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Photoluminescent and Electroluminescent Properties of Cd$_{0.95}$Mn$_{0.05}$Se Electrodes

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Prepared for Publication in Journal of Luminescence

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PHOTOLUMINESCENT AND ELECTROLUMINESCENT PROPERTIES OF Cd$_{0.95}$Mn$_{0.05}$Se ELECTRODES

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1. INTRODUCTION

Photoluminescence (PL) and electroluminescence (EL) can be used to characterize electric fields in semiconductor electrodes through their influence on electron-hole (e^-h^+) pair recombination. Solid solutions of II-VI compounds such as n-CdS and n-CdSe have provided a useful family of tunable band gap materials for such studies. We have extended these studies to emissive electrodes derived from a solid solution of MnSe and CdSe. In this paper we report that PL from n-Cd$_{0.95}$Mn$_{0.05}$Se electrodes used in photoelectrochemical cells (PEC's) can be used to map the electric field in these solids, and that EL obtained from the electrodes originates, on average, nearer the semiconductor-electrolyte interface than PL.

2. SYNTHESIS AND CHARACTERIZATION

Single-crystal samples of n-Cd$_{0.95}$Mn$_{0.05}$Se were grown by a modified Bridgman method; samples with carrier concentrations, n, ranging from $10^{16}$-$10^{18}$ cm$^{-3}$ (Hall method) were etched with 1:20 (v/v) Br$_2$/MeOH prior to use. When excited with ultraband gap light ($E_g 1.75$eV$^4$), the samples emit with $\lambda_{max}$-694nm, Fig.1. The spectral maximum is near $E_g$ and blue-shifts to -665nm at 77 K; radiative quantum efficiencies, $\phi_r$, for the edge emission generally range from $10^{-5}$ to $10^{-4}$.

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3. PL PROPERTIES IN A PEC

When the solid serves as the photoanode of a PEC employing diselenide electrolyte, its PL intensity can be quenched by applied potential. Figure 1 presents photocurrent - PL intensity - voltage data (iLV curves) for a n-Cd$_{0.95}$Mn$_{0.05}$Se-based PEC; the potential-independent spectral distribution permits PL to be monitored at $\lambda_{\text{max}}$. Quenching of PL in PEC's has been described using a dead-layer model originally applied to semiconductor-metal, Schottky barrier systems: $e^-h^+$ pairs formed within a distance on the order of the depletion width do not contribute to PL; this model thus relates PL intensity to the thickness of the electric field in the electrode$^{5,6}$. The quantitative form of the model is given by eq. (1), where $\phi_r$ and $\phi_{rFB}$ are radiative efficiencies in circuit and at flat-band potential (assumed to be open circuit), respectively; D is the dead-layer thickness; and $\alpha' = \alpha + \beta$ with $\alpha$ and $\beta$ the solid's absorptivities for the exciting and emitted light.

Although ultraband gap absorptivities have not been measured for n-Cd$_{0.95}$Mn$_{0.05}$Se, values of $\alpha$ can be estimated by blue-shifting the CdSe absorption spectrum by -25nm, since the solids have similar electronic structures. The PL quenching resulting from a given excitation wavelength then leads, in conjunction with the estimated value of $\alpha$ and eq. (1), to a value for D. For the Fig. 1 data, D is calculated to be -1200Å ($\alpha$ is taken to be 1.7 x $10^5$ and 0.63 x $10^5$ cm$^{-1}$ for 458 and 646nm, respectively) at -0.7V vs SCE in accord with a calculation of the depletion width. In general, good agreement of PL quenching with the dead-layer model was found and a consistent set of values for $\alpha$ was obtained for all samples. When the experimental curves were compared to curves calculated by assuming that all of the applied potential appears in the semiconductor$^5$, good accord was found, indicating that applied potential appears predominantly in the solid.

4. EL PROPERTIES

When used as a dark cathode in aqueous, OH$^-$/S$_2$O$_8^{2-}$ electrolyte, samples of n-Cd$_{0.95}$Mn$_{0.05}$Se exhibit red EL. The electrode's EL spectrum, Fig. 1, is similar to its PL spectrum, but exhibits a spectral mismatch in the high-energy tail. As with n-Cd$_x$Se$_{1-x}$ (0 $\leq$ X $\leq$ 1) samples, we attribute this mismatch to self-absorption effects: the enhanced intensity at short wavelengths is consistent with the origin of EL, on average, nearer the semiconductor-electrolyte interface than PL$^2$. Measured EL efficiencies are ~10$^{-5}$ to 10$^{-6}$.$^2$
FIGURE 1

Left: Uncorrected PL (solid curve) and EL (vertical lines) spectra of n-Cd_{0.95}Mn_{0.05}Se obtained in the same sample geometry in OH-/S_{0}^{2-} electrolyte (295K). The PL spectrum (632.8-nm excitation) was taken out of circuit; the EL spectrum, scaled to match the PL intensity at \( \lambda_{\text{max}} \), was acquired by repetitively pulsing the electrode between 0.0 V (1.5 s) and -1.3 V vs. SCE (1.0 s).

Right: Relative photocurrent (bottom panel) and PL intensity (top panel; monitored at \( \lambda_{\text{max}} \)) as a function of potential for an n-Cd_{0.95}Mn_{0.05}Se-based PEC employing diselenide electrolyte. The electrode (n-4 \times 10^{16} cm\(^{-2}\)) was excited with 457.9- ("A" curves) and 646-nm ("B" curves) light in an identical geometry. PL intensities and photocurrents were arbitrarily matched at "100" open circuit; photocurrent densities (quantum yields) at -0.7 V vs. SCE are 7mA/cm\(^2\) (0.7) and 3mA/cm\(^2\) (0.5) for curves A and B, respectively. These IV curves were swept at 10mV/s.

REFERENCES


