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BREAKDOWN LUMINESCENCE OF PURE AND COBALT-DOPED ZnO ELECTRODES IN SUPPORTING ELECTROLYTE UNDER PULSED ANODIC EXCITATION

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An intense breakdown current occurs at 9.7 V vs. SCE with pure ($N_D=5\times10^{18}\text{cm}^{-3}$) and Co-doped n-ZnO electrodes in supporting electrolyte. A simultaneous light emission is observed, extending over the visible and near IR regions, which decays in 1 and 30 ms respectively. The exp ($-b\times V^{-1/2}$) potential dependence of the electroluminescence intensity suggests an impact-ionization mechanism.

II-VI compounds are electroluminescent materials whose properties have been extensively studied in solid-state junctions called light emitting diodes (LEDs).[1] Their electroluminescence (EL) emission can also be monitored at a semiconductor/electrolyte interface, whose electrical characteristics can easily be compared to those of a Schottky barrier.

Although the EL emission of various wide bandgap n-type semiconductors was largely studied in photoelectrochemical cells during persulfate reduction,[2-4] i.e. arising from hole injection into the valence band, only few studies were reported in which the EL arises from an electron injection from the solution into the conduction band.[5,6]

We report, here, the EL properties of n-ZnO electrodes in an indifferent electrolyte under strong anodic polarization. A pulsed potential technique is used to polarize the electrodes in order to prevent electrochemical decomposition. The EL mechanism at the semiconductor/electrolyte interface is discussed by comparison with solid-state EL, and the dependence of EL and current intensities on the potential, pulse frequency and time is put forward. The influence of the doping of ZnO by cobalt on the EL emission is studied and related to the visible photocurrent that was observed in a PEC cell.[7]

The polycrystalline ZnO samples are sinters prepared by firing high purity (99.99%) pellets at 1200 °C. The resistivities of the undoped samples range between 1 and 10 Ω cm while that of the ZnO:Co ones are ca. 10^2 Ω cm. The donor concentration N_D of the undoped ZnO electrode used here is found,[8] from capacitance measurements, to be $5\times10^{18}\text{cm}^{-3}$. The electrolyte is 1.0 M KCl. The EL experiments are carried out in a single compartment cell, the standard three electrodes configura-

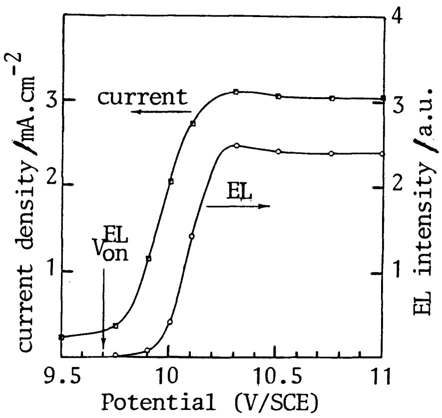


Fig.1. EL intensity and anodic current density vs. potential for a n-ZnO electrode pulsed between 0 V (10 ms) and a positive upper limit (1 ms). Electrolyte: 1.0 M KCl (pH 5.7)

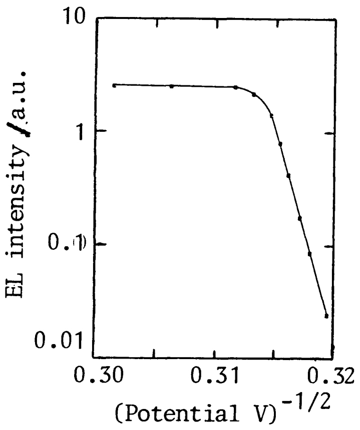


Fig.2. EL intensity as a function of $(V)^{-1/2}$.

tion being used with a saturated calomel electrode (SCE) as reference. The electrochemical cell is put in place of the usual cell holder of a Perkin-Elmer MPF-44B spectrofluorimeter. The EL emission of the n-ZnO/electrolyte junction is monitored by pulsing the electrode between 0 V (where the dark current density is of the order of 10 to 100 nA cm^{-2}), and a fixed anodic potential by means of a P.A.R. model 173 potentiostat monitored by a P.A.R. model 175 programmer.

