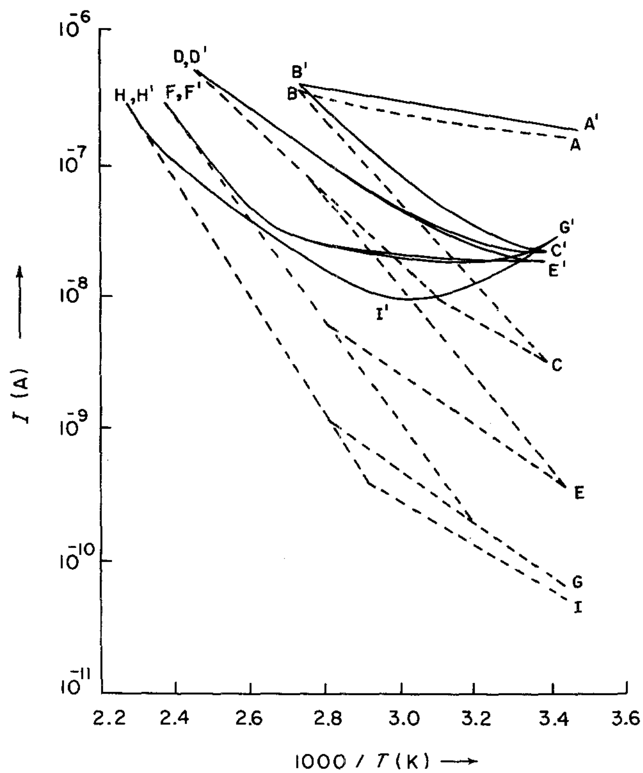

Figure 1 Effect of thermal cycling on I_D (dotted line) and I_L (solid line) for five temperature cycles corresponding to a T_p of 90, 130, 145, 165 and 180° C, respectively.

shows the typical thermal cycling curve with log I_D and log I_L plotted against $1/T$. Starting with raw samples at room temperature, i.e. point A, the I_D follows the path A–B–C–D–E–F–G–I (dashed curve) while I_L follows A′–B′–C′–D′–E′–F′–G′–I′ (solid curve) when the heat treatment described above is applied. It is thus seen that the current in dark conditions decreases considerably (four orders of magnitude) with thermal treatment whereas the photocurrent in illuminated conditions decreases slightly in the beginning for the first cycle but then remains more or less constant at room temperature after further cycles. Thus the photosensitivity ($S = I_L/I_D$) at room temperature is tremendously enhanced by the thermal treatment.

There are some interesting observations worth noting regarding the shape of the curves in Fig. 1. Whereas in the case of I_D, the curve remains more or less linear, the slope of which increases after every thermal cycle; the curve for I_L changes drastically from a linear one with a small slope to a sharply bent one showing a dip at about 60° C. It thus appears that there is thermal quenching of photoconductivity in the annealed samples. This behaviour of I_L with temperature is exactly the reverse of that observed for orthorhombic PbO [3]. The temperature dependence of I_d on the other hand is very similar to that noted for yellow PbO but for the fact that the changes in I_D with every cycle are more pronounced in the present case.

The effect of annealing temperature, T_p, on the dark-conditions conductivity (represented by I_D itself) and photosensitivity, S, is shown in Fig. 2. It is seen that as T_p is increased, I_D decreases and S increases until T_p reaches 250° C, but that for values of T_p greater than 250° C, I_D increases and S decreases thus indicating that there is a critical value of T_p, at which optimum photosensitivity is attained. At the critical T_p of 225° C, I_D is 10^{-11} A, four orders of magnitude lower and S is two orders higher than the original values.

Fig. 3 shows the effect of thermal treatment on the spectral response of photoconductivity in the visible region. Curves 1 to 4 shows the photocurrent normalized for constant intensity (1 μW cm^{-2}) at various wavelengths (400 to 700 nm) for a T_p of 150, 200, 225 and 250° C, respectively. It can be seen that for low T_p (Curve 1) the photocurrent shows a broad peak at 575 nm and is otherwise small at other wavelengths. On the other hand when T_p is increased to 200° C or above, the overall photosensitivity increases,

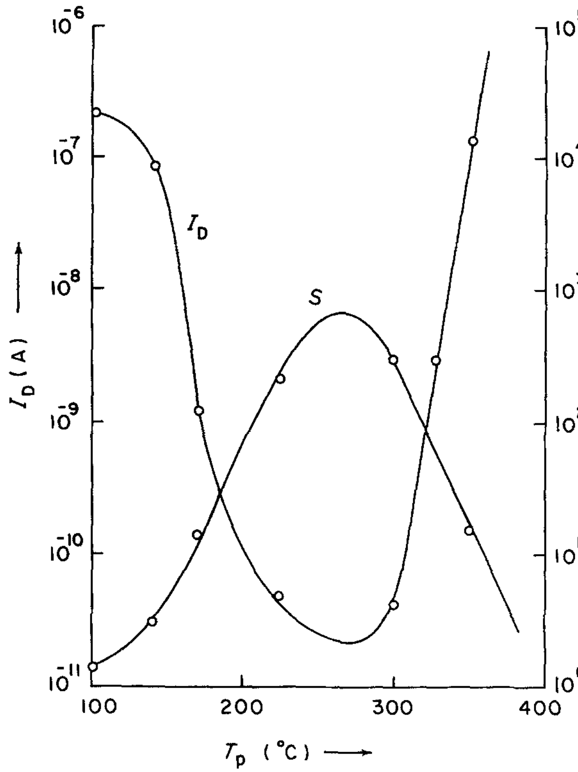

Figure 2 The effect of annealing temperature on dark-condition conductivity (I_D) and photosensitivity (S).

