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Optically pumped lasing in ZnSe epilayers grown by OMVPE

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Blue lasing emission in ZnSe thin films under optically pumped excitation has been observed. The films were grown on (1 0 0) GaAs substrates by organometallic vapor phase epitaxy (OMVPE). These epitaxial films have been characterized using low temperature photoluminescence (PL) and electrical transport as well as deep level transient spectroscopy (DLTS) measurements. It has been found that deep level PL bands are strongly dependent on the growth temperature, and the near band edge (NBE) emission predominated the entire PL spectrum only at the growth temperature near 285°C. The lasing emission spectrum from the ZnSe cavity has been measured at 77 K under various excitation levels by the 337.1 nm line of a N_2 laser. Only one emission band E_s at 445 nm appears under low excitation level. With increasing excitation level a new band P follows at 448.5 nm below the E_s band, which is ascribed to the interaction of excitons. The lasing emission from OMVPE films which originates from the P band with 0.75 MW/cm^2 threshold power has been reported for the first time and it can be operated up to 150 K.

1. Introduction

ZnSe has been widely studied because of its potential as an efficient blue light emitter. However, it has not yet been possible to fabricate a blue p–n junction diode laser because of the problems to form p-ZnSe. In recent years there has been considerable progress in characterizing and understanding the stimulated and lasing properties of bulk and film ZnSe by optical or electron beam pumping [1,2]. The lasing properties of MBE and OMVPE ZnSe films pumped by an electron beam have been reported [3]. Recently, we devoted ourselves to studying the blue electroluminescence of ZnSe epitaxial films grown by OMVPE [4]. In this paper high quality ZnSe thin films with a strong near band edge emission, no detectable donor–acceptor pair (DAP) emission and much weaker deep level emission have been grown by atmospheric pressure OMVPE. We present optical and electrical transport properties of these ZnSe epilayers and the lasing characteristic at 77 K excited by the 337.1 nm line of a N_2 laser for the first time.

2. Experimental

The dimethyl zinc (DMZ) and hydrogen selenide (H_2Se) were used as Zn and Se source and palladium diffused hydrogen as the carrier gas. The ZnSe heteroepitaxial growth was performed in a horizontal radiant heated reactor under atmospheric pressure, the substrate was placed on a graphite susceptor. The growth temperature (T_g) was variable from 200–500°C and the flow ratio of H_2Se to DMZ was changeable from 1–4, the GaAs (1 0 0) wafer served as the substrate because of its small lattice mismatch to ZnSe as well as comparable thermal expansion coefficient.

The spectral distribution of the luminescence was measured using a 44 W grating monochromator with a C31034 cooled photomultiplier. PL was excited either by the 365 nm line from a Hg arc lamp or by the 337.1 nm line from a N_2 laser with a peak power of 3 MW/cm^2. The sample was mounted on a copper holder and immersed in a pumped liquid nitrogen dewar with transparent windows.

3. Results and discussion

3.1. Dependence of PL and electrical properties on the growth temperature

The photoluminescence spectra at 77 K excited by the 365 nm line of a mercury arc lamp are shown in fig. 1. It can be seen from the figure that both the NBE emission band and the deep level emission bands are strongly dependent on the growth temperature. These deep level emission bands are ascribed to various defects (such as dislocations, stacking faults, impurities and vacancies) which were formed in epitaxial processes. Only when T_g is near 285°C the NBE exciton-related emission band predominates the entire spectrum with a narrow feature due to neutral donor bound excitons [5] while the DAP emission band (at about 462 nm) cannot be detected and the deep level emission bands (more than 490 nm) is much weaker than the NBE emission band.

The carrier concentration n, the electron mobility μ and the resistivity ρ of the as-grown ZnSe epilayers are measured by the Van der Pauw method at room temperature. As seen from fig. 2 low resistivity of about 1 $\Omega \cdot$ cm could be obtained with T_g in the range 270–300°C. When T_g is out of this region the resistivity increases rapidly. A maximum electron mobility of 300–400 $cm^2 \cdot V^{-1} \cdot s^{-1}$ and a carrier concentration of the order of 10^{16} cm^{-3} are obtained in the same T_g range.

Figure 3 shows the DLTS spectrum of an Au/ZnSe Schottky diode from low resistivity ZnSe epilayer. As seen from the figure, there is a single deep level located at $E_c - 0.33$ eV with the concentration of 2.4×10^{11} cm^{-3} which is associated with Se vacancy [6].

