Observation of the Forbidden Second-Harmonic Generation in Resonance with 2P Wannier Exciton in ZnSe Thin Films

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We have observed for the first time a drastic enhancement of the normally forbidden second-harmonic-generation signal when twice the incident photon energy is resonant with the excitation energy of a $2P$ exciton in thin ZnSe crystals. Measurements were performed, using a titanium-sapphire laser, at 4.2 K in such a geometrical configuration, $x(zz, x \text{ or } y)z$ or $x(yy, x \text{ or } y)z$, that transitions are forbidden by the usual selection rules. The results are shown to be well accounted for in the framework of a time-dependent perturbation formalism.

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Up until now, second-harmonic-generation (SHG) coefficients, expressed as the usual third rank tensor d_{ijk}, have been measured in a large number of crystals lacking inversion symmetry with a view to searching for new nonlinear optical materials. The frequency dispersion of d_{ijk} has also attracted much interest [1]. This includes a resonant effect of d_{ijk}, i.e., an enhancement of SHG which occurs when one of the relevant photon energies is resonant with that of a specific one-photon allowed state such as an S-type Wannier exciton [2,3] in inorganic crystals and a Frenkel exciton [4,5] in molecular crystals. The involvement of a polariton effect has also been studied in detail and a relationship to two-photon absorption has been previously discussed [6–9]. However, no resonant SHG phenomenon concerning a state forbidden by one-photon absorption has been reported until now.

In this Letter, we report that a dramatic enhancement of the "configuration forbidden" SHG signal has been observed in thin ZnSe films when twice the incident photon energy, $2\hbar\omega_i$, coincides with the excitation energy of a $2P$ exciton. It is known [10,11] that in ZnSe the $2P$ exciton is a one-photon forbidden but two-photon allowed transition, and that the reverse is true for the $1S$ exciton. In other words, the two-band model [12] is established to be valid for Wannier excitons in II-VI and III-V compounds [13]. This work therefore represents a first demonstration of resonant enhancement of a SHG signal at one-photon forbidden levels. All measurements were performed in such scattering configurations that the SHG signal due to the first-order process was not observed in the off-resonance case.

Single-crystal samples of ZnSe were grown by metal-organic chemical-vapor deposition (MOCVD) on a single-crystal substrate of GaAs, with one (z axis) of the cubic axes perpendicular to the film. The experimental data discussed here were obtained from two samples: a 2-μm-thick and a 5-μm-thick film. These samples were directly immersed in liquid helium using a cryostat. A custom-made titanium-sapphire laser pumped by output pulses of 532-nm wavelength from a Q-switched Nd-doped yttrium-aluminum-garnet laser (Quantronix model 532) was employed as a wavelength-tunable source for excitation. The representative characteristics of the titanium-sapphire laser were 0.5-kW output peak power, 30-ns pulsewidth, and 3-kHz repetition rate. The tuning accuracy of the laser was about 1 Å at $\sim$880 nm, corresponding to a $\sim$0.3-meV uncertainty in the energy determination of $2\hbar\omega_i$. The 90° scattering geometry [14] was adopted in which the incident laser beam propagated along one axis (x axis) of the crystal and scattered light was observed in a direction (z axis) perpendicular to the film. The scattered signal was collected by a lens, dispersed by a monochromator (Ritsu Co., MC-25N), and then detected by a gated optical multichannel detector (Tracor-Northern Co., TN 6133) cooled to $-30\,^{\circ}$C.

Examples of the emission and scattered signal spectra are shown in Fig. 1, which were obtained from the 5-μm-thick sample in the resonant case where $2\hbar\omega_i$ approximately coincides with the excitation energy of a $2P$ exciton. The spectra were observed in the configuration of $x(yy, \text{unp})z$ in the Porto notation, where the symbols in the parentheses, yy and unp refer to the polarization directions of incident and scattered light, respectively, the latter being "unpolarized." It is clearly seen that in addition to the recombination emissions of free and bound $1S$ excitons, a strong signal manifests itself just at $2\hbar\omega_i$, as $2\hbar\omega_i$ approaches the energies of 2.8182 and 2.8156 eV. As will be seen below, those values correspond exactly to the excitation energies of the $2P$ excitons, which are split due to residual strain in the ZnSe film. Under the same detecting conditions, the "SHG" signal was below the noise level when the value of $2\hbar\omega_i$ was remote from the $2P$ exciton energies. Both x- and y-polarized SHG signals were observed.

