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Generation of resonant second harmonic in multiple Si/SiO₂ quantum wells

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(Submitted 28 September 1995)

Zh. Éksp. Teor. Fiz. 109, 1240–1248 (April 1996)

The paper presents a spectroscopic study of optical second harmonics generated in multiple amorphous Si/SiO₂ quantum wells with a various thicknesses of silicon layers. The spectral dependence of the Fourier components of the second-harmonic intensity versus azimuthal angle has a resonant peak close to the double energy of the optical transition in the Si/SiO₂ quantum well. These spectra indicate that the intensity of the second harmonic is sensitive to the quantum-size effects in such structures. The resonant energies vary with the silicon layer thickness, and this dependence is in qualitative agreement with the calculation using the simple model of a rectangular quantum well. © 1996 American Institute of Physics. [S1063-7761(96)01204-8]

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1. INTRODUCTION

Recently much attention has been focused on low-dimensional semiconductor structures, such as quantum dots and wells, as well as multiple quantum wells and superlattices, which have been extensively used in both fundamental and applied research. Electronic states in such structures are fundamentally different from those in bulk semiconductors. The confinement of charge carriers in potential wells results in so-called quantum-size effects, which essentially change the electronic spectrum, for example, generating subbands or discrete levels in the valence and conductance bands of the quantum-well semiconductor. The progress in semiconductor technology has brought forth devices using quantum-size effects. Presently devices based on multiple quantum wells show promise in various fields of micro- and optoelectronics.

Various optical and modulation techniques are extensively employed in studies of electronic spectra of multiple quantum wells.¹ The efficiency of nonlinear optical techniques in this field has been demonstrated recently. The generation of second and third harmonics has been studied both experimentally and theoretically.^{2–6} The spectroscopy of optical harmonics generated in semiconductor structures has been successfully used to investigate transitions between different subbands, the more so since the efficiency of the harmonic generation is several orders higher around a resonance.² This effect has been studied mostly in quantum wells built from III-V (such as GaAs/AlGaAs) and II-VI (ZnSe/ZnCdSe) semiconductors. Unlike these thoroughly investigated crystalline materials, there are few publications about amorphous quantum wells.^{7–10} The interest in amorphous multiple quantum wells, such as Si/SiO₂ quantum

wells, arises because that they can be built from materials with lattices that do not match in crystalline states, hence crystalline quantum wells cannot be fabricated from them. Si/SiO₂ quantum wells are more interesting since the potential barrier height in them is an order of magnitude larger than in previously studied quantum wells and superlattices.⁷

Some properties of Si/SiO₂ multiple quantum wells have been investigated using linear optical techniques. In particular, it was demonstrated by Zayats *et al.*⁸ that the quantum-size effects affected photoluminescence and excitation luminescence spectra, and therefore the energies of interband transitions could be estimated. These energies were derived from modulated absorption and reflection spectra.^{7,9,10}

All this indicates that nonlinear optical studies of Si/SiO₂ multiple quantum wells, particularly the second-harmonic generation, may provide new interesting information. The parameters of the second harmonic are highly sensitive to both structure and electronic spectra of interfaces and surface layers.¹¹ An important point is that the second-harmonic intensity depends on properties of any interface, including an interface between two solids. It has been demonstrated in recent years that the second-harmonic technique yields a lot of information about the Si/SiO₂ interface.^{12–16} On the other hand, little information about the nonlinear optical properties of Si/SiO₂ multiple quantum wells has been available.^{17,18}

The paper presents a spectroscopic investigation of the resonant second harmonic generated in Si/SiO₂ multiple quantum wells with different thicknesses of silicon and silicon oxide layers in the 2.9–3.4-eV range of the second-harmonic energy. We have found that some features of the

