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New Strategies for Display Devices Based on II-VI Materials

by

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Vapor-phase diffusion and ion implantation provide versatile synthetic techniques for preparing spatially inhomogeneous n-CdS_xSe_{1-x} samples. The color-coded nature of PL and EL from these materials and the susceptibility of the emission to perturbation by electric fields gives rise to novel electro-optical effects: the spectral distribution can be altered by applied potential and can serve as the basis for patterned, multi-colored emissive displays thorugh the use of chemical and photoelectrochemical etching techniques.

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NEW STRATEGIES FOR DISPLAY DEVICES BASED ON II-VI MATERIALS

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INTRODUCTION

Spatially inhomogeneous, emissive semiconductors afford an opportunity to control the color of photoluminescence (PL) and electroluminescence (EL) by use of applied potentials and etching techniques. Over the past few years we have demonstrated these principles using solid solutions of n-CdS_xSe_{1-x}. Formed from CdS and CdSe, these materials exhibit band edge PL and EL spanning the green to the red portion of the spectrum. In fact, the band maxima vary linearly with composition according to eq. 1,

$$\lambda_{max}\text{ (nm)} = 718 - 210\,x \qquad (1)$$

permitting a homogeneous alloy's composition to be identified by its emission to within about a percent.[1,2]

In this paper we summarize our research with graded n-CdS_xSe_{1-x} samples, showing that the spectral distribution can be altered by applied potential when the materials are used as electrodes in suitable electrolytes. The next section reveals that patterned, multicolored display devices can be constructed from the graded samples using chemical and photoelectrochemical etching techniques. The final segment demonstrates the use of ion implantation as a technique for controlling the depth and concentration of n-CdS_xSe_{1-x} alloy compositions.

Graded n-CdS_xSe_{1-x} Samples

Short-term, vapor-phase diffusion of S into single-crystal samples of n-CdSe (typically, a heat treatment at 700°C for 15 min) yields a graded semiconductor.[3,4] At this stage, however, the sample has lost its conductivity; by subsequently heating the sample in the presence of Cd metal (700°C for 15 min), conductivity is restored, presumably by increasing the concentration of chalcogen lattice vacancies. Two lines of experimental evidence support the production of a near-surface graded region. First, Auger electron spectroscopy (AES)/Ar^+ sputter etching reveals that the surface analyzes as CdS and that over a distance of about 1 micron the composition monotonically increases in Se content until the CdSe substrate is reached. Second, the PL spectrum, shown in Fig. 1, spans the spectral region from green to red, evidencing contributions from all of the alloy compositions comprising the graded region. It is noteworthy that we do generally see

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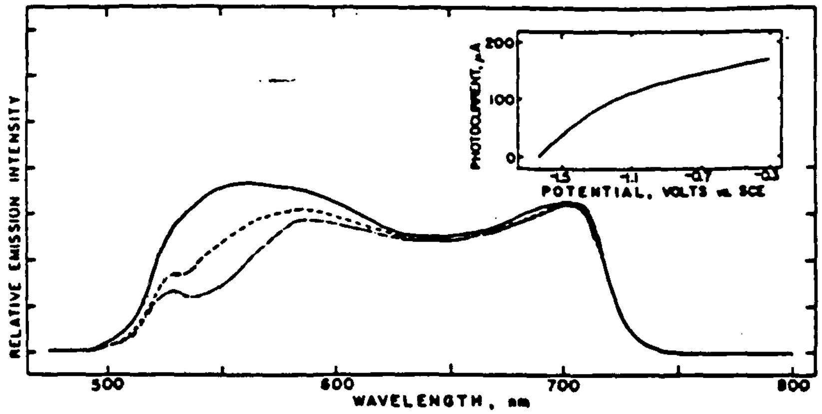

Figure 1. PL spectra and current-voltage properties of a graded CdS_x-Se_{1-x} sample (CdSe/S). The inset shows current-voltage properties obtained with 457.9-nm excitation of the electrode when incorporated into a PEC employing 1 M OH^-/1 M S^{2-} electrolyte. Corresponding, uncorrected PL spectra obtained at open circuit (solid curve), -1.0 V (dashed curve), and -0.3 V vs. SCE (dot-dashed curve) are shown in the main panel of the figure. All spectra were taken in an identical sample geometry. Additional details are given in ref. 4, from which this figure is adapted.

some lateral inhomogeneity: PL spectra vary slightly from spot to spot when a focused laser beam is used for excitation.