A plot of the forbidden SHG signal intensity as a function of $2\hbar\omega_i$, i.e., a two-photon excitation spectrum of the SHG, is presented in Fig. 2. For simplicity, no corrections were made for variation of the effective coherence

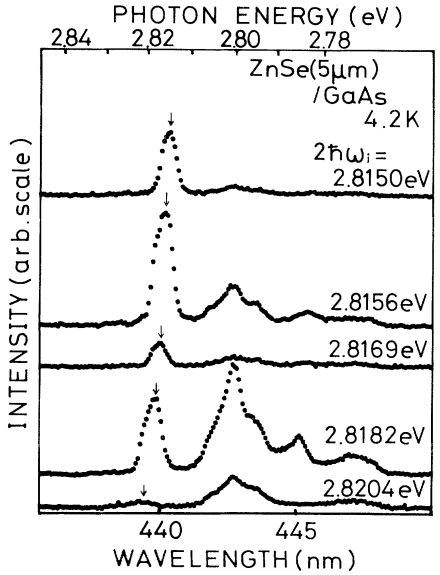

FIG. 1. Examples of SHG profiles of the 5-μm-thick ZnSe film for the $x(yy,\ \mathrm{unp})z$ configuration. The signals around 442.5 nm are recombination emissions from free and bound $1S$ excitons. The arrows indicate the SHG signals. The spectral resolution is 8 Å.

length [2,3] expressed as $l_c=(|\Delta\mathbf{k}|^2+\alpha^2)^{-1/2}$ with wavelength, where α is the absorption coefficient for the signal and $\Delta\mathbf{k}=2\mathbf{k}_i-\mathbf{k}_s$ with $\mathbf{k}_i$ ($\mathbf{k}_s$) being the wave vector of the incident (scattered) wave. This is because $|\Delta\mathbf{k}|$ is 1 order of magnitude larger than α ($\sim 3\times 10^4$ cm^{-1} for the $2P$ exciton region) [15], and l_c is dominated by $\Delta\mathbf{k}$. For comparison, two-photon absorption spectra obtained from the same sample are also shown in Fig. 2. Because of internal stress caused by the lattice mismatch between ZnSe and GaAs, the $2P$ exciton state is found [16] to split into two states (i.e., the heavy- and light-hole $2P$ exciton states), separated by about 2.5 meV. The polarization dependence indicates that the high-energy peak corresponds to the heavy-hole $2P$ exciton and the low-energy peak to the light-hole one [16]. From Fig. 2, it is evident that the forbidden SHG signal emerges as the result of strong resonance with the $2P$ excitons. The fact that the polarization selection rules for the SHG is the same as those for the two-photon absorption strongly suggests that both transitions involve the same states as intermediates. As for the sample of 2 μm thickness, similar results were also obtained (aside from the energy separation of $\sim$3.7 meV) between the two $2P$ peaks (Fig. 3). The possibility that the signal originates from recombination emission from the $2S$ exciton existing closely to the $2P$ exciton, rather than the inherent SHG, may be ruled out. This is because in comparison to the recombination emission from the $1S$ exciton, the intensity should be at least 2 orders of magnitude smaller reflecting the faster nonradiative decay and smaller oscillator strength, but experimentally this is not the case as can be seen from Fig. 1. More importantly, the signal is found to shift with changes in the excitation photon energy.