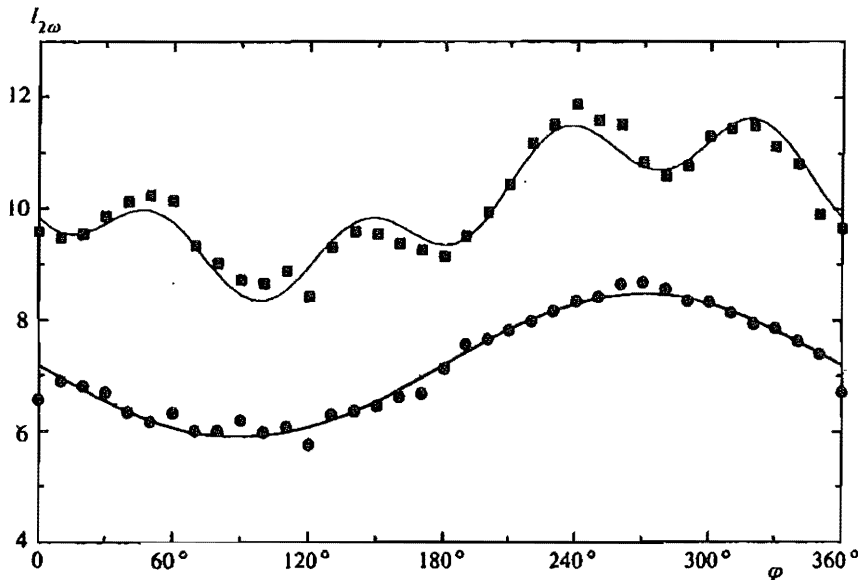


FIG. 1. Intensity of p -polarized second harmonic generated by p -polarized fundamental beam (p - p curves) at wavelengths of 737 nm (full squares) and 798 nm (full circles) versus azimuthal angle measured in the 11/10 sample (points) and calculated by Eq. (2) (solid lines).

second-harmonic spectrum in multiple quantum wells are due to the quantum-size effects.

2. EXPERIMENT

Amorphous multiple quantum wells were fabricated by magnetron sputtering¹⁹ on Si (100) substrates with silicon layer thicknesses of 5.5 or 11 Å and SiO₂ thickness of 10 Å. The total number of wells was forty, and the upper and lower layers were SiO₂. In the text we will denote these structures as 5.5/10 and 11/10.

The second optical harmonic was generated by a fundamental radiation of a titanium-sapphire laser operating in the 710–840 nm spectral range at an average power of 0.1 W and a repetition rate of 82 MHz generating pulses with a width of 100 fs. Given this pulse width, the spectral resolution of our measurements was limited to 15 nm. The fundamental beam was focused on a sample by an achromatic lens with a focal length of 30 cm to a spot about 200 μm in diameter. The second harmonic was recorded in the reflection configuration by a cooled PMT, and the signal was processed by a photon-counting system.

The angle of incidence of the pumping beam was 45°. In order to detect structural features of the quantum wells, both fundamental and second-harmonic radiation could be p - or s -polarized and the second-harmonic intensity versus the azimuthal angle was recorded by rotating the sample around its normal.

To normalize the intensity of the second harmonic generated at different wavelengths, we measured the intensity of the second harmonic generated in a quartz plate in the reflection configuration.

3. ANALYSIS OF EXPERIMENTAL DATA

In the case of multiple quantum wells built from totally amorphous silicon and silicon dioxide layers deposited on a Si(100) substrate, one can expect the second-harmonic intensity as a function of the azimuthal angle to be isotropic if it

is generated only in the quantum wells (this is possible if the penetration depth of either the fundamental beam or the second harmonic in the structure is less than its total thickness), or to have fourth-order symmetry if a part of the signal is generated in the substrate.

We found (Fig. 1) that for our samples with multiple quantum wells, the second-harmonic intensity as a function of the azimuthal angle has four maxima and is overlaid with an additional function with one peak. This feature on the curve of the second-harmonic intensity versus angle is probably due to the fabrication technique, since the substrate was not rotated in the process of magnetron sputtering that might produce a specific axis in the sample plane.

For the symmetry of these samples, we may express the second-harmonic intensity as

$$I_{2\omega} = |A + B \sin(\varphi + \varphi_1) + C \sin(4\varphi + \varphi_4)|^2, \quad (1)$$

where A , B , and C are complex constants, φ is the azimuthal angle, and φ_1 and φ_4 are the phases of respective anisotropic components.

Fourier transforms of the azimuthal dependence demonstrated that their first and fourth harmonics are smaller than the zeroth component, and other harmonics of the Fourier series are comparable with the noise intensity. Thus we have $A \gg B$ and $A \gg C$, so that Eq. (1) can be transformed to

$$I_{2\omega} = |A|^2 + 2 \operatorname{Re}(AB) \sin(\varphi + \varphi_1) + 2 \operatorname{Re}(AC) \times \sin(4\varphi + \varphi_4), \quad (2)$$

where the terms with the factors B^2 , C^2 and BC are omitted. In this notation the amplitudes of the zeroth, first, and fourth Fourier coefficients are expressed as $a_0 = |A|^2$, $a_1 = 2 \operatorname{Re}(AB)$, and $a_4 = 2 \operatorname{Re}(AC)$.

