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journal or publication title	Journal of Applied Physics
volume	94
number	9
page range	5805-5808
year	2003-11-01
URL	<a href="http://hdl.handle.net/10228/573">http://hdl.handle.net/10228/573</a>

doi: 10.1063/1.1618932

# Intrinsic excitonic photoluminescence and band-gap engineering of wide-gap *p*-type oxychalcogenide epitaxial films of LnCuOCh (Ln=La, Pr, and Nd; Ch=S or Se) semiconductor alloys

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(Received 24 April 2003; accepted 21 August 2003)

The optical spectroscopic properties of layered oxychalcogenide semiconductors LnCuOCh (Ln = La, Pr, and Nd; Ch=S or Se) on epitaxial films were thoroughly investigated near the fundamental energy band edges. Free exciton emissions were observed for all the films between 300 and  $\sim 30$  K. In addition, a sharp emission line, which was attributed to bound excitons, appeared below  $\sim 80$  K. The free exciton energy showed a nonmonotonic relationship with lattice constant and was dependent on lanthanide and chalcogen ion substitutions. These results imply that the exciton was confined to the  $(\text{Cu}_2\text{Ch}_2)^{2-}$  layer. Anionic and cationic substitutions tune the emission energy at 300 K from 3.21 to 2.89 eV and provide a way to engineer the electronic structure in light-emitting devices. © 2003 American Institute of Physics. [DOI: 10.1063/1.1618932]

## I. INTRODUCTION

Wide-gap III-V or II-VI semiconductors have been intensively investigated for optoelectronic devices such as light-emitting diodes and laser diodes, which operate in the short-wavelength region from green to ultraviolet.<sup>1</sup> In order for wide-gap semiconductors to control the emission wavelength for specific applications, these materials must tune the band gaps. Alloy systems are employed for this purpose because changing the ratios of the constituent components continuously controls the band-gap energies. Interestingly, such systems can form superlattice structures that enhance the emission efficiency by confinement effects.<sup>2</sup> Currently, AlGaIn-InGaIn is a well-known system that is capable of tuning emission wavelengths and forms artificial superlattice structures. Thus, it is widely used in commercial optoelectronic devices.<sup>3</sup> However, several issues are not resolved; for example, it is difficult to form heavily hole doped  $p^{(+)}$  layer for low-resistive ohmic contacts.

A series of oxychalcogenides, LnCuOCh (Ln = lanthanides, Ch=S or Se), is a wide-gap *p*-type semiconductor and exhibits sharp emission in the ultraviolet to blue region, which originates from excitons even at room temperature.<sup>4</sup> An interesting feature of this type of compound is that along the *c*-axis it has layered structures, composed of alternating stacks of wide-gap insulating  $(\text{Ln}_2\text{O}_2)^{2+}$  layers and semiconducting  $(\text{Cu}_2\text{Ch}_2)^{2-}$  layers.<sup>4,5</sup> Since the hole transport path is in the  $(\text{Cu}_2\text{Ch}_2)^{2-}$  layer,<sup>6</sup> this structure is expected to exhibit unique properties that arise from the two-dimensional confinement effects based on the natural super-

lattice structure. This is an advantage over current compound semiconductors such as GaN because expensive preparation processes are not required to fabricate multi-quantum-well structures. In fact, the exciton binding energy of LnCuOCh has been estimated to be  $\sim 50$  meV.<sup>7</sup> The large binding energy is probably due to the stabilization by the quantum confinement effects in the sandwiched structure. Mg-doped LaCuOSe exhibits wide-gap *p*-type metallic conduction while maintaining a moderately large hole mobility, which may be explained by the natural modulation doping and also originates from the layered structure.<sup>7</sup> Thus, it is expected that LnCuOCh compounds will exhibit additional optical characteristics inherent to the layered structure, which are favorable for optoelectronic device application. A detailed optical study on high quality epitaxial films, however, has not been performed, except for polycrystalline samples.<sup>4,8,9</sup>

This paper details the optical properties associated with excitons of LnCuOCh epitaxial films. Sharp emission lines associated with free and bound excitons were observed at temperatures from 10 to 300 K. The exciton energy exhibited unusual behavior with the crystal structure, and these characteristics are discussed with respect to the specific layered structure of LnCuOCh semiconductor alloys.