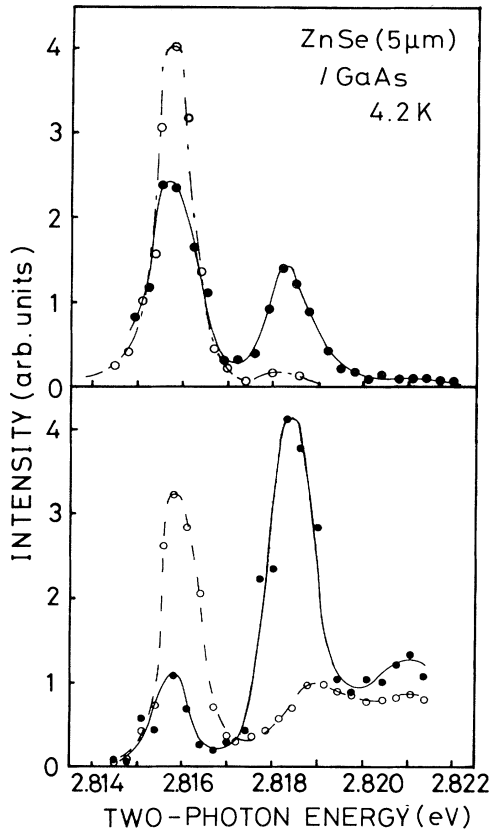

FIG. 2. Upper part: SHG intensities from the 5-μm-thick ZnSe film as a function of $2\hbar\omega_i$ for $x(zz,\ \mathrm{unp})z$ (open circles) and $x(yy,\ \mathrm{unp})z$ (solid circles) configurations. Lower part: two-photon absorption spectra of the 5-μm-thick ZnSe film obtained for the z-polarized incident beam, i.e., $\mathbf{E}_i\|\mathbf{z}$ (open circles), and for $\mathbf{E}_i\|\mathbf{y}$ (solid circles). The lines are guides for the eye.

Now, let us consider the mechanism responsible for this observed phenomenon. As already described, the appearance of a SHG signal in the nonresonance region should be forbidden in the present geometrical configuration and in the electronic-dipole approximation, since the nonvanishing SHG tensor components are only off-diagonal ones, i.e., $d_{xyz}=d_{yzx}=d_{zxy}$, being a result of the $\bar{4}3m$ symmetry. However, a weak SHG signal, originating from a quadrupolar term [17,18] such as $\chi_{ijlm}E_j\nabla_l E_m$ or $i\chi_{ijlm}k_l E_j E_m$, should appear. Consequently, the SHG signal can emerge in the present configuration (direction) with the relevant coherence length, $l_c=\pi/|2\mathbf{k}_i-\mathbf{k}_s|$, being of the order of $\lambda/2$ with λ the wavelength of the incident wave. The polarization of the SHG signal is theoretically predicted to be parallel to the x axis in this process.

Therefore, a clue to understanding the presence of this

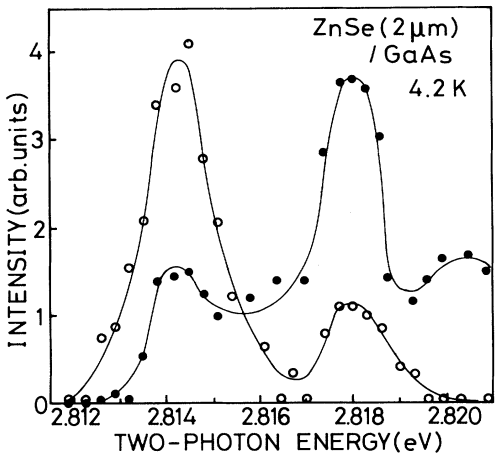

FIG. 3. SHG intensity from the 2-μm-thick ZnSe film as a function of $2\hbar\omega_i$ in the $x(yy, \text{unp})z$ geometry (open circles) and two-photon absorption spectrum for $\mathbf{E}_i \| \mathbf{y}$ (solid circles). The lines are guides for the eye.

weak SHG signal might be to invoke a quadrupolelike transition [19] for one of three successive virtual electronic transitions involved in the time-dependent perturbation formalism. In this case, the dominant contribution to the forbidden SHG tensor d_{jlm} comes from terms such as

$$d_{jlm} \propto \sum_I \frac{\langle g|e^{-2\mathbf{k}_i\cdot\mathbf{r}}\mathbf{e}_j\cdot\mathbf{p}|2p\rangle\langle 2p|\mathbf{e}_l\cdot\mathbf{p}|I\rangle\langle I|\mathbf{e}_m\cdot\mathbf{p}|g\rangle}{(E_{2P}-2\hbar\omega_i+i\Gamma_{2P})(E_I-\hbar\omega_i)} \tag{1}$$

for the $2P$ resonance, where $\mathbf{e}_j$ is a unit polarization vector of the light beam $\mathbf{E}_j$, Γ_{2P} represents the damping constant of the $2P$ exciton, and I refers to the intermediate states with the energy E_I which can be reached by one-photon absorption. According to the $\mathbf{k}\cdot\mathbf{p}$ perturbation theory, the matrix element for the transition $|2p\rangle \rightarrow |g\rangle$ may be written as

