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OPTICAL SPECTROSCOPY OF EXCITONS IN QUANTUM WELLS

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Main aspects of the electric-field effects on excitons in GaAs-GaAlAs quantum wells by spectroscopic studies are presented, including thickness dependence and coupling between excitonic states.

1. INTRODUCTION

Research on quantum structures was initiated with a proposal by Esaki and Tsu[1] in 1969 for an "engineered" semiconductor superlattice (SL): a one-dimensional periodic structure consisting of alternating ultrathin layers as shown in the insert of Fig. 1. The idea occurred to them while examining the feasibility of structural formation by epitaxy for quantum wells (QWs) and barriers, thin enough to exhibit resonant electron transport. The superlattice was considered a natural extension of multi-barrier structures where quantum effects are expected to prevail. An important parameter relevant to the observation of such effects is the phase-coherent distance which depends strongly on bulk and interface quality of crystals and also on temperature. As schematically illustrated in Fig. 1, if characteristic dimensions such as SL periods and well widths are reduced to less than the phase-coherent distance, the entire electron system will enter a "mesoscopic" quantum regime of reduced dimensionality, between the macroscopic and microscopic scales.

Heteroepitaxy is essential for the SL and QW formation. Advances in growth techniques such as MBE (molecular beam epitaxy), MOCVD (metalorganic chemical vapor deposition) and their combination, MOMBE, have made possible predesigned, high-quality quantum structures. The resulting great precision has cleared the access to the "mesoscopic" quantum regime. Thus, the new field in semiconductor physics of QWs and SLs has made remarkable progress for the last decade, inspiring a number of ingenious studies which lead to unprecedented transport and optoelectronic devices.

Transport and optical measurements on "engineered" quantum structures have revealed the salient features arising from the electronic structure of quasi-two-dimensional character.[2] Chang, Esaki and Tsu[3] observed resonant electron tunneling in double-barriers, confirming the existence of bound states at expected energies, and Esaki and Chang[4] measured quantum transport properties in an SL having a tight-binding potential. Subsequently, Dingle et al.[5] observed pronounced structure in the optical absorption spectrum with several excitonic peaks representing bound states in QWs. Tsu et al.[6] measured photocurrent in SLs, revealing also the presence of bound states. More recently, Miller et al.[7] first reported the observation of excited states of excitons, followed by Dawson et al.[8] and Moore et al.[9]

In 1982, Mendez et al.[10] performed the first study of electric-field effects on photoluminescence (PL) in GaAs-GaAlAs QWs, observing two significant effects with increasing the field: decrease in the PL intensity and Stark

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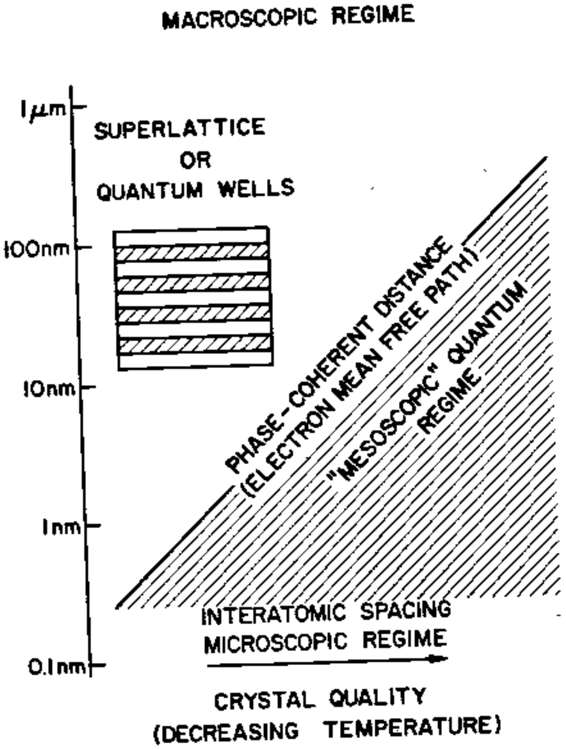

Fig. 1 Schematic illustration of a "mesoscopic" quantum regime (hatched) with a superlattice or quantum wells in the insert.

shifts in the peak positions to lower energies, as shown in Fig. 2. The field, here, was applied perpendicular to the layers, whereas the effect was less dramatic in a parallel configuration. Since then, the interest in the field effect for confined carriers has grown considerably, and a variety of techniques such as photoluminescence excitation (PLE), optical absorption, photocurrent (PC) and electroreflectance have been employed for its investigation.