All the potential values given in the text are referred to SCE.

The steep current increase observed at + 9.7 V (Fig. 1) suggests an avalanche breakdown. This mechanism of current generation is supported by a strong gas (O_2) evolution together with a partial dissolution of the electrode and an increase of the temperature of the electrolyte. As it occurs only for band-bendings eV_s c.a. three times greater than E_g, if the potential drop prevails in the semiconductor rather than in the Helmholtz layer, then a band-to-band (VB → CB) electron tunneling can be ruled out. Also, the distance for the electrons to travel through would be ca. 130 Å. Thus, it seems that electrons from the solution would be injected, through the fully depleted layer, into the conduction band, provided that the tunneling distance is short enough.

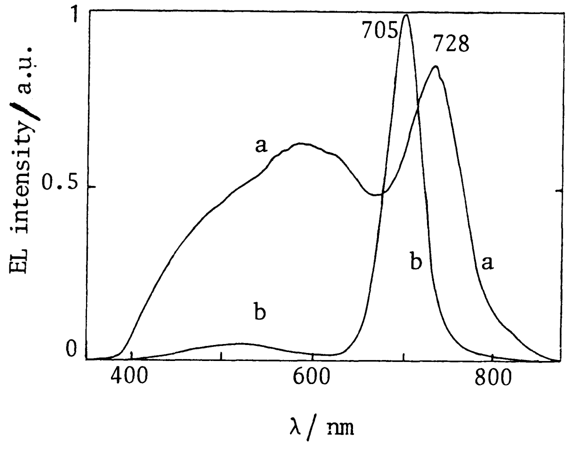
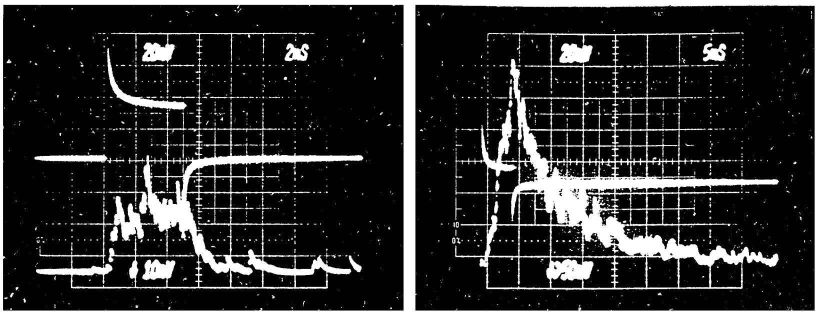


Fig.3. EL spectra of (a) pure ZnO and (b) Co-doped ZnO electrodes pulsed between 0V (5 ms) and + 10.3 V (1 ms).

Electron injection from the electrolyte results in the oxidation of the injecting species or of the electrode itself. Since the junction



(a) (b)

Fig.4. EL emission (noisy signal) and current time transients of a ZnO electrode during a stationary pulse between 0 V (50 ms) and + 10.3 V (5 ms). Monitoring wavelength: (a) 500 nm (2 ms/div); (b) 728 nm (5 ms/div).

is an oxide in contact with water, the surface is totally hydrated, and it is very likely that the surface oxygen atoms, ($O^{2-}_{surf.}$) are the injecting agents (as the distance to tunnel through is now 40 Å) :

$$O^{2-}_{surf.} \longrightarrow 1/2\ O_2 + 2e^-_{CB} \qquad (1)$$

Depending on their ZnO and H_2O origin, either the electrode or the electrolyte is decomposed according to reactions :

$$ZnO_{surf.} \xrightarrow{0.7\ V\ (pH\ 7)} Zn^{2+} + 1/2\ O_2 + 2\ e^-_{CB} \qquad (2)$$

$$H_2O_{surf.} \xrightarrow{0.8\ V\ (pH\ 7)} 2\ H^+ + 1/2\ O_2 + 2\ e^-_{CB} \qquad (3)$$

