

Growth of Zinc Sulfo-Selenide Single Crystals and Their Near Band-Edge Photoluminescence

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High-purity $\text{ZnS}_x\text{Se}_{1-x}$ ($0 \leq x \leq 0.15$) single crystals have been grown by the sublimation method. Sharp emission due to free-exciton (Ex) has been observed for the first time in $\text{ZnS}_x\text{Se}_{1-x}$. The bound-exciton (I_2 and I_1^{deep}) line and the LO-phonon replicas of I_1^{deep} line have also been observed. Energies of their peaks shift towards higher energy with the increase of composition parameter x ($0 \leq x \leq 0.15$). With increasing x , the I_1^{deep} emission line becomes broader and approaches a Gaussian shape. The intensity of I_1^{deep} line decreases with increasing x and becomes hardly observable for x above 0.12.

§1. Introduction

Zinc sulfo-selenide ($\text{ZnS}_x\text{Se}_{1-x}$) is a solid solution of two binary compounds, ZnS and ZnSe, where the band-gap energy changes continuously with the composition x . This ternary compound has the advantage of being a direct-type wide gap semiconductors which is favorable for the realization of blue light emitting devices. Much interest has been focussed on single crystals of $\text{ZnS}_x\text{Se}_{1-x}$, and extensive efforts have been made on the crystal growth and study of the luminescent properties of the $\text{ZnS}_x\text{Se}_{1-x}$ system.¹⁻⁵⁾ As for the luminescent properties, the free-exciton emission, which is observed on many II-VI binary compounds, has not been reported in ternary compound $\text{ZnS}_x\text{Se}_{1-x}$. In addition, no detailed studies on the luminescence of $\text{ZnS}_x\text{Se}_{1-x}$ with $x < 0.2$ are reported. The free-excitons are easily trapped by impurities or imperfections to form bound-excitons.⁶⁾ Therefore, in order to observe the sharp free-exciton emission spectrum, highly pure and highly perfect $\text{ZnS}_x\text{Se}_{1-x}$ single crystals must be grown.

In this paper are described the growth method of highly pure single crystals of $\text{ZnS}_x\text{Se}_{1-x}$ ($0 \leq x \leq 0.15$), together with their photoluminescence spectra. Furthermore, the main features of the photoluminescence spectra observed on the specimens with different composition x of $\text{ZnS}_x\text{Se}_{1-x}$ are discussed.

§2. Experimental Procedure

Polycrystals of the component compounds ZnS and ZnSe were synthesized at about 1000°C by chemical reaction of the constituent elements; sulfur having nominal purity 6-nine refined by the sublimation method, zinc with 6-nine grade and selenium of 5-nine up grade. Synthesized polycrystals of ZnS and ZnSe were refined by repeating sublimation 2 or 3 times. ZnS and ZnSe were ground and mixed to a desired composition ratio and then vapor-transported at 1010°C in a quartz ampoule. By these procedures, homogeneous polycrystalline solid solutions

of $\text{ZnS}_x\text{Se}_{1-x}$ were obtained. $\text{ZnS}_x\text{Se}_{1-x}$ single crystals were grown by the sublimation method using these solid solutions as the source materials. The temperatures of the source chamber and of the crystallization chamber were kept at 1010°C and at about 1003°C, respectively. The growth ampoules were quenched in water. The compositions x of the grown crystals were measured by an X-ray micro-analyzer.