Authors, such as Mruanio [7] and Yao [8] have demonstrated that the conductivity of ZnSe epi-

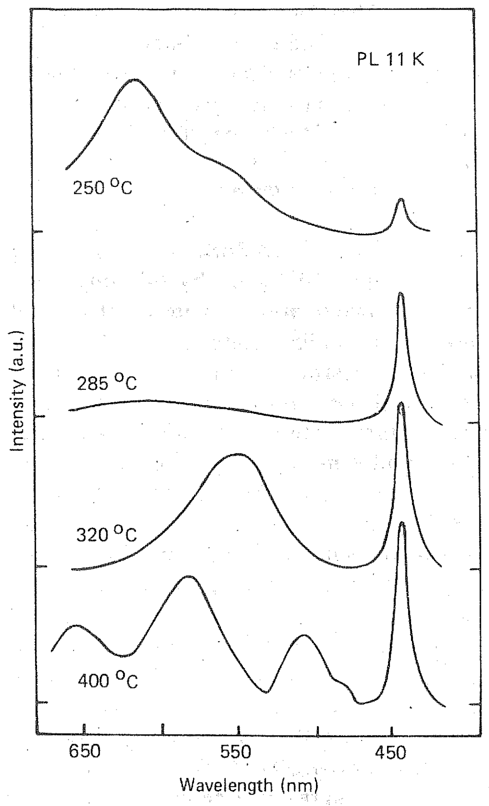

Fig. 1. The dependence of ZnSe films PL spectra on the growth temperature.

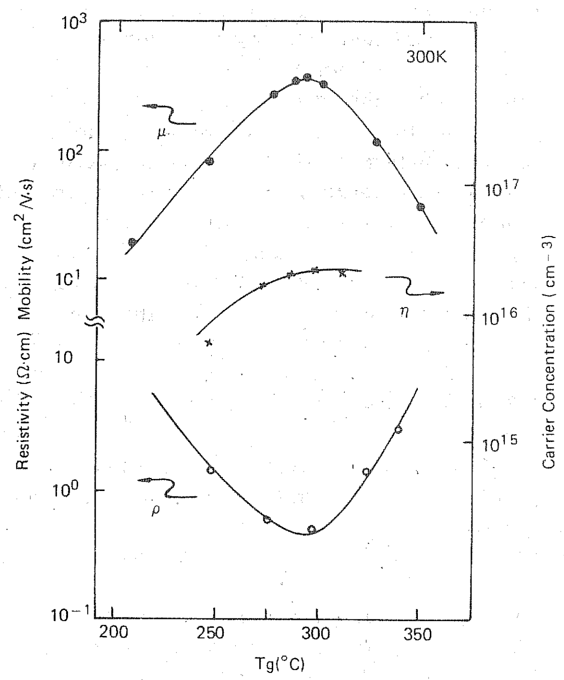

Fig. 2. The dependence of ZnSe film electrical properties at T_g under 300 K.

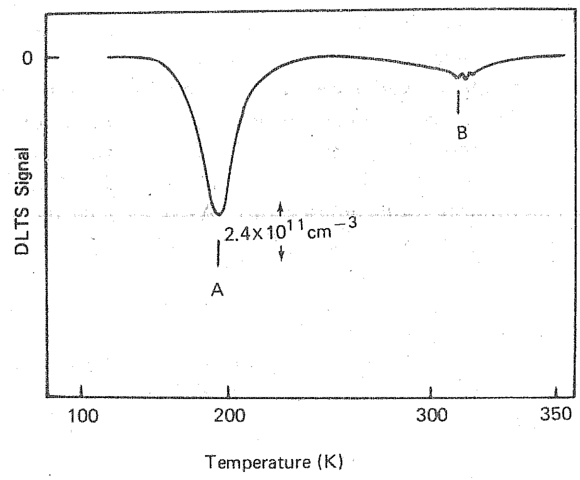

Fig. 3. DLTS spectrum of an Au/ZnSe Schottky diode from low resistivity epilayer.

taxial films is ascribed to Ga diffusing out of the GaAs substrate and Se vacancy as native donor, respectively.