In this paper, based on our experimental results recently obtained with high-quality QW-embedded p-i-n samples, the main aspects of the field effects are presented; dependence of Stark shifts on the well thickness[11] and coupling of the excited states of the heavy-hole exciton with the ground state of the light-hole exciton.[12]

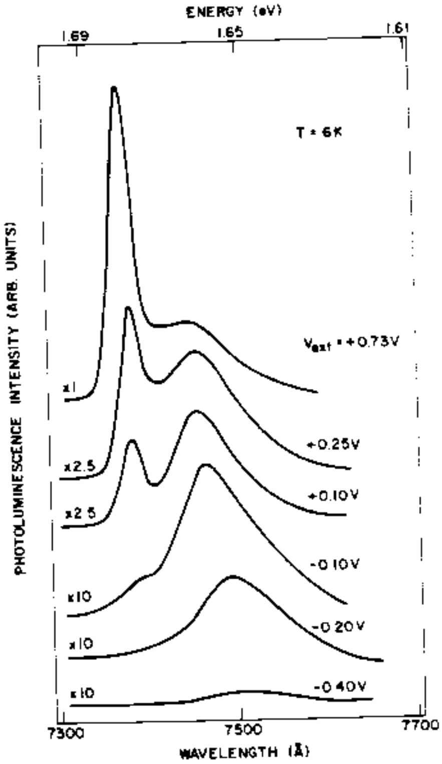

Fig. 2 Photoluminescence intensity versus emission wavelength in GaAs quantum wells (35Å) at various fields represented by applied voltages. The spectra indicate two peaks associated, respectively, with exciton and impurity-related recombination; with increasing field, the peaks shift to lower energies and their intensity decreases.

2. STARK SHIFTS AND EXCITONIC COUPLING

As the electric field is applied to GaAs-GaAlAs QWs, observed is a strong quenching of the dominant PL peak being assigned to the free heavy-hole exciton. A further increase in the field quenches the donor-bound exciton, but simultaneously makes resolvable a third peak which is attributed to an acceptor-bound exciton. Fig. 3 shows the Stark shifts of the dominant peak with the electric field in the PL spectra for four samples. A larger shift with increasing well thickness, as noticed, is expected from perturbation-theory arguments. The Stark effect results in a shift of the excitonic recombination below the bulk GaAs exciton, whose energy is indicated by a dotted line in the figure. The results of variational calculations (dashed lines) [13] and the exact numerical solutions (solid lines)[11] are in good agreement with measurements.

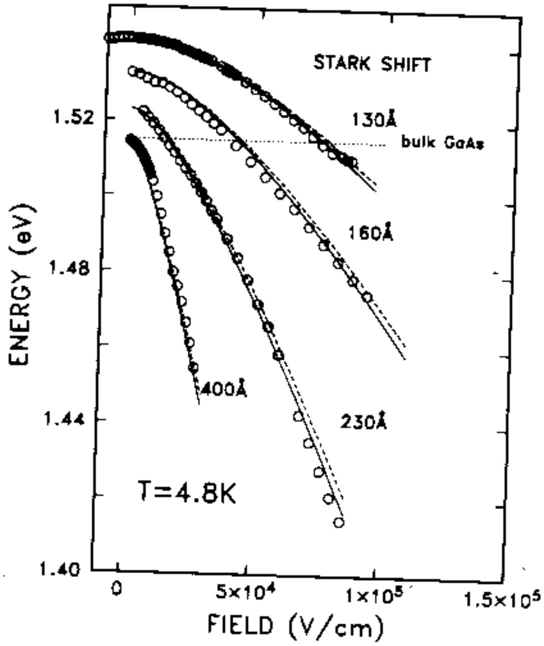

Fig. 3 Stark shifts of heavy-hole exciton energies for four different well widths. Two calculations are shown by dashed and solid lines.

