

PHOTORESPONSE MEASUREMENTS OF A SEMICONDUCTING ZnO-ELEKTROLYTE JUNCTION

A. H. ABOU EL ELA, M. EL BAHAY

*Physics Department, Islamic Girls College, Nasr City, Cairo,
and*

S. M. EL-RAGHY

Metallurgy Department, Faculty of Engineering, Cairo University, Cairo, Egypt

Received 20 December 1981

UDC 538.95

Original scientific paper

Photoresponse measurements of the characteristics of ZnO semiconducting electrode were carried out for ZnO layers obtained by anodic oxidation of zinc metal in different electrolytes. The characteristics of the growth process and the properties of ZnO layer were investigated, and the effect of organic medium on the photoresponse and the process of decomposition of ZnO electrode was discussed. Moreover, the power characteristics and the stability of the photoelectrode were analyzed.

1. Introduction

Much research and attention have been devoted to the semiconductor-electrolyte junction, with the rather recent interest in solar energy conversion¹⁻³. The recent demonstration of workable wet photovoltaic cells employing semiconducting anodes by a number of groups⁴⁻⁶ have evoked considerable interest.

One of the fundamental aspects of the problem of applying photoelectrochemical cells to solar energy conversion is defining the materials properties of the photosensitive electrode necessary to optimize its performance. A simple photoelectrochemical cell consists of a semiconducting electrode, a metallic electrode and an

electrolyte, as shown in Fig. 1. When the semiconducting electrode is illuminated electrons are excited from the valence band to the conduction band by the absorbed photons. In the depletion region there exists an electric field which is necessary to separate the optically excited electrons in the conduction band from the holes in the valence band before they can recombine. The electrons then flow through the electrical load impedance R_L to the metallic cathode and drives an electrochemical reaction, while the holes flow to the semiconductor surface driving another reaction.

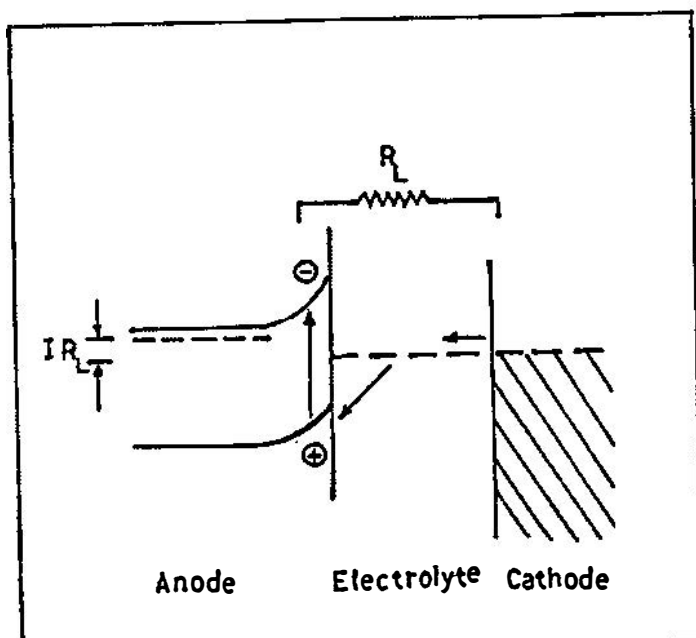


Fig. 1. Energy level diagram for photoelectrochemical cell.

Butler and Ginley⁶⁾ had shown that, in the case of metal oxide photosensitive electrodes, the generation and separation of carriers in the semiconductor is the rate limiting step rather than the chemical kinetics at the interface and the semiconductor-electrolyte junction can be treated exactly as a solid state Schottky junction.

In the present work photoresponse measurements were carried out in order to investigate the growth process and the bulk properties of ZnO film grown by anodic oxidation of zinc metal. The power characteristics and the stability of the semiconducting electrode were studied. ZnO is a *n*-type semiconductor⁷⁾ presumably due to excess zinc causing anion (O^-) vacancies, and its forbidden gap is about 3.2 eV. In an earlier paper⁸⁾ X-ray diffraction technique has been used to study the structural changes and processes which take place during the growth of ZnO layer, and the effect of electrolyte concentration and anodizing voltage on the composition of ZnO layers.

2. Experimental

The experimental work consists of three phases:

- i) Zinc oxide film growth,
- ii) Measurement of the polarization characteristics, and
- iii) Photoresponse measurements.

Zinc oxide layers were prepared by anodic oxidation of zinc metal in different anodizing electrolytes: potassium hydroxide, sodium hydroxide and sodium borate in aqueous solutions with different concentrations: 0.1, 0.5, 1 and 2 molar. A conventional electrochemical cell was used whose anode is made from a circular zinc sheet 0.37 mm thickness and 1 cm² cross sectional area. The zinc surface was polished and then etched in 0.5 N HCl for a half a minute, then it was carefully washed by distilled water. A rectangular platinum cathode was used, and both electrodes were connected to the measuring circuit, which consists of a stabilized dc power supply (0–300 V) and a sensitive ampermeter, and the potential across the cell electrodes was measured using a sensitive digital voltmeter. Anodic oxidation was carried out for 30 minutes under different anodizing voltages 1, 2 and 3 V and the anodizing currents were stabilized during ZnO film growth (0.1 mA/cm² for anodizing in 0.1 M KOH and 1.8 mA/cm² for anodizing in 1 M KOH).

Measurements of the polarization characteristics of the cell and its photoresponse were carried out in the dark and under illumination from a medium pressure mercury lamp (200 W), where ZnO layers were placed in the focused spot.

3. Results and discussion

A — Characteristics of the process of growth of ZnO layers

Various processes may affect the growth of ZnO semiconducting layer. The growth rate can be controlled by the dissolution of metal, by the growth of a new phase or product, or by the electrolyte resistance to current flow. In the case when metal dissolution is the predominant factor which controls the growth rate, the current decreases exponentially with time at constant potential⁹⁾. Figure 2 shows the time dependence of the current density, the current firstly decreases abruptly and then decreases exponentially with time reaching a saturation value. The shape of the curves indicates that metal dissolution controls the growth rate of ZnO layer.