These samples, denoted CdSe/S, exhibit several fascinating electro-optical properties.[3-5] As shown in the inset of Fig. 1, the materials can serve as electrodes in photoelectrochemical cells (PEC's) employing stabilizing, aqueous, (poly)chalcogenide electrolytes. The body of the figure reveals that the PL spectral distribution is altered as the applied potential is varied; a modest color change can be perceived visually. We have interpreted the change in spectral distribution as a map of the effective electric field (EEF) in the solid; our use of the term "EEF" reflects the fact that the field consists of contributions from band edge and effective mass gradients as well as from space-charge formation and applied voltage.[6,7] The EEF map is based on the color-coded nature of the emission and is readable as follows: the potential-dependent family of curves all coalesce at about 600 nm. This wavelength corresponds to a CdS_xSe_{1-x} composition of about x = 0.5, which, from AES/Ar^+ sputter etch data, occurs about 0.2 microns (2000 Å) from the surface. Our results indicate, then, that the EEF can be influenced to a depth of about 2000 Å from the surface over the applied potential range employed.

A more dramatic visual effect is observed when the CdSe/S samples are used as dark cathodes in an aqueous, alkaline peroxydisulfate ($S_2O_8^{2-}$) electrolyte for EL experiments;[4,5] use of this oxidant results in hole injection into the semiconductor's valence band (presumably from an intermediate like the sulfate radical anion), and subsequent recombination with conduction band electrons leads to emission.[8] Figure 2 demonstrates that the EL spectral distribution is remarkably

