Two-photon absorption spectrum of AlAs-GaAs monolayer crystals

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The excitation spectrum of two-photon absorption of 1.1 ± 0.1:9.4 ± 0.6 AlAs:GaAs monolayer crystals was measured by the luminescence technique. The observed transitions to the $n = 1$ exciton are attributed to the three-band model. The 5.3-meV splitting of the exciton is primarily due to the splitting of the two hole bands by the periodic potential, which is also responsible for an upward shift of the band gap relative to a random alloy having the same average composition. The band to band two-photon absorption spectrum has the characteristics of the two-band model previously found for GaAs. The two-photon absorption spectrum thus indicates that while the band structure of the monolayer crystal has certain similarities to the band structures of bulk GaAs and the random alloy, the details may be significantly different.

In this paper we report the observation of two-photon absorption (TPA) spectra in an AlAs:GaAs monolayer crystal.[1-5] The band gaps of bulk AlAs at 4.2 °K are higher than those of GaAs [3.13 eV (Ref. 6) vs 1.519 eV (Ref. 7) for the direct gap], and in a layered structure the difference in the band gaps is distributed between the valence and conduction bands.[8] A potential difference persists down to monolayer layer thicknesses so that, normal to the layer plane, the electrons and holes experience a periodic potential having a period determined by the spacing of the superlattice. The layered nature of these new materials introduces significant variations in the optical properties,[1,3] phonon spectra,[2] and electron[1] and x-ray[4] diffraction relative to the corresponding random alloys, and are of considerable current interest.

We find that the excitons involving the heavy and light holes are split by the periodic potential, and occur at a higher energy than expected for an alloy having a similar average composition. The two-photon transition mechanism of the excitons is identified with the three-band model, and the band-to-band TPA is due to the two-band model.

The monolayer crystal was grown as an optical waveguide in a molecular-beam apparatus incorporating a motor-driven shutter arrangement which interrupted alternately the molecular beams from the Al and the Ga ovens.[1,9] The arsenic beam was not shuttered. The waveguide was grown on a (001)-oriented GaAs substrate. The oven and substrate temperatures and the shutter times were adjusted so that the central guiding region consisted of 1.1 ± 0.1 monolayer of AlAs alternating with 9.4 ± 0.6 monolayers GaAs having a total thickness of 1.4 μm. A monolayer is 2.83 Å thick. The two cladding layers consisted of 3.4 ± 0.3 monolayers AlAs and 7.3 ± 0.5 monolayers GaAs, each 1.4 μm thick. The monolayer thicknesses were obtained from interferometric measurement of the total AlAs and GaAs thickness divided by the number of times the shutter had been opened. The possible error of this measurement yields the uncertainty in the monolayer thickness. The higher average Ga content of the guide, relative to the cladding, provides the necessary refractive-index difference for waveguiding. The relatively low Al content and high quality of the central layer allowed the exciton structure to be resolved at low temperatures.

The TPA shown in Fig. 1 was measured by monitoring the band-gap luminescence as the pump energy is varied in the region of half the band-gap energy. Small bars, 1–2 mm long, with $(1\bar{1}0)$ entrance and exit faces, were cleaved from the wafer (see insert in Fig. 1.) Radiation from a temperature-tunable optical parametric oscillator was end coupled into the guide using a combination of spherical and cylindrical lenses to produce an astigmatic image on the entrance edge of the guide. The samples were mounted in a variable-temperature cryotip refrigerator and were estimated to be at ~10 °K. The recombination radiation was detected in the [001] direction.

The emission at 1.68 eV, where the maximum luminescence from the monolayer crystal occurred, was isolated by an interference filter. The focal-spot size was somewhat larger than the width of the guide. Consequently, a considerable fraction of the pump radiation passed into the substrate where, due to consecutive two photon absorption involving deep impurity levels, an intense luminescence signal at 1.51 eV is generated. A small fraction of this emission is transmitted by the filter and appears in Fig. 1 as a smoothly varying background signal beginning at $2\hbar\omega = 1.519$ eV.

