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# A Study on ZnSSe : Te/ZnMgSSe DH Structure Blue and Green Light Emitting Diodes

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**Abstract** : The optical properties of $ZnS_ySe_{1-x-y}:Te_x$ ($x<0.08$, $y\sim0.11$) alloys grown by molecular beam epitaxy (MBE) have been investigated by photoluminescence (PL) and PL-excitation (PLE) spectroscopy. Good optical properties and high crystal quality were established with lattice match condition to GaAs substrate. At room temperature, emission in the visible spectrum region from blue to green was obtained by varying the Te content of the ZnSSe:Te alloy. The efficient blue and green emission were assigned to $Te_1$ and $Te_n$ ($n\geq2$) cluster bound excitons, respectively. Bright blue (462 nm) and green (535 nm) light emitting diodes (LEDs) have been developed using ZnSSe:Te system as an active layer.

**Key words** : Light emitting diode, Blue, Green, ZnSSe:Te, Molecular beam epitaxy

## 1. Introduction

As a wide and direct band-gap material of II-VI family, Te-doped ZnSe and related semiconductors with a strong blue-green emission band are promising materials for visible light emitting devices. A considerable phenomena were found in the ZnSe:Te crystals[1]-[3], which is related to two emission bands due to the efficient radiative recombination of localized excitons bound to Te atom ($Te_1$ emission) and $Te_n$ ($n\geq2$) cluster ($Te_n$ cluster emission) in the luminescence spectra. In the ZnSe:Te epitaxial layers grown on GaAs substrates by molecular beam epitaxy (MBE), the strong emission band can be seen only in the low temperature region[4], because the Te-doped ZnSe films included high density of macro- and micro-scopic point defects due to a substantial lattice-mismatch in the ZnSe:Te-GaAs system. To utilize this efficient blue~green emission property in visible light emitting devices (laser diodes and light emitting diodes), the characteristics of ternary compounds (ZnSSe:Te) have been studied, focussing on the control of the lattice-matched condition and microscopic

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point defects.

In this article, optical properties of blue and green emission in the ZnSSe:Te epilayers with high crystallinity are presented. And, ZnSSe:Te/ZnMgSSe double-heterostructure (DH) LEDs with an efficient blue (462 nm) ~ green (535 nm) emissions at room temperature are also demonstrated.

## 2. Experimental Procedure

All the samples used in this study were $ZnSe_{1-x}:Te_x$ ($x$=0.002-0.041) and $ZnS_ySe_{1-x-y}:Te_x$ ($x$=0.004-0.042, y~0.11) epilayers, grown on (100) GaAs substrates by MBE. Solid sources of ZnSe (5N), ZnS (6N), Mg (6N), and ZnTe (6N) were used. $ZnCl_2$ was used as an n-type doping source, and the p-type layers were obtained using active nitrogens produced by a radio-frequency (RF) plasma source. In the detailed sample structure, the GaAs substrate surfaces were thermally cleaned (Temp.=~600℃), and then a Zn source beam was irradiated on the substrate surfaces for 60 seconds, followed by the growth of a 120Å-thick undoped ZnSe buffer layer. On top of the ZnSe buffer layer, a ZnSSe:Te layer (about 0.9μm-thick) was grown by varying the Te composition from 0.4 to 4.2%. The samples grown at 200℃ were primarily used in this study. Temperature dependent photoluminescence (PL) measurements were performed to investigate the optical characteristics of the excitonic blue and green emission. The PL experiments (11~300K) were performed under excitation with the 325-nm line of a He-Cd laser. The elemental compositions of the specimens were determined by electron-beam probe microanalysis (EPMA). Double crystal X-ray diffraction (DCXRD) measurements were carried out to confirm the crystal quality of the epitaxial films. Further electroluminescence (EL) experiments were also employed to analyze the emission mechanism of the LEDs.

## 3. Results and Discussion

### 3.1 Comparison of crystal quality between ZnSe:Te and ZnSSe:Te epilayer

Fig. 1 shows the compositional dependence of full-width at half maximum (FWHM) of the X-ray rocking curves and lattice constants for the Te-doped $ZnSe_{1-x}:Te_x$ (binary) and $ZnS_ySe_{1-x-y}:Te_x$ (ternary) epitaxial layers. The FWHM values of the Te-doped binary films increase abruptly with increasing Te concentration. On the other hand, the values in the ternary epilayers show gradual increase with Te composition. The lattice constants are analyzed using the (400) and (115) X-ray diffraction lines. The lattice constant of the binary epilayers with respect to that of GaAs substrate increases linearly with Te concentration. As can be seen in this figure, the $ZnSe_{0.96}:Te_{0.04}$ specimen has mediocre crystal quality (FWHM 〉 1000 arcsec), and which is due to a large lattice mismatch factor ($\Delta a/a$ 〉 +1.1%).

