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Third-order optical nonlinearity originating from room-temperature exciton in layered compounds LaCuOS and LaCuOSe

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We have studied the third-order optical nonlinearity ($\chi^{(3)}$) of epitaxial thin films of layered compounds LaCuOS and LaCuOSe at room temperature by a spectrally resolved degenerative four-wave mixing technique with femtosecond time resolution. The $\chi^{(3)}$ values in both films are sharply resonant to optical absorption bands in the ultraviolet (UV) light region due to room-temperature exciton. The peak values are evaluated to be as large as $2-4 \times 10^{-9}$ esu with a fast time response of 250–300 fs. These findings indicate that LaCuOS and LaCuOSe are promising materials for emerging optical nonlinear devices that operate in the UV light region compatible for GaN-based lasers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1646221]

Since demonstrations of a photoexcited laser oscillation in ZnO epitaxial film¹ and an ultraviolet (UV) light emitting diode composed of an all oxide *pn* heterojunction,² transparent semiconducting oxides and oxychalcogenides have attracted much attention for their applications to light emitting devices operating in the blue-UV light region, and their emission characteristics around the band edge region associated with excitons have been studied intensively. On the contrary, only few studies have been conducted to date regarding the optical nonlinearity, although a huge amount of similar studies have been performed for semiconductors and organic compounds to search for materials with large nonlinearity to realize all optical switching or signal processing devices. These studies have revealed that optical nonlinearity is enhanced at the resonant energy of the exciton, especially when the exciton has a large binding energy [e.g., ZnO (Ref. 3) with ~ 60 meV] or is confined in a quantum well or nanoparticle.^{4,5} Excitons with large binding energy are particularly favorable for practical application because enhancement takes place even at room temperature.

Oxychalcogenides LaCuOS and LaCuOSe (LaCuOS/Se) are wide band gap materials with *p*-type conductivity and UV emission due to exciton at room temperature.^{6,7} They have a tetragonal system (space group: *P4/nmm*) and are composed of an alternate stack of $(\text{La}_2\text{O}_2)^{2+}$ and $(\text{Cu}_2\text{S}_2)^{2-}$ or $(\text{Cu}_2\text{Se}_2)^{2-}$ [$(\text{Cu}_2\text{S}_2/\text{Se}_2)^{2-}$] layers along the *c* axis as shown in Fig. 1.⁸ Band calculations and photoemission spectra have indicated that the conduction band minimum (CBM) and the valence band maximum (VBM), respectively, are constructed of Cu 4*s* orbitals and a mixture of Cu 3*d* and S 3*p* (or Se 4*p*) orbitals.⁹ There are noticeable band discontinuities at both the CBM and VBM, leading to the view that they are naturally formed quantum wells in which the

$(\text{Cu}_2\text{S}_2/\text{Se}_2)^{2-}$ layer acts as a well sandwiched by the $(\text{La}_2\text{O}_2)^{2+}$ barrier layers.¹⁰ The optical absorption spectra show a sharp peak around the band gap energy (3.1 eV for LaCuOS, 2.8 eV for LaCuOSe) even at room temperature, which is attributed to the exciton with large binding energy (~ 50 meV)¹¹ confined in the conductive $(\text{Cu}_2\text{S}_2/\text{Se}_2)^{2-}$ layer. These characteristics lead one to expect that LaCuOS/Se has large optical nonlinearity in the UV light region at room temperature. In this letter, we focus on the spectral intensity and time response of the nonlinearity, represented by third-order optical susceptibility $\chi^{(3)}$, in LaCuOS/Se epitaxial thin films using a femtosecond time-resolved degenerative four-wave mixing (DFWM) technique around the band gap energy at room temperature.

The epitaxial LaCuOS/Se films used for this study were

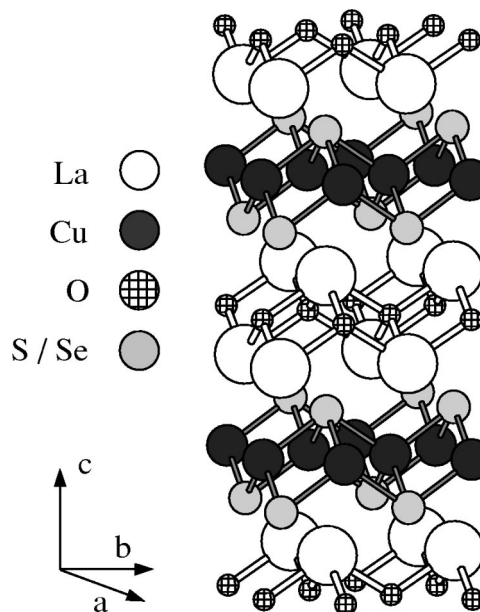


FIG. 1. Crystal structure of LaCuOS and LaCuOSe.