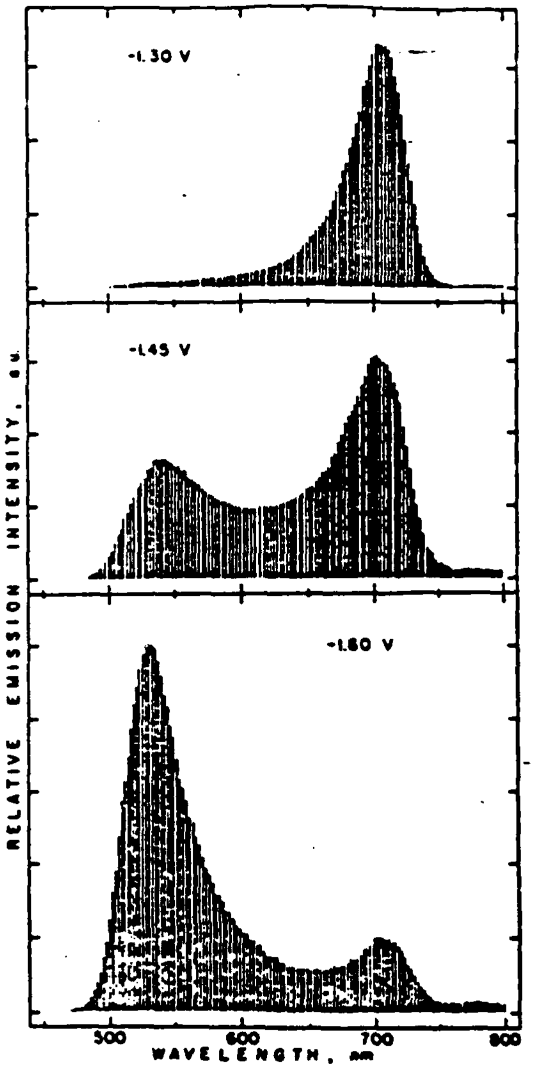

Figure 2. Uncorrected EL spectra of a graded CdS_xSe_{1-x} electrode (CdSe/S). The series of vertical lines that constitute the spectra were obtained in 5 M OH^-/0.1 M $S_2O_8^{2-}$ electrolyte by repetitively pulsing the electrode between 0.00 V (11 s) and -1.30 V (top panel), -1.45 V (middle panel) or -1.60 V (bottom panel) for 1 s while scanning the emission monochromator at 12 nm/min. The -1.30-V spectrum was obtained at both the beginning and end of the experiment to demonstrate reproducibility. All spectra were taken in an identical sample geometry; however, the -1.45-V spectrum was taken at twice the sensitivity used to obtain the -1.30- and -1.60-V spectra. This figure is adapted from ref. 4.

sensitive to the potential used to initiate the process: a difference of 0.3 V causes the observed color to change from green to red! In particular, at the most positive voltage, the red Se-rich EL observed indicates that injected holes can travel a distance on the order of a micron into the electrode before they suffer recombination; in contrast, at the most negative potential used in Fig. 2, the green S-rich EL observed suggests that most of the injected holes recombine at the surface. These effects, which are reversible with changes in potential, indicate that in essence we can direct hole "traffic" in the solid by use of applied potential.

A natural companion to the CdSe/S system is prepared by vapor-phase diffusion of Se into single-crystal n-CdS.[9] A similar two-step heat treatment is employed to yield CdS/Se graded samples. Use of AES/Ar^+ sputter etch data confirmed that the surface had been converted to a Se-rich alloy and that a graded zone of micron-length thickness had been produced. In contrast to the broad PL of the CdSe/S system, however, samples of CdS/Se exhibit a relatively narrow Se-rich PL spectrum. We attribute this difference to the directions of the band edge gradients: if most of the gradient is assumed to occur in the valence band, holes will seek the small band gap compositions to minimize their energy. For CdSe/S samples, holes were thus driven toward the bulk substrate and could recombine in any of the alloy compositions en route; for CdS/Se samples, holes will tend to stay and recombine in the near-surface, Se-rich compositions. The CdS/Se compositions do allow for frontside or backside excitation, the latter with light below the CdS bandgap energy. Nonuniform quenching of PL intensity was observed with use of CdS/Se electrodes in PEC's (frontside or backside excitation), but the effect on spectral distribution is subtle, since only a limited spectral range is affected. Similarly, EL showed a disappointingly negligible effect of applied potential on spectral distribution.

Display Devices from Graded n-CdS_xSe_{1-x} Samples

Besides their potential-induced changes in PL and EL spectral distribution, the graded n-CdS_xSe_{1-x} samples can be used to create patterned, multi-colored display devices.[9,10] The strategy is that by spatially controlling the etching of the materials, different strata are exposed that emit different colors. Our first efforts involved use of chemical etchants: after masking portions of the surface with nail polish, solutions of Br_2 or HCl in water were used to etch the unmasked regions. The etching was done incrementally, with EL observed after each etch treatment so that the extent of removal of the graded layer could be estimated. After removal of the mask with acetone, the electrode exhibited two-toned EL.

An alternative etching technique is based on the photoanodic decomposition that many n-type semiconductors undergo in aqueous electrolytes. Photoelectrochemical etching (PEC etching[10,11]) can be conducted with the graded electrodes at reverse bias in non-stabilizing aqueous NaOH electrolyte; the chemistry involves oxidation of the lattice to yield Cd^{+2} and the chalcogen, which is removed from the surface by reaction or solvation. Projection of ultrabandgap light through a mask will yield an image on the semiconductor surface that will result in an etch pattern of roughly the same geometry, as shown in Fig. 3. Moreover, by keeping track of the coulombs passed in the external circuit during PEC etching, a rough idea of the etching depth may be obtained. Nonetheless, the sample would still need to have its EL spectrum recorded periodically to better gauge the depth of etching.