The value of the dark current depends on the rate of dissolution of ZnO layer, and the rate of dissolution increases on illumination. Figures 3, 4 and 5 show the dependence of the current density of the cell on the concentration of the anodizing electrolyte at different anodizing voltages in the dark and under illumination using two polarizing electrolytes: 0.1 M KOH and 0.1 M sodium borate. From the figures it is clear that the maximum photocurrent (the difference between the current under illumination and in the dark) is observed for ZnO layers prepared by oxidation of zinc metal in anodizing electrolyte concentration 1 M KOH. Moreover, the photocurrent for the cell with 0.1 M KOH polarizing electrolyte is higher than with 0.1 M sodium borate. It is known that the number of defects increases

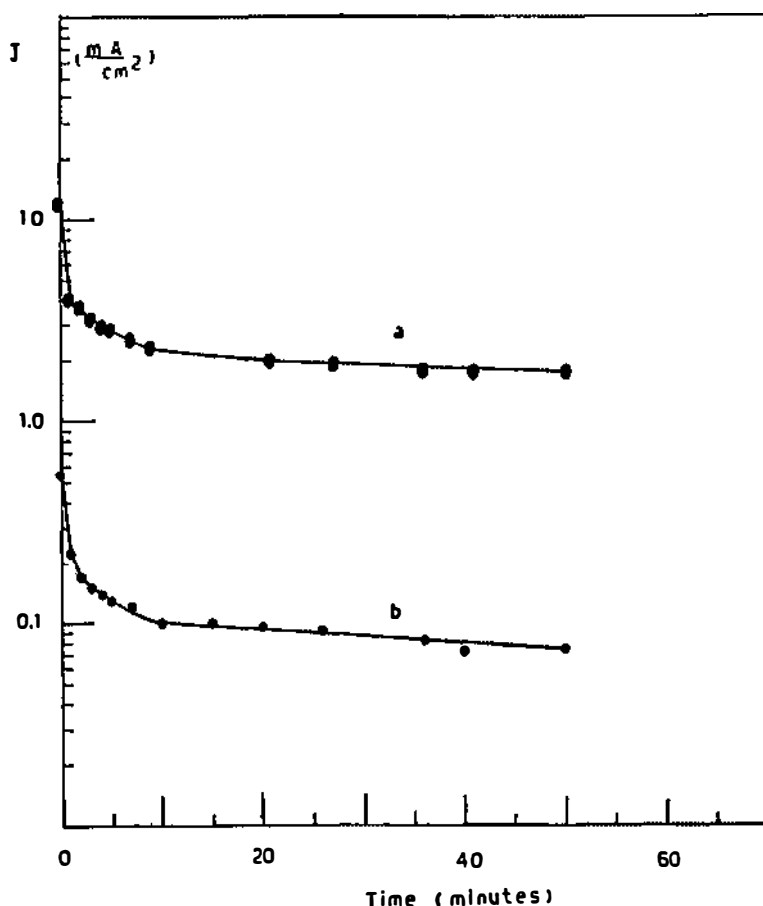


Fig. 2. The dependence of current density on time at anodizing voltage 2 V and different electrolyte concentration: a) 1 M KOH b) 0.1 M KOH.

with the concentration of the electrolyte, and the decrease of the current when the concentration of the electrolyte becomes higher than 1 M KOH, may be attributed to the increased number of defects which act as trapping centres.

The dependence of the current density of the cell on the anodizing voltage is shown in Fig. 6, in the dark and under illumination. Maximum values of the photocurrent are obtained at 2 V anodizing voltage. From a comparison between the values of the photocurrent density for ZnO layers obtained at different oxidation conditions and different polarizing electrolytes, one concludes that the optimum conditions for maximum photocurrent are: 1 M KOH for anodizing electrolyte, 2 V for the anodizing voltage and 0.1 M KOH for the polarizing electrolyte.

Gerisher¹⁰⁾ and Gomes, Freund and Morrison¹¹⁾ had shown that the photocurrent can be increased by the addition of organic medium, they indicate the

possibility of noncorrosive charge exchange at the semiconductor electrode and current doubling. To investigate the effect of organic medium on the characteristics of ZnO layer, methyl and ethyl alcohols were added to the electrolyte in the following concentration by volume: 90% alcohol + 10% water + 0.1 M KOH, also 0.1 M sodium borate solution was used as electrolyte. Experimental measurements of the photocurrent (Fig. 7) and the ratio of the photocurrent to the dark current (Fig. 8) show that the photocurrent is higher than in the case when 0.1 M KOH electrolyte is used alone. This result agrees with the data of Morrison and Freund¹²⁾ on ZnO single crystal electrode with formic acid and KCl electrolyte.