On the other hand, the ternary $ZnS_{0.11}Se_{0.85}:Te_{0.04}$ (with a close lattice match to GaAs substrates) exhibits a good crystal quality (FWHM 〈 150

arcsec). Here, the lattice mismatch factor ($\Delta a/a$) in ZnSSe:Te ternary samples is found to be within 0.2%. Thus, we can confirm a remarkable improvement of crystal quality using Te-doped ternary compounds ($ZnS_ySe_{1-x-y}:Te_x$, $x$=0.04, $y$=0.11), enabling us to develop high-efficiency and long-lived light-emitting devices.

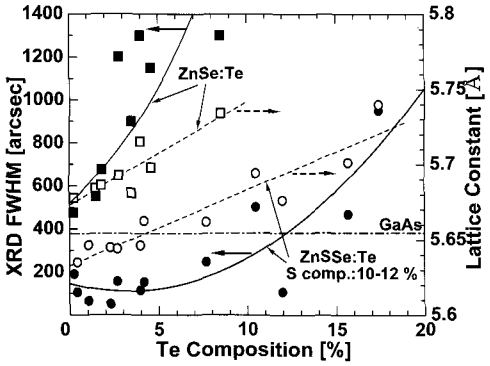


**Fig. 1 Full-width at half maximum (FWHM) of X-ray diffraction (XRD) measurements and lattice constant in $ZnSe_{1-x}:Te_x$ and $ZnS_ySe_{1-x-y}:Te_x$ epitaxial layers as a function of Te composition. A dash-dotted line indicates the lattice constant of GaAs substrate at 300 K**

### 3.2 Optical properties of ZnSSe:Te epilayer

In order to investigate the emission-transition process on the Te-bound exciton systems, PL experiments were employed. Typical temperature dependence of PL spectra from the Te lightly doped $ZnS_ySe_{1-x-y}:Te_x$ ($x$=0.004, $y$=0.103) epitaxial films is shown in Fig. 2 (solid lines). The PL spectrum at 11 K consists of a broad emission band at around 2.63 eV (blue band) with FWHM of 163 meV. Note that for $x$<1% in the binary $ZnSe_{1-x}:Te_x$ alloys the probability of forming $Te_n$ cluster is less than 0.01%[4]. Therefore, it is conceivable that the broad blue emission (2.63 eV) in the$ZnS_ySe_{1-x-y}:Te_x$ (Te=0.4%) with very high efficiency is attributed to the radiative recombination of the exciton bound at two isolated Te atoms ($X/Te_2$). As temperature increases, the intensity of the blue emission band decreases monotonically and the peak energy shifts to the lower energy side.

As the temperature is increased further to 300 K, most of the excitons in the form of $X/Te_2$ states are dissociated into the $X/Te_1$ states. In addition, an emission related to deep level is not observed at room temperature. The most important point in this optical property is that the blue emission at 2.72 eV (see, A of Fig. 2) with FWHM of 68 meV clearly exists even at room temperature. This reflects a highly improved crystal quality of the ternary ZnSSe:Te system (FWHM of XRD<150 arcsec).

Next, temperature dependent PL spectra from the Te heavily doped $ZnS_ySe_{1-x-y}:Te_x$ ($x$=0.042, $y$=0.112) thin films are shown in Fig. 2 (dashed lines). In the PL spectrum at 11 K, one broad emission band is observed at 2.49 eVwith a linewidth (FWHM) of 190 meV. This emission band is attributed to the exciton bound to the $Te_n$ clusters (formed by two or more Te atoms) bonded to the same Zn atom ($Te_n$ cluster emission)[5],[6]. As temperature increases, the peak energy of the $Te_n$ cluster emission shifts to the lower energy side (redshift), and the intensities of all peaks decrease monotonically. On the other hand, the value of FWHM increases with temperature. At room temperature (300

K), the broad emission band peaking at 2.48 eV (see, B of Fig. 2) is observed, which is also assigned to the $Te_n$ cluster emission. The most important point in these optical studies is that the $Te_n$ cluster green emission is kept even at 300 K, and this also reflects highly improved crystal qualities in the Te-doped ternary ZnSSe:Te epitaxial films.

