Two-photon spectroscopy in GaAs/$Al_xGa_{1-x}As$ multiple quantum wells

I. M. Catalano, A. Cingolani, R. Cingolani, and M. Lepore
Dipartimento di Fisica, Università degli Studi di Bari, via Amendola 173, 70126 Bari, Italy

K. Ploog
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany
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The excitation spectrum of two-photon absorption in GaAs/$Al_xGa_{1-x}As$ multiple quantum wells was measured by means of the nonlinear luminescence technique. We found a strong excitonic effect overlapping the interband two-photon spectrum. The parity selection rules of the nonlinear transitions allow the direct observation of excitonic $2p$ states providing new information on these excited states in confined systems.

In recent years a great deal of interest has been devoted to the nonlinear optical properties of semiconductor quantum wells (QW's). The confinement properties of the electronic and excitonic wave functions allow us to achieve high values of the nonlinear susceptibility[1] leading to strong optical nonlinearities. In this class of processes, the two-photon absorption (TPA) in multiple quantum wells (MQW's) has not been investigated in detail. To our knowledge, only the TPA spectrum of GaAs/AlAs monolayer crystals has been reported in an early paper by van der Ziel and Gossard,[2] who measured the TPA spectrum showing a spectral dependence similar to the one already found for bulk GaAs with some excitonic contribution to the total transition probability. More recently, Fröhlich *et al.* have performed TPA experiments at the excitonic resonance in the presence of a strong magnetic field.[3]

From the theoretical point of view, there are only two recent papers on the spectral dependence of the TPA coefficient for interband transitions in quantum wells.[4,5] Both papers are based on a perturbative approach in the effective-mass approximation. They predict a nonmonotonic increase of the TPA with the energy of the absorbed photons ($2\hbar\omega$), showing distinct spectral features at energies corresponding to the transitions between quantized states and neglecting the excitonic contributions.

In this paper we report the first two-photon excitation spectra in GaAs/$Al_xGa_{1-x}As$ MQW's obtained by monitoring the luminescence induced by the nonlinear absorption process.[6] The TPA emission in the energy range of the quantized states in the well has been detected at the energy of the fundamental $n=1$ heavy-hole confined exciton E_{11h}. (In the following we shall use the notation $E^q_{i,j,h\,(l)}$ for the optical transitions, where i is the electronic subband, j the hole subband, h and l stand for heavy and light hole, respectively, and q indicates the state of the exciton $1s$, $2s$, $2p$, etc.)

The investigated samples are high-quality GaAs/$Al_xGa_{1-x}As$ MQW's consisting of 60 periods of 4.7-nm GaAs sandwiched between 5.7 nm of $Al_{0.38}Ga_{0.62}As$ (sample A) and ten periods of 10-nm GaAs sandwiched between 11-nm $Al_{0.36}Ga_{0.64}As$ (sample B). Details on the samples growing, on the linear luminescence properties, and on optical reflectance are reported in Ref. 7. The samples were mounted in a variable-temperature cryostatic He refrigerator operating in the range 7.5–300 K.

The laser source was a Quantel neodymium-doped yttrium aluminum garnet (Nd:YAG) laser whose second harmonic pumped a Quantel Datachrome dye laser with 9-ns pulse duration and 10-Hz repetition rate. The useful spectral range for TPA processes in GaAs MQW's ($1.5 < 2\hbar\omega < 1.8$ eV) was achieved by using a low-pressure hydrogen Raman shifter which provided the frequency down conversion of the dye-laser radiation in the range $0.6 < \hbar\omega < 1.3$ eV. The output power density in the second-order Stokes wavelength range used in this experiment was a few MW cm^{-2} after focusing. The tuning accuracy of the dye-laser head was about 2 Å, corresponding to ± 1 meV uncertainty in the energy determination of $2\hbar\omega$. The excitation configuration employed in the experiment was with the laser beam at 45° with the growth axis of the samples. The luminescence was detected perpendicular to the excited direction. In this configuration, owing to the transverse polarization of the laser source, the exciting electric field has both the polarization components parallel and perpendicular to the QW layer.

