LUMINESCENCE EXCITATION MECHANISMS IN CdS FROM DEPENDENCE OF PHOTOLUMINESCENCE AND THERMOLUMINESCENCE ON PERSISTENT CONDUCTIVITY STORED CHARGE STATE

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Experiments are reported on excitation-spectroscopic time-resolved photoluminescence and thermoluminescence in high resistivity CdS as a function of persistent conductivity associated stored-charge state.

1. INTRODUCTION
The details of the mechanisms for energizing donor-acceptor (D,A) pairs which result in recombination luminescence are still not completely understood. Recent work on CdS has indicated that polaritons play the principal role in the D',A' to D,A° charging process, and that the luminescence emanates from the near-surface (~1 μm) regions. Experiments we report here indicate that polaritons also generate the stored charge associated with persistent conductivity phenomena observed in high resistivity CdS. It is shown that generation of stored charge in the near-surface region is a precondition for polariton-energized edge emission actually to occur.

It is further shown that the stored charge associated with persistent conductivity is the source of the low temperature thermoluminescence, with the free-to-bound high energy series (HES) and the bound-to-bound low energy series (LES) peaking at different temperatures. These results establish a low activation energy localized electron state as the source of the persistent conductivity stored charge.

2. RESULTS
The LES luminescence intensities for a series of excitation energies as a function of time after initial excitation from the equilibrium dark state were measured. Long times were required for the growth of LES under long wavelength excitation.

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low absorption coefficient $\alpha(\lambda)$, implying an electron and/or hole storage mechanism for an intermediate state which produces edge luminescence upon subsequent excitation. The nearly instantaneous rise of luminescence for $\lambda_{\text{exc}} < 480$ nm indicates that the storage state must reach a critical density in the region within $[\alpha(480\text{nm})]^{-1}$, or ~1 $\mu$m, of the surface (the "near surface region"), which is in excellent agreement with previous work and preliminary reports.

Simultaneous with the luminescence, the sample conductance as a function of time was measured. Light of wavelength 485-490 nm produced the highest differential conductance per incident photon, demonstrating that the spatial surface region important for the generation of persistent conductivity carriers is larger (10-150 $\mu$m, the "far surface region") than the region for luminescence. This would indicate that the intermediate storage states fill the far surface region, with the density in the near surface region critical for generation of edge luminescence. The absence of luminescence for zero persistent conductivity carrier density supports this.

It has been demonstrated that exciton-polaritons can efficiently propagate across macroscopic distances and produce luminescence at surfaces in these type crystals. Using these results to determine the polariton flux at the far side of a crystal excited with $\lambda<480$nm light, the persistent conductivity was measured on the far surface and compared with the persistent current generated on the near (directly excited) surface. The results were found to scale with polariton flux.

Low temperature thermoluminescence was investigated to determine trap position and relative occupied number. Figure 1 shows glow curves for PC saturated samples at an initial temperature of 4.2K. The spectral dependence indicated only a thermally broadened edge emission; no additional luminescence was observable. A plausible interpretation is that electrons stored on PC centers are activated to recombine radiatively with A's either directly from the conduction band or, if they are captured onto D's before this occurs, from D's. Applying a moderate electric field produced only the HES, consistent with this interpretation.
Using first order kinetics we can determine the trap energies quantitatively. Isothermal thermoluminescence gave activation energies of 2.5±0.5 meV for the LES and 4.5±0.5 for the HES. The trap is remarkably shallow and thus should appear in the luminescence spectra if different from either a donor or acceptor.

We propose a candidate center similar to the model proposed by Lang and Logan\(^4\) that allows charge storage onto traps with a large lattice distortion. We propose that the charge storage states are donor-related defects that trap free electrons and thus inhibit direct radiative recombination with holes. Preliminary results have shown excitation from the Stokes-shifted center to the conduction band verifying the proposed model.

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