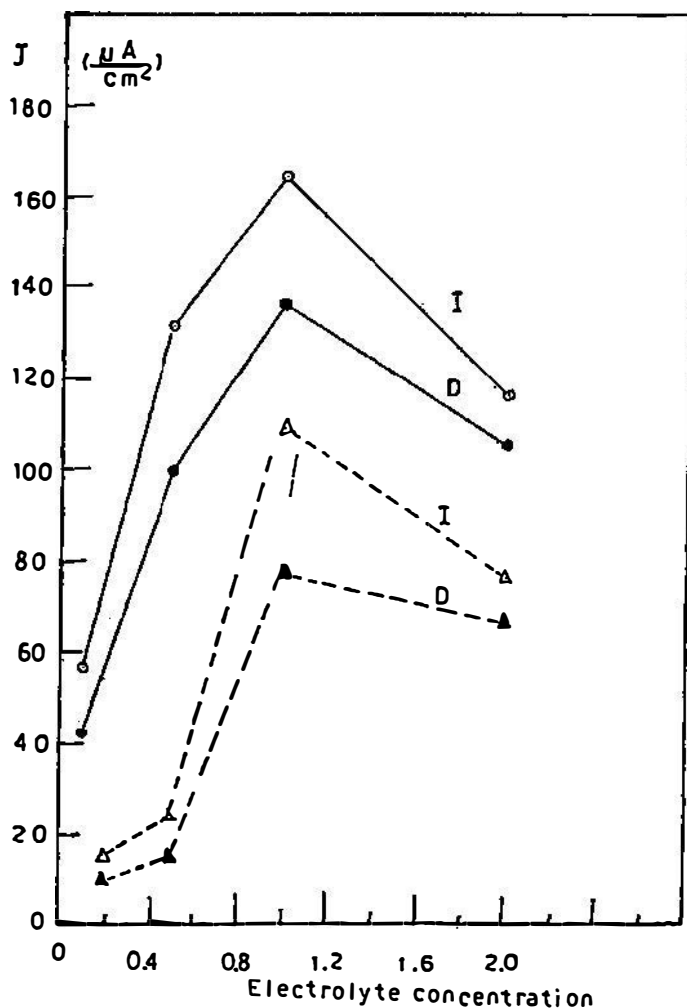


Fig. 3. The dependence of the current density on the anodizing electrolyte concentration (KOH) at anodizing voltage 1 V in the dark (D) and under illumination (I) and for different polarizing
 ● 0.1 M KOH and ▲ 0.1 M sodium borate.

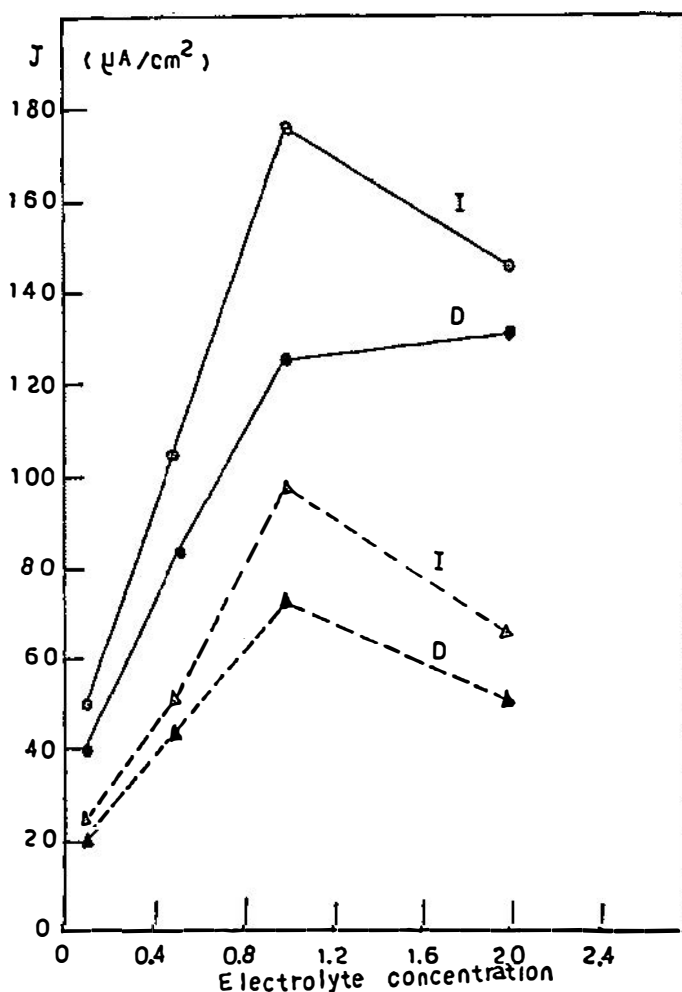


Fig. 4. The dependence of the current density on the anodizing electrolyte concentration (KOH) at anodizing voltage 2 V in the dark (D) and under illumination (I), and for different polarizing electrolytes: ● 0.1 M KOH and ▲ 0.1 M Na borate.

Structural analysis of the investigated ZnO layers using X-ray technique⁸⁾, shows that the addition of methyl and ethyl alcohols inhibits the decomposition of ZnO and the formation of zinc hydroxide.

The process of dissolution of ZnO can be quantitatively estimated by plotting the variation of the weight of ZnO layer electrode versus time. Fig. 9 shows the time dependence of the weight of ZnO layer with 0.1 M KOH cell in the dark and under illumination, where the weight gain (or loss) is given by the difference in weight between the ZnO layer and the weight result after different time intervals of self polarization of the cell. It appears from the curves that a salted level begins to appear after 18 h. Moreover, the weight gain after 18 h is amounted

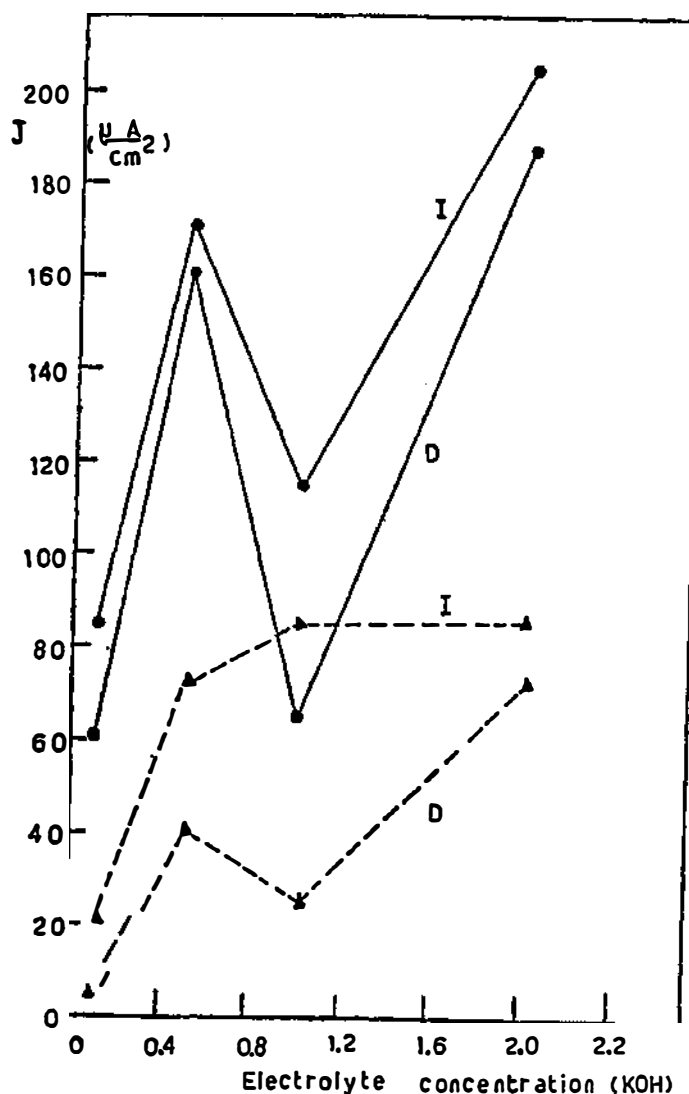
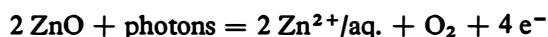