The luminescence emitted was detected by using a double monochromator equipped with a 60 ER response photomultiplier tube while the incident beam was monitored by a fast response photodiode. Both signals were stored and processed by a computer controlled data-acquisition system. To reduce the effects of fluctuations in the input beam intensity, a ratio of the photomultiplier signal to the square of the monitor signal was used. Moreover, the quadratic behavior of the detected luminescence signal versus excitation intensity was checked at each experimental point and, for each of them, different measurement runs were carried out. The signal-to-noise ratio was better than 200 for each run. In Fig. 1 we show the TPA luminescence excitation spectrum obtained from sample A at 10 K. The spectrum exhibits a steplike behavior fol-

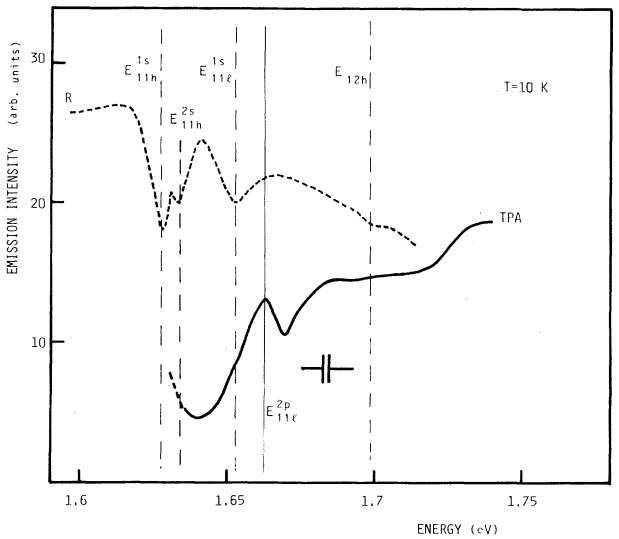

FIG. 1. Two-photon absorption luminescence excitation spectrum of sample A vs $2\hbar\omega$ at 10 K (TPA curve). The curve is compared with the reflectance spectrum (R curves) taken from Ref. 7. Solid and dashed vertical lines indicate the excitonic transitions, respectively, allowed and forbidden in TPA processes.

lowing the density of states involved in the interband transition probability. In addition, a strong excitonic contribution is observed around 1.663 eV in the energy region of the E_{11l} exciton. A shoulder around 1.7 eV is also observed at an energy corresponding to the E_{12h} transition. Approaching $2\hbar\omega$ to the top of the well, the effect of the continuum of states on the transition probability leads to a further increase of the luminescence signal.

The peaks in the TPA curve can be compared with the excitonic resonances observed in the reflectance spectrum (R line in Fig. 1). The comparison of the two spectra does not show a close correspondence of the excitonic structures observed in the TPA experiment with the energy positions of the fundamental (1s states) excitons already observed and assigned in low- and high-intensity linear luminescence and reflectivity.[7] In the TPA excitation spectrum of Fig. 1 the light-hole exciton appears at about 9 meV higher energy than the corresponding 1s state of the E_{11l} feature observed in reflectivity and luminescence.

Similar results have been obtained in the case of sample B (Fig. 2). In particular, we observe the excitons associated with the $n=2$ subbands. The E_{22h} and E_{22l} features in the TPA spectrum appear at an energy position 7 meV higher than the 1s states observed in reflectivity with the E_{22l} peak which is much more intense than the E_{22h} peak. In this sample the E_{11l} is not too close in energy to the detection wavelength and is not well resolved in the TPA spectrum. It should be pointed out that in the case of one-photon absorption processes, we have found a close coincidence in the energy positions of the 1s state of the excitonic resonance in reflectivity and photoluminescence spectra of the same sample.[7]

It is worth noting that in the TPA spectrum of sample B, other structures can be observed such as the E_{21l} and the E_{13l} transitions around 1.665 and 1.71 eV, respectively, which will be discussed in the following. However, in