Once injected in the conduction band, the electrons are accelerated by the high electric field strength until they have sufficient kinetic energy to impact-excite (or ionize) the host lattice or an impurity. The radiative recombinations of the resulting electron-hole pairs, either directly or via traps, yield the observed luminescence. This impact-ionization process, which has been primarily defined onto solid-state devices, is supported by the exponential voltage relation $i_{EL} \alpha \exp(-b\ V^{-1/2})$ found here with the ZnO/electrolyte junction (Fig. 2). This dependence which characterizes an impact-ionization phenomenon in II-VI diodes follows, usually, the Alfrey-Taylor$^{9)}$ relationship discussed in reference$^{10)}$:

$$B = B_o \exp(-b\ V^{-1/2})$$

where B is the brightness, V the applied potential, B_o and b being constants.

Figure 3 shows that pure (a) and Co-doped (b) electrodes have very similar EL spectra. The weak visible (400 to 600 nm) EL emission of the Co-doped sample probably results from a semiconductor self-absorption process, since the material is strongly coloured in green. This can be taken as the indication that the EL emission takes place at, or very near, the surface. On the other hand, the presence of an intense EL band at 728 nm (1.67 eV) for the undoped ZnO electrodes clearly demonstrates that the corresponding EL center is not directly related to the cobalt atoms but rather to a native defect band at midgap, as we have postulated$^{7)}$ previously to account for the visible photocurrent observed. Its lifetime appears to be much longer (30 ms) than any other EL band of the spectra (1 ms) as shown in Figure 4. This would indicate that carriers are trapped in lattice sites where they can stay up to 30 ms; since a large number of free electrons are injected into the semiconductor under EL conditions, it seems likely that the trapped carriers are holes.

The electroluminescence mechanism can be summarized as shown in Figure 5. We have pointed out, in this figure, that the same hot electron can impact-excite one or several electroluminescent centers (C_1, C_2 and C_3, for instance as shown in the figure) depending on its kinetic energy and its mean free path. In short, this mechanism would be the following : (1) electron injection from the $O^{2-}_{surf.}$ atoms into the conduction band (electron tunneling); (2) acceleration of the injected electrons by the high electric field; (3) impact-ionization of the electroluminescence centers C_i (Figure 5); (4) radiative recombination of the electron-hole pairs.

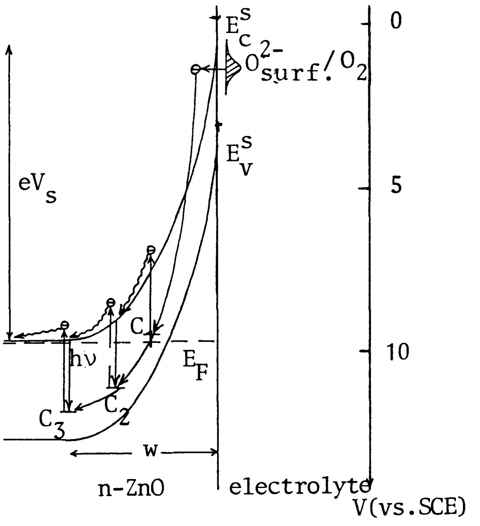


Fig.5. Mechanism of the breakdown luminescence of the n-ZnO/aqueous electrolyte junction under + 9.7 V vs. SCE.

In conclusion, an intense luminescence, due to electron injection from the $O^{2-}_{surf.}/O_2$ redox couple into the conduction band and followed with an impact-excitation process, is observed at the ZnO/electrolyte interface under a pulsed potential of + 10 V/SCE. Detailed characterization of the electroluminescence of these systems is under current investigation.

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