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grown on MgO(001) substrates through a two-step growth process, called the *reactive solid-phase epitaxy* technique.¹² High-resolution x-ray diffraction and a cross-sectional electron microscopy confirm the high-quality heteroepitaxial growth of the films with LaCuOS/Se(001)[110]/MgO(001)[110].^{11,13} The film thicknesses were 160 and 140 nm for LaCuOS and LaCuOSe, respectively. We also prepared a 50-nm-thick epitaxial ZnO thin film on a sapphire (11 $\bar{2}$ 0) substrate by pulse laser deposition, and it was used as a reference for the $\chi^{(3)}$ measurements.

The femtosecond time-resolved DFWM measurements were carried out in a conventional pump-probe configuration at room temperature. We employed the second harmonic of a mode locked Ti:sapphire laser (tunable from 350 to 450 nm) with a pulse width of ~ 100 fs and repetition rate of 80 MHz as the light source. The pulse was split into two, chopped at different frequencies (f_1, f_2) and focused onto a spot on the sample with a diameter of ~ 50 μm and a crossing angle of 8° between the propagated directions \mathbf{k}_1 and \mathbf{k}_2 . The excitation power density was 1.8×10^7 W/cm². The DFWM signal refracted in the forward direction $2\mathbf{k}_1 - \mathbf{k}_2$ due to a grating that transiently formed in the sample that was measured as a function of the time delay between the two split pulses using a photomultiplier connected to a digital lock-in amplifier synchronized at the sum frequency ($f_1 + f_2$). The absolute value of $\chi^{(3)}$ for LaCuOS/Se was determined by comparing the DFWM signal I to the signal I_r from a silica glass plate (used as a standard, 1 mm in thickness), measured under identical experimental conditions using the following equation:¹⁴

$$\chi^{(3)} = \chi_r^{(3)} \left[\frac{l_r}{l} \right] \left[\frac{n}{n_r} \right]^2 \left[\frac{I}{I_r} \right]^{1/2} \frac{\alpha l \exp(\alpha l/2)}{1 - \exp(-\alpha l)}, \quad (1)$$

where $\chi_r^{(3)}$ ($= 3.7 \times 10^{-14}$ esu)¹⁵ is the susceptibility of silica glass. The interaction length l_r in the silica glass plate is estimated from $l_r = [8\lambda/\pi][F/D]^2 \sqrt{e-T}$, assuming the effective power density is $\geq e^{-1} I_0$ under Gaussian beam treatment. In these equations, I_0 is the power density at the beam waist, and F and D represent the focal length (70 mm) and net beam width (20 mm) in front of the focusing lens, respectively.¹⁶ l is the film thickness. The refractive index (n) values for LaCuOS/Se, determined from ellipsometry measurements, vary in the range of 2–3 with a dull peak around the energy band gap, while a constant value ($n_r = 1.5$) is employed for silica glass in those wavelength regions. Absorption coefficients α of $1-2 \times 10^5$ cm⁻¹ at the exciton band peaks in LaCuOS/Se are nearly equal to that in our ZnO film at 3.3 eV (1.8×10^5 cm⁻¹, which agrees well with reported values).¹⁷ The α values of the films should be verified carefully since the calculated $\chi^{(3)}$ value is critically sensitive to α . The time dependences of photoluminescence intensities were measured using a streak camera with picosecond time resolution.

Figure 2 shows the $\chi^{(3)}$ values of the LaCuOS/Se films as a function of excitation wavelength in the fundamental absorption region at room temperature compared with optical absorption spectra of the films. Those of the ZnO film are also shown as a reference. The absorption spectrum of LaCuOS shows an exciton peak at band edge energy of 3.2 eV. On the other hand, two absorption bands around 2.9 and

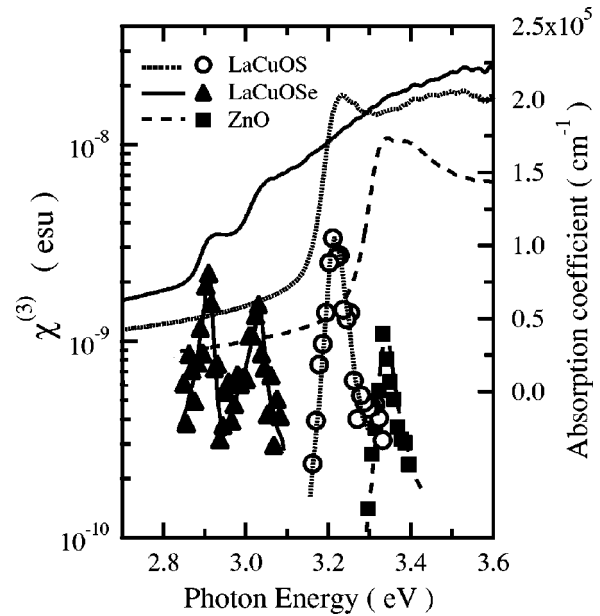


FIG. 2. $\chi^{(3)}$ and absorption spectra of LaCuOS, LaCuOSe and ZnO epitaxial thin films as a function of the excitation energy at room temperature.