The waveguide configuration results in a tight confinement of the pump radiation and the recombination radiation is generated in the thin

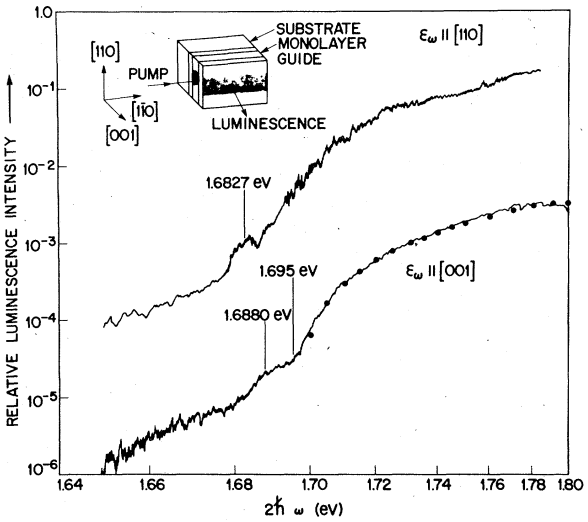

FIG. 1. Polarized TPA spectrum obtained by monitoring the luminescence from the monolayer. Curves are separated to show detail. Transitions at 1.6827 and 1.688 eV correspond to the $n=1$ excitons of the heavy- and light-hole bands, respectively. The points in the $\mathcal{E}_\omega \| [001]$ curve are the calculated values of the TPA based on the two-band model, and were fitted to the experimental curve using the 1.695-eV band gap. The orientation of the monolayer and the input and output beams is shown in the insert.

waveguide thus minimizing the effect of self-absorption. The use of the cladding layers reduces the nonradiative surface recombination normally present at a GaAs-air interface.

The energies of the sharp excitons agree quite closely with the exciton peaks at 1.683 and 1.6876 eV observed in σ-polarized linear absorption in a part of this crystal which had a small circular region of the substrate removed by a selective etch. Thus, as was found for pure GaAs,[10] the TPA absorption is associated with transitions to the $n=1$ exciton states which can occur via the allowed-allowed transition mechanism in the three-band approximation.[11,12] For this mechanism the transition strength to the s states of the higher-energy excitons decreases like n^{-3}.[11] The observed lack of significant strength for transitions to these states is consistent with this decrease in intensity. Two-photon transitions to the $n=2$ states can also occur via the allowed-forbidden mechanism in the two-band approximation.[11,12] The estimated strength for this mechanism is an order of magnitude weaker than for the allowed-allowed transition to the $n=2$ state,[11] and so is too weak to be observable.

The 5.3-meV splitting of the excitons results primarily from the splitting of the light- and heavy-hole bands by the periodic potential. The polarization data show that the heavy-hole band edge has the lowest energy. The effect of strain on the central layer due to differential thermal contraction of the cladding and substrate, from the growth to the measurement temperature, also contributes to the splitting. However, previous studies using similar molecular beam epitaxy random alloy compositions, grown at the same temperature indicate that the strain splitting is ~1 meV (Ref. 13) and is thus not the dominant cause of the splitting.

The band gaps were calculated using the Kronig-Penney model with the bulk effective masses of AlAs and GaAs, and assuming 15% and 85% of the direct band-gap discontinuity is attributed to the valence and conduction bands, respectively.[8] The calculated splitting of the heavy- and light-hole band edges is 10.7 meV with the heavy-hole band edge having the lowest energy. This is about twice the measured value.

The energies of the band edge of $Al_xGa_{1-x}As$ random alloys for $x<0.5$ are to a good approximation given by[14]

$$E_{gd} = 1.519 + 1.24x. \tag{1}$$

The average Al content of the monolayer used in this study is $x=0.105\pm0.015$, and from Eq. (1) corresponds to an alloy band gap of 1.649 ± 0.019 eV. This is 46 meV smaller than the measured $E_{gd}=1.695$ eV of the monolayer. For the Kronig-Penney model the conduction–heavy-hole band edge is at 1.77 eV which is 75 meV larger than the measured value. The calculated and measured values of the band-edge splitting and the shift of the band edge have the same signs, but as might be expected from the simple one-dimensional Kronig-Penney model, the agreement with the experimental magnitudes is poor.

The results of a recent pseudopotential calculation of an AlAs-GaAs monolayer structure are quite different.[15] This pseudopotential calculation yields monolayer direct and indirect gaps smaller than the gaps of corresponding alloys. In addition, an anisotropy in the $\epsilon_2\omega^2$ spectrum was calculated; however, the splitting of the band edge resulting from the periodic potential was not found. Our experimental results thus appear to indicate the need for more sophisticated band-structure calculations.