The samples for the photoluminescence measurements were cut from the grown single crystals along the cleavage planes and etched by the method reported by Satoh and Igaki.⁷⁾ The photoluminescence spectra were measured at 4.2 K or 2 K using Xe-lamp as the excitation source. The reflection spectra were measured at 2 K using a W-lamp. In these measurements at 4.2 K were used a grating monochromator with a reciprocal dispersion of 1.5 nm/mm and HTRV-292 photomultiplier and at 2 K monochromator with a reciprocal dispersion of 0.05 nm/mm and HTRV-106 UH photomultiplier.**

§3. Experimental Results

The $\text{ZnS}_x\text{Se}_{1-x}$ single crystals grown in 8 days are pale yellow-green clear rods with typical dimensions about $10.0 \times 6.5 \times 4.5 \text{ mm}^3$. The $\text{ZnS}_x\text{Se}_{1-x}$ single crystals have zincblende structure with their growth direction along $\langle 111 \rangle$ determined from Weissenberg X-ray diffraction photographs. The compositions x of the grown crystals of $\text{ZnS}_x\text{Se}_{1-x}$ were examined by X-ray micro-analyzer within the standard error ± 0.004 . The grown crystals were known to be homogeneous.

The near band-edge photoluminescence spectra and reflection spectra at 2 K for $\text{ZnS}_x\text{Se}_{1-x}$ ($0 \leq x \leq 0.15$) single crystals are shown in Fig. 1. The luminescence and reflection spectra of a pure ZnSe single crystal ($x=0$) are shown in Fig. 1(a). The prominent peak at 2.8010 eV and the small shoulder at 2.8150 eV in the reflection spectrum have been interpreted⁸⁾ as due to creation of excitons in the ground state ($n=1$) and the first excited state ($n=2$),

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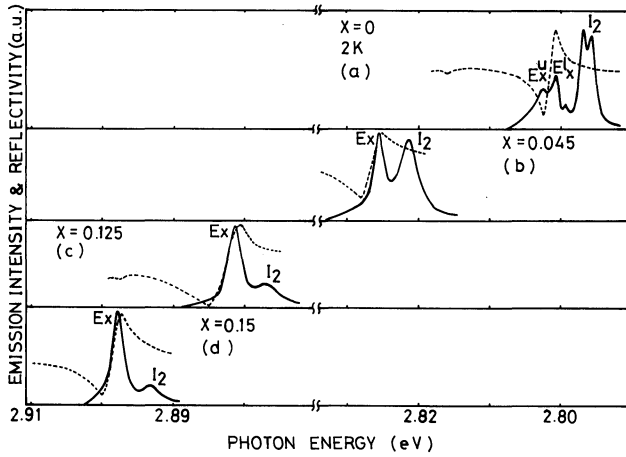


Fig. 1. Free-exciton and bound-exciton luminescence spectra and reflection spectra of $\text{ZnS}_x\text{Se}_{1-x}$ ($x=0-0.15$), at 2 K.

—: The luminescence spectra; ----: The reflection spectra.

respectively. The two emission peaks at 2.8034 eV and 2.8011 eV are very close to the maximum position in the reflection spectrum, and hence are attributable to the free-exciton emissions. Two structures can be interpreted as the radiative decays of excitonic polaritons distributed in the upper and lower branches near the bottleneck.⁹⁾ They are labelled Ex^u (peaking at 2.8034 eV) and Ex^l (at 2.8011 eV), respectively. The I_2 line appearing on the lower energy side of the free exciton emission is composed of two emission peaks at 2.7969 eV and 2.7954 eV. They are considered to be due to the radiative recombination of excitons bound to neutral donors.^{10,11)}

Figure 1(b)–(d) shows the near band-edge photoluminescence and reflection spectra for $\text{ZnS}_x\text{Se}_{1-x}$ ($x=0.045-0.15$). The emission (Ex) which is observed very close to the position of reflection peak is considered to be due to the radiative recombination of the free-exciton. The peak energies of I_2 line for $\text{ZnS}_x\text{Se}_{1-x}$ are located at 4.5 to 4.7 meV lower than those of Ex. The intensity of Ex is smaller than that of I_2 for $x=0$, but becomes larger for $x=0.125$ and 0.15 than that of I_2 emission as seen in Fig. 1.

