Two-Photon Absorption Spectroscopy in GaAs Quantum Wells

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Two-photon absorption spectroscopy was performed in GaAs quantum wells with photon energy $\hbar\omega$ near half the band gap E_g. For the case of incident light polarized perpendicular to the confinement direction $\hat{\epsilon} \perp \hat{z}$, the onset of two-photon absorption occurs at the $2P$ state of the lowest-energy heavy-hole exciton and the absorption increases linearly with $2\hbar\omega - E_g$. For $\hat{\epsilon} \parallel \hat{z}$, the two-photon spectrum is stepped with superpositions of sharp $1S$ exciton features at odd ΔN light-hole–conduction-band transitions. These results are used to accurately determine exciton binding energy, successive subband energy splittings, and band offsets.

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Two-photon absorption spectroscopy is a powerful method of investigating electronic properties of solids. Because the transition selection rules are different from those ruling linear absorption, levels which are not accessible in conventional one-photon spectroscopies can be observed. Also, the added flexibility in the choice of the frequency, polarization, and propagation vector of light can yield detailed information on the symmetry and other properties of initial and final states involved in the transition. These advantages have been illustrated in several beautiful experiments performed in bulk semiconductors.[1]

In this Letter, we apply two-photon absorption spectroscopy to the study of quantum well (QW) structures. As will be illustrated with GaAs/AlGaAs QW's, this technique is well suited for extracting several important parameters of these artificial structures. The first parameter is the heterojunction conduction- and valence-band offsets, which is of great interest and is controversial even in GaAs/AlGaAs QW's despite the considerable number of spectroscopic studies performed on this material.[2-9] The offsets can be accurately deduced if the energy splittings between successive quantized conduction and valence subbands are known. This quantity $X_N - X_{N'}$ (X_N denotes the Nth subband energy of conduction C, heavy-hole H, or light-hole L band) is not easily extracted from one-photon spectroscopies, because transitions between conduction and valence subbands with $\Delta N = N' - N \neq 0$ are forbidden. On the other hand, two-photon transitions for the incident light polarized parallel to the confinement direction $\hat{\epsilon} \parallel \hat{z}$ obey the selection rule $\Delta N = \pm 1, \pm 3$,etc. The subband splittings $C1$-$C2$ and $L1$-$L2$ are independently measured in the GaAs/$Al_{0.35}Ga_{0.65}As$ QW's studied in this Letter.

A second parameter is the exciton binding energy E_b, which is increased in quasi-two-dimensional systems relative to the bulk material due to the forced confinement of electrons and holes in the same thin layer. The determination of exciton binding energy has so far been rather indirect because of the difficulty in determining the band edge from one-photon processes.[9-13] However, the band edge can be accurately determined from two-photon absorption with the polarization of light in the plane of quantum wells $\hat{\epsilon} \perp \hat{z}$. This is because for $\hat{\epsilon} \perp \hat{z}$ the two-photon transition rate is linear with $2\hbar\omega - E_g$ and the strongly one-photon-allowed $1S$ exciton is forbidden. Consequently E_b is directly obtained by the separation of the $1S$ state apparent in one-photon absorption from the band edge in the two-photon spectrum.

The experimental arrangement, shown in Fig. 1, employs a waveguide geometry to allow long interaction length and, more importantly, to permit either the $\hat{\epsilon} \parallel \hat{z}$ or $\hat{\epsilon} \perp \hat{z}$ polarization configuration. The samples consist of 160 periods of GaAs wells and 150-Å-thick $Al_{0.35}Ga_{0.65}As$ barriers embedded between two 1-μm-thick $Al_{0.35}Ga_{0.65}As$ lower-refractive-index layers grown by molecular-beam epitaxy. The incident light from a tunable Tl:KCl color center laser was coupled into the waveguide by focusing on a cleaved edge of the sample.

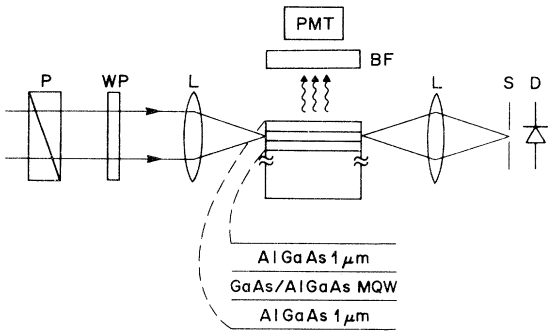

FIG. 1. Experimental setup and waveguide sample geometry. P, polarizer; WP, zero-order half-wave plate; L, lens; S, slit; D, InGaAs photodiode; BF, 10-nm bandpass filter, and PMT, photomultiplier tube. The transmission band of the filter coincides with the sample luminescence, which was premeasured by a monochromator and exhibited a single-peak structure of 2.5–3 nm wide due to the recombination of the $1S$ $H1$-$C1$ exciton.