Figure 4 shows a low-field PLE spectrum for a 160Å-wide well, covering the spectral region from the ground to the excited states of the light-hole exciton. Also depicted is the heavy-hole PL, which shows a rising background from the p⁺-GaAs PL on its low energy side. The dominant peaks in this spectrum are extremely sharp, with a full width at half maximum of 0.5 meV, comparable to the thermal broadening, reflecting the exceptional quality of the sample. In the presence of an electric field, the QWs become asymmetric and forbidden transitions ($\Delta n \neq 0$) appear.[14] The peak labeled h_{12a} corresponds to one of such transitions, between the $n=2$ heavy-hole and the n=1 electron. Based on agreements with published experimental[7,8] and theoretical data,[7,8,9,15] the shaded structures in the spectrum are assigned to the excited states of the heavy- and light-hole excitons, $h_1^{(2s)}$ and $l_1^{(2s)}$, respectively. Calculations of the oscillator strength give a ratio of the excited to the ground states of 0.11,[15,16] in reasonable agreement with the experimental value of 0.07.

PLE spectra for different voltages, in the spectral range covering the l_1 and $h_1^{(2s)}$ excitons, are shown in Fig. 5. At zero field, $h_1^{(2s)}$ lies 1.5meV higher than l_1, and the ratio of their oscillator strengths is ≈ 0.25. With increasing the electric field, $h_1^{(2s)}$ shifts more than l_1, because of its heavy-hole character; their relative energy spacing decreases, and their intensities become comparable. At still higher fields the excitons separate; $h_1^{(2s)}$ moves to the low-energy side of l_1, reversing the original order, and its intensity decreases steadily.

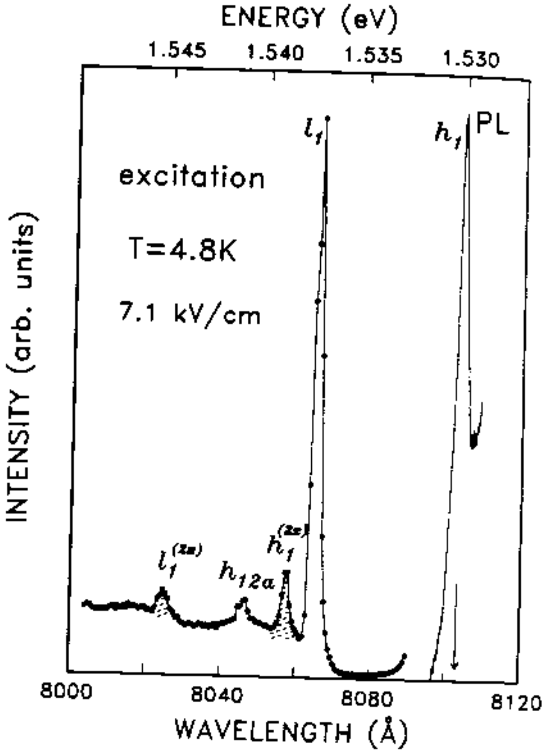

Fig. 4 Excitation spectrum with the photoluminescence of the heavy-hole exciton, where h_1,$h_1^{(2s)}$-l_1 and $l_1^{(2s)}$ denote the ground and excited states of the heavy- and light-hole excitons, respectively, and h_{12a} corresponds to an exciton related to the n=1 conduction and n=2 heavy-hole valence bands.