Fig. 5. The dependence of the current density on the anodizing electrolyte concentration (KOH) at anodizing voltage 3 V in the dark (D) and under illumination (I), for different polarizing electrolytes: ● 0.1 M KOH and ▲ 0.1 M Na borate.

to 5×10^{-4} g/cm², while the weight loss after the same time is 12×10^{-4} g/cm² under continuous illumination, which emphasised that the dissolution rate is increased by illumination. Gerisher¹²⁾ had shown that ZnO decomposes under illumination according to



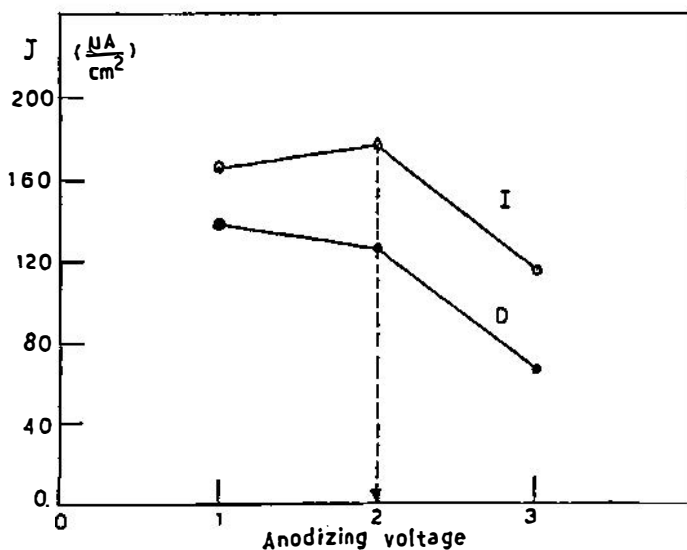


Fig. 6. The dependence of the current density on the anodizing voltage in the dark (D) and under illumination (V) for electrolyte concentration 0.1 M KOH.

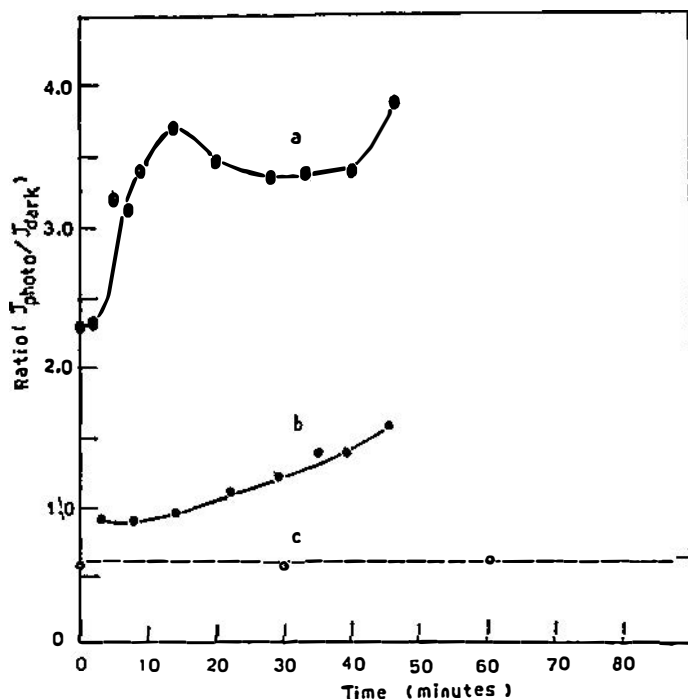


Fig. 7. The effect of alcohol addition on the time dependence of the ratio of the photocurrent to the dark current: (a) 0.1 M KOH + 90% methyl alcohol + 10% water, (b) 0.1 M KOH + 90% ethyl alcohol + 10% water (c) 0.1 M KOH.

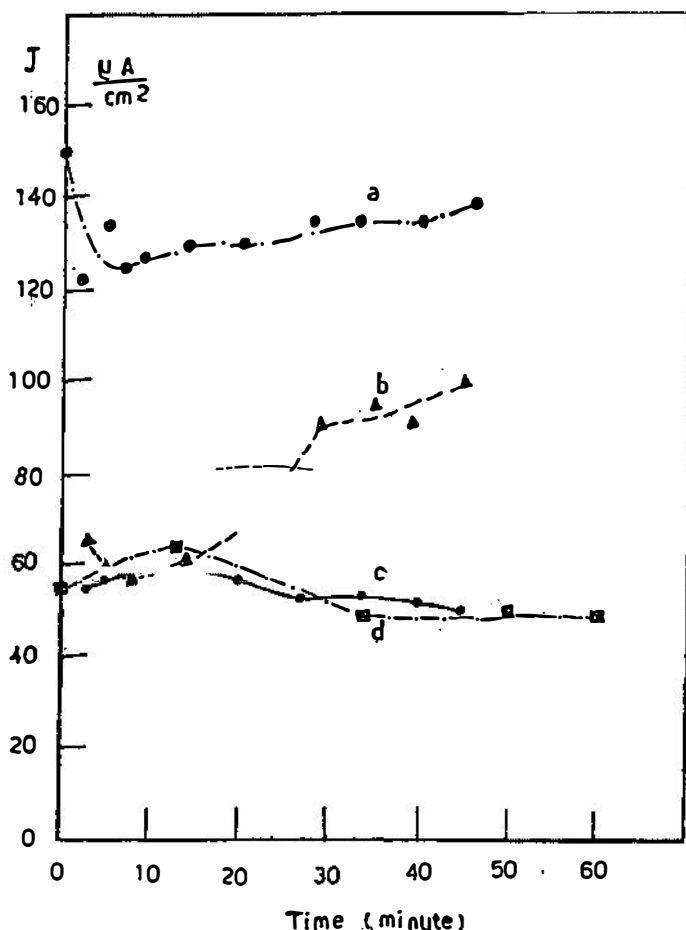


Fig. 8. Time dependence of the photocurrent density for ZnO electrode in different electrolytes a, b, c as in Fig. 7.

