SLOW RESPONCE PHOTOCONDUCTIVITY OF CHEMICALY DEPOSITED ZnO THIN FILM

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Abstract:

The slow responce photoconductivity of chemicaly deposed ZnO thin film was investigated. The spectral sensitivity was found to show two maxima, the small one (3, 2 eV) coresponds to the band gap energy, and the bigger one (3, 02 eV) has an energy less than band gap. The decay time of slow responce photoconductivity was found to be not exponential in time t, but exponential in t^n*, with* $n < 1$*.*

INTRODUCTION

Chemicaly deposed films of Cu_2O[1], CdS[2] and ZnO[3] show pronaunced slow responce photoconductivity, with light to dark conductivity ratio as high as 10^4. The examination of time decay of conductivity is very convenient for ZnO thin film, since it shows a weak fast responce photoconductivity and has very small dark conductivity, thus the whole conductivity atained after illumination comes from slow processes in ZnO.

PREPARATION OF THE SAMPLES OF ZnO THIN FILMS

The film used in the measurements of slow responce photoconductivity were prepared from aquaeous solutions of apropriate chemicals by the method described elsevere[3]. The 1st solution was ammonium complex of $ZnCl_2$. A clean glass slides were successively immersed in a cold ammonium complex and then in a hot water (95 – 99°C). After 80 – 90 immersions a thin ZnO film with a thickness of 0,8 – 0,9 μm was deposited on the both faces of the glass slide. Such a film has very small dark conductivity (10^8 Ω cm). Film with a higher dark conductivity (10^6 Ω cm) were prepared by doping with Sn^{++}, performed by addition of 10 cm^3 of 0,1 M $SnCl_2$. The electrodes were made by silver paste painted as two strips 0,2 cm apart each other. Since silver doesn't give ohmic contact with ZnO, a thin layer of HgS was chemicaly deposed prior to the painting.

THE MEASUREMENTS OF SLOW RESPONCE PHOTOCONDUCTIVITY

The rise and fall of conductivity was measured every 10 s at the begining, every minute after 1st minute, and every 5 minutes in the later time. The rise of photoconductivity in time after put on of stationary illumination, and decay of photoconductivity in time after turn off of the illumination is presented of Fig. 1. The measurements were performed by sun light (80 mW/cm^2) and monochromatic light ($8 \cdot 10^{-6}$ W/cm^2) in the range of 200 – 800 nm. Up to 80 mW/cm^2, the stationary value photoconductivity was found to be linear with light intensity. The spectral sensitivity (Fig. 2) shows two peaks, a small one corresponds to the band gap energy 3,2 eV, and the bigger one with the energy 3,02 eV. This showes that the free carriers are created by photons with energies less than band gap, i.e. the slow processes are connected with the impurity levels.

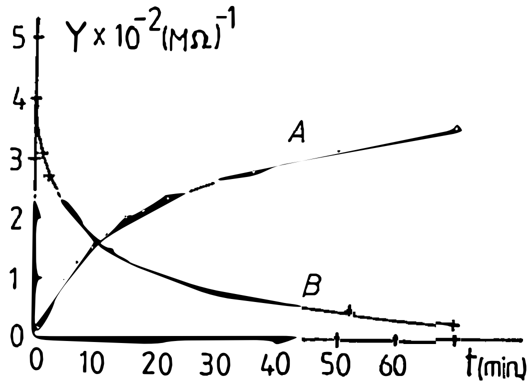

Fig. 1. The rise of photoconductivity after put on illumination – A, and decay of photoconductivity after turn off the illumination – B.

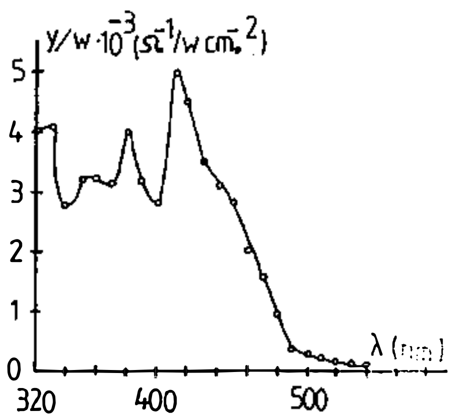

Fig. 2. Spectral sensitivity show two peaks: small corresponds to the band gap energy (3,2 eV) and bigger to the energy of 3,02 eV.