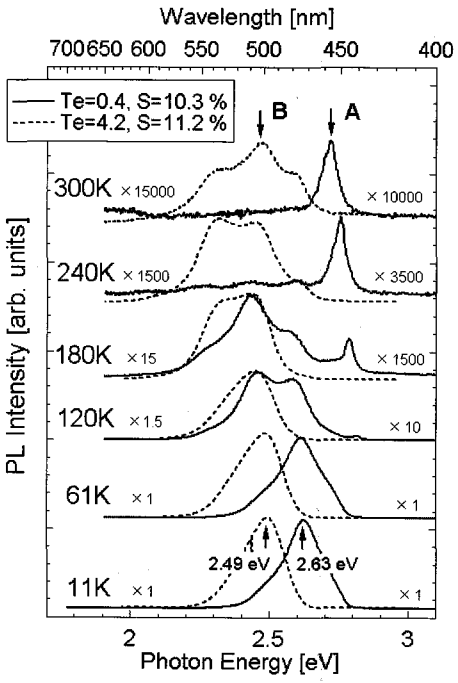


**Fig. 2 Temperature dependent PL spectra for the ZnSSe:Te epitaxial layers. The solid lines result from the $ZnS_ySe_{1-x-y}:Te_x$ ($x$=0.004, $y$=0.103), and dashed lines are $ZnS_y$ $Se_{1-x-y}:Te_x$ ($x$=0.042, $y$=0.112)**

On the basis of PL (photoluminescence) and PL-excitation experiments, we can explain the origin of the blue and green emission by using a configuration coordinate (CC) diagram (see, Fig. 3). In case of Te (~4 %) doped epitaxial layer, electron and hole pairs (excitons) are generated from the ground state to free exciton (F. E.) state (or $Te_1$ bound exciton state) and then relax to the lowest $Te_n$ cluster state (B), accompanied by the lattice relaxation. Thus, we can observe strong green emission even at room temperature (RT) because the $Te_n$ cluster bound exciton has a large thermal activation energy (300 ~ 400 meV). For the case of ZnSSe:Te epitaxial layer with low Te-density (~0.4 %), the origin of blue emission can be explained as follows

i) 10〈T〈100 K, a broad blue-green emission band (due to $Te_n$ cluster) is dominant.

ii) 100〈T〈200 K, the broad blue-green and a rather sharp blue emission are mixed. Here some excitons jump-back from $Te_n$ cluster (B) to $Te_1$ state (A), by thermal dissociation process.

iii) This thermal dissociation becomes dominant around room temperature. Thus, we can see only strong blue emission (due to $Te_1$ state) peaking at 2.72 eV (see, A of Fig. 2).

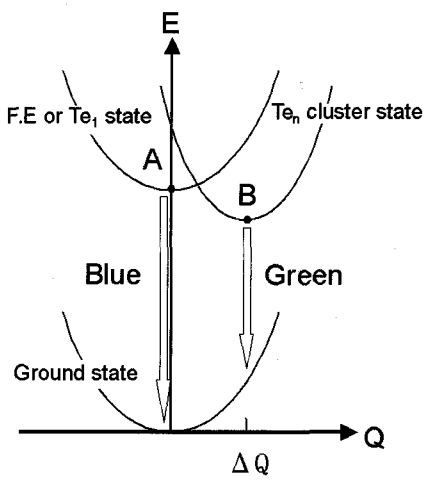


**Fig. 3 Configuration coordinate energy diagram in the ZnSSe:Te epitaxial layer**

### 3.3 Characteristics of ZnSSe:Te-based LEDs

Fig. 4 shows schematic structure of blue and green light emitting devices. The Te-doped $ZnS_ySe_{1-x-y}:Te_x$ ($x$=0.004-0.04, $y$~0.11) alloy has been used as an active layer, which has a good crystalline and a close lattice-match to GaAs substrate. The ZnSSe:Te active layer (0.1~0.3 μm-thick) is sandwiched with n- and p-ZnMgSSe cladding layers. The effective carrier concentrations of n-ZnMgSSe (lower cladding layer) and p-ZnMgSSe (upper cladding layer) were $6\times10^{17}$ $cm^{-3}$ and $2\times10^{16}$ $cm^{-3}$, respectively. On the top surface, a superlattice electrode (SLE) consisting of p-ZnTe/p-ZnSe multiple quantum wells (MQWs) is formed as p-type ohmic contact layer, which is one important factor in obtaining low voltage operation of bright LED devices. Deposited Au-film and In-alloy are used for top and bottom metal electrodes, respectively.

