Second-harmonic generation investigations of $Zn_{1-x}Cd_xSe$/ZnSe asymmetric coupled quantum wells

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Second-order nonlinear optical properties of strained $Zn_{1-x}Cd_xSe$/ZnSe asymmetric coupled quantum wells (ACQW's) have been investigated by using the reflective second-harmonic generation (SHG) technique. Compared with the SHG intensities in ZnSe bulk material, a significant enhancement of the signals was observed in ACQW's due to the centrosymmetry-breaking effect resulting from the strong-coupling interaction between adjacent quantum wells. The second-harmonic intensity was also found to increase with decreasing cadmium concentration x because of the second-harmonic off-resonance effect. Moreover, the SHG intensity versus the sample azimuthal angle shows an obvious in-plane anisotropy with a period of 180°, and our numerical calculations of the SHG dependence on azimuthal or polarization angle agreed well with experimental results.

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I. INTRODUCTION

Over the past decade there has been a growing interest in the nonlinear optical properties of wide-band-gap ZnSe-based II-VI semiconductor quantum wells (QW's) because of their applications for laser diodes and other photonic devices operating in the blue-green region of the visible spectrum.[1–4] The previous theoretical calculations and experimental work have demonstrated that the nonlinear optical coefficients, particularly the second-order susceptibility, are many times larger than those for bulk materials when asymmetry is introduced by a compositionally graded band gap or coupled wells.[5,6] However, little effort has been made to study the dependence of nonlinear optical properties on QW parameters for ZnSe-based materials. Studies of the relation between nonlinear optical properties and QW parameters such as the degree of asymmetry, interwell coupling, and in-plane anisotropy can help us in the design of desired nonlinear optical components.

Second-harmonic generation (SHG), being extremely sensitive to the symmetry of materials, is widely used to study the second-order properties of surface and interfaces (such as quantum wells) as a nondestructive and noncontact probe. In this paper, we observed anisotropic features of SHG intensity depending on the azimuthal angle of samples, and obtained the SH dependence on coupling effects, cadmium concentration, and incident polarization angle through measurements of SHG intensities in strained $Zn_{1-x}Cd_xSe$/ZnSe asymmetric coupled quantum wells (ACQW's). The experimental data are in good agreement with our predictive results obtained from theoretical formulas.

II. EXPERIMENTAL DETAILS

During our experiments, all QW samples were grown by molecular-beam epitaxy on GaAs (100) substrates, including four samples (1–4) with single asymmetric coupled quantum wells (SACQW's) and two samples (5 and 6) with multiple asymmetric coupled quantum wells (MACQW's). A 500-nm-thick undoped ZnSe buffer layer was first grown on a GaAs (100) substrate in every sample. Then the ZnCdSe/ZnSe SACQW's or MACQW's were grown on the buffer layers, and at last a 60-nm-thick undoped ZnSe cap layer concluded the growth. Each SACQW consists of two $Zn_{1-x}Cd_xSe$ wells ($x=0.24$) with thicknesses of L_1 and L_2 ($L_1 \neq L_2$), respectively, which are separated by a ZnSe barrier with thickness B (for samples 1–4, $L_1=3.8$ nm, $L_2=10$ nm, and $B=10$, 5, 2.5, and 1.25 nm, respectively). Each MACQW consists of ten periods of SACQW's separated by a ZnSe layer of thickness E between every two adjacent ones, as shown in Fig. 1. For comparison, a SHG study was also performed on a 500-nm-thick undoped ZnSe buffer layer (sample 7) grown under identical conditions to the QW samples. The absorption spectra of the MACQW's were measured by using a Shimadzu 365 spectrophotometer.