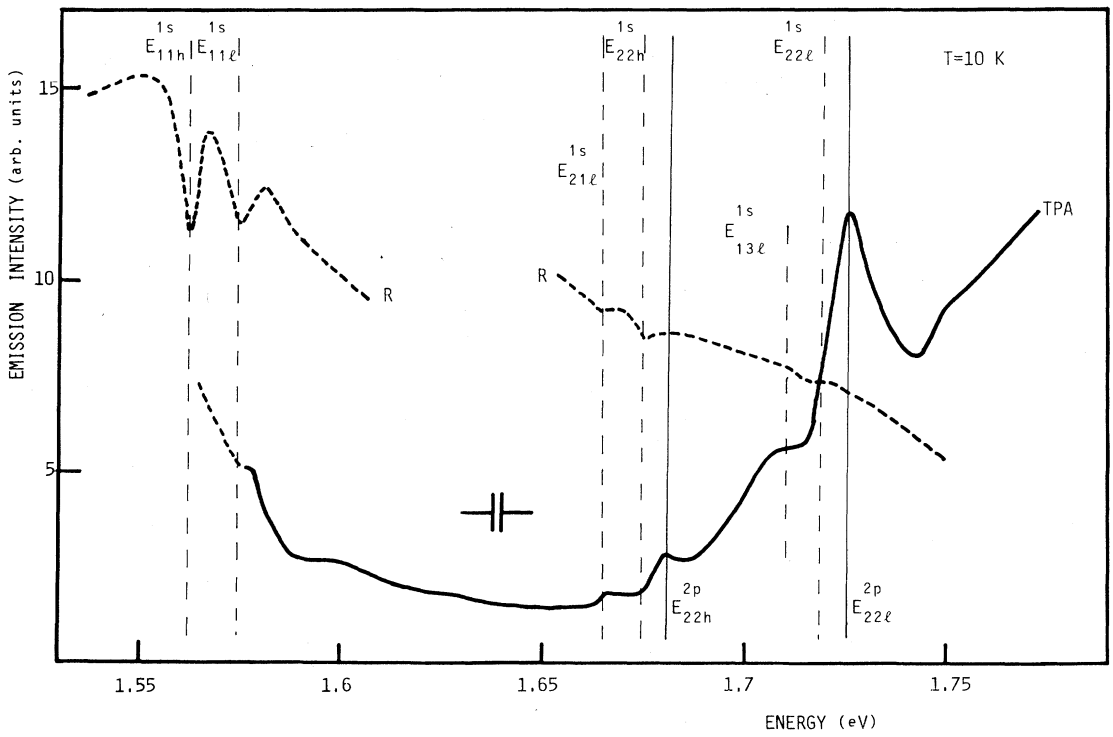

FIG. 2. The same as Fig. 1 for sample B. The high-energy part of the reflectance spectrum has been amplified for comparison.

the region $2\hbar\omega < 1.65$ eV the luminescence efficiency is low owing to the small TPA coefficient near the absorption edge. The obtained faint structures are not well resolved in the flat TPA spectrum.

The interpretation of these TPA spectroscopy data allows us to obtain new important information on the basic transition mechanisms involving nonlinear absorption processes in semiconductor MQW's. First, we note that the excitonic contribution to the total transition amplitude is dominant in the spectrum when $2\hbar\omega$ is close to resonance with the excitonic states. This feature assumes a considerable importance in view of a more complete theory which should take excitonic effects into account. Second, we note that the interband TPA spectrum in these structures follows the expected steplike density of states owing to the quantization of the electronic states. In addition, the TPA transitions undergo different parity selection rules compared to the case of the linear absorption processes. Allowed transitions in two-photon processes involve states having the same parity since the intermediate states must have opposite parity to the initial and final states. Conversely, one-photon processes always link states having opposite parity. It is therefore expected that in semiconductor QW's the results of TPA spectroscopy give complementary information on the excited states of the excitons associated to the various subbands. In the case of interband transitions, the parity of the state is $P_{c,v}=P_kP_f$, where the subscripts c and v indicate the conduction or valence band. P_k is the Bloch state parity (odd for the conduction states and even for the valence ones), and P_f is the envelope function parity (even for the odd index subbands and odd for even index subbands in the QW). In the case of excitonic transitions the parity of the state is $P_{\rm exc}=P_cP_vP_{\rm env}$, where $P_{\rm env}$ is the parity of the exciton envelope function (related to the parity of the exciton orbital: even for the $1s$ and $2s$ state, odd for the $2p$ state).

Evaluation of $P_{c,v}$ and $P_{\rm env}$, taking the odd parities of the absorbed photons into account, leads to the result that parity conservation is satisfied in TPA processes only if the $2p$ states of the excitons are involved, while transitions between $1s$ states are forbidden. On the contrary, for the case of linear absorption processes, only transitions between fundamental excitonic states ($1s$) are allowed. This finding can explain the energy shift of the E_{11l} exciton peak observed in the TPA spectrum of sample *A*. In particular, the energy difference of about 9 meV is comparable to the energy separation between the $2p$ and $1s$ states of the E_{11l} exciton recently observed by Viña *et al.*[8] in the linear photoluminescence excitation spectra of a 1.6-nm GaAs QW sample. Furthermore, theoretical calculations of Greene *et al.*[9] give a $2p$-$1s$ splitting of about 7.5 meV for a 5-nm GaAs.