The color center laser was pumped by a Q-switched neodymium-doped yttrium-aluminum-garnet laser and had a tuning range from 1.45 to 1.56 μm, a pulse duration of 300 ns, and a pulse energy of several μJ. Because of the limited laser tuning range, we used quantum confinement spectral shift in two samples with well thickness of 40 and 110 Å to study different spectral regions of quantum wells. The well thickness l_z was determined by transmission electron microscopy. The rate of two-photon absorption was measured as a function of wavelength by monitoring the subsequent sample luminescence due to the recombination of the $1S$ state of the $H1$-$C1$ exciton (two-photon excitation spectroscopy). The signal was divided by the square of the laser intensity as measured at the exit edge of the sample. As expected for the two-photon excitation the signal was directly proportional to the square of the guided laser intensity in the range of the measurements. Attentuation of the laser intensity by two-photon absorption over the sample length of 2 mm was negligible. Typical spectra recorded at $T=5$ K are shown in Figs. 2 and 3, together with the linear spectrum.

The two-photon absorption in the bulk GaAs [14] has been shown to result predominantly from transition terms which are described in the framework of a two-band model.[15] Schematically, the first photon induces a virtual interband transition to the $n=1$ (lower case n denotes the hydrogenic principal quantum number) exciton or higher-lying terms with an S-like envelope function including the ionization continuum. The second photon completes the electronic transition by coupling to the envelope function of the electron-hole pair. The second transition is denoted as the intraband transition. Since the intraband transition changes the parity of the envelope function, the lowest-energy final state is the $2P$ exciton. Because of the weak binding energy ($\sim n^{-2}$) and small oscillator strength ($\sim n^{-3}$) of the final $n=2$ excitons, the two-photon spectrum corresponding to the band edge is rather featureless.

In the two-dimensional case, one must distinguish between the $\hat{\epsilon} \| \hat{z}$ and $\hat{\epsilon} \perp \hat{z}$ polarization configurations because of the difference in the selection rules.[16,17] For $\hat{\epsilon} \perp \hat{z}$, the situation is essentially the same as in the 3D case, except for an overall blue shift of transitions energies due to confinement. The intraband transition alters the parity of the envelope function in the x-y plane and thus the two-photon transitions obey selection rule $\Delta N=0$. The onset of two-photon absorption occurs at $2\hbar\omega$ equal to the $H1$-$C1$ band edge. Including the exciton effect, the lowest bound state reached is the $2P$ state of the $H1$-$C1$ exciton as in the 3D case. Because there is no gain in binding energy or oscillator strength for the $n=2$ state of the exciton due to confinement (in contrast to the $n=1$ term), no distinct exciton feature is expected in two-photon absorption as for bulk GaAs. In Fig. 2, one-photon and two-photon absorption spectra are shown as functions of $\hbar\omega$ and $2\hbar\omega$, respectively, near the band edge of the $l_z=40$ Å sample. It is noted that the strongly one-photon-allowed $1S$ state of the $H1$-$C1$ exciton is absent in the two-photon spectrum. The onset of two-photon absorption occurs at the $2P$ exciton feature shown as the shaded area in Fig. 2. The $2P$ state assignment is confirmed by the weak $2S$ state feature seen in the linear spectrum, which disappears when $T>50$ K.

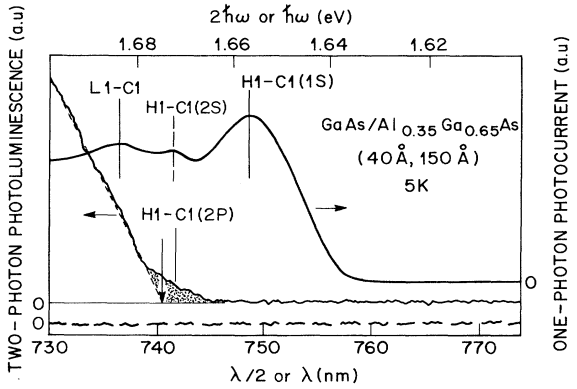

FIG. 2. One-photon (solid line) and two-photon (solid and dashed line) absorption spectra of GaAs/$Al_{0.35}Ga_{0.65}$As QW's with $l_z=40$ Å. One-photon spectrum was measured with light incident normal to the sample. Two-photon absorption for $\hat{\epsilon} \| \hat{z}$ (dashed line) was found to be zero in the spectral range shown. Nonvanishing two-photon absorption was obtained only for $\hat{\epsilon} \perp \hat{z}$ (solid line). Vertical lines position the observed exciton features. Vertical arrows indicate the $H1$-$C1$ band edge from the linear extrapolation indicated by the dashed line. The shaded area is the broadened $2P$ state. The $1S$ state splitting between $H1$-$C1$ and $L1$-$C1$ agrees with numerical calculations.

