

## Interfacial Phenomena at ZnO : CoO Electrodes

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The admittance of a cobalt-doped ZnO crystal/NaOH electrolyte interface has been studied as a function of frequency for various electrode potentials. Analysis of the admittance data gives evidence of a continuum of surface states, the density of which reaches a maximum for an energy 0.30 eV lower than the energy of the conduction-band edge. However, appropriate surface states are involved in the charge transfer processes of carriers photogenerated in the visible, between the  $\text{Co}^{2+}$  states and the  $\text{O}_2/\text{OH}^-$  level, and can stabilize as a consequence the electrode against photocorrosion. © 1988 Academic Press, Inc.

### Introduction

It is well known that ZnO suffers photo-dissolution in contact with 1M NaOH electrolyte under anodic polarization.

According to Gerischer the anodic dissolution potential of ZnO lies in the bandgap and thus makes the semiconductor thermodynamically unstable (1).

We have recently shown that the substitution of 1 at.% of  $\text{Co}^{2+}$  in the tetrahedral sites of the wurtzite-type ZnO lattice leads to a large extension of the photoresponse toward the visible light region for the corresponding electrodes (2, 3). This visible photoresponse involves a  $d-d$  transition within the  $\text{Co}^{2+}$  ion itself, followed by the transfer of both photogenerated electrons into the semiconductor conduction band and the photoexcited holes toward the semiconductor/electrolyte interface via the midgap  $\text{Co}^{2+} : d$  band (Fig. 1) (2, 3).

As a consequence the charge transfers occurring at the  $\text{Co}^{2+}$ -doped ZnO/electrolyte interface should involve  $d$  orbitals while  $\text{O}_{2p}$  orbitals are related to ZnO itself. Thus the stability is likely to be improved for  $\text{Co}^{2+}$ -doped ZnO.

Therefore it was worthwhile as a first stage to investigate the influence of  $\text{Co}^{2+}$  doping upon the electrode stability against visible light photocorrosion.

On the other hand, it is well known that surface states can also participate in the charge transfer processes at the semiconductor/electrolyte interface (4). Thus we will also study the influence of  $\text{Co}^{2+}$  doping on formation of surface states. A nonlinear least-squares analysis of complex admittance of the semiconductor/electrolyte interface is used for this purpose.

The investigation will be carried out on 1%  $\text{Co}^{2+}$ -doped ZnO single crystals (symbolized as ZnO : Co).

## Experimental

ZnO:Co single crystals have been prepared by chemical vapor transport (CVT) of 99% ZnO and 1% CoO (molar proportions) in a sealed ampoule under 100 Torr chlorine pressure. Crystal growth requires about 70 hr.

The considered samples were cut perpendicularly to the *c*-axis from the original ingot so as to have the shape of hexagonal wafers with approximately 1 mm thickness and 5 mm diameter.

The room temperature conductivity ( $10^{-1} \Omega^{-1} \text{ cm}^{-1}$ ) of the ZnO:Co samples was measured by a two-probe method using a high impedance Keithley multimeter.

The electrode preparation for the electrochemical cell was described elsewhere (5). A 0.1 M NaOH aqueous electrolyte was used and all potentials were referred to a saturated calomel electrode (SCE).

Impedance measurements were performed in the range of 1 to  $2 \times 10^5$  Hz under potentiostatic conditions using a Solartron 1174 frequency response analyzer connected to a HP 1000 computer.

## Results and Discussion

As pointed out ZnO photocorrodes in NaOH aqueous solutions under anodic polarization.

On the other hand, ZnO:Co immersed in the electrolyte and submitted to polychromatic visible irradiation ( $\lambda > 450$  nm) gives evidence under anodic polarization ( $-0.2$  V/SCE) of a photocurrent stable for 10 days. This photocurrent corresponds to a charge of 10 C passing through the electrode. Neither cobalt nor zinc are detected by atomic absorption in the solution (30 ml).

### Thermodynamic Aspect

The stability of semiconductors against photocorrosion can be estimated from thermodynamic data (1, 6, 7).