## II. EXPERIMENT

Two series of LnCuOCh epitaxial films, LaCuOS<sub>1-x</sub>Se<sub>x</sub> ( $x=0-1$ ) and LnCuOS (Ln=Ce, Pr, and Nd) were prepared on MgO (001) substrates by reactive solid-phase epitaxy technique.<sup>10</sup> In this paper, CeCuOS is not referred to, but will be described elsewhere,<sup>11</sup> because it exhibits completely different electrical and optical properties from the other samples. All the films were grown in conditions similar to those previously reported.<sup>7,12</sup> High-resolution x-ray diffraction analyses verified that each film was a single phase and grown heteroepitaxially on MgO (001) with the crystallo-

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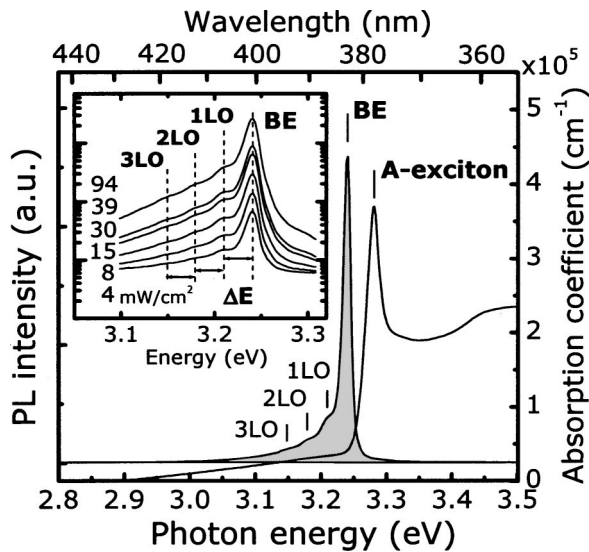


FIG. 1. PL and absorption spectra of LaCuOS epitaxial film at 10 K. The inset shows the PL spectra of LaCuOS epitaxial film dependence on excitation power in a logarithm scale. Excitation power are shown at the left of the spectra.

graphic orientation of (001)[110] LnCuOCh|(001)[110] MgO. Optical absorption and photoluminescence (PL) spectra were measured in a temperature range from 10 to 300 K by conventional spectrophotometers. The excitation source for PL was a 325-nm lasing line from a He-Cd laser with an energy of 30 mW/cm<sup>2</sup>.

### III. RESULTS AND DISCUSSION

Figure 1 shows the PL and absorption spectra of the LaCuOS epitaxial film at 10 K. A single, sharp PL line peaking at 3.24 eV (denoted BE) with a full width at half-maximum (FWHM) of  $\sim 10$  meV was observed, and the peak energy is Stokes-shifted by  $\sim 40$  meV from that of the free exciton absorption peak (A-exciton). Broad luminescence from deep centers, as reported for polycrystalline bulks,<sup>4,9</sup> was not observed, which revealed that the epitaxial film had a highly crystalline quality with a low defect density. In addition, three weak bands that have equal energy spacing ( $\Delta E$ ) of  $\sim 31$  meV ( $\sim 250$  cm<sup>-1</sup>) were detected in the lower energy region of the BE line. Since the energy spacing was nearly the same as the LO phonon energies in sulfides such as chalcopyrites (I-III-VI)<sup>13</sup> and II-VI semiconductors,<sup>14</sup> the observed replica structure was most likely phonon sidebands associated with the LO phonon in the Cu-S plane. The inset shows the PL spectra dependence on the excitation power. The integrated PL intensity linearly increased with the power without an observable peak shift, which is evidence that the BE line is not due to a donor-acceptor-pair emission. This fact, the small Stokes shift, and the small BE line width were consistent with the conclusion that the line is attributed to a bound exciton emission. Since the LaCuOS exhibits *p*-type conduction without intentional acceptor doping, the (Cu<sub>2</sub>S<sub>2</sub>)<sup>2-</sup> layer may have Cu<sup>1+</sup> vacancies.<sup>4</sup> It is likely that the bound exciton is trapped at the

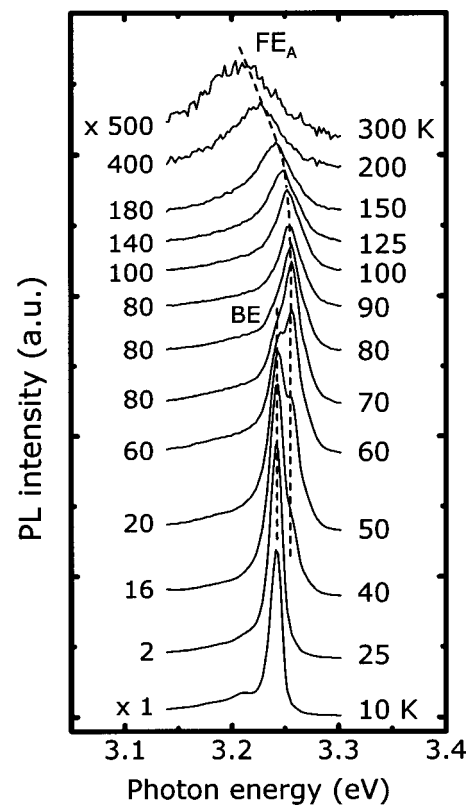


FIG. 2. Variations in PL spectra of LaCuOS epitaxial film in the near-band-edge region with temperature. Magnifications of spectra and temperatures measured are shown at both sides of each spectrum, respectively.