Similar conclusions can be drawn for the TPA spectrum of sample *B*. In this case, we resolve very well the E_{22h} and the E_{22l} exciton peaks displaced at higher energy with respect to the corresponding reflectivity resonances and linear luminescences. The $1s$-$2p$ separation for this sample amounts to about 7 meV.

No previous experimental results on the $2p$ excitons associated to higher-order quantized subbands are available, therefore it is not possible to perform a quantitative comparison. On the other hand, few theoretical treatments have been reported on the exciton states associated with higher subbands in the well.[9,10] Extrapolation from the theory of Matsuura and Shinozuka[10] for the binding energy of the E^{2p}_{22h} and E^{2p}_{22l} gives a $2p$-$1s$ splitting of about 7 meV for the investigated sample, in agreement with our observations.

These data indicate that the splitting of the $1s$-$2p$ excitonic states increases in the narrow wells. This finding is in agreement with the results of a recent experimental work by Koteles and Chi[11] where the $2s$-$1s$ splitting of the E_{11h} exciton in GaAs QW's is found to decrease monotonically with the well width. In particular, the quantitative comparison between the data of Ref. 11 and our results for the $2p$-$1s$ splitting has been performed taking into account the very small energy separation between the $2s$ and $2p$ excitonic states (0.4 meV as measured by Viña *et al.*[8]).

It is worth noting that thermal ionization of the E^{2p}_{22h} exciton occurs around 14 K and the luminescence peak in the spectrum can be well resolved only below 10 K. This result indicates a binding energy for the $2p$ state of the E_{22h} exciton of about 1.2 meV, in good agreement with the values of about 1.5 meV obtained in variational calculations of Refs. 9 and 10. In addition, considering the experimental $2s$-$2p$ splitting and the $2s$ binding energy measured in Refs. 8 and 11, respectively, we obtain a $2p$ exciton binding energy of the order of 1 meV, in agreement with our direct experimental observation.

This result accounts well for the emission intensity ratio observed at 10 K between the E^{2p}_{22h} and the E^{2p}_{22l} exciton peaks (Fig. 2). According to Refs. 9 and 10, it is indeed expected that the $2p$ states of the light-hole exciton have a slightly higher binding energy than the heavy-hole ones (about 20% larger[9]) leading to a less efficient thermal ionization of the E^{2p}_{22l} exciton at 10 K.

Finally, we want to briefly discuss the presence of some $\Delta n \neq 0$ transitions (where n is the index of the subbands in the well) in the TPA spectra of Figs. 1 and 2. We suggest that these transitions are due to the polarization component of the exciting field parallel to the superlattice growth axis ($\mathbf{E}\|\mathbf{z}$), which is always present in our experimental configuration. As calculated by Pasquarello and Quattropani[5] for the component of light polarized parallel to the confinement direction, TPA transitions involve subbands having different quantum numbers n. Hence in our excitation condition it is expected that, although the variation of the refractive index at the interface $Al_xGa_{1-x}As/GaAs$ is not favorable for guiding radiation along the z direction, this small polarization component causes the excitation of the $\Delta n \neq 0$ transitions.

For this kind of configuration, parity selection rules, owing to the different P_f parity of the subbands involved in the transitions, lead to allowed TPA transitions between $1s$ states while absorption between $2p$ states becomes forbidden. This prediction is apparently confirmed by the energy positions of the E_{12h} and E_{21l} peaks observed in the TPA spectra of Figs. 1 and 2, which coincides with the resonances ($1s$ states) in the reflectance spectra. Detailed experiments on these transi-

tion mechanisms and on the polarization dependence of the TPA spectroscopy are now in progress and will be the subject of future work.

We conclude that the TPA spectroscopy is a powerful tool to study the excited states of exciton associated with quantized levels in semiconductor quantum wells. Our results shine light on the dominant role of the excitonic transitions in the TPA processes, providing the first direct observation of the $2p$ excited states associated to the quantized subband of higher index n (also showing the importance of including excitonic transitions in the theoretical models for the TPA processes). A reliable value of the binding energies of these excited states, in satisfactory agreement with recent theoretical models, has been obtained with these measurements. Further studies should be performed on TPA processes in order to study the well size dependence of the binding energy of the excitated states in confined excitons.

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