Quantitative dissolution experiments carried out by Morrison and Freund¹³⁾ on single crystal ZnO had shown that the steady state dissolution in 0.1 M KCl with 0.1 Acetate buffer electrolyte, is about 5×10^{-5} g/cm².

Measurements of the time dependence of the cell conductivity (Fig. 7) show that the conductivity under continuous illumination is greater than in the dark.

B — Photoresponse measurements of the characteristics of the grown ZnO layers

The current-voltage characteristics of ZnO-electrolyte junction are shown in Fig. 11, in the dark and under illumination. The shape of the curves indicates that the transfer of electrons is energetically much more favorable from ZnO to the chemisorbed species than in the reverse direction. Also it may be concluded

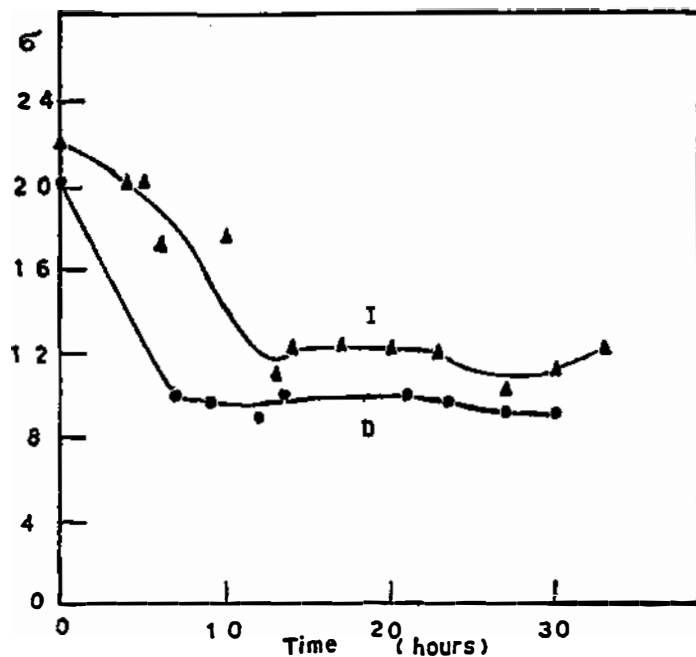


Fig. 10. Time dependence of the cell conductivity in the dark (D) and under illumination.

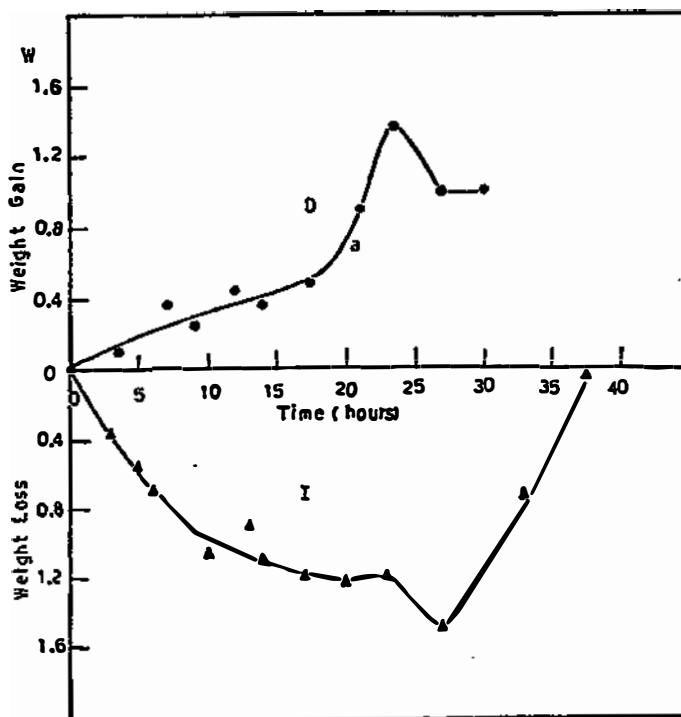


Fig. 9. Time dependence of the weight loss (or gain) of ZnO layer with 0.1 M KOH electrolyte.

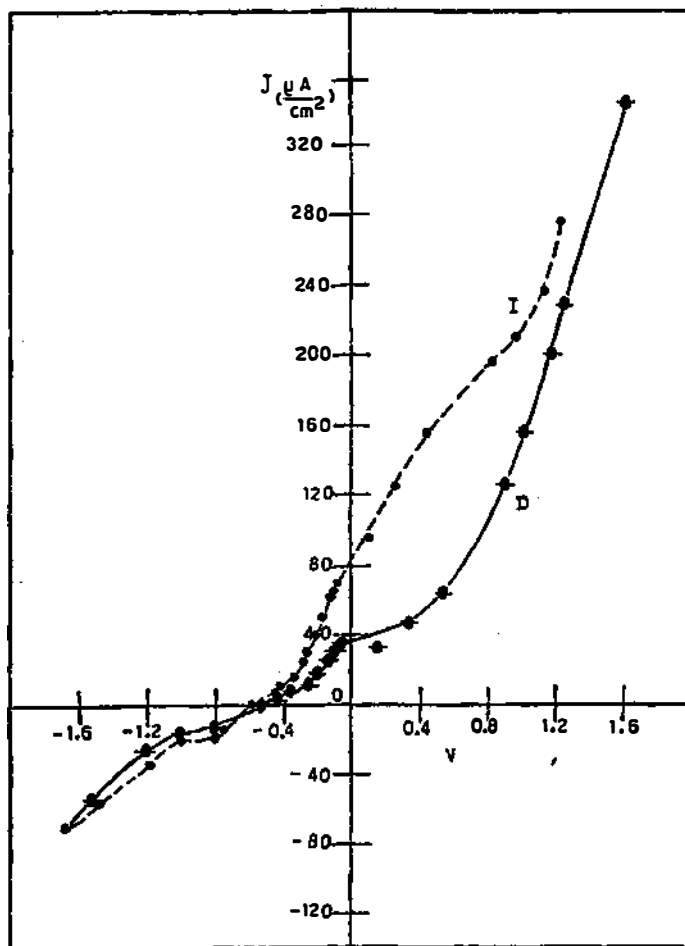


Fig. 11. The variation of the current density with the electrode potential in 0.1 M KOH: D — Dark current and I — current under illumination.