A further refinement in this regard is provided by the CdS/Se samples. As illustrated in Fig. 4, the etching depth in these samples can be controlled simply by the color of light employed in the PEC etching experiment.[9,10] For example, red light will cause very little etching, since it is below the band gap of all but the most Se-rich compositions and will no longer be absorbed once those compositions have been etched away. In general, etching will only proceed until a composition whose band gap roughly matches the photon energy is exposed to the electrolyte. Without optimizing these techniques, we have prepared multi-colored, patterned displays with resolution on the order of 0.1 mm. In principle, the use of other II-VI alloy families derived from ZnS and ZnSe, e.g.) can extend the accessible spectral range to higher visible photon energies.

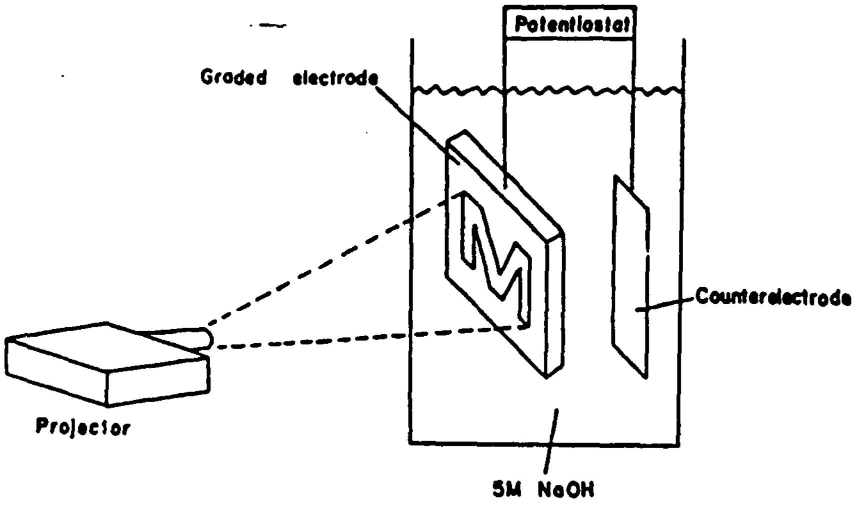

Figure 3. Schematic of a setup used for PEC etching of a semiconductor electrode.

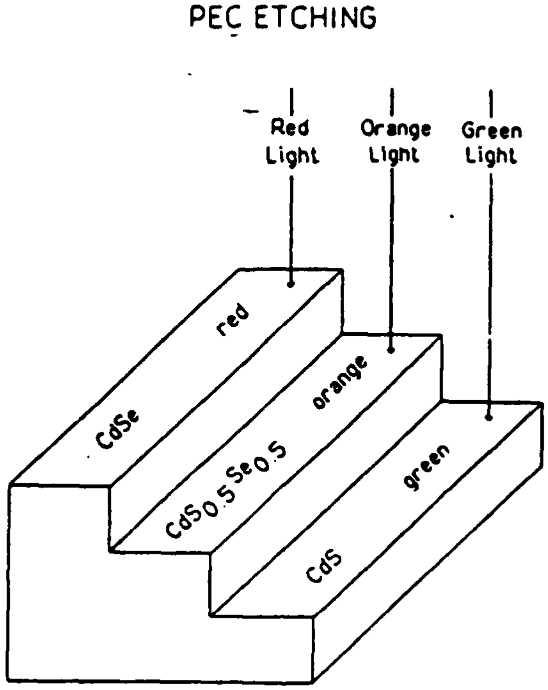

Figure 4. Schematic of a CdS/Se sample undergoing spatially-controlled PEC etching. The depths to which representative colors of light will etch the solid are indicated as is the color of light each exposed surface will emit. When the etching is complete, the electrode will exhibit patterned, multi-colored emission.