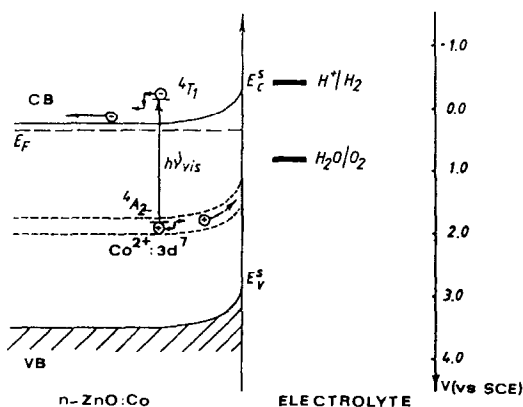
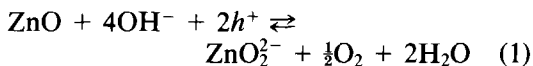


FIG. 1. Energy diagram of the *n*-ZnO:Co/aqueous electrolyte interface under visible irradiation at a low reverse bias.

According to Pourbaix the anodic dissolution reaction of the ZnO electrode at pH = 13 can be written as



The standard free energy for this reaction is

$$\Delta G_{\text{dec}}^\circ(\text{ZnO}) = -80.2 \text{ kJ mole}^{-1}.$$

Thus the corresponding standard dissolution potential is

$$V_{\text{diss}}^\circ(\text{ZnO}) = 0.42 \text{ V/ENH} = 0.16 \text{ V/SCE}.$$

The dissolution potential depends upon the activities of ionic species in the electrolyte:

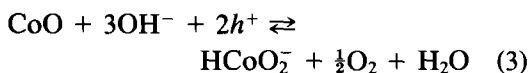
$$V_{\text{diss}}(\text{ZnO}) = V_{\text{diss}}^\circ(\text{ZnO}) + \frac{RT}{2F} \ln \frac{a_{\text{ZnO}_2^{2-}}}{a_{\text{OH}^-}^4}. \quad (2)$$

At pH = 13,  $a_{\text{ZnO}_2^{2-}} = 1.66 \times 10^{-4}$  (7) and  $V_{\text{diss}}(\text{ZnO})$  is found to be

$$V_{\text{diss}}(\text{ZnO}) = 0.05 \text{ V/SCE}.$$

Assuming that the dissolution of CoO in ZnO:Co occurs in a similar way as that of intrinsic CoO, the dissolution reaction of

CoO present in ZnO : Co at pH = 13 can be expressed in first approximation as (7)



$$\Delta G_{\text{dec}}^{\circ}(\text{CoO}) = 266 \text{ kJ mole}^{-1}.$$

In the same way as for ZnO the corresponding decomposition potential is given at pH = 13, assuming that  $a_{\text{OH}^-} = 1$  by

$$V_{\text{diss}}(\text{CoO}) = 0.35 + 0.03 \log a_{\text{HCoO}_2^-} \quad (4)$$

with

$$a_{\text{HCoO}_2^-} = 7.94 \times 10^{-7}.$$

Thus

$$V_{\text{diss}}(\text{CoO}) = 0.17 \text{ V/SCE}.$$

These decomposition potentials should be compared with the oxygen evolution potential at pH = 13:

$$V(\text{O}_2) = 0.21 \text{ V/SCE}.$$

As a consequence

$$V_{\text{diss}}(\text{ZnO}) < V(\text{O}_2) \approx V_{\text{diss}}(\text{CoO}).$$

The higher value obtained for  $V_{\text{diss}}(\text{CoO})$  would imply that the  $\text{Co}^{2+}$  ions indeed play a role in the stabilization of ZnO against anodic photodecomposition under visible light irradiation.

Nevertheless this value is very near that of  $V(\text{O}_2)$  and an improvement of the charge transfer speed has to be taken into account for doped ZnO.

#### Surface States and Their Role in Charge Transfer Processes

In fact fast charge transfer of holes, photogenerated in the  $\text{Co}^{2+}$  energy states, to the  $\text{O}_2/\text{OH}^-$  redox level can be expected if surface states are situated at the vicinity of the redox level.

The measurement of  $a-c$  admittance of the semiconductor-electrolyte interface is a method well suited to characterize the surface states (4, 8-16): this means that one

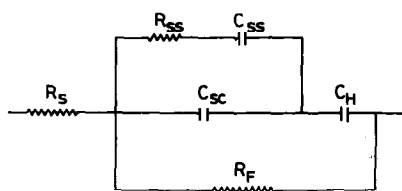


FIG. 2. Equivalent circuit of the ZnO-Co/electrolyte junction at pH = 13.

has to determine from admittance diagrams the most appropriate equivalent circuit of the investigated interface for a wide frequency range and for various potentials.