Figure 6, where the energies of $h_1^{(2s)}$ and l_1 are plotted as a function of field, shows clearly the coupling between these excitons, manifesting itself as an anticrossing. The solid and dotted lines represent calculations of the Stark shifts of uncoupled heavy- and light-hole excitons, respectively. As seen in the figure, the excitons follow closely the theoretical predictions outside of the range of strong coupling. The inset in the figure shows the integrated intensity of $h_1^{(2s)}$, normalized

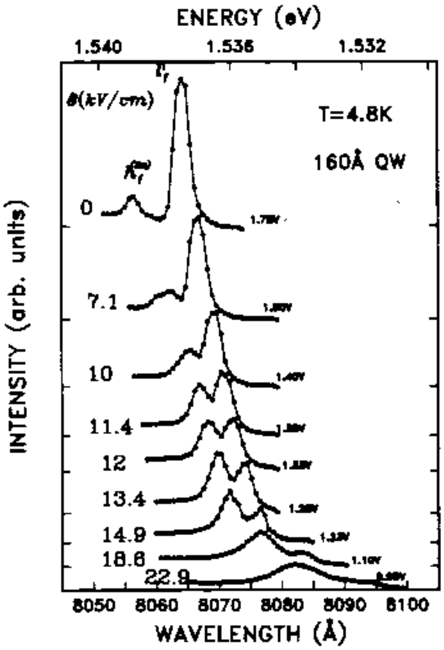

Fig. 5 Excitation spectra for several biases, ranging from flat band (1.75V) to 22.9kV/cm (0.95V), in the spectral range of the ground light-hole exciton, l_1, and the excited states of the heavy-hole exciton, $h_1^{(2s)}$.

to that of l_1, as a function of electric field. A strong correlation exists between the maximum in the intensity and the minimum in the energy separation of the excitonic structures. The minimum separation between l_1 and $h_1^{(2s)}$, 0.7 ± 0.2 meV, indicates an enhancement of the exchange interaction between these excitons by a factor of two with respect to bulk GaAs.[17] In addition, as a consequence of the interaction, further fine structure is resolved as a doublet in the excited states of the heavy-hole exciton, which is not shown here. We attributed the high- (low-) energy component of the doublet to the 2s (2p) state of the h_1 exciton. Their energy separation, ≈0.45 meV, agrees with the calculated difference of their binding energies. [9, 15]

PC measurements[14] for the similar sample have also provided useful information complementary to the above-described PL and PLE results. The combination of PL and PC techniques[18] allowed us to establish the role of impurities in the Stokes shift between absorption and emission measurements. Also, the PC measurements, because of their high sensitivity, revealed two excitonic peaks in the energy range of the parity- forbidden h_{12} exciton, which provided evidence of mixing between the second heavy- and the first light-hole valence subbands. A possible model for the mixing is that it occurs between h_{12} and an excited state of the l_1 exciton.

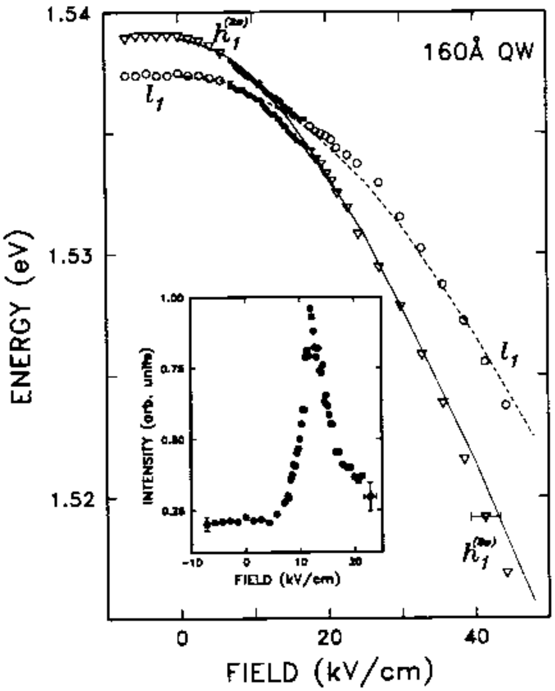

Fig. 6 Stark shifts of the light-hole exciton, l_1 (open circles), and the excited states of the heavy-hole exciton, $h_1^{(2s)}$ (open triangles). The data are shown as solid circles in the region of strong coupling. The lines correspond to calculations in the envelope-function approximation. The integrated intensity of $h_1^{(2s)}$, normalized to that of l_1, is shown in the inset.