$$\langle g|e^{-\mathbf{k}_s\cdot\mathbf{r}}\mathbf{p}|2p\rangle \simeq \left(-\hbar\mathbf{k}_s\cdot\mathbf{r}_{v,c}+\frac{\partial\mathbf{p}_{v,c}}{\partial\mathbf{k}}\cdot\right)_{k=0}\left(\frac{\partial\Phi_{2p}}{\partial\mathbf{r}}\right)_{r=0}, \tag{2}$$

where c (v) refers to the conduction (valence) band, and Φ_{2p} is the hydrogenic envelope function of the $2p$ type. The first and second terms in Eq. (2) lead respectively to the quadrupole and weakly allowed dipole transitions. The magnitude of $\nabla_k\mathbf{p}_{v,c}$ could be roughly estimated from the two-photon absorption coefficient for $1S$ exciton resonances or band-to-band transitions near the band edge. Such an estimation reveals that the magnitude of the matrix element for the weakly allowed transition in ZnSe is of the same order of magnitude as that for the quadrupole transition, and is about 3 orders of magnitude smaller than that for the usual dipole-allowed transitions (e.g., the transition $|1s\rangle \rightarrow |g\rangle$). However, it should be noted that a striking enhancement of the signal should be expected by a factor of $E_{2P}-2\hbar\omega_i+i\Gamma_{2P}$. This factor can become as small as ~ 1 meV judging from the spectral widths from the two-photon absorption spectra for $2P$ excitons. Compared to the off-resonance case $E_{2P}-2\hbar\omega_i \sim 1$ eV, therefore, a nearly thousandfold enhancement in d_{ijk} is expected under the resonance. Consequently, the magnitude of the forbidden SHG tensor under the resonance should become comparable to that of the usual SHG tensor. This could be the reason why an anomalously strong SHG signal has been observed in the present experiment. The polarization property of the signal, which is found to be polarized in both x and y directions, is one characteristic of the $2P$ resonance. In ZnSe, it is well known that a p-like envelope and a hole spin are strongly coupled [10]. It can be shown from symmetry considerations that both x- and y-polarized signals should be observed when the transition occurs via envelope-hole coupling states as intermediates. Thus, we are led to the conclusion that the above interpretation is perfectly reasonable. So far, corrections due to reabsorption of the signal and variation of l_c with wavelength have been neglected for simplicity. Obviously, those corrections are needed for accurate discussions. A quantitative analysis including this will be presented in a forthcoming paper.

As mentioned above, there exist small strains in ZnSe films due to the lattice mismatch between ZnSe and GaAs. Thus one may think that the normally forbidden SHG signal appears as a result of stress-induced changes in the bulk of the film. However, this is not true in our case. Under in-plane biaxial stress, the crystal symmetry of the ZnSe film changes from $\bar{4}3m$ to $\bar{4}2m$. The SHG tensor d_{ijk} in the $\bar{4}2m$ system obeys the same symmetry restrictions as that in the $\bar{4}3m$ system [19]. Consequently, the SHG is still forbidden in the present configuration. There is another possibility that the surface layers may contribute to the appearance of the SHG. However, this contribution seems to be very small, because the surface SHG is not allowed for the present polarization [20]. Further, this conclusion is also borne out by the fact that the SHG excitation peaks coincide exactly with the two-photon absorption peaks in the bulk of the film.

Next, we briefly mention that resonant SHG signals were also observed in the $1S$ exciton region, which were somewhat less intense than those due to $2P$ excitons. The result exhibits rather complicated features, indicating that polariton effects are undoubtedly involved. This is very reasonable because of strong exciton-photon interaction with the dipole-active $1S$ excitons, as evidenced for excitons in molecular crystals [5,6] as well as in inorganic crystals [7]. In contrast, it may not be necessary to take into account polariton effects when considering the $2P$ exciton, because the transverse-longitudinal splitting estimated from the oscillator strength is much smaller than the homogeneous width of the $2P$ exciton line [10]. This may be also justified by the fact that no strong SHG sig-

nal due to phase matching was observed in the forward direction.

The present phenomena will provide a new spectroscopic tool for studying electronic states, through $2P$ excitons, in thin-film samples recently developed, such as quantum wells. The measurement gives rather direct information compared to emission-probed two-photon absorption because unknown relaxation mechanisms are not involved. Moreover, the fact that the signal should appear just at $2\hbar\omega_i$ seems quite attractive from the spectroscopic point of view, because the measurement would not be hampered by other complicated emission lines.

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