Figure 2 is the equivalent circuit of the semiconductor/electrolyte interface. The influence of the bulk subband-gap energy states, such as the  $\text{Co}^{2+}$  energy ground states, is neglected because the previous capacitance-voltage measurements give linear Mott-Schottky plots (4, 5). In the circuit, surface states are represented by a series combination of a resistance  $R_{ss}$  and a capacitance  $C_{ss}$ .  $C_{sc}$  and  $C_H$  represent the space charge layer capacitance and Helmholtz layer capacitance, respectively.  $R_F$  symbolizes the dark current resistance.

The technique of equivalent conductance  $G_p$  (the in-phase component of the total admittance) used by the previous authors (9-13) is not adequate for the data analysis because of the complexity of our circuit. Therefore we have adopted a nonlinear least-squares method by fitting separately the imaginary and the real parts of the admittance at each potential (4) (Fig. 3).

The values of the relevant parameters thus obtained in the potential range of -0.5 to 0.5 V ( $I < 1 \mu\text{A}/\text{cm}^2$  in this range) are listed in Table I. Note that the  $C_H$  value is in good agreement with that estimated by Dewald on ZnO (16).

The density of surface states is determined by

$$N_{ss} = \frac{C_{ss}}{e} \quad (5)$$

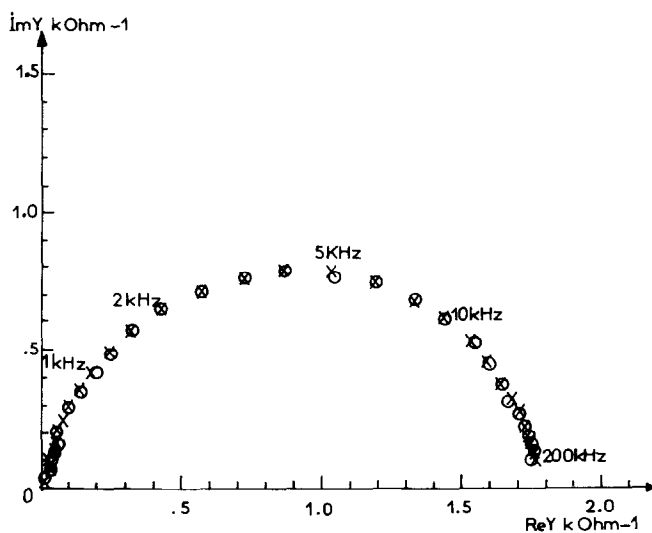


FIG. 3. Complex plane plot of the admittance measured at 0V/SCE and pH = 13. (X) Experimental data, (O) least-squares fit according to the equivalent circuit in Fig. 1.

and is shown in Fig. 4. The dependence of  $N_{ss}$  vs  $V$  clearly shows the existence of a continuous distribution of states in the forbidden gap, as it has similarly been observed by other authors in  $n$ -TiO<sub>2</sub>,  $n$ - and  $p$ -WSe<sub>2</sub>,  $n$ -MoSe<sub>2</sub>, and  $n$ -MoTe<sub>2</sub> (12, 13).

As shown in Fig. 4, the density of surface states for charge transfer (i.e., in the vicin-

ity of  $V(O_2/OH^-)$  is large enough ( $1.7 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ ) so that they can efficiently participate in the charge transfer processes of photogenerated carriers from the  $Co^{2+}$  states to the  $O_2/OH^-$  level.

On the other hand, such a situation does not occur for nondoped ZnO since the density observed in the capacitance-voltage plots is much lower (14).