The experimental setup used for reflective SHG measurements is also shown in Fig. 1. The incident fundamental beam of 40 ps pulse width, 10 Hz repetition rate, and 1.5 mJ/pulse energy at 1.06 μm from an actively model-locked Nd:YAG (yttrium aluminum garnet) laser was directed by a telescope onto the samples as a spot of diameter 1 mm and at a fixed incident angle 45°. The SHG signals at 532 nm were detected by a water-cooled photomultiplier tube (PMT) and a boxcar averager and then displayed on an x-y recorder. An infrared-blocking filter $F1$ and a 532 nm interference filter $F2$ were inserted to ensure that only the second-harmonic radiation was detected. The SHG intensities from the samples were normalized to those from a z-cut quartz plate reference to eliminate the measurement errors caused by laser power fluctuations. The polarization angle α_p between the incident fundamental polarization direction and the incident plane could be changed by rotating $\lambda/2$ plates. Rotating the sample around the surface normal could change the azimuthal angle ϕ between the GaAs [110] direction and the incident plane. The analyzer polarization angle α_a between the output SHG polarization direction and the incident plane

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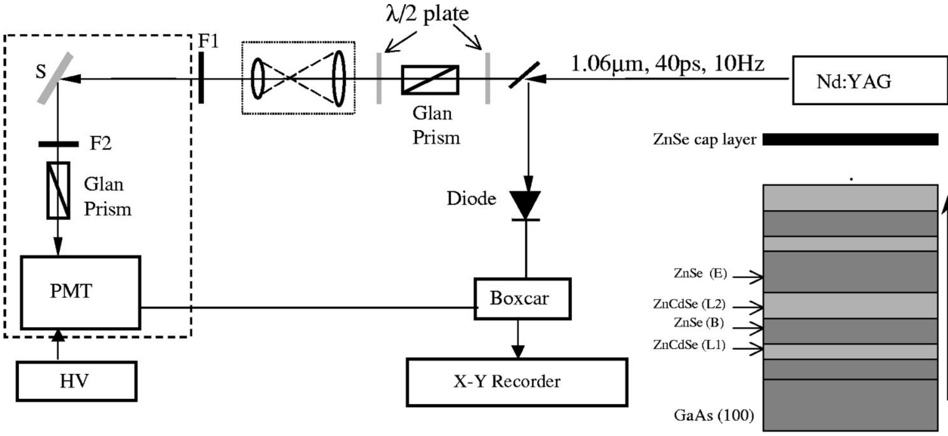

FIG. 1. Reflective SHG experimental setup and a structural diagram of the ACQW samples.

could be changed by rotating the analyzer (Glan prism), as shown in Fig. 2, where the z axis is along the surface normal and the y axis in the incident plane.

All the SHG experimental results were obtained at room temperature.

III. THEORY

It is well known that an unalloyed ZnSe crystal has the zinc-blende structure, a CdSe crystal has the wurtzite structure, and the alloy $Zn_{1-x}Cd_xSe/ZnSe$ has the zinc-blende structure for small cadmium concentration x.[7] So the structure of all parts in our ACQW samples could be regarded as zinc blende with a C_{4v} point group. The nonzero components of the second-order susceptibility $\chi^{(2)}$ in bulk material and ACQW's are given in Table I.[8]

In the mean-field approximation there are only three independent nonzero $\chi^{(2)}$ elements and the second-order polarization $P^{(2)}$ has been given previously as[3]

$$P_x^{(2)}=\chi_{xxz}^{(2)}E_xE_z\,,\quad P_y^{(2)}=\chi_{xxz}^{(2)}E_yE_z\,,$$

$$P_z^{(2)}=\tfrac{1}{2}[\chi_{zxx}^{(2)}(E_x^2+E_y^2)+\chi_{zzz}^{(2)}E_z^2]. \tag{1}$$

Here E is the electric field of the fundamental wave. With the coordinate system shown in Fig. 2, we can write