The solid lines in Fig. 1 are fits to experimental data calculated using Eq. (2) for the intensity of the p -polarized second harmonic generated in the 11/10 sample by a p -polarized fundamental beam (p - p curves) at wavelengths 737 and 798 nm.

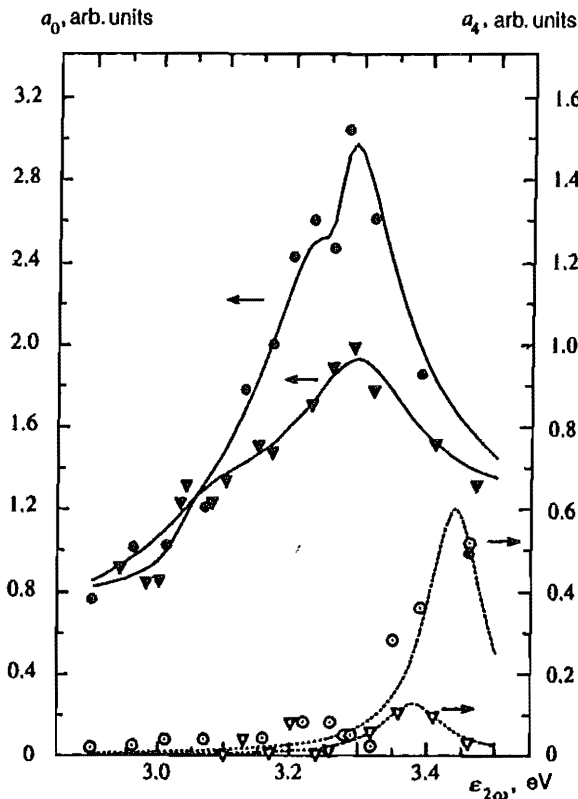


FIG. 2. Amplitudes of Fourier components a_0 (filled symbols) and a_4 (open symbols) versus the second-harmonic photon energy in the p - p configuration. The points mark measurements of samples 11/10 (triangles) and 5.5/10 (circles), the solid lines are calculations of a_0 via Eq. (6) (left vertical scale; the parameters of resonances in multiple quantum wells are listed in Table I), the dotted lines are fits of Lorentzian contours to experimental data (right vertical scale).

Figure 2 shows the factors a_1 and a_4 measured in the p - p configuration versus wavelength (in our experiments the error for a_0 and a_1 was 5% and for a_4 20%). These curves have well defined resonances, which will be discussed in the next section.

Figure 3 shows the Fourier coefficients a_1 in the p - p configuration and a_0 in the s - p configuration (p -polarized second harmonic generated by an s -polarized fundamental beam) versus the second-harmonic photon energy. The spectrum of the coefficient a_1 also has a peak centered at the same energy as the peak of a_0 . The coefficient a_0 in the s - p configuration is a monotonic function of the fundamental frequency. The intensity of the s -polarized second harmonic could not be distinguished against the noisy background for s - or p -polarized fundamental beams.

4. DISCUSSION

In the spectral range studied, the second harmonic of the silicon substrate has resonances, so the spectra of the second harmonic generated in the quantum wells must be separated from the spectrum that is due to the substrate to study their peaks.

The second harmonic generated in crystalline silicon has a resonance at 3.37 eV due to the transition between the bands Λ_1 and Λ_3 in the Γ - L direction of the Brillouin zone

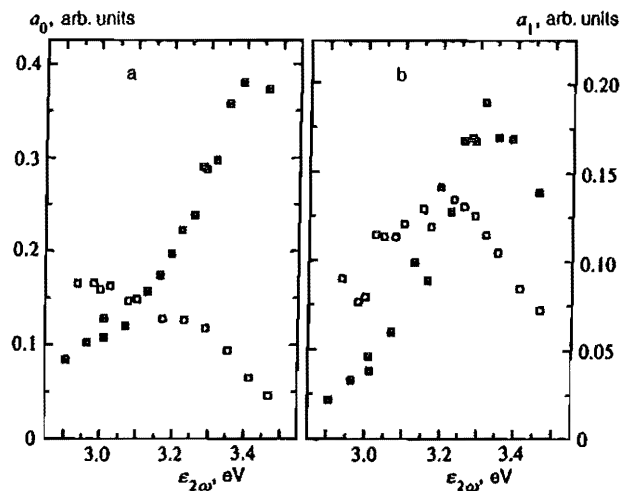


FIG. 3. Amplitudes of Fourier components a_0 measured in (a) s - p and (b) p - p configurations versus the second-harmonic photon energy. Filled squares denote measurements for the 5.5/10 sample, open squares for the 11/10 sample.

