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CHARACTERIZATION OF PVT GROWN ZnSe BY LOW TEMPERATURE PHOTOLUMINESCENCE

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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_1^{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_{Zn}^x 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_1^{deep} line at 2.783 eV. The origin of the I_1^{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_1^{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 monotonicaly in the direction of the gravitational field, while the I_1^{deep} line stays pretty much plat. This gives a hit 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_1^{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 seemss 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.

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