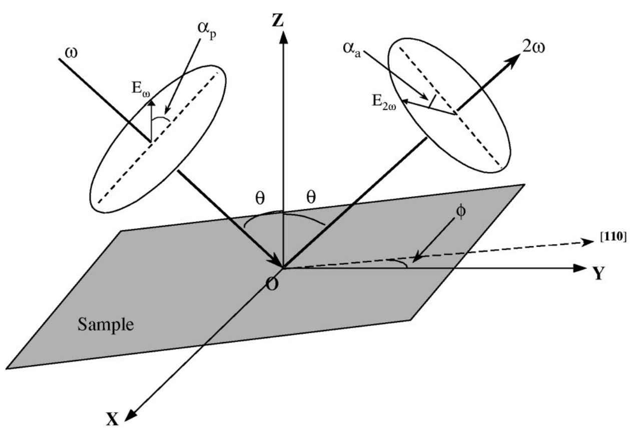

FIG. 2. Geometry of the reflective SHG measurements.

$$(E_x,E_y,E_z)=(E\sin\alpha_p, E\cos\alpha_p\cos\theta, E\cos\alpha_p\sin\theta). \tag{2}$$

The SHG intensity as a function of α_p, ϕ, and α_a can be written[9]

$$I(\alpha_p,\phi,\alpha_a)=K|P_x\sin\alpha_a-P_y\cos\theta\cos\alpha_a + P_z\sin\theta\cos\alpha_a|^2, \tag{3}$$

where K is a constant determined by the QW parameters.

Taking $\theta=45°$, $\phi=0°$, and $\alpha_a=0°$ or 90° in Eq. (3), we obtain

$$I_{p\ \mathrm{out}}(\alpha_p,0°,0°)=\tfrac{1}{16}K|(\chi_{zzz}^{(2)}-\sqrt{2}\chi_{xxx}^{(2)}-\chi_{zxx}^{(2)})\cos^2\alpha_p + 2\chi_{zxx}^{(2)}|^2E^4, \tag{4}$$

$$I_{s\ \mathrm{out}}(\alpha_p,0°,90°)=2K|\chi_{xxz}^{(2)}\sin(2\alpha_p)|^2E^4. \tag{5}$$

IV. RESULTS AND DISCUSSION

A. Dependence of SHG intensity on interwell coupling (barrier width)

The measured ratio of p in to p out $(\alpha_p=0°,\alpha_a=0°)$ SHG intensity versus barrier width B for SACQW samples 1–4 is shown in Fig. 3 with a fixed azimuthal angle $\phi=0°$; there were almost no signals from ZnSe bulk (sample 7) under the identical conditions. The SHG intensity and thus $\chi^{(2)}$ increase slowly as the barrier width B decreases from 10 to 5 nm, and then grow quickly when the barrier width continues to decrease. Since $\chi^{(2)}$ of a single QW should be zero due to the centrosymmetry of electronic and hole wave functions,[8] a larger degree of interwell coupling would break the symmetry and thus enhance the SHG signals.

TABLE I. Symmetry of second-order susceptibility $\chi^{(2)}$ in bulk material and ACQW.

Symmetry	$\chi^{(2)}$
O_h (bulk)	0
C_{4v} (ACQW)	$\chi_{zxx}^{(2)}=\chi_{zyy}^{(2)}$, $\chi_{xxz}^{(2)}=\chi_{yyz}^{(2)}$, $\chi_{xzx}^{(2)}=\chi_{yzy}^{(2)}$, $\chi_{zzz}^{(2)}$

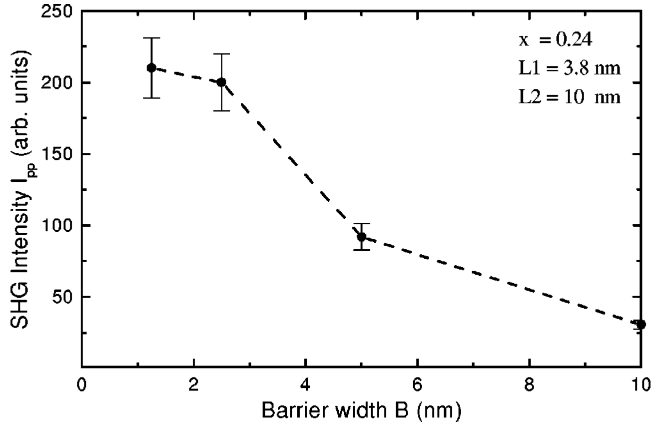

FIG. 3. Measured dependence of the ratio of *p* in to *p* out SHG intensity from the SACQW samples on barrier width *B* with $\alpha_p = 0°$, $\phi = 0°$, $\alpha_a = 0°$.