3. SUMMARY

Stark shifts in QWs exhibits the strong dependence on both the well thickness and the origin of the involved excitonic transition. The energy shift from zero field in the peak of the free heavy-hole exciton exceeds 0.1eV at an electric field of 100kV/cm. The study on Stark shifts enables us to observe coupling between excited states of the heavy-hole and the ground state of the light-hole excitons. An anticrossing behavior with sharing of oscillator strength for fields of the order of 10kV/cm has been shown. A doublet resolved in the excited states of the heavy-hole exciton is assigned to its 2s and 2p states.

It should be reminded that the study of these extraordinary phenomena in quasi-two-dimensional carriers was made possible only with high-quality structures offered through advanced material engineering. The results reported here demonstrate that optical spectroscopy in solid-state quantum systems can approach the level of resolution found in atomic physics.

REFERENCES

1. L. Esaki and R. Tsu, IBM Research Note RC-2418 (1969); IBM J. Res. Develop. 14 (1970) 61
2. L. Esaki, IEEE J. Quantum Electron. QE-22 (1986) 1611
3. L.L. Chang, L. Esaki, and R. Tsu, Appl. Phys. Lett. 24 (1974) 593
4. L. Esaki and L.L. Chang, Phys. Rev. Lett. 33 (1974) 495
5. R. Dingle, W. Wiegmann, and C.H. Henry, Phys. Rev. Lett. 33 (1974) 827; R. Dingle, A.C. Gossard, and W. Wiegmann, Phys. Rev. Lett., 34 (1975) 1327
6. R. Tsu, L.L. Chang, G.A. Sai-Halasz, and L. Esaki, Phys. Rev. Lett. 34 (1975) 1509
7. R.C. Miller, D.A. Kleinman, W.T. Tsang, and A.C. Gossard, Phys. Rev. B 24 (1981) 1134
8. P. Dawson, K.J. Moore, G. Duggan, H.I. Ralph, and C.T.B. Foxon, Phys. Rev. B34 (1986) 6007
9. K.J. Moore, P. Dawson, and C.T. Foxon, Phys. Rev. B 34 (1986) 6022
10. E.E. Mendez, G. Bastard, L.L. Chang, and L. Esaki, Phys. Rev. B 26 (1982) 7101
11. L. Vina, E.E. Mendez, W.I. Wang, L.L. Chang, and L. Esaki, J. Phys. C: Solid State Phys. 20 (1987) 2803
12. L. Vina, R.T. Collins, E.E. Mendez, and W.I. Wang, Phys. Rev. Lett. 58 (1987) 832
13. G. Bastard, E.E. Mendez, L.L. Chang, and L. Esaki, Phys. Rev. B 28 (1983) 3241.
14. R.T. Collins, K.v. Klitzing and K. Ploog, Phys. Rev. B 33 (1986) 4378; R.T. Collins, L. Vina, W.I. Wang, L.L. Chang, L. Esaki, K.v. Klitzing and K. Ploog, Phys. Rev. B 36, in press.
15. Y. Shinozuka and M. Matsuura, Phys. Rev. B 28 (1983) 4878
16. R.L. Greene, K.K. Bajaj, and D.E. Phelps, Phys. Rev. B 29 (1983) 1807
17. C.J. Jagannath and E.S. Koteles, Solid State Commun. 58 (1986) 417
18. L. Vina, R.T. Collins, E.E. Mendez, and W.I. Wang, Phys. Rev. B 33 (1986) 5939