The emission spectra at 4.2 K for $\text{ZnS}_x\text{Se}_{1-x}$ single crystals are shown in Fig. 2. The very strong line observed at 2.7835 eV in Fig. 2(a) is known as the I_1^{deep} line for ZnSe, which is due to the radiative recombination of excitons bound to neutral acceptors.^{12,13)} The strong LO-phonon replicas of I_1^{deep} line are observed with a separation of the LO-phonon energy 31.5 meV. The intensity of I_1^{deep} line decreases with the increase in x , whereas the intensity of $I_1^{\text{deep-LO}}$ line increases, and the intensity of $I_1^{\text{deep-LO}}$ line is stronger than that of I_1^{deep} line for x larger than 0.06, as seen in Fig. 2(b)–(d). I_1^{deep} line becomes hardly observable and appears as a broad peak near 2.80 eV for x larger than 0.12 as seen in Fig. 2(e).

Peak energies of Ex and other photoluminescence peaks are plotted in Fig. 3 as a function of x . From Fig. 3, the energies of Ex, I_2 , I_1^{deep} and $I_1^{\text{deep-LO}}$ line vary linearly with x , the slopes of I_1^{deep} and $I_1^{\text{deep-LO}}$ line with x are smaller than those for Ex and I_2 . Change of the half-width of I_1^{deep} line is shown in Fig. 4 as a function of composition x . The half-width increases linearly with x ($0 \leq x \leq 0.06$), this increase will be discussed in the next section.

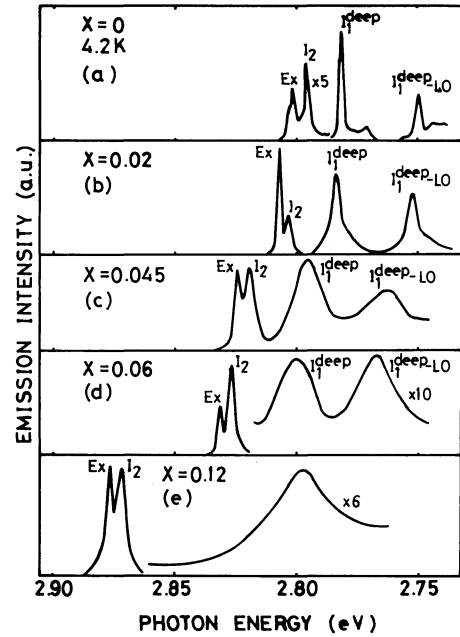


Fig. 2. Near band-edge emission spectra of $\text{ZnS}_x\text{Se}_{1-x}$ ($x=0-0.12$), at 4.2 K.

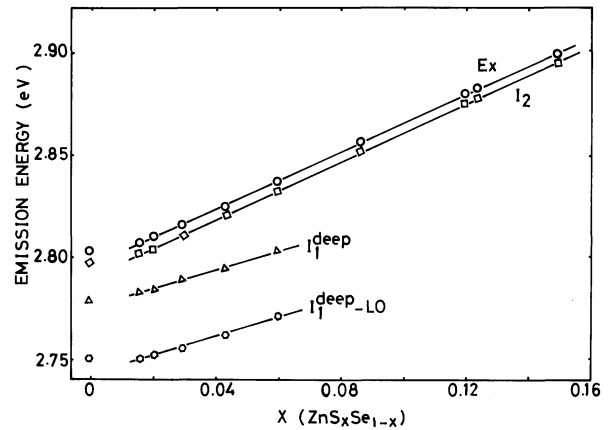


Fig. 3. Composition dependence of emission energies of Ex, I_2 , I_1^{deep} and $I_1^{\text{deep-LO}}$ line.

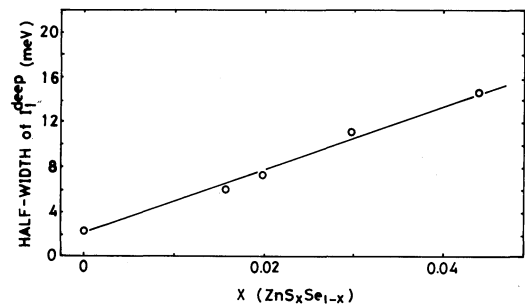


Fig. 4. Composition dependence of half-width of I_1^{deep} line.