TABLE I  
VALUES OF THE TERMS OF THE EQUIVALENT CIRCUIT GIVEN IN FIG. 2

$V$ (V/SCE)	$R_s$ ( $\Omega$ )	$R_{ss}$ ( $\Omega$ )	$C_{ss}$ (nF)	$10^{+6} \times \tau_{ss}$ (sec)	$C_{sc}$ (nF)	$R_F$ (k $\Omega$ )	$C_H$ ( $\mu$ F)
0.5	564	4513	22.75	102.70	67.42	700	4.2
0.4	563	4425	23.77	105.18	69.67	665	4.2
0.3	560	4110	25.75	105.83	72.36	760	4.2
0.2	551	3650	27.43	100.12	75.38	200	4.2
0.1	547	3108	29.73	92.40	78.80	395	4.2
0.0	546	2530	33.00	83.49	82.48	297	4.2
-0.1	543	2275	37.38	85.04	87.04	240	4.2
-0.2	525	1725	45.34	78.21	92.25	244	4.2
-0.3	523	1484	50.52	74.97	89.80	305	4.2
-0.4	454	1344	72.80	97.84	106.00	875	4.2
-0.5	454	1070	79.14	84.68	117.40	850	4.2

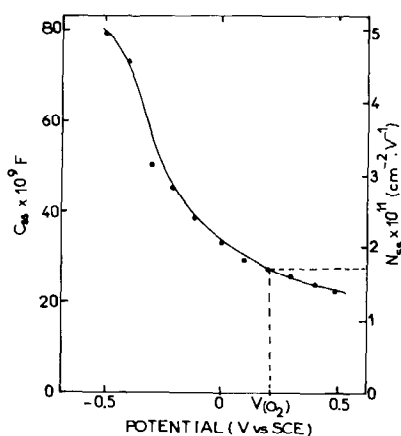


FIG. 4. Space-charge capacitance and surface state density versus voltage curves at pH = 13.

### Characterization and Identification of the Surface States

The surface state densities in  $\text{Co}^{2+}$ -doped ZnO reach a maximum for an energy  $E_{ss}$ .  $E_{ss}$  could be approximated by the following relation which describes the single level trap states in the semiconductors (17):

$$\tau_{ss} = \tau_0 \exp\left(\frac{E_c - E_{ss}}{kT}\right). \quad (6)$$

Here,  $E_c$  is the energy of the conduction band edge.

If one considers the mean value of  $\tau_{ss}$  ( $= R_{ss}C_{ss}$ ) being  $9.2 \times 10^{-5}$  sec (Table I), the corresponding energy  $E_{ss}$  must be located about 0.3 eV below  $E_c$  assuming that (17, 18)

$$\tau_0 = (\sigma_n V_n N_c)^{-1} \approx 10^{-9} \text{ sec}, \quad (7)$$

where  $\sigma_n$  is the electron capture cross section,  $V_n$  is the thermal velocity of the electrons, and  $N_c$  is the effective density of states at the conduction band.

Furthermore,  $\sigma_n$  determined from the relation (7) is about  $2.4 \times 10^{-17} \text{ cm}^2$  ( $V_n = 10^7 \text{ cm sec}^{-1}$ ,  $N_c = 4.12 \times 10^{18} \text{ cm}^{-3}$  (8)).

The estimated capture cross section rules out the possibility that the ion  $\text{OH}^-$  would

act as a surface state at one of the sites on the crystal surface: in fact for repulsive centers such as  $\text{OH}^-$  one expects a  $\sigma_n$  value of the order of  $10^{-20} \text{ cm}^2$  (19).

On the other hand, the surface states concerned in this study cannot be attributed to " $\text{Zn}_i^{+}$ " ions located at interstitial positions, since the corresponding discrete donor levels are situated 0.2 eV below  $E_c$  (20). The surface states can neither be attributed to chemisorbed oxygen which forms acceptor states 0.72 eV below the conduction band (21).

Our results are rather consistent with Gomes and Cardon's results (9); these authors have indeed demonstrated that the surface nonuniformity causes the surface states located at 0.31 eV below the conduction band.

Therefore the surface states could be ascribed to a lattice disorder occurring particularly at the electrode surface as a gradient concentration of  $\text{Co}^{2+}$  occurs likely near the surface (22).

### Conclusion

Finally, it appears that the ZnO:Co electrode does not photocorrode in the visible because the charge transfer mechanism of the photogenerated holes from the  $\text{Co}^{2+}$  states to the  $\text{O}_2/\text{OH}^-$  redox couple is favored not only by the vicinity of these levels, but also by surface states which are close to the  $\text{O}_2/\text{OH}^-$  level.

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