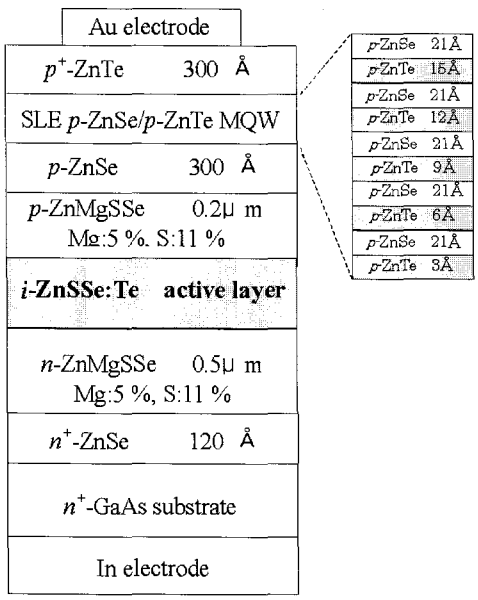


**Fig. 4 Schematic structure of ZnSSe:Te-based DH structure LEDs grown by molecular beam epitaxy**

Fig. 5 demonstrates the electroluminescence (EL) spectra at room temperature for typical ZnSSe:Te-based LEDs for the blue (2.68 eV, 462 nm; Te=0.4%), blue-green (2.48 eV, 500 nm; Te=2-3%) and green (2.31 eV, 537 nm; Te=4.2%) emissions. The blue-green and green emission in LEDs are related to the $Te_n$ cluster bound excitons ($Te_n$ cluster emission), and blue emission relates to the exciton bound to a single Te atom ($Te_1$ emission). These strong blue and green emissions at 300 K due to $Te_1$ and $Te_n$ clusters indicate highly improved crystal qualities in the ternary ZnSSe:Te system.

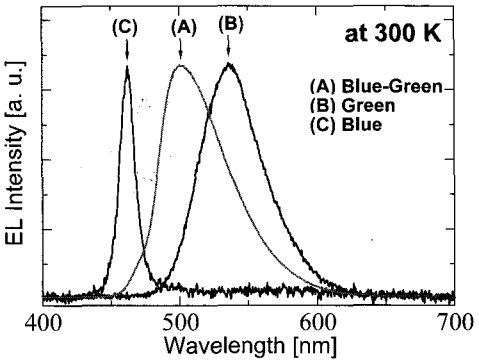


**Fig. 5 EL spectra of ZnSSe:Te-based LEDs at 300K: (a) blue-green (b) green (c) blue**

## 4. Conclusions

Systematic investigations were carried out on crystal qualities and optical properties of the $ZnS_ySe_{1-x-y}:Te_x$ ($x$=0.004~0.042, y~0.11) epitaxial layers grown on (100) GaAs substrates by molecular beam epitaxy.

From the double crystal X-ray diffraction (DCXRD) measurements, the

Te-doped ternary $ZnS_ySe_{1-x-y}:Te_x$ ($x<0.05$) epilayers have represented a high crystal quality (FWHM < 150 arcsec) and a close lattice matching to GaAs substrate ($\Delta a/a$: ±0.2%). Those values are improved drastically in comparison with the Te-doped binary compounds.

From the optical properties (PL measurements) and the detailed temperature dependence, the blue emission (at 2.72 eV) is assigned as $Te_1$ exciton emission process. This blue emission can be obtained in the Te lightly doped $ZnS_ySe_{1-x-y}:Te_x$ (Te=0.4%) epilayers. In addition, the strong green emission band, which is attributed to the Ten cluster bound exciton, is observed at 300 K in the Te heavily doped $ZnS_ySe_{1-x-y}:Te_x$ (Te=4.2%) epilayers. These strong blue and green emissions due to $Te_1$ and $Te_n$ clusters indicate highly improved crystal qualities in the ternary ZnSSe:Te system.

It has been successfully fabricated that efficient blue (462 nm), blue-green (500 nm) and green (535 nm) ZnSSe: Te/ZnMgSSe DH structure LEDs grown by MBE, introduced the $ZnS_ySe_{1-x-y}:Te_x$ ternary epilayers as an active layer.

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