n-CdS_xSe_{1-x} Samples Prepared by Ion Implantation

An alternative strategy for preparing n-CdS_xSe_{1-x} samples is to make use of ion implantation technology. This technique provides control over the depth and concentration of an invasive ion. We have recently implanted Se^+ into single-crystal CdS (denoted CdS/Se^+) and shown that after thermal annealing (250°C under 3:1 H_2S/N_2 for 10 min, followed by heating with Cd at 400°C for 30 min) the samples exhibit PL and photoelectrochemical properties characteristic of CdS_xSe_{1-x} alloy compositions.[12] Typical results obtained with Se^+ ions implanted at 185 keV at dosages of 6.5×10^{16} ions/cm^2 are alloy compositions that extend to a distance of ~0.5 microns into the sample. A maximum alloy content in this near-surface zone of about 50% Se is estimated from secondary ion mass spectroscopy (SIMS). The corresponding value from PL is about 30%; the PL maxima correspond to a Se content of 10-20% based on the use of eq. 1. When the implanted samples were used as electrodes, we found that their PL spectra were quenched uniformly by applied potential and that their EL and PL spectral distributions were similar.

A logical extension of these implantation studies with CdS/Se^+ materials is to implant S^+ into single-crystal CdSe (CdSe/S^+ samples). We have recently carried out such experiments using conditions similar to those outlined above.[13] For samples implanted at 101 keV at dosages of 6.5×10^{16} ions/cm^2, the PL after annealing is broadened relative to the spectrum of unimplanted CdSe, with a shoulder corresponding to a maximum S content in the alloy of 25%. Data from AES/Ar^+ sputter etching experiments support this conclusion, revealing an alloy zone of 0.3 microns in thickness with a maximum S content of 25% occurring about 0.1 microns (1000 Å) from the surface. When these samples are used as PEC electrodes, the high energy shoulders of their PL spectra are quenched preferentially. The EL spectral distribution shows growth of the alloy band as the sample is pulsed to more negative potentials, as shown in Fig. 5.

CONCLUSION

Vapor-phase diffusion and ion implantation provide versatile synthetic techniques for preparing spatially inhomogeneous n-CdS_xSe_{1-x} samples. The color-coded nature of PL and EL from these materials and the susceptibility of the emission to perturbation by electric fields gives rise to novel electro-optical effects: the spectral distribution can be altered by applied potential and can serve as the basis for patterned, multi-colored emissive displays through the use of chemical and photoelectrochemical etching techniques.

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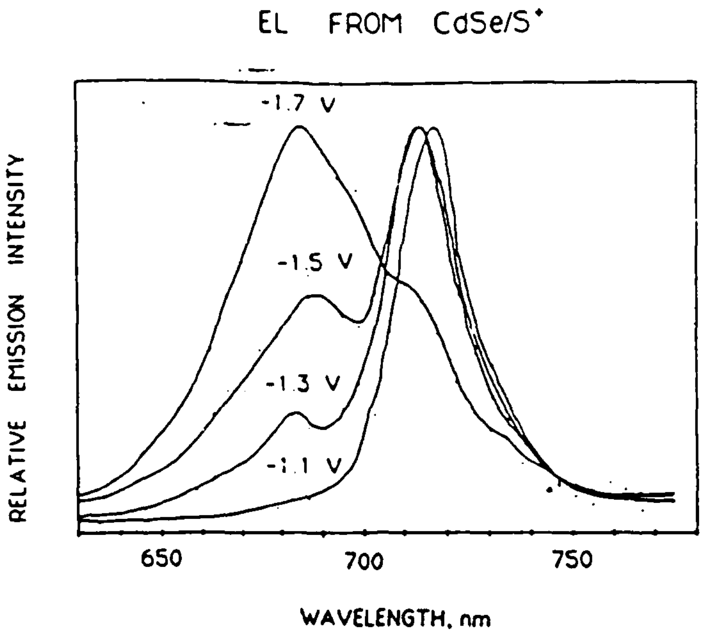

Figure 5. Uncorrected EL spectra of an ion-implanted CdSe/S^+ electrode. The spectra were obtained in 5 M OH^-/1.0 M $S_2O_8^{2-}$ electrolyte by repetitively pulsing the electrode between -0.4 V (10 s) and one of the potentials indicated in the figure (1 s) for each spectrum while scanning the emission monochromator at ~20 nm/min. All spectra were taken in an identical sample geometry. The -1.1-V spectrum was obtained at both the beginning and end of this experiment to demonstrate reproducibility. The spectra are all normalized to a common maximum intensity.

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