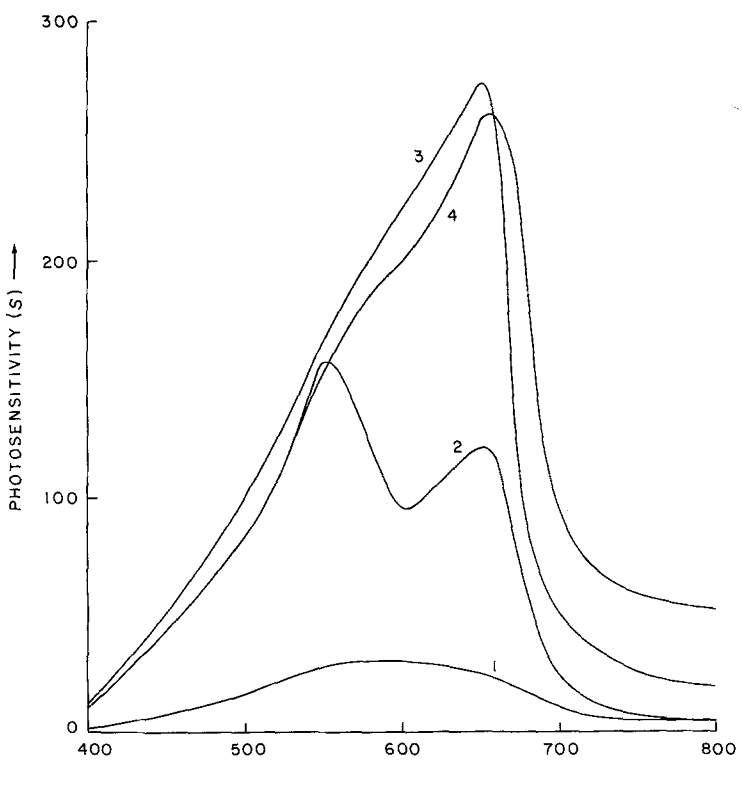

Figure 3 The spectral response of photoconductivity in samples annealed at different temperatures. Curves 1 to 4 correspond to a T_p of 150, 200, 225 and 250° C, respectively. The photosensitivity is normalized for constant intensity of 1 μW cm^{-2}.

especially at longer wavelengths, and in fact a new peak appears at 650 nm in the photocurrent spectra for a T_p of 250° C. This suggests that there may be new centres created by thermal treatment which increase the photosensitivity in the samples at longer wavelength. Since the thermal treatment was carried out in an ambient atmosphere and the starting material was in pure condition, one can envisage that the creation of these new centres is due to incorporation of oxygen in the samples. Such oxygen impurity sensitization is known in many photoconducting materials [9] and it is also quite likely to be present in PbO. The sharp fall in the photosensitivity at shorter wavelengths, i.e. for photon energies higher than at the absorption edge which lies at 630 nm for red PbO [10] is due to strong surface recombination effects which arise because of the large number of photons absorbed near the surface.

In order to investigate the various processes involved in the photoconductivity such as trapping and recombination, the rise and decay transients of the photocurrent were studied with respect to annealing temperature as well as ambient temperature. Fig. 4 shows the photocurrent transients at constant intensity (50 lux) and wavelength (600 nm) for samples annealed at various temperatures. Curves A, B and C correspond to values of T_p of 200, 250 and 300° C, respectively. It is seen that the photocurrent in the case of $T_p = 200°$ C rises uniformly and then saturates to a constant value, while for $T_p = 250°$ C it first rises rapidly and then slowly decreases to the saturation limit thus showing a peak or overshoot in the photocurrent transient. For $T_p = 300°$ C, this overshoot becomes quite sharp as is evident from Curve C. Also in the decay portion some significant changes have been noted for various values of T_p. Whereas the decay is uniform and gradual for $T_p \leqslant 200°$ C, the decay for higher values of T_p appears to consist of two steps, a rapid one first followed by a slow one extending over a long period. The former may be attributed to recombination processes whereas the latter is due to trapping at deeper levels. Some interesting features were observed in the photocurrent transients when studied at different temperatures. Fig. 5 shows the photocurrent transients recorded for annealed samples ($T_p = 250°$ C) at various ambient temperatures. Curves A to E are for temperatures of 20, 35, 45, 60 and 70° C, respectively. It can be seen that as the temperature is increased the overshoot observed in the rising portion of the transient decreases gradually, and finally for high temperatures ($\geqslant 70°$ C) is practically absent. Further, it can be seen that there is an overall decrease in the value of the photosensitivity as the temperature is increased.