§4. Discussion

Excitons in highly excited states come down to the bottom of the exciton band as a result of phonon scattering or are trapped by impurities or defects. The zero-phonon radiative exciton annihilation gives rise to narrow emission lines with energies corresponding to the bottoms of the exciton band. The intensity of free exciton emission (Ex)

depends on the population of exciton at $K=0$. Therefore, the intensity of Ex directly depends on the concentration of impurities and defects in crystal. It is seen from Fig. 1 that the free exciton emission spectra are sharp and very strong. This shows that the relatively large number of excitons are in the bottom of the exciton band and that the grown crystals are of high quality.

The shifts of peaks of Ex, I_2 and I_1^{deep} line towards the higher energy side with increasing x shown in Figs. 1 and 2, correspond to the change of the band gap energy with x . The smaller slope of I_1^{deep} line with x compared to those of Ex and I_2 shown in Fig. 3, means that the energy level of neutral acceptors responsible for the I_1^{deep} line becomes deeper with increasing x . In $\text{ZnS}_x\text{Se}_{1-x}$, the bottom of the conduction band is predominantly composed of the 4s level of Zn, and the upper valence bands consist of the 3p levels of S and 4p levels of Se. Therefore, in the solid solutions of $\text{ZnS}_x\text{Se}_{1-x}$, the variation of the band-gap energy with x is supposed to arise predominantly from a shift of the valence band, while the energy of conduction band is nearly fixed. The shallow donor level responsible for the I_2 line is situated below the bottom of the conduction band, Therefore the observed linear changes in the energy of I_2 and Ex with x directly reflect the linear change of the band gap energy of $\text{ZnS}_x\text{Se}_{1-x}$ with x ($0.02 \leq x \leq 0.15$).

The half-width of I_1^{deep} lines increases linearly with x ($0 \leq x \leq 0.06$), as shown in Fig. 4. The broadening of I_1^{deep} line is considered to be caused by the following two factors: first, the nonuniformity in the number of sulfur atoms present within the orbit of an exciton bound to neutral acceptors; second, the shortening of the lifetime of excitons caused by the scattering into states by phonons, since lifetime Γ is inversely proportional to $|W|^2$, where W is the exciton-phonon scattering interaction¹⁴⁾ and is considered to increase which the depth of the level responsible for the I_1^{deep} line. The approach of the shape of I_1^{deep} line to a Gaussian shape with increasing x is in agreement with the theoretical result by Toyozawa¹⁵⁾ who studied the relation between the exciton lifetime and shape of exciton emission spectrum and predicted the Gaussian shape of exciton emission spectrum when a strong exciton-phonon coupling exists.

have been observed on the sublimation grown high purity $\text{ZnS}_x\text{Se}_{1-x}$ single crystals.

The band gap energy of $\text{ZnS}_x\text{Se}_{1-x}$ ($0.02 \leq x \leq 0.15$) increases linearly with composition x .

With increasing x ($x \leq 0.06$) the intensity of I_1^{deep} line decreases, whereas the intensity of I_1^{deep} -LO line increases, and I_1^{deep} line is hardly observed for x larger than 0.12, and the composition dependence of the energy of I_1^{deep} line is smaller than that of Ex and I_2 . These results can be accounted for by the fact that the energy level of neutral acceptor of I_1^{deep} line becomes deeper and exciton-phonon coupling increases with increasing x .

The half-width of I_1^{deep} line increases linearly with x ($0 \leq x \leq 0.06$). This behavior is considered to arise from the nonuniformity in the amount of sulfur atoms present in the radius of excitons bound to neutral acceptors and from the shortening of exciton lifetime.

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