(E_1 -transition). This resonance, which we will call a bulk resonance, also appears in linear optical effects, and its energy was measured using ellipsometry and electric-field-modulation reflection spectroscopy.²⁰ The second resonance has an energy of 3.3 eV and is called a surface resonance. It was first observed in the spectrum of the second harmonic generated on various silicon surfaces²¹ and is due to the same transition but is in the surface layer, where the inversion symmetry is broken and the lattice parameters are different from those in the bulk.^{22,23}

The nonzero Fourier coefficient a_4 obtained for our samples indicates that a fraction of the second-harmonic signal is generated in the substrate with a fourth-fold symmetry. Since the nonlinear dipole response of the Si(100)/SiO₂ interface does not contain anisotropic components,²¹ the four-fold symmetry of the second-harmonic anisotropic dependences should be due to bulk Si(100).

By approximating the spectral curve of a_4 for the 11/10 sample with a Lorentzian with a maximum at 3.37 eV, we have obtained a line width of about 0.1 eV. The maximum of spectral curve for a_4 for the sample 5.5/10 is shifted to the high-energy side, and we approximated it with a Lorentzian with a maximum at 3.43 eV. There may be several causes for this shift. First, the coefficient a_4 in the Fourier series of the second-harmonic intensity is a function of C and A and the phase difference between these two complex parameters. For example, if the phase difference is a function of frequency (which is typical of resonances), the peak shape may be altered and the resonant energy may shift. Second, the shape and position of the resonant peak depends on linear characteristics of multiple quantum wells, such as absorption.

Let us discuss the spectral dependence of the coefficient a_0 for multiple quantum wells in the samples 11/10 and 5.5/10 recorded in the p - p configuration. The curves in Fig. 2 can be seen to differ from each other and from the bulk-silicon spectrum.

Both curves have maxima around 3.3 eV. Since a fraction of the second-harmonic signal originates from the substrate, the spectra of our samples should contain surface resonances due to the silicon substrate. Apparently, these 3.3-eV peaks are due to the surface resonance.

The spectrum of a_0 for the 11/10 sample has a well defined shoulder around 3.05 eV. Since the second-harmonic spectrum due to bulk silicon is monotonic in this range, we ascribe this feature to the transition between the first subbands of the quantum well.

The spectrum of a_0 for the 5.5/10 sample is also different from that of bulk silicon. Firstly, the width of the resonant peak in the 3.2–3.3-eV range is notably larger than for bulk silicon (in silicon the resonance FWHM is 0.1 eV²¹); second, the peak frequency is shifted to the low-energy side. Therefore, it is quite natural to interpret this peak as a superposition of two resonances: the first one due to the silicon substrate with a fixed resonance energy and width, and the second one due to multiple quantum wells. The parameters of the second resonance must be determined.

In order to describe spectra of nonlinear optical parameters of the samples, we must determine their nonlinear susceptibilities as functions of light frequency. Consider a quantum well containing one subband in the valence band and one subband in the conduction band of the semiconductor. The wave functions and energies of their states are $\varphi_v(z)e^{i\mathbf{p}\mathbf{r}}$ and $E_v - p^2/2m^*$ in the valence band, and $\varphi_c(z)e^{i\mathbf{p}\mathbf{r}}$ and $E_c - p^2/2m^*$ in the conduction band, respectively (here z -axis is perpendicular to the quantum-well layers, \mathbf{r} lies in the horizontal plane, \mathbf{p} is the two-dimensional quasi-momentum, and m^* is the effective mass of electron). Strictly speaking, the electron wave function in an amorphous material is not a plane wave because of the disordered atomic structure. Nonetheless, we hope that this approach can be used as an approximate description of amorphous layers. Assume that the resonant energy $E_c - E_v$ is close to the fundamental photon energy. In this case the nonlinear susceptibility of the quantum well is

$$\chi_{\text{qw}}^{(2)} = \alpha \int \frac{\theta(\hbar\omega - (E_c - E_v)) d\omega'}{\omega - \omega' + i\delta_{\text{qw}}}. \quad (3)$$

Here ω is the fundamental radiation frequency, $\theta(x)$ is the Heaviside step-function, the constant δ_{qw} determines the line width, and the coefficient α is proportional to the resonance amplitude. After integration we have

$$\chi_{\text{qw}}^{(2)} = \alpha \left\{ \frac{1}{2} \ln \left[\frac{(\omega - (E_c - E_v)/\hbar)^2 + \delta_{\text{qw}}^2}{\Omega^2} \right] + i \left[\frac{\pi}{2} + \tan^{-1} \frac{\hbar\omega - (E_c - E_v)}{\delta_{\text{qw}}} \right] \right\}. \quad (4)$$

Here Ω determines the energy scale in the system. The parameter $\hbar\Omega$ equals several electronvolts; it is included in Eq. (4) as the argument of a logarithmic function, so its exact value is not essential.