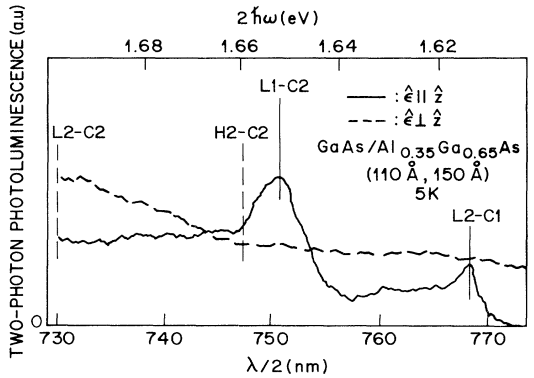

FIG. 3. Two-photon absorption spectra of GaAs/$Al_{0.35}$-$Ga_{0.65}$As QW's with $l_z=110$ Å for the $\hat{\epsilon} \| \hat{z}$ (solid line) and $\hat{\epsilon} \perp \hat{z}$ (dashed line) configurations. Vertical lines position the exciton features observed in two-photon (solid line) and in one-photon (dashed line) absorption. Other exciton features seen in linear absorption, $L1$-$C1$, $H1$-$C1$, and $H3$-$C3$, are at 1.552, 1.565, and 1.815 eV, respectively.

The linear increase of two-photon absorption at higher energy—to be contrasted with the plateaus seen in linear absorption—is in agreement with recent calculations[17] of band-to-band two-photon transitions in quantum wells, and is due to the linear k dependence[17] of the intraband transition matrix element. In Fig. 2, the band edge of the $H1$-$C1$ transition is easily obtained with an accuracy of 0.3 meV by linear extrapolation as indicated by the dashed line. The exciton binding energy, which corresponds to the separation between the $1S$ state and two-photon band edge, is found here to be 17.6 ± 0.3 meV. This is to be compared with a value of 14 meV reported[9] for the same well thickness by (linear) photoluminescence excitation technique. However, the latter method relies on the $1S$-$2S$ energy separation and consequently assumes a hydrogenic relation, a condition which is seldom verified in crystal. Also, the extraction of E_b from the first two terms ($1S$ and $2S$) under the assumption of a hydrogenic series can be performed simply in the true 2D or 3D case only. Finally, in the linear spectrum there is an uncertainty in determining the center position of the weak $2S$ state due to presence of the broadened ionization plateau. The two-photon technique which measures directly the exciton ionization energy avoids these uncertainties and therefore yields more accurate value of E_b.[18]

For $\hat{\epsilon} \parallel \hat{z}$, other properties specific to the quantum confinement become apparent. In this polarization configuration, the intraband step of the two-photon transition is not allowed because the polarization vector is orthogonal to the in-plane k vector. However, the intersubband transitions[16,17,19] of odd ΔN, which change the parity of the envelope functions along $\hat{z}$, are allowed. Therefore, the onset of two-photon transition should occur at the $L2$-$C1$ transition, which is higher in energy than the $H1$-$C1$ edge, the onset for the $\hat{\epsilon} \perp \hat{z}$ configuration. (The $H2$-$C1$ transition with an energy lower than $L2$-$C1$ is forbidden because for $\hat{\epsilon} \parallel \hat{z}$ the interband transition is not allowed between the heavy-hole and conduction bands due to the angular momentum conservation.) The next allowed transition is from $L1$ to $C2$. Experimental results shown in Figs. 2 and 3 agree with these expectations. In Fig. 2, two-photon absorption for $\hat{\epsilon} \parallel \hat{z}$ is zero because $2\hbar\omega$ within the laser scanning range is always lower than the $L2$-$C1$ transition for the $l_z = 40$ Å sample. In Fig. 3, for the $l_z = 110$ Å sample with reduced confinement energy, the two-photon spectrum for $\hat{\epsilon} \parallel \hat{z}$ shows an abrupt rise at 1.615 eV and consists of two plateaus from the $L1$-$C2$ and $L2$-$C1$ band-to-band transitions and two corresponding $1S$ exciton peaks. The plateaus are due to the fact that the intersubband matrix element is independent of k.[17] For the $\hat{\epsilon} \perp \hat{z}$ configuration, the two-photon spectrum in Fig. 3 still scales with $2\hbar\omega - E_g$ and shows no distinct exciton structure. Note, however, that a change of slope occurs beyond the $H2$-$C2$ exciton (a feature observed in one-photon measurements) in agreement with the model of Ref. 17.