Cu<sup>1+</sup> vacancy sites. This discussion of the phonon replica further supports the hypothesis that the exciton is associated with the (Cu<sub>2</sub>S<sub>2</sub>)<sup>2-</sup> layer.

Figure 2 shows temperature dependence of the PL spectra of the LaCuOS epitaxial film. Only one sharp emission, originating from BE, was observed at 10 K with phonon replicas. As the temperature was increased to  $\sim 40$  K, a weak emission band (3.26 eV) appeared at an energy higher than that of the BE line. This emission was assigned to free exciton emission (FE<sub>A</sub>) since the low energy edge of the absorption band significantly overlaps with the high energy edge of the emission band. However, small Stokes shifts ( $\sim 20$  meV) were observed in terms of peak positions of the absorption and emission bands. The emission intensity of the free exciton gradually increased as the temperature increased to 80 K. On the contrary, the BE line intensity decreased and disappeared around 90 K. The decrease of the BE line intensity was caused by the thermal excitation of the bound exciton to the free exciton due to the small localization energy ( $\sim 20$  meV). The intensity of the FE<sub>A</sub> peak decreased as the temperature increased, and was gradually shifted to lower energy side.

Figures 3(a) and 3(b) show the temperature dependence of the peak energies for the A-exciton absorption line, FE<sub>A</sub>, and BE emission lines in LaCuOS<sub>1-x</sub>Se<sub>x</sub> ( $x=0, 0.4, \text{ and } 1$ ) and LnCuOS (Ln=La, Pr, and Nd) epitaxial films. Since the A-exciton absorption peak in these materials, except for LaCuOS, splits into two peaks due to spin-orbit interaction,<sup>15</sup> the peak energy of lower energy side was plot-

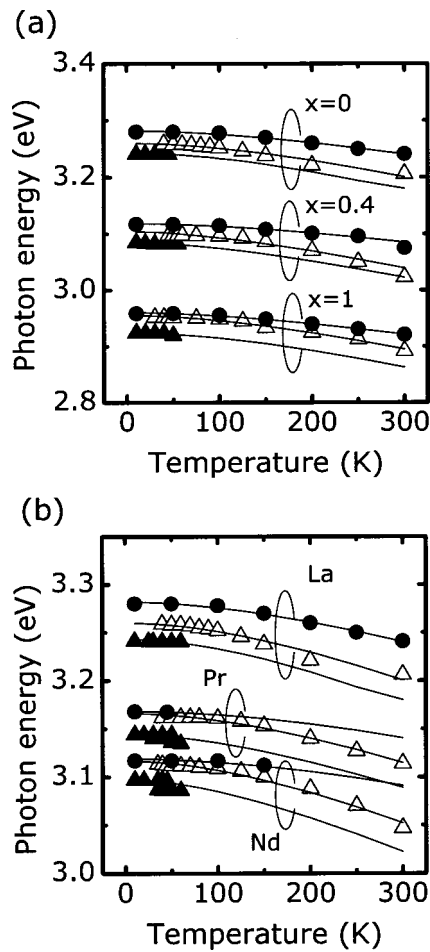


FIG. 3. Temperature dependence of exciton energies of A-exciton (filled circle),  $FE_A$  (open triangle), and BE (filled triangle) of (a)  $LaCuOS_{1-x}Se_x$  epitaxial films and (b)  $LnCuOS$  ( $Ln=La, Pr, Nd$ ) epitaxial films. The temperature dependence, calculated by Varshni's empirical model, is shown as solid curves and reproduces the experimental values.

ted in Fig. 3. The plotted data was fitted as solid curves using the Varshni's empirical relationship.<sup>16</sup> The  $FE_A$  and BE emission lines were clearly resolved in all samples and the intensities of these emission lines showed similar temperature dependencies, except for their peak energies. The BE lines were thermally excited and were converted into the  $FE_A$  at  $\sim 50$  K. The Stokes shift between the A-exciton absorption peaks and the  $FE_A$  emission peaks became slightly larger in all the samples as the temperature increased, which indicates a thermal influence on energy dispersion of exciton. The FWHMs of the BE lines of  $LaCuOSe$  and  $LnCuOS$  ( $Ln=Pr$  and  $Nd$ ) at 10 K were  $\sim 30$ – $40$  meV, which was larger than that of  $LaCuOS$  ( $\sim 10$  meV) and was probably due to the Auger interaction with the residual hole carriers.<sup>7,12</sup> The PL intensities of the other films did not noticeably differ from  $LaCuOS$  and emissions from the lanthanide ions were not detected, indicating that the  $4f$  electrons did not act as emission quenchers.