However, our measurements suggest that the conductivity in normally undoped ZnSe epitaxial films is attributed to extrinsic donor impurities, rather than Ga from the GaAs substrate or native donor such as the Se vacancy. These donors originate from the Zn and Se source or contamination of the growth process. The acceptor-like defects such as a Zn vacancy and its complexes created at high T_g compensate the extrinsic donors to form high resistivity materials. Therefore when the acceptor-like concentration decreases at a suitable T_g, the electrons are released from the compensation and they exist as free carriers.

3.2. *Spontaneous and stimulated emission*

Spontaneous emission was recorded at 77 K pumped by the 337 nm line from a N_2 laser under low excitation power. There is one band, E_s, at 445 nm, and a new band P at 448.5 nm appears with increasing excitation level. Stimulated emission was recorded from the cleaved edge of the ZnSe epilayer under the same condition. In comparison with the two kinds of emission spectra it is found that the P emission band is about 20 meV below the E_s band. This energy is just equal to the free exciton binding energy of ZnSe [9], it could be assumed that when two excitons collide one of them gets an energy equal to the binding energy and becomes a free electron–hole pair, meanwhile the other one looses the same energy and emits a photon to form the P band. On the other hand, the E band is due to free exciton emission scattered by a carrier. As a result the position of the P band is the binding energy below the E band. The appearance of the P band shows clearly that the interaction between excitons occurs.

The optical gain was measured like Shaklee reported [10]. The unsaturated gain coefficient g is about 30 cm^{-1} at about 1.1 MW/cm^2 excitation level. In contrast to the optical gain of 300 cm^{-1} in bulk ZnSe reported by Catalano et al. [11] our experimental result is rather small. They used, however, a high efficiency resonant dye laser as a pumping source rather than the 337.1 nm line of a N_2 laser. They have not detected any stimulated emission from ZnSe crystal under the 337.1 nm line of a N_2 laser and they considered that a high density of excitons could not be achieved for excitation of the 337.1 nm line of a N_2 laser.

3.3. *Blue lasing emission*

The cavities of the ZnSe film laser for optical pumping were fabricated by thinning the GaAs substrate down to approximately 200 μm and then cleaving the wafer along the (1 1 0) cleavage planes into rectangles with a width of 100–500 μm. The optical feedback of the cavity was provided by the natural reflection of the cleavage planes.

When a beam of pumping light from a N_2 laser was incident on the front surface of the sample, the lasing emission would pass out of the cleaved plane of the sample. The lasing emission spectra of the ZnSe films are similar to stimulated emission spectra.

The emission intensity from the P band rises rapidly with the excitation level further increasing meanwhile the full width at half maximum (FWHM) of the P band from a broadened spontaneous emission gets to a narrow peak as shown in fig. 4. This narrowing behavior of the emission spectrum demonstrated the onset of lasing.

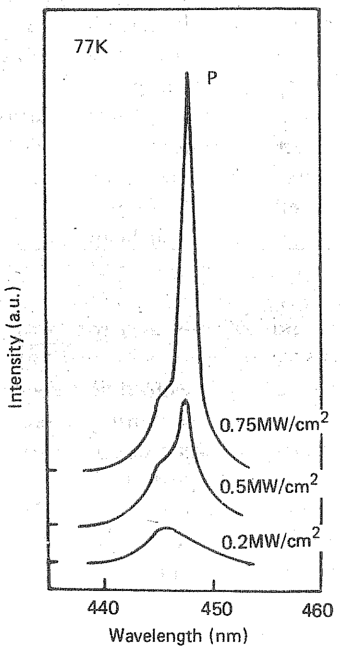

Fig. 4. Lasing emission spectra of a ZnSe epilayer under various excitation levels.

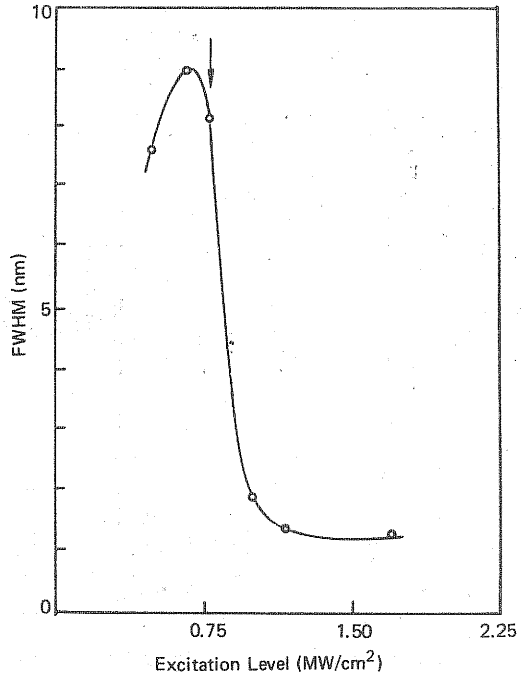

Fig. 5. PL FWHM versus the excitation levels for an optical pumping cavity.