Consider the determination of the subband splittings and band offsets. The conduction-subband splitting $C1$-$C2$ equals the energy difference between the $L1$-$C2$ exciton (apparent in two-photon absorption) and the $L1$-$C1$ exciton (apparent in linear absorption) and is 84 meV.[20] Similarly, the light-hole subband splitting $L1$-$L2$ is 48 meV, obtained from the positions of the $L2$-$C1$ and $L1$-$C1$ excitons or from the $L2$-$C2$ and $L1$-$C2$ excitons. Thus the subband splittings for conduction and valence bands are obtained in the same measurement. Then using the standard procedure for particles in a box, the band offsets ΔE_c and ΔE_v are independently determined[21] to be 330 and 107 meV with a ratio of $(75/25) \pm 1\%$ using $m_e^* = 0.0665 m_e^6$ and $0.0957 m_e^6$ and $m_{lh}^* = 0.094 m_e^6$ and $0.109 m_e^6$ for GaAs and $Al_{0.35}Ga_{0.65}As$, respectively. Previously, there were many reports on the band offsets on GaAs QW's primarily determined by fitting heavy- and light-hole exciton spectral positions seen in linear absorption. The fitting procedure is not sensitive to the offset ratio used as an adjustable parameter especially for wide wells ($l_z > 40$–50 Å) and requires accurate knowledge of l_z and ΔE_g. The wide spread of published offset ratio[2–9] ranging from 88/12 to 50/50 reflects the difficulty in determining the offset ratio by linear spectroscopies.[22] This difficulty should become even worse in other types of quantum wells with less well characterized constituents. We believe that two-photon absorption increases the accuracy in the determination of the offset ratio by roughly 1 order of magnitude for GaAs QW's for the following reasons. (1) It does not require the same accurate knowledge of l_z as in linear spectroscopy. Indeed, the uncertainty in l_z only affects the offset ratio to the second order due to the similar electron- and light-hole masses. (2) The *a priori* knowledge of the gap difference between the well and barrier materials is not necessary. We note, however, as a check of consistency that the sum of ΔE_c and ΔE_v obtained here agrees with the difference between 1.955 and 1.519 eV, the reported gap energies for $Al_{0.35}Ga_{0.65}As$ and GaAs, respectively.[23] (3) The offsets in the conduction and valence bands are determined independently and with no adjustable parameter. Using the offset ratio of 75/25, all excitons observed in our samples, up to $N = 3$ subbands, fall within 3 meV of the numerical calculations.

Finally, consider $\chi^{(3)}$ for $\hbar\omega \sim E_g/2$ in GaAs QW's. In this midgap region, linear absorption (α) is very low so that the ratio of $\chi^{(3)}/\alpha$, which is the figure of merit for optical nonlinearity, could be very large. The luminescence technique employed here does not yield a quantitative measure of two-photon absorption rate, which is related to the imaginary part of $\chi^{(3)}$.[24] However, $\mathrm{Im}\chi^{(3)}$ for the $\hat{\epsilon} \perp \hat{z}$ configuration in QW's is similar to the bulk $\mathrm{Im}\chi^{(3)}$ value at a similar detuning from the gap

$(2\hbar\omega - E_g)$. Consequently, one can determine the excitonic enhancement of $\chi^{(3)}$ due to quantum confinement for $\hat{\epsilon} \| \hat{z}$ over $\chi^{(3)}$ in the bulk. In Fig. 3, a factor of 2 enhancement is seen at the $L2$-$C2$ exciton peak. Larger enhancement can be expected since the present results are limited by the inhomogeneous exciton linewidth.

In conclusion, we have shown that two-photon absorption spectroscopy can yield crucial information on quantum wells. This method improves the accuracy of exciton binding energy, subband splittings for both the conduction and valence bands, and band offsets in the extensively much studied GaAs quantum wells. It is expected that this method should be even more valuable in the new type of quantum wells for which less background knowledge is available.

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