that during illumination electron injection occurs from the adsorbed negatively charged species into the ZnO layer by a recombination process, while the holes in the valence band are generated by illumination. The values of the current in Fig. 11 are higher than those obtained by Hauße and Range¹⁴⁾ for single crystal ZnO with 10^{-4} M quinhedrone in an acetate buffered 0.5 M KCl electrolyte, moreover, the shape of the curves differs, since no saturation is observed in the present work, which may be attributed to surface recombination. Furthermore, the shape of the curves in the dark and under illumination shows that ZnO layer undergoes decomposition in the corrosive electrolyte, the decomposition reactions are known^{8, 15, 16)} and they are caused by electrons and holes.

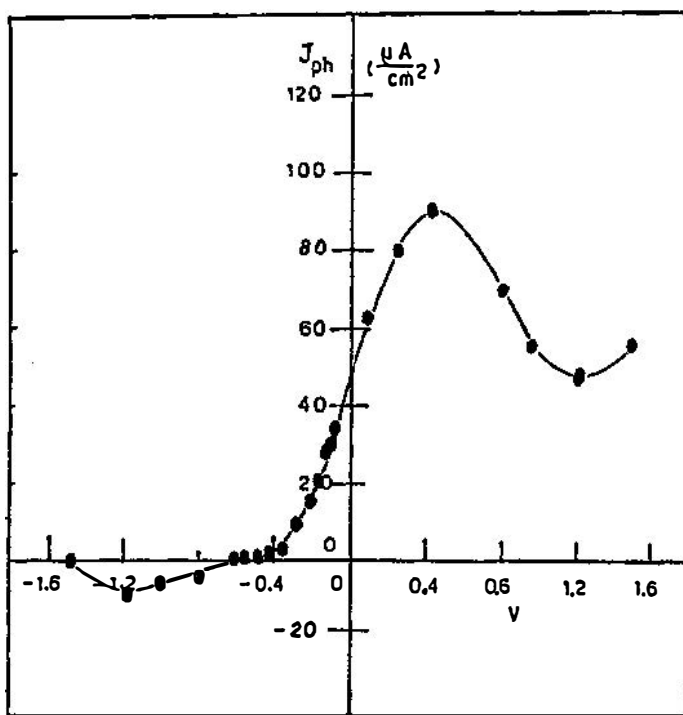


Fig. 12. The dependence of the photocurrent density on the electrode potential.

The dependence of the photocurrent on the electrode potential is shown in Fig. 12. The photocurrent tends to zero at about -0.5 V and increases with voltage reaching maximum near 0.4 V. Generation of the minority carriers by illumination will cause a photocurrent if the minority carriers can react at the interface with the electrolyte. Otherwise, charge separation will create a counter voltage that will compensate the voltage drop in the space charge layer such that electron-hole pair generation is compensated for by recombination. In most systems¹⁷⁾, minorities react with the electrolyte or cause electrolytic decomposition of the semiconductor. A model for the photocurrent¹⁷⁾ yields the relation

$$J_{ph} = e \Phi_0 [1 - (1 + \alpha L_p) \exp(-\alpha W)]$$

where α is the light absorption coefficient, Φ_0 is the incident photon flux, $W = L_D ((V - V_{fb})/kT)^{1/2}$ is the space charge width and $L_D = (2\epsilon\epsilon_0 kT/e N_D)^{1/2}$ is its Debye length, and $L_p = (D_p \tau_p)^{1/2}$ is the diffusion length of holes. The limitations of this model are that effects such as recombination at the interface are ignored. Wilson^{18,19)} has included surface recombination in the Schottky model, and Laser and Bard²⁰⁾ and Reiss²¹⁾ had taken into consideration the electrochemical kinetics as well as surface recombination. They indicated that recombination process is the fundamental process responsible for the shape of the photocurrent voltage characteristics.

C — Power characteristics and stability of the grown ZnO layers

The characteristics of the grown ZnO layers can be clarified more by their operation as a photovoltaic cell. Figure 13 shows the power characteristics (current-voltage output under variable load) of the cell with two different electrolytes (0.1 M KOH and 0.1 M KOH + 90% methyl alcohol + 10% water). At maximum output power ($\partial I/\partial V = -I/V$) and $P_{max} = I_{sc} V_{oc} f$, where I_{sc} is the short circuit current, which is determined by the number of photons absorbed less the losses in the system, V_{oc} is the open circuit voltage and f is the fill factor, which depend on the relative positions of the energy levels in both the semiconductor and the electrolyte, and on the type of the electrolyte. The fill factor for the first electro-