Figure 5 shows the dependence of PL line width (FWHM) on the excitation levels. One can see from the figure that for an excitation level less than 0.75 MW/cm^2, the FWHM is broad up to 9 nm, while it decreases drastically to 1.3 nm for an excitation level of more than 0.75 MW/cm^2. Therefore, the lasing emission occurs where the FWHM of the P band reduces drastically and the lasing threshold is indicated by a vertical arrow.

Typical PL intensity from a cavity versus excitation levels is plotted in fig. 6. There are three regions included in the curve, the first region excited at the lowest level, is linear, the second region excited at a higher level is superlinear and the third region excited at the highest level is saturating. As seen from the figure the lasing threshold is determined by the change from linear to superlinear behavior near about 0.75 MW/cm^2 indicated by the arrow.

In general, the lasing threshold depends on the configuration of the cavity and material quality. As for the ZnSe quality, we consider the ZnSe epitaxial film with strong NBE emission, no DAP emission and much weaker deep level emission are necessary for the low lasing threshold. Because the interaction of various defects and impurities produces deep electronic levels in ZnSe which can act as carrier traps or deep recombination centers, these defects and impurities might detract from the efficient production of the NBE emission which is needed for lasing. However, it is not quite clear whether there might be a correlation between a low lasing threshold and a strong NBE emission intensity.

The lasing emission can be continuously operated up to 150 K with increasing measuring temperature. However, when the temperature rises beyond 150 K the emission intensity falls into spontaneous emission with broadened FWHM under the same excitation level.

It is possible to lower the threshold power and to raise lasing operation temperature through the OMVPE ZnSe superlattice structure. High quality ZnSe superlattice films can be produced under a low temperature growth process, which are

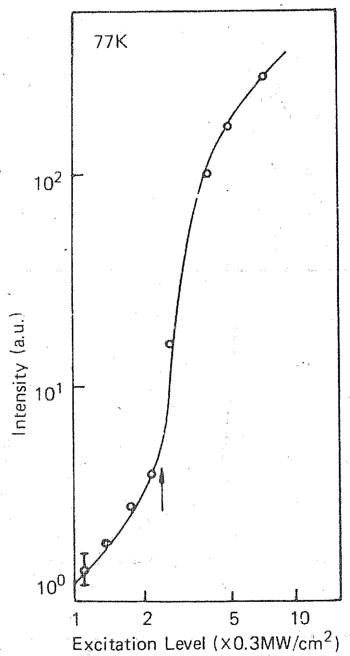

Fig. 6. The dependence of emission intensity of ZnSe epitaxial layer laser on the excitation level.

sufficiently free of defects, high efficient PL and high electrical mobility, the PL from the impurities and the defects are drastically restrained in the superlattice structure [12] and binding energy of free exciton in the superlattice structure is larger than that of bulk ZnSe. On the other hand, we believe that the threshold power would also be able to reduce if a resonant dye laser was used as a pumping source.

4. Conclusion

We have investigated the dependence of the optical and electrical properties of ZnSe epilayers depending on the growth temperature conditions. High quality ZnSe thin films with strong NBE emission, no detectable DAP emission and much weaker deep level emission have been grown at 285°C. In this kind of epitaxial films there is only one emission band E_s at 77 K under low excitation level, while the P band appears about 20 meV below the E_s band under higher excitation level. The E_s and P are attributed to free excitons scattered by carriers and the interaction between excitons, respectively.

We have first reported blue lasing emission from OMVPE ZnSe at 77 K originating from the P band. The threshold of the lasing emission is about 0.75 MW/cm^2 power level and the lasing can be operated up to 150 K. Moreover, we have discussed to improve the lasing threshold and the operation temperature by means of both producing ZnSe superlattice films and using dye laser excitation.

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