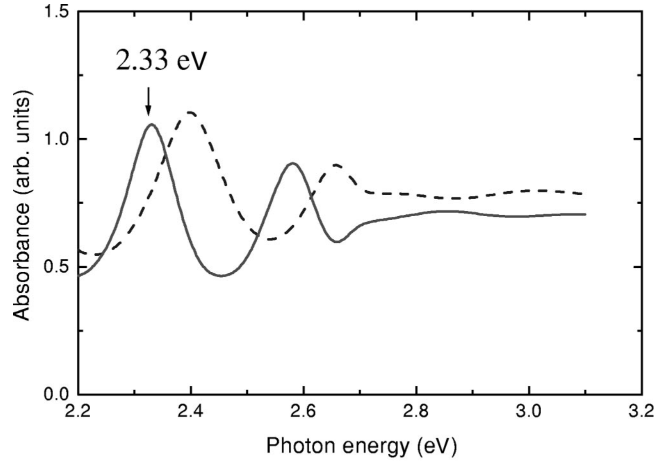

FIG. 4. Absorbance spectra of the ACQW samples (5, solid line; 6, dashed line).

B. Dependence of SHG intensity on cadmium concentration *x* (barrier height)

Barrier height (or well depth) will increase with increasing Cd composition *x*, while the band gap of the coupled QW's decreases.[10] The measured SHG intensities of I_{pp} (*p* in/*p* out, $\alpha_p = 0°$, $\phi = 0°$, $\alpha_a = 0°$) and I_{sp} (*s* in/*p* out, $\alpha_p = 90°$, $\phi = 0°$, $\alpha_a = 0°$) from MACQW's 5 and 6 measured at room temperature and the sample parameters are given in Table II. The table shows that a larger cadmium concentration *x* (barrier height or well depth) leads to smaller SHG intensities I_{pp} and I_{sp}.

To further clarify the relation between SHG intensities and cadmium concentration (or the band gap of the coupled QW's), we measured the absorption spectra of samples 5 and 6, as shown in Fig. 4. The absorption peak of sample 6 (2.34 eV or 529 nm) is closer to the SH photon energy 2.33 eV (or 532 nm) than that of sample 5 (2.40 eV or 517 nm). The smaller SHG intensities I_{pp} and I_{sp} from sample 5 than those from sample 6 were caused mainly by the second-harmonic off-resonance effect.[11]

C. Dependence of SHG intensity on azimuthal angle

The ratios *p* in of *p* out and *s* in to *p* out SHG intensities from sample 6 are changed by changing the sample azimuthal angle ϕ, as shown in Figs. 5 and 6, respectively. An obvious in-plane anisotropy with a period of 180° was observed and the *p* in/*p* out intensities were two orders of magnitude larger than the *s* in/*p* out ones. Notice that the SHG intensities from ZnSe bulk (sample 7) are at least one order of magnitude smaller than those from MACQW sample 6 due to its centrosymmetry.

TABLE II. SHG intensities I_{pp} and I_{sp} in quantum wells with different Cd compositions *x*.