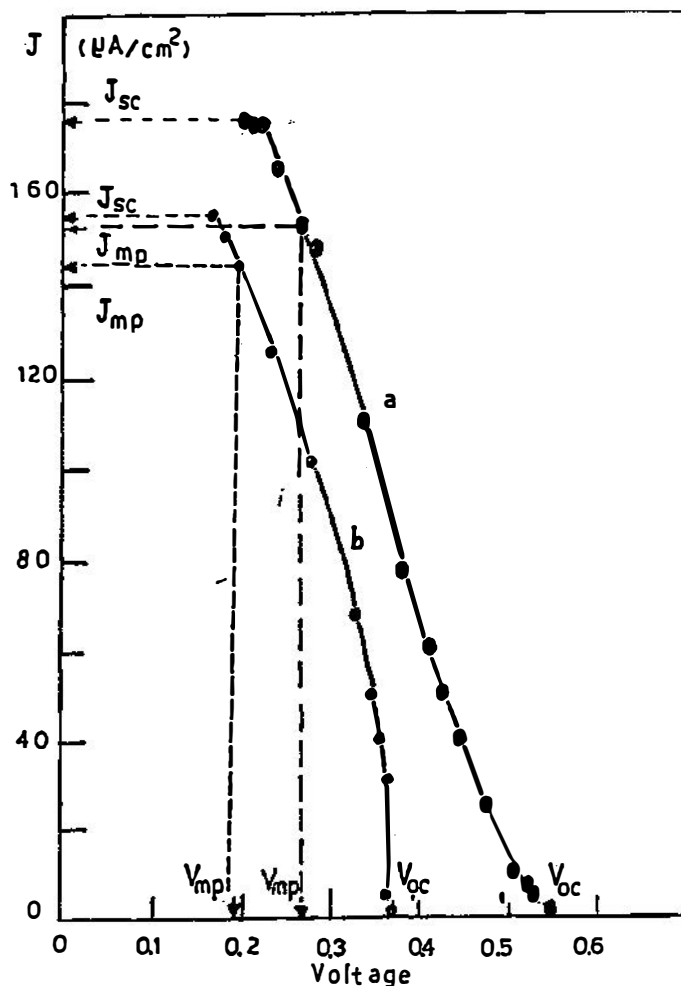


Fig. 13. Power characteristics of the cell with ZnO electrode and different electrolytes:
 (a) 0.1 M KOH (b) 0.1 M KOH + 90% methyl alcohol + 10% water.

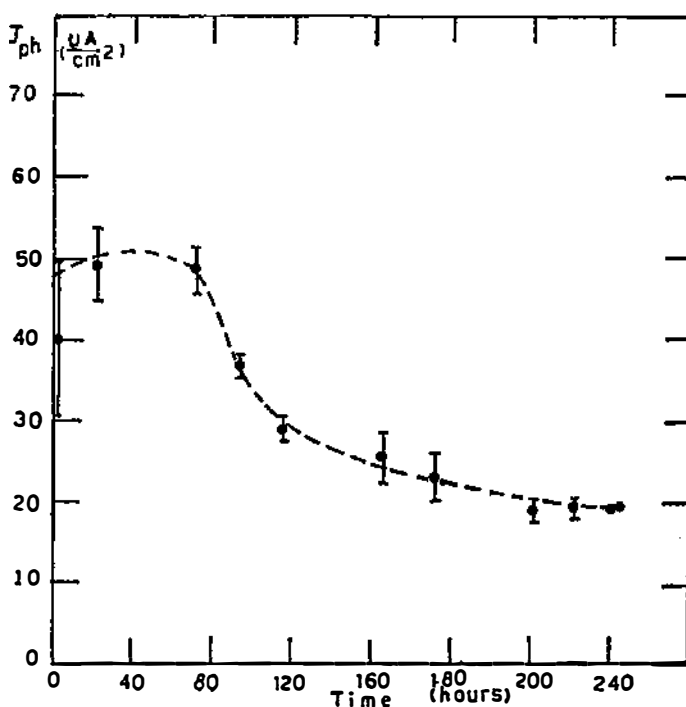


Fig. 14. Ageing effect: The variation of the photocurrent density with time.

lyte (0.1 M KOH) is 0.42, while for the second electrolyte is 0.5, which indicates that the addition of alcohol increases the fill factor of the cell.

The stability of ZnO photoelectrode can be investigated through long term ageing process. Gerisher and Gobrecht²²⁾ have recently shown that long-term ageing of non-oxide photoanodes as CdS and can cause phase changes in the surface layer. Concurrent with the phase changes were significant reduction in the photocurrent. In the present work measurements of the photoresponse were carried out under long-term continuous polarization of the ZnO layer for about 12 days. Figures 14, 15 and 16 show the time dependence of the photocurrent, V_{oc} , I_{sc} and the fill factor of the whole cell. The characteristic features of the curves can be summarized as:

1. The photocurrent decreases rapidly with time,
2. The open circuit voltage, the fill factor, and the cell conductivity decreases rapidly with time and becomes nearly constant after a time interval of about 5 days.

Ageing effects can be attributed to the changes which occur in the ZnO photoanode and photodecomposition. Structural analysis⁸⁾ shows that long-term self polarization of ZnO layers enhances the decomposition of ZnO and the formation of zinc hydroxide. Stability can be increased by the addition of organic medium which inhibits the formation of zinc hydroxide⁹⁾.

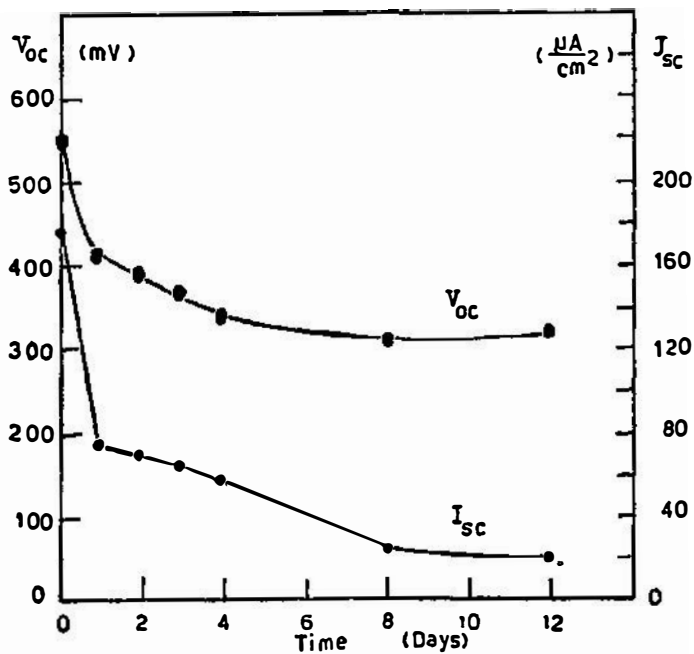


Fig. 15. The variation of V_{oc} and J_{sc} with time.