3.1 eV were observed in LaCuOSe. Symmetry analysis verifies that the degenerative exciton state in LaCuOS is split into two singlet states in LaCuOSe due to spin-orbit interaction in the Se ion.¹⁰ Thus, these absorption bands are also attributed to excitons that are thermally stable even at room temperature due to the large binding energy.

The $\chi^{(3)}$ values for LaCuOS/Se depend strongly on the excitation wavelength and show sharp peaks just below these absorption band peaks, which clearly indicates $\chi^{(3)}$ resonance with the exciton absorption. The $\chi^{(3)}$ values of the LaCuOS/Se films at the peaks, determined according to Eq. (1), are enhanced to $2-4 \times 10^{-9}$ esu, which is larger than that of the ZnO film ($= 1 \times 10^{-9}$ esu),¹⁸ whereas LaCuOS/Se has smaller exciton binding energy. The larger $\chi^{(3)}$ values in LaCuOS/Se presumably are attributable to increases in the density of exciton states caused by exciton confinement in the $(\text{Cu}_2\text{S}_2/\text{Se}_2)^{2-}$ layer. These $\chi^{(3)}$ values are comparable with those for semiconductor CdS/Se nanoparticles dispersed in a glass matrix.¹⁹ The formation of solid solution for LaCuOS and LaCuOSe results in a modulation of the valence bands and, accordingly, the exciton resonance energy can be varied from 2.9 to 3.2 eV (390–430 nm).⁷ This region of energy just overlaps the working area of GaN-based laser. That is, the resonant nature of the $\chi^{(3)}$ spectrum in LaCuOS_{1-x}Se_x ($0 \leq x \leq 1$) is quite attractive for emerging applications such as an optical switching device that operates in UV light region.

The time response profile of the DFWM signals for LaCuOS/Se and ZnO as a function of the delay time between the pump and probe pulses are shown in Fig. 3. The excitation energies were fixed at the absorption band peaks of LaCuOS/Se and ZnO (3.35 eV), respectively. The response times (τ) are $\sim 250/300$ fs for LaCuOS/Se at room temperature, slightly larger than that of ZnO (~ 120 fs). On the other hand, the population decay time (τ_1) of excitons has been estimated as 30 ps for LaCuOS and 41 ps for ZnO through single exponential fitting for the photoluminescence decay curves shown in the inset. The large dissociation of τ from τ_1

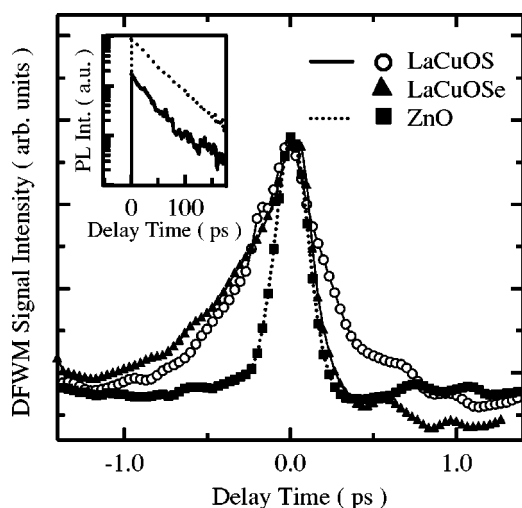


FIG. 3. DFWM signals as a function of the time delay at the absorption peak energy for LaCuOS, LaCuOSe and ZnO. The inset shows the photoluminescence (PL) decay profiles at PL peak energy 3.16 eV for LaCuOS and 3.27 eV for ZnO.

in both samples reveals that the DFWM response time is dominated not only by energy decay but also by the dephasing time (τ_2) of the transient grating induced by nonlinear polarization from the intense laser pulse irradiation, described by the relation $\tau = \tau_2/4$ in the exciton distribution with inhomogeneous broadening.²⁰

In conclusion, we have performed DFWM experiments in high-quality epitaxial thin films of layered compounds of LaCuOS/Se in the band gap energy region at room temperature. The $\chi^{(3)}$ spectrum of LaCuOS exhibits a sharp peak, resonant to the absorption band due to room-temperature exciton. On the other hand, the LaCuOSe spectrum has two sharp peaks, both of which are resonant to the excitons split by the spin-orbit interaction in the Se ion. The peak values are in the range of $2-4 \times 10^{-9}$ esu with an ultrafast relaxation time of 250–300 fs. The peak $\chi^{(3)}$ values of LaCuOS/Se are larger than that of epitaxial ZnO film, presumably reflecting the exciton confinement in the layer

($\text{Cu}_2\text{S}_2/\text{Se}_2$)²⁻. The large $\chi^{(3)}$ value at room temperature, fast relaxation time and controllability of the resonance energy for the $\chi^{(3)}$ peak from 2.9 to 3.2 eV by changing the Se content in $\text{LaCuOS}_{1-x}\text{Se}_x$ make them promising materials for nonlinear optical devices that operate in the UV light region.

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