CHARACTERIZATION OF PVT GROWN ZnSe BY LOW TEMPERATURE PHOTOLUMINESCENCE

Prepared by: Ling Jun Wang, Ph.D.
Academic Rank: Associate Professor
Institution and Department: University of Tennessee at Chattanooga
Department of Physics, Geology and Astronomy

NASA/MSFC:
Lab: Space Sciences Laboratory
Division: Microgravity Science and Applications
MSFC Colleagues: Ching-Hua Su and S. L. Lehoczky
Introduction

ZnSe, a II-VI semiconductor with a large direct band gap of 2.7 eV at room temperature and 2.82 eV at 10 K, is considered a promising material for optoelectric applications in the blue-green region of the spectrum. Photoemitting devices and diode laser action has been demonstrated as a result of decades long research. [1-6]. A key issue in the development of II-VI semiconductors is the control of the concentration of the various impurities. The II-VI semiconductors seem to defy the effort of high level doping due to the well known self compensation of the donors and the acceptors. A good understanding of roles of the impurities and the behavior of the various intrinsic defects such as vacancies, interstitials and their complexes with impurities is necessary in the development and application of these materials [7]. Persistent impurities such as Li and Cu have long played a central role in the photoelectronic properties of many II-VI compounds, particularly ZnSe. The shallow centers which may promote useful electrical conductivity are of particular interest. They contribute the richly structured near gap edge luminescence, containing weak to moderate phonon coupling and therefor very accessible information about the energy states of the different centers. Significance of those residual impurities which may contribute such centers in II-VI semiconductors must be fully appreciated before improved control of their electrical properties may be possible.

Low temperature photoluminescence spectroscopy is an important source of information and useful tool of characterization of II-VI semiconductors such as ZnSe. The low temperature photoluminescence spectrum of a ZnSe single crystal typically consists of a broad band emission peaking at 2.34 eV, known as the Cu-green band, and some very sharp lines near the band gap. These bands and lines are used to identify the impurity ingredients and the defects. The assessment of the quality of the crystal based on the photoluminescence analysis is then possible. In this report we present the characterization of a ZnSe single crystal as grown by physical vapor transport method, with special intention paid to the possible effects of the gravitational field to the growth of the crystal.

Experimental

The low temperature photoluminescence measurements were performed on a as grown ZnSe single crystal cooled to below 10 °K by a CRYO Industries of America, Inc. system. The single crystal is usually cooled to below 10 kelvin with helium vapor. The ultraviolet 364 nm line of an Coherent Innova 300 argon laser is selected for excitation. The energy of this UV line is 3.4 eV, well above the 2.82 eV band gap of ZnSe at 6 kelvin. The photoluminescence spectra were recorded using a Spex 1877D spectrometer which is interfaced to an IBM desktop computer. The position of the sample can be translated by two micrometers with an accuracy of 0.05 mm. The movable sample stage enables us to study the morphology of the sample surface. The sample is translated....
vertically by a step of 0.5 mm and horizontally by a step of 0.254 mm (10 mil). The two
dimensional scan is carried out in the spectral range between 22430 cm$^{-1}$ to 22650 cm$^{-1}$
(2.78 eV to 2.81 eV) that cover the three major peaks (EX, I$_2$ and I$_{\text{deep}}$). The broad
spectrum is taken from 15000 cm$^{-1}$ to 22650 cm$^{-1}$ (1.86 eV to 2.81 eV) to study the
general features of the luminescence.

Results

The low temperature luminescence spectra show the typical features seen in the pure
ZnSe crystals. The well known Cu-green emission band that peaks at 2.34 eV is clearly
seen. This band is believed to be associated with residual copper impurity in ZnSe,
resulting from the recombination of an electron in the conduction band with a hole
captured at a Cu$_{\text{Zn}}$ center, located 0.35 eV above the valance band. [8-12].

One of the important peaks observed is the broad peak at 2.803 eV, which is the
intrinsic free exciton (EX) emission of ZnSe [13,14]. The most dominant peak of the
spectra is the I$_2$ peak at 2.796 eV. This broad peak is actually the superposition of a few
narrower peaks associated with neutral and ionic donor-bound excitons (DBE) or with
native defects [13-23]. The second most prominent peak is the I$_{\text{deep}}$ line at 2.783 eV. The
origin of the I$_{\text{deep}}$ line is thought to be exciton annihilation at Cu acceptors made by Cu
atoms occupying Zn lattice sites (CuZn) or at Zn vacancies (VZn). [13,14,17, 22, 24,26-28].

Although the intensity of these prominent peaks reflect the concentration of the
impurity and the defects, it depends heavily on the surface condition of the crystal that
necessarily affects the efficiency of signal collection. Since the EX peak is related to the
recombination of the intrinsic free exciton which has nothing to do with any impurity or
defects, we then take the intensity ratios of the I$_2$ peak and the I$_{\text{deep}}$ peak over the EX
peak as indications of the relative strength of these peaks. The sample crystal is scanned
along the direction of the gravitational field in the spectrum range of 22400 cm$^{-1}$ to 22650
cm$^{-1}$ (2.779 eV to 2.810 eV). The plots of the intensity ratios show a nearly linear
dependence on the gravity. The I$_2$ line, decreases monotonically in the direction of the
gravitational field, while the I$_{\text{deep}}$ line stays pretty much plat. This gives a hint that the
gravity might play a role in the growing process of the semiconductor crystals.

Conclusions

Low temperature photoluminescence offers an effective tool and an important source
of information for characterization of II-VI semiconductors such as ZnSe. The sharp near
band edge spectrum lines, especially the neutral donor bond exciton line I$_2$ at 2.799 eV,
the neutral acceptor bond exciton line I$_{\text{deep}}$ at 2.783 eV, and the intrinsic free exciton line
at 2.802 eV can prove the most useful lines for such characterization. These lines are very
prominent and persistent. They stay within 20 meV, a pretty short range for practical scan
of the samples within reasonable time constrain. These peaks are heavily investigated
experimentally and theoretically, and therefore are the best candidates for more credible
quality assessment of the crystal. No conclusive identification, however, has been ventured in the literature. This is partially due to the fact that the photoluminescence spectra are sensitive to the growing method, the post treatment and the sample preparation. The reliability of photoluminescence characterization is crucially dependent upon the identification of the spectrum lines and bands. The spectrum lines have to be carefully studied and a database prepared before one can have a handy and confident scheme of crystal characterization.

The most reliable but expensive and time consuming way of line identification is of course the doping experiments. The correlation experiments offer the less expensive alternatives. For example, one can study the correlation of the spectrum lines with respect to annealing and aging, or with the change of the excitation energy and the sample temperature. The lifetime studies of the individual peaks can prove to be very fruitful tool to identify these peaks.

Our investigation show that the gravitational field might play a role in the crystal growth. Since the growing ampoule usually has a typical diameter in the order of one centimeter, it seems hardly conceivable that the difference in gravitational field over such small distance can affect the growing process in any significant way. However, it is well known that the physical properties of the semiconductors are extremely sensitive to the concentration of the impurities and the defects, which are usually a few orders of magnitude smaller than the lattice concentration. A very slight change in the partial pressure of the ingredients in the physical vapor can cause changes in the relative concentration of the impurities and the defects.

References