The resonance due to bulk silicon can be described by a Lorentzian with a resonant frequency $\omega_{\text{Si}} = 3.3$ eV and a half-width $\delta_{\text{Si}} = 0.1$ eV:

TABLE I. Parameters of transitions in quantum wells and substrates.

Sample	Parameters of transitions in wells	Parameters of transitions in substrates	Nonresonant susceptibility
11/10	$E_c - E_v = 1.52$ eV $\delta_{\text{qw}} = 0.015$ eV $\alpha = 0.06$	$\hbar\omega_{\text{Si}} = 3.3$ eV $\delta_{\text{Si}} = 0.1$ eV $\beta = 0.02$	$\chi_{\text{nr}}^{(2)} = 0.57i$
5.5/10	$E_c - E_v = 1.63$ eV $\delta_{\text{qw}} = 0.01$ eV $\alpha = 0.41$	$\hbar\omega_{\text{Si}} = 3.3$ eV $\delta_{\text{Si}} = 0.1$ eV $\beta = 0.015$	$\chi_{\text{nr}}^{(2)} = 0.06 - 0.56i$

$$\chi_{\text{Si}}^{(2)} = \frac{\beta}{2\omega - \omega_{\text{Si}} + i\delta_{\text{Si}}}, \quad (5)$$

where β is the resonance amplitude.

Beside these two resonances, our spectra contain a nonresonant background described by the nonlinear susceptibility component $\chi_{\text{nr}}^{(2)}$, which is independent of the light frequency. If we ignore the dispersion of linear optical parameters of multiple quantum wells, the second-harmonic intensity is described by the following equation:

$$I_{2\omega} \propto |\chi_{\text{qw}}^{(2)} + \chi_{\text{Si}}^{(2)} + \chi_{\text{nr}}^{(2)}|^2. \quad (6)$$

The solid lines in Fig. 2 show calculations by Eq. (6) with parameters listed in Table I. These curves demonstrate a satisfactory agreement of our approximate calculations with spectroscopic measurements of the second harmonic generated in multiple quantum wells. Note also that the resulting transition energies are in a good agreement with parameters reported in the earlier publication,⁸ in which they were derived from measurements of modulated absorption and luminescence excitation spectra.

The width of the band gap in SiO_2 is very large (about 9 eV), so the tunneling across the 1-nm oxide layer may be neglected and the transition energy $E_c - E_v$ may be estimated using the simple model of a single rectangular quantum well. Taking the band-gap width in amorphous silicon to be 0.9 eV and the electron effective mass to be unity, we obtain a transition energy of about 1.3 eV in the 11/10 sample and about 2.1 eV in the 5.5/10 sample. These parameters correlate qualitatively with the experimental data. The discrepancy is probably due to the inadequacy of the rectangular-well model.

In this connection, we note that a rectangular potential well is symmetrical with respect to the reversal of the z -axis, so the dipole susceptibility in such wells must be zero. Given that the intensity of the second harmonic generated in such a structure is quite considerable, the real potential well should be asymmetrical. This asymmetry may be caused by the preparation technique, mechanical strain, or built-in charge in the layers of multiple quantum wells.

There are no resonances in the spectrum of a_0 in the s - p configuration, probably because in the general case different components of the quadratic susceptibility tensor correspond to different transitions and therefore are described by different spectral functions.

The spectrum of a_1 has peaks at the same second-harmonic energies as a_0 . This means that the parameter B in Eq. (2) is either described by the same spectral function or is not resonant at all.

5. CONCLUSION

In this paper we have reported on the investigation of nonlinear optical characteristics of amorphous Si/SiO₂ multiple quantum wells. Our data demonstrate that the second-harmonic intensity is sensitive to the quantum-size effects in these structures. For the first time interband transitions in such structures have been detected through the second-harmonic generation. The resonance parameters have been estimated using the simple rectangular-well model.

The authors are indebted to L. V. Keldysh and E. A. Vinogradov for helpful discussions and to F. A. Pudonin, who supplied the samples with quantum wells. This work was supported by the Solid-State Nanostructures and Low-Dimensional Systems Programs, and by grants from the National Science Foundation (No. 95-02-05893-a), INTAS-93370, and International Science Foundation (M12300).

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Translation was provided by the Russian Editorial office.