Sample	L_1 (nm)	*B* (nm)	L_2 (nm)	*E* (nm)	*x*	I_{pp}	I_{sp}
5	1.2	1.2	2.4	6.0	0.38	1.7	0.02
6	1.2	1.2	2.4	6.0	0.30	20	0.6

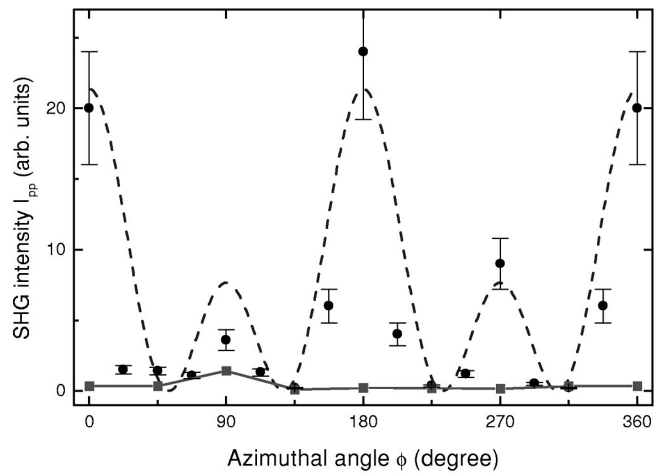

FIG. 5. Measured dependence of the ratio of *p* in to *p* out SHG intensity from (a) MACQW (sample 6, dots) and (b) ZnSe bulk (sample 7, squares) on the azimuthal angle ϕ. The broken line represents the theoretical calculation.

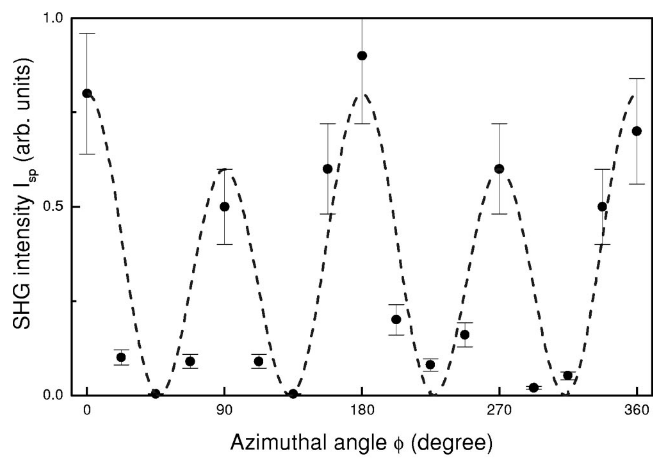

FIG. 6. Measured dependence of the ratio of *s* in to *p* out SHG intensity from MACQW sample 6 (dots) on the azimuthal angle ϕ. The broken line represents the theoretical calculation.

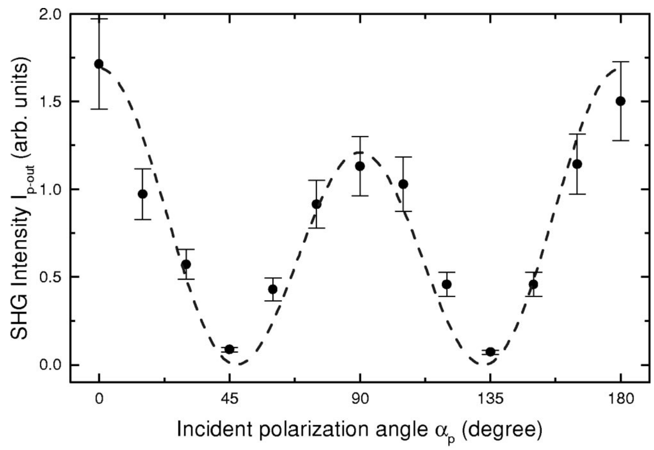

FIG. 7. Measured dependence of the p out SHG intensity from MACQW sample 5 (dots) on incident polarization angle α_p. The broken line represents the theoretical calculation.