Figure 4 shows the peak energy of the free exciton emission at 300 K as a function of the  $a$ -axis length for  $LaCuOS_{1-x}Se_x$  and  $LnCuOS$  ( $Ln=Pr$  and  $Nd$ ) epitaxial films. The inset shows the band-gap energies of wide-gap semiconductor alloys as a function of lattice constant from

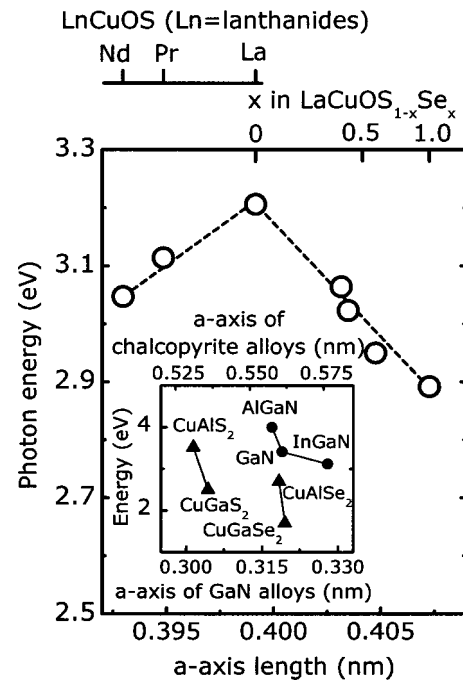


FIG. 4. PL peak energies of epitaxial films of  $LnCuOCh$  alloys at 300 K as a function of  $a$ -axis length. Top axis shows alloy compositions. The inset shows relationship between the  $a$ -axis and energy gaps of representative wide-gap semiconductors for comparison.

Refs. 3 and 17 for comparison. In the  $LaCuOS_{1-x}Se_x$  region, the emission energies almost linearly decreased as the  $a$ -axis length increased, which allows the emission energy to be continuously tuned from 3.21 eV (386 nm) to 2.89 eV (429 nm) by changing the Se content. The decrease in the emission energy was attributed to the electronic structure change of the valence band maximum from a hybridized orbital composed of  $Cu\ 3d-S\ 3p$  to that of  $Cu\ 3d-Se\ 4p$ .<sup>6,7</sup> This type of the band-gap control or band engineering is commonly performed in III-V and II-VI alloys such as  $GaInAs_{1-x}P_x$ <sup>18</sup> and  $ZnMgS_{1-x}Se_x$ .<sup>19</sup>

On the contrary, the emission energy is decreased from 3.21 eV (386 nm) to 3.05 eV (407 nm) by changing the lanthanide ions in the order of La, Pr, and Nd, although the  $a$ -axis shrinks. In III-V and I-III-VI alloy systems such as  $In_xGa_{1-x}N$ ,  $Al_xGa_{1-x}N$ ,<sup>3</sup>  $CuAl_xGa_{1-x}S_2$ , and  $CuAl_xGa_{1-x}Se_2$ ,<sup>17</sup> band-gap energy monotonically decreased as the lattice constant by cation substitution increased, as shown in the inset of Fig. 4. However, the present result demonstrates the opposite behavior for the chalcogen and lanthanide ion substitutions. The behavior is explained by the natural superlattice structure composed of the  $(Ln_2O_2)^{2+}$  and the  $(Cu_2Ch_2)^{2-}$  layers, in which the chalcogen and lanthanide ion substitutions play different roles. The substitution of lanthanide ions in a  $(Ln_2O_2)^{2+}$  layer does not directly change the electronic structure around the energy band gap, but the shrinkage of the  $(Ln_2O_2)^{2+}$  layer may induce internal stress in  $(Cu_2S_2)^{2-}$  layer. If it is the case, the situation is analogous to a strained layer superlattice.

#### IV. CONCLUSIONS

The excitonic properties of wide-gap  $p$ -type  $LnCuOCh$  epitaxial films were examined. A single, sharp bound exciton

emission peaking at 3.24 eV was observed in LaCuOS at 10 K. The bound excitons are thermally released from the trapped acceptors to the free exciton and smear above 80 K. The bound exciton is accompanied by a LO phonon replica, which is associated with a LO phonon in the Cu–S plane. Different anionic and cationic models explain the exciton energy shift upon ion substitutions. These results, along with the large exciton binding energy, strongly suggest that the excitons are two-dimensionally confined in the  $(\text{Cu}_2\text{Ch}_2)^{2-}$  layer. The appropriate ion substitution can tune the emission energy between 2.89 and 3.21 eV. These features and the wide range control capability of *p*-type electrical conduction from an insulator to a degenerate semiconductor, make LnCuOCh very promising in light-emitting devices.

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