Synthesis and Spectroscopic Characterization of TM Doped II-VI Materials

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Motivation

- Transition metal ($\text{Cr}^{2+}$, $\text{Fe}^{2+}$) doped II-VI (II-Zn; VI-S, Se) semiconductors are effective media for broadly tunable, mid-IR lasers
- Promise under optical, and possibly direct electrical excitation
- Timely, predictable method for preparation of bulk crystals is needed
- *Thin film, quantum well, and quantum dot* structures should provide increased efficiency in energy migration from host crystal to TM dopant ions
Two Experiments

- Synthesis of bulk Fe:ZnS crystals by *electrolytic coloration*

- Comparison of fluorescence properties of Cr:ZnSe bulk and thin film materials
One:
Electrolytic Coloration
Electrolytic Coloration

Background

- past samples prepared from melt, vapor-growth techniques, or post-growth thermal diffusion
- each method has disadvantages
- *Electrolytic Coloration* increases uniformity of concentration and decreases annealing time
Electrolytic Coloration (cont.)

Experiment: setup

- **3 kV** to ground
- High voltage power supply
- Tungsten needle electrode
- ZnS crystal
- Iron (Fe) foil
- Thermal couple
- Ceramic insulator
- Spring adjustment system
- To ground
Electrolytic Coloration (cont.)

Experiment: procedure

- vacuum pressures ($\sim 10^{-5}$ torr)
- heated to 500-650°C continuously under voltage (3.0 kV)
- annealed for 30 minutes to one hour
Electrolytic Coloration (cont.)

Results

Transmission spectra:
(A) taken from two different places on Fe:ZnS prepared by electrolytic coloration
(B) thermo-diffusion doped Fe:ZnSe
Two: Bulk vs. Thin Film Fluorescence
Bulk vs. Thin Film

Background

- Thin films, because of smaller dimensions, should exhibit increased efficiency of energy migration to TM dopant ions.

- Therefore, thin films are a better candidate for fluorescence under electrical excitation.
Bulk vs. Thin Film (cont.)

Experiment: setup

- Spectrograph
- PbS detector
- Chopper (800 Hz)
- Cylindrical lens (f = 15cm)
- Lens (f = 5cm)
- Cr:ZnSe film (thickness 1 µm)
- Ge filter
- GaAs substrate
- Brewster angle (68°)
Experiment: procedure

- cw Er-fiber laser modulated at 800 Hz used as pump beam
- thin film spectra taken at two different geometries: at zero degrees and normal to the monochromator slits
Bulk vs. Thin Film (cont.)

Experiment: procedure (cont.)

- **DETECTOR**
  - normal geometry
  - zero degree geometry
Bulk vs. Thin Film (cont.)

Results

Fluorescence spectra of (A) normal geometry thin film, (B) zero degree geometry thin film, (C) bulk sample

(At Right)
Top: Output intensity at 2000 nm as function of pump power
Bottom: (A) Transmission of thin film (B) difference in fluorescence spectra of zero degree and normal geometry thin film
Conclusions

- Evidence of diffusion by electrolytic coloration was obtained for Fe doped ZnS in a period of 30 minutes.

- Differences in the fluorescence spectra of bulk and normal geometry thin film Cr:ZnSe as well as zero degree and normal geometry thin films were detected and explained due to cavity effect.
Conclusions (cont.)

- Similarities in the fluorescence spectra of bulk and zero degree geometry thin film were explained by the fact that spontaneous photons of thin film imaged on the slit are not perturbed by the cavity.

- Enhancement of thin film fluorescence at wavelengths matching cavity resonances was observed.

- It was demonstrated that the stimulated processes are not responsible for enhancement of thin film fluorescence.
Questions?