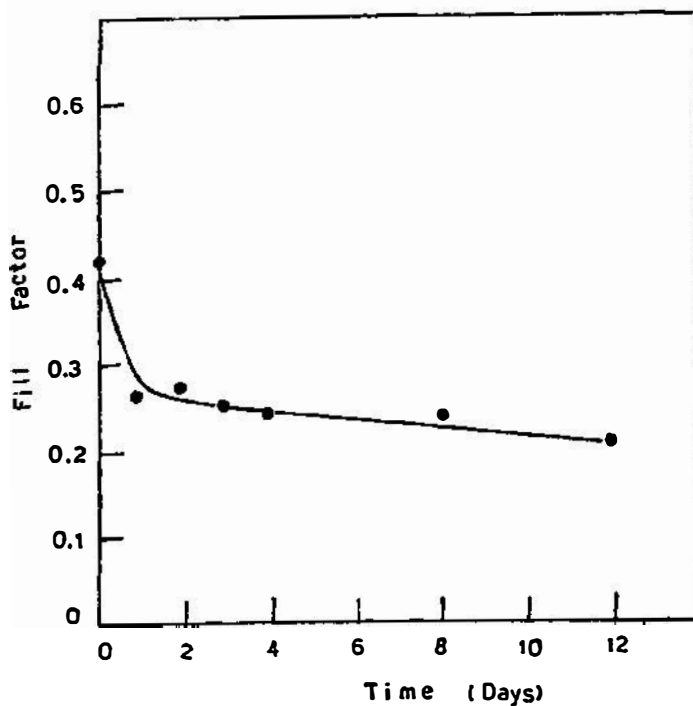


Fig. 16. The variation of the fill factor with time.

4. Conclusions

Photoresponse measurements were carried out on ZnO photosensitive anodes prepared by anodic oxidation of zinc metal. The layers undergo electrolytic decomposition as a photovoltaic cell and the rate of dissolution increases on illumination. The process of decomposition can be inhibited partially by the addition of organic medium, and results in better stability of the layers.

References

- 1) C. G. B. Garrett and W. H. Brattain, *Phys. Rev.* **99** (1955) 376;
- 2) W. H. Brattain and C. G. B. Garrett, *Bell System. Tech. J.* **34** (1955) 129;
- 3) H. Gerisher, in: *Solar Energy Conversion*, Ed. B. O. Seraphin, Springer-Verlag, New York 1979, p. 119;
- 4) B. Miller and A. Heller, *Nature (London)* **262** (1976) 680;
- 5) A. B. Ellis, S. W. Kaiser and M. S. Wrighton, *J. Am. Chem. Soc.* **98** (1976) 1635;
- 6) M. A. Butler and D. S. Ginley, *J. Mater. Science* **15** (1980) 1;
- 7) W. P. Gomes and F. Cardon, in *Semiconductor-Liquid Junction Solar Cells*, Ed. A. Heller. The Electrochemical Society, 1977, Princeton N. J., p. 120;
- 8) A. H. Abou El Ela, S. M. El-Raghy and M. Elbahay, *J. Mater. Science* **16** (1981) 2726;
- 9) D. A. Verimlyea, *Advances in Electrochemistry and Electrochemical Engineering* vol. **3**, Ed. P. Delahay et al. Louisiana, 1963, p. 211;
- 10) H. Gerisher, *Surface Science* **18** (1969) 97;
- 11) W. P. Gomes, T. Freund and S. R. Morrison, *J. Electrochem. Soc.* **115** (1968) 431;
- 12) H. Gerisher, *Advances in Electrochemistry and Electrochemical Engineering* vol. **1**, p. 139, Ep. P. Delahay, Interscience Publishers, New York (1961);
- 13) S. R. Morrison and T. Freund, *J. Chem. Phys.* **47** 1543 (1967); *ibid* **13** (1968) 1343;
- 14) K. Hauße and J. Range, *Ber. Bunsenges. Phys. Chem.* **71** (1967) 690;
- 15) H. Gerisher, *Proc. Conf. on Electrochemistry and Physics of Semiconductor-Liquid Interfaces*, Airlic, Virginia, May 1977, Ed. A. Heller, *Proc. vol. 77, 3*, Princeton: The Electrochemical Society (1977) 1;
- 16) H. Gerisher, D. M. Kolb and J. K. Sass, *Advances in Physics*, 1978, vol. **27**, No. 3, pp. 437;
- 17) M. A. Butler, *J. Appl. Phys.* **48** (1977) 1914;
- 18) R. H. Wilson, *J. Appl. Phys.* **48** (1977) 4292;
- 19) R. H. Wilson in *Semiconductor-Liquid Junction Solar Cells*, Ed. A. Heller, *Proceedings of a Conference held at Airlic, May 1977, Proc. vol. 77*, The Electrochemical Society, 1977, Princeton N. J.;
- 20) D. Laser and A. J. Bard, *J. Electrochemical Society* **123** (1976) 1837;
- 21) H. Reiss, *J. Electrochemical Society* **125** (1978) 937;
- 22) H. Gerisher and J. Gobrecht, *Ber. Bunsenges Phys. Chem.* **80** (1976) 327.

MJERENJE FOTOODGOVORA SPOJA ZnO ELEKTROLIT

A. H. ABOU EL ELA, M. EL BAHAY i S. M. EL-RAGHY

Physics Department, Islamic Girls College, Nasr City, Cairo, Egipat

UDK 538.95

Originalni znanstveni rad

Poluvodička elektroda ZnO dobivena anodnom oksidacijom uronjena je u elektrolyte različitih sastava. Mjeren je fotoodgovor, istražene su karakteristike rasta ZnO slojeva, ustanovljen je utjecaj prisustva organskog medija na fotoodgovor. Također je proučavan proces dekompozicije ZnO elektrode. Načinjena je analiza električke efikasnosti i stabilnosti dobivenih fotoelektroda.