ANALIZE OF TIME DECAY OF THE PHOTOCONDUCTIVITY

For all the samples (more than 30) we found that the decay of conductivity is not simple exponential in time but it has more complex behavior, similar to the behavior of Cu_2O[1] and As_2S_3[4]. Graphic presentation of ln $\ln(R/R_o)$ v.s. ln t gives a straight line (Fig. 3) with an tangens $n < 1$ for the interval from 0 — 180 minutes. This means that the

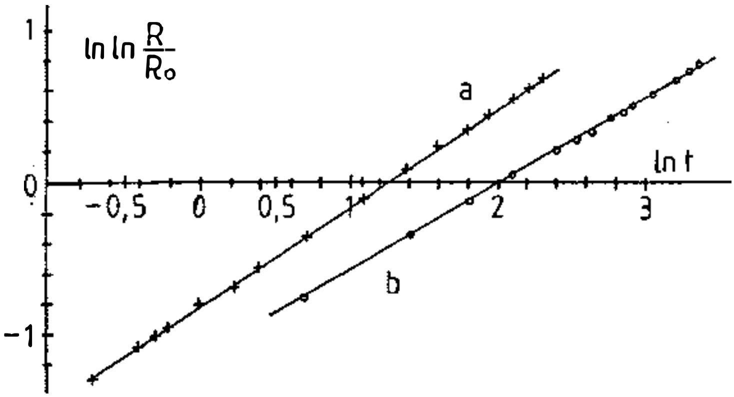

Fig. 3. Presentation of ln ln (R/R_o) v.s. ln t for high intensity illumination (a), and for monochromatic illumination (b).

conductivity decay can be expresed by $Y = Y_o \exp(-at^n)$, where Y_o — is stationary photoconductivity, and n is tangens of the straight line. In the case of sun light illumination (80 mW/cm^2) $n = 0{,}66$, and for monochromatic illumination ($8 \cdot 10^{-6}$ W/cm^2) it is 0,5. For the case of high intensity excitation (sun light illumination), the decay of photoconductivity is

$$Y = Y_o \exp(-at^n)$$

which was found to be true for undoped and doped ZnO films, with a thickness from 0,5 — 0,9 μm. If one assumes constant electron mobility in time, the decay of photoconductivity can be described to the decay of concentration of the electrons $n = n_o \exp(-at^{2/3}$. The rate of the concentration decay is

$$\frac{dn}{dt} = -\frac{2}{3} a t^{-1/3} n$$

which can be taken as differential equation for time evolution of electron concentration. This equation can be considered as equation for linear carrier recombination in which the concentration of the recombination centers is time dependent, i.e.

$$\frac{dn}{dt} = -A \cdot n \quad \text{where } A = \frac{2}{3} a t^{-1/3}$$

The rate of change of recombination centers A is

$$\frac{dA}{dt} = -\frac{2}{9} at^{-4/3} \text{ i.e. } \frac{dA}{dt} = -\frac{9}{8}\frac{A^4}{a\,3}$$

which is differential equation for four particle recombination. Thus the mechanism of the carrier (electron) recombination in the case of slow responce photoconductivity, excited by high light intensity is complex one. First of all four particle recombine and give recombination center for the free electron. The free electron recombine and the decay in photoconductivity take place.

For the case of low intensity excitation, which was the case of monochromatic light illumination the decay of photoconductivity was found to be $Y = Y_0 \exp(-at^{1/2})$, where Y_0 – is stationary value conductivity. In a similar way one obtaines:

$$\frac{dn}{dt} = -\frac{1}{2} at^{-1/2} n, \text{ and } \frac{dA}{dt} = -\frac{1}{4} at^{-3/2} \text{ i.e. } \frac{dA}{dt} = -\frac{2 \cdot A}{a^2}$$

which can be taken as equation for tree particle recombination. Thas the decay of slow responce photoconductivity in the case of low level excitation is complex process in which tree particle recombine and create recombination center for the free electrons.

In the paper[5] confirmation is given that the slow processes in ZnO sintered sample are connected with the adsorbtion of oxygen and chemical reaction of the adsorbed oxygen with the interstitial Zn, which othervice acts like donor. In the case of high intensity excitation the process involvs four particles:

$$Zn^{++} \text{ (interstitial)} + 2e + \frac{1}{2} O_2 \text{ (adsorbed)} \rightarrow ZnO$$

Similarly, in the case of low intensity excitation, the processes involve tree particles:

$$Zn^{+} \text{ (interstitial)} + e + \frac{1}{2} O_2 \text{ (adsorbed)} \rightarrow ZnO$$

As far as Zn^{++} or Zn^{+} exsist the free electrons can recombine with this donor centers.

Conclusion:

The slow responce photoconductivity of ZnO thin film is a complex process in which interstitial Zn and adsorbed oxygen take part. The interstitial Zn plays a role of donor, which can be thermaly or opticaly ionized, giving one or two electrons. The adsorbed oxygen can be chemicaly bounded forming ZnO. In the case of monochromatic illumination the interstitial ZnO can be disociated by photons with the energy $h\nu_1 = 3{,}02$ eV, i.e.

$$ZnO + h\nu_1 \rightarrow Zn^{+} + \frac{1}{2} O_2 + e,$$

for the case of sun light illumination the following process goes

$$ZnO + h\nu_2 \rightarrow Zn^{++} + \frac{1}{2} O_2 + 2e,$$

where $h\nu_2 = 3{,}2$ eV.

In the case of cease of the excitation a reverse process goes up, which destroys donor levels Zn^{++}, Zn^{+}. The destruction of this levels is governed by tree or four particle recombination, which conforms by the examination of photoconductivity in the case of low level excitation (monochromatic light illumination) and also in the case high level excitation (sun light illumination).

LITERATURE

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