The single-photon absorption and TPA of the excitons exhibit a significant polarization effect. In GaAs the selection rules for single-photon transitions between the Γ_5^v ($j=\frac{3}{2}$) valence and Γ_1^c ($j=\frac{1}{2}$) conduction band are determined by symmetry.[7] As indicated above, the light- and heavy-hole bands are split by the periodic potential and strain and this splitting is large compared with the exchange splitting ($j=0.05\pm0.05$ meV for

bulk GaAs).[7] The transition in GaAs involving the heavy-hole band, corresponding to $j_z = \frac{3}{2}$, has relative strength 3 in σ polarization, and the light-hole-band transitions have strengths 1 and 4 in σ and π polarization, respectively.[7] Single-photon σ-polarized absorption in the monolayer with radiation propagating normal to the layers confirm the σ-polarized selection rule, with the strongest σ-polarized heavy-hole transition occurring at 1.683 eV. In the three-band model of TPA the transition from the ground to the intermediate state will have the same selection rules as determined by single-photon absorption.[12] This is qualitatively observed in Fig. 1 where the σ-polarized absorption strength ($\mathcal{E}_\omega \| [110]$) has approximately a 3:1 ratio for the 1.6827 and 1.688 eV excitons, respectively.

In an earlier study,[10] the band-to-band TPA of high-purity GaAs was attributed to the allowed-forbidden mechanism of the two-band model which has a spectral dependence proportional to $(2\hbar\omega - E_g)^{3/2}/\hbar\omega$.[6] The corresponding band-to-band TPA of the three-band model has a weaker dependence given by $(2\hbar\omega - E_g)^{1/2}$.[11] The two-band expressions of Fossum and Chang were used to calculate the TPA of the monolayers.[16] The best fit to the $\mathcal{E}_\omega \| [001]$ spectrum, shown by the points in Fig. 1, was obtained using $E_{gd} = 1.695$ eV, and the bulk GaAs effective masses. The good agreement confirms the two-band approximation for the band-to-band transitions and yields an exciton binding energy of 7 meV. The calculated spectral dependence is found to be a relatively weak function of the effective masses. Using values of the effective masses corresponding to a linear interpolation of the masses in GaAs and AlAs, consistent with the average Al content, did not give a significantly different spectral shape.

The exciton binding energy of 7 meV for the $\mathcal{E}_\omega \| [001]$ polarization is larger than the value 4.2 meV of pure GaAs.[7] The larger energy is consistent with the trend observed in ultrathin GaAs layers isolated by $Al_{0.2}Ga_{0.8}As$ barriers where binding energies up to 9 meV have been found.[8]

The anisotropy of the intensity of the TPA can best be expressed in terms of the imaginary part of the third-order nonlinear susceptibility.[10] The intensities for [110] and [001] polarized inputs are related by

$$\frac{I([110])}{I([001])} = \frac{2\chi''_{xxyy} + \chi''_{xyyx} + \chi''_{xxxx}}{2\chi''_{xxxx}}. \quad (2)$$

The measured band-to-band intensity ratio at 1.78 eV is 1.48 ± 0.03. In order to make a comparison with prior results which involve isotropic band gaps, the intensity of the [110] polarization was measured at 1.775 eV and [001] polarization at 1.78 eV yielding an intensity ratio of 1.24 ± 0.03. Thus for equal energies above the band gaps $(2\chi''_{xxyy} + \chi''_{xyyx})/\chi''_{xxxx} = \chi''_{xxxx} = 1.48 \pm 0.06$. This agrees with the ratio of the susceptibilites of 1.45 ± 0.06 found for bulk GaAs,[10] and indicates that the additional anisotropy of the third-order nonlinear susceptibility is attributable to the splitting of the light-and heavy-hole bands by the periodic potential.

In summary, we have shown that the TPA spectrum of AlAs-GaAs monolayer materials is in many respects similar to the spectrum of pure GaAs. In both cases the transitions involving the $n = 1$ excitons are due to the three-band model, and the band-to-band transitions to the two-band model. However, the one-dimensional periodic potential present in the monolayer introduces a significant modification of the one- and two-photon absorption spectra. The potential causes a splitting of the light- and heavy-hole bands introducing an anisotropy in the absorption. Together with the ordering of the monolayer structure, relative to the random distribution of the cations in the alloy, the periodic potential increases the band gap of the monolayer as compared to a random alloy having the same average Al composition. Thus, the energy bands of the monolayer material are not only different from the random $Al_xGa_{1-x}As$ alloy of the same composition, but also different from bulk GaAs. These differences appear to be qualitatively explained by a one-dimensional Kronig-Penney model. Using a pseudopotential calculation Carruthers and Lin-Chung[15] predicted a modification in the band structure for alternating monolayers which is somewhat different from the results found here. Similarly, Schulman and McGill,[17] using a tight-binding calculation, have also implied a modification of the band structure. Additional work in this area would clearly be of considerable interest in obtaining a better understanding of these new monolayer materials.

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