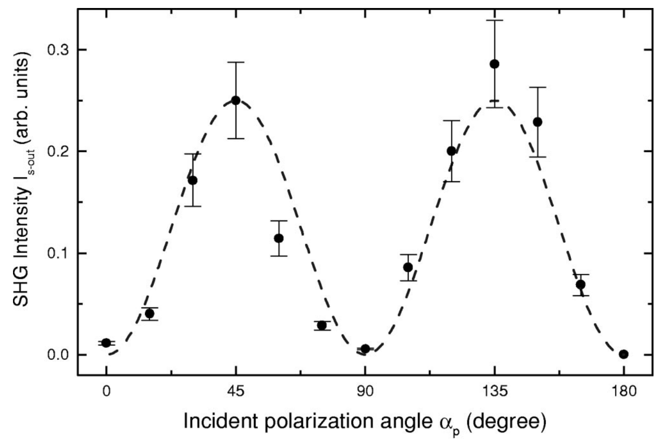

FIG. 8. Measured dependence of the s out SHG intensity of MACQW sample 5 (dots) on incident polarization angle α_p. The broken line represents the theoretical calculation.

In the electric-dipole approximation, the dependence of p in/p out and s in/p out SHG intensities from ACQW's on the azimuthal angle ϕ was deduced by Qu *et al.*[10,12] as

$$I_{pp}(\phi)\propto|c_{pp}^{(0)}+c_{pp}^{(2)}\cos(2\phi)+c_{pp}^{(4)}\cos(4\phi)|^2, \qquad (6)$$

$$I_{sp}(\phi)\propto|c_{sp}^{(0)}+c_{sp}^{(2)}\cos(2\phi)+c_{sp}^{(4)}\cos(4\phi)|^2, \qquad (7)$$

where the coefficients $c_{pp}^{(m)}$ and $c_{sp}^{(m)}$ give rise to the m-fold rotational symmetry of $E_{pp}^{(2\omega)}(\phi)$ and $E_{sp}^{(2\omega)}(\phi)$, respectively, and $c_{pp}^{(0)}$ and $c_{sp}^{(0)}$ represent the isotropic contribution. The electric-quadrupole contributions $c_{pp}^{(4)}$ and $c_{sp}^{(4)}$ can be neglected because they are much smaller than the electric-dipole contribution.[10] The results for $I_{pp}(\phi)$ and $I_{sp}(\phi)$ calculated by using Eqs. (6) and (7), as shown by the broken lines in Figs. 5 and 6, agreed well with the experimental data.

D. The dependence of SHG intensity on polarization angle

The measured SHG intensities $I_{p\text{ out}}(\alpha_p,0°,0°)$ and $I_{s\text{ out}}(\alpha_p,0°,90°)$ from sample 5 are shown in Figs. 7 and 8, respectively. The s out SHG intensity displays a periodic feature, $I_s(\alpha_p)\propto|\sin(2\alpha_p)|^2$, while the p out SHG intensity varies in a relatively complex way with two maxima at $\alpha_p=0°$ and 180°, two minima at $\alpha_p=45°$ and 135°, and a small peak at $\alpha_p=90°$. They all agree well with the theoretical values calculated from Eqs. (4) and (5), represented by the broken lines in Figs. 7 and 8. These properties are also in a good agreement with results of Refs. 13 and 14.

V. CONCLUSIONS

Our experimental results show that SHG intensity in strained $Zn_{1-x}Cd_xSe/ZnSe$ asymmetric coupled quantum wells is at least one order of magnitude larger than that from bulk ZnSe due to the centrosymmetry-breaking effect resulting from the strong interwell coupling interaction. It is also strongly dependent on the QW parameters. SHG intensity was found to increase with decreasing barrier width or cadmium concentration x (barrier height, well depth). Furthermore, an obvious in-plane anisotropy was observed with a period of 180° in our measured ratios of p in to p out and s in to p out SHG intensities. The s out SHG intensity versus the incident polarization angle displayed a periodic feature, $I_s(\alpha_p)\propto|\sin(2\alpha_p)|^2$, while the p out SHG intensity varied in a relatively complex way, which agreed well with the theoretical calculations.

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