The various features described above may be explained on the basis of sensitization of photoconductivity by impurity or defect centres [11]. Typically in an n-type material there may be various impurity or defect sites which can act as

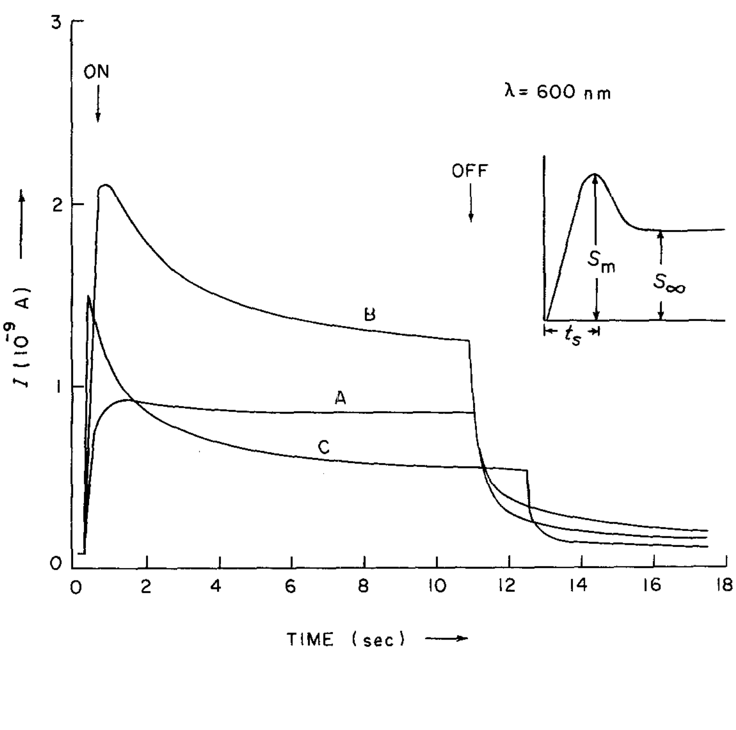

Figure 4 Transient response of photocurrent for samples annealed at various temperatures. Curves A to C correspond to a T_p of 200, 250 and 300° C, respectively.

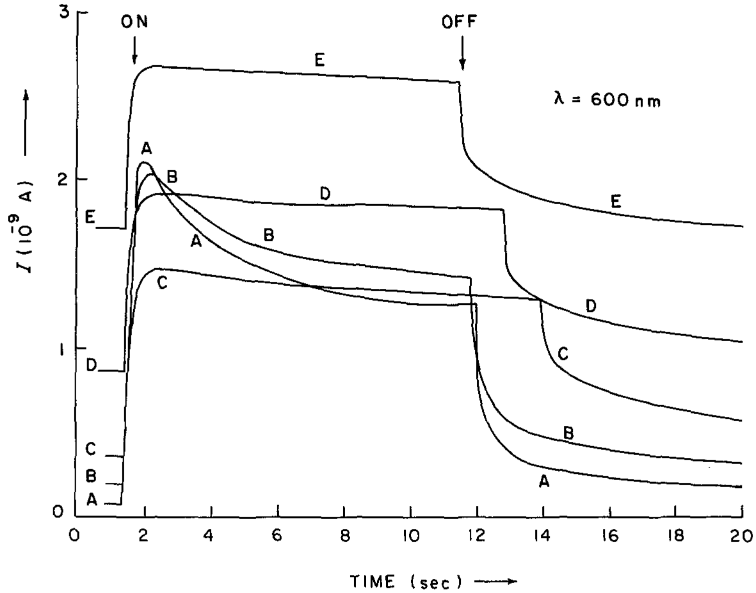

Figure 5 The transient response of photocurrent for the critically annealed sample (T_p = 250° C) at various ambient temperatures. Curves A to E are for temperatures of 20, 35, 45, 60 and 70° C, respectively.

trapping or recombination centres for either electrons or holes, depending on their energy level with respect to valence or conduction bands and the Fermi level [12]. The centres with energy levels close to the conduction band usually act as trapping centres for electrons. Additionally there may be centres (Type I) present in the intermediate region which act as recombination centres. The addition of centres (Type II) with $C_n > C_p$, where C_n and C_p are the trapping cross-sections for electrons and holes, respectively, has the following effect. If the demarcation level is below Type II levels then the photoconductivity is greatly enhanced and if the demarcation level moves from below Type II levels to above them, as in the case when temperature is increased, then the photoconductivity is quenched.

From the above discussions it may be concluded that heating of tetragonal PbO gives rise to creation of two types of centres, one of which acts as a trapping centre and the other as a recombination centre for the majority carriers (electrons) in the material. This is supported not only by the occurrence of a new peak in the spectral response of the photocurrent but also the photocurrent transients, with overshoot phenomena for the critically annealed samples. However, the exact origin of the creation of these centres is not yet known.

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