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Determination of the valence-band offset of GaAs-(Ga,In)P quantum wells by photoreflectance spectroscopy

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This work reports on growth, characterization, and calculation of the electronic structure of GaAs-(Ga,In)P quantum wells, where the two semiconductors share neither a common anion nor a common cation. Metal organic molecular-beam epitaxy was the growth method that we used. The composition of the disordered alloy was close to 50 at.% indium. We have determined the valence-band offset in such structures. We have found $\Delta E_c/\Delta E_v = 0.4$, and have calculated the influence of the spin-orbit split-off states on the light-hole confinement. We found that these deep valence states significantly reduce the light-hole confinement.

During the last two decades, the physics of semiconductors has been dominated by investigations of prospective heterostructures. In particular, the GaAs-(Ga,Al)As system, where the ternary alloy (Ga,Al)As is nearly lattice matched to GaAs for all compositions, is currently subjected to worldwide developments to incorporate it in low-cost integrated devices.[1] However, (Ga,Al)As compounds suffer from multiple drawbacks. The most important defects are donor-related deep traps such as $EL2$ and DX,[2] which are observed when the Al content in the alloy is greater than 30 at.%. Another frequently related problem is the high reactivity of these compounds with oxygen, which causes difficulties in the control of some processes widely used for the fabrication of devices from these materials.[3] (Ga,In)P has recently emerged as a potential alternate high-band-gap material for the realization of barriers on GaAs.[4] This material is *a priori* not lattice matched to GaAs. Lattice matching occurs only for a particular composition of the ternary semiconductor, close to $(Ga_{0.5},In_{0.5})P$. For that composition, the band-gap energy is close to the direct band gap of $(Ga_{0.7},Al_{0.3})As$. An important parameter for the use of heterostructures in the buildup of devices like lasers[5] or heterostructures bipolar transistors[6] is the band lineup between the two semiconductors. In the case of GaAs-(Ga,Al)As, the ratio of the conduction-band offset ΔE_c to the valence-band offset ΔE_v is now well established: $\Delta E_c/\Delta E_v \sim 2$. The situation is not at all so clear for GaAs-(Ga,In)P lattice-matched heterostructures, where the values published for ΔE_c vary between 0.03 (Ref. 7) and 0.39 eV,[8] the band-gap difference being of the order of 0.45 eV. Recently, Lee *et al.*[9] have performed a determination of ΔE_c for such heterostructures from a study of the current-voltage characteristics of GaAs-$(Ga_{0.5},In_{0.5})P$ double-heterojunction bipolar transistors and found a value of 0.21 eV. They confirmed this value by internal photoemission measurements on the same samples. A tight-binding calculation of band lineups at GaAs-(Ga,In)P lattice-matched heterostructures was performed by Foulon *et al.*[10] This calculation yielded a value for ΔE_c that varies between 60 and 130 meV, depending on the detailed interface atomic structure. Indeed, this calculation confirmed that for such a heterostructure where the two semiconductors share neither a common anion nor a common cation [contrary to GaAs-(Ga,Al)As], the band lineups are highly dependent on the interface dipole, and thus on the interface chemical bonding.

In this paper, we report on a study of the optical properties of GaAs-(Ga,In)P quantum wells by the technique of photoreflectance spectroscopy. The epitaxial layers were grown by metal-organic molecular-beam epitaxy (MOMBE). Reflection high-energy electron diffraction (RHEED) was used *in situ* during the growth to characterize the various materials that were grown, and in particular to control the GaAs quantum well thicknesses, from the intensity oscillations of the specular beam. X-ray diffraction was used *a posteriori* to check that the (Ga,In)P barriers were lattice matched to GaAs. Lattice matching occurs for a composition close to $(Ga_{0.5},In_{0.5})P$. Detailed information of the growth procedures used to obtain these quantum wells are given elsewhere.[11] Photoreflectance spectroscopy is a differential method which has been used previously to study band lineup problems in GaAs-(Ga,Al)As and (Ga,In)As-GaAs quantum wells and heterostructures.[12–17] The principles of the method have been reviewed in Ref. 18. The photoreflectance data shown in Fig. 1 were taken at 2 K, using the 325-nm radiation of a helium-cadmium laser. The sample is a multiple quantum well structure with five GaAs wells with thicknesses of 70, 35, 25, 15, and 10 Å, separated from each other by 450-Å-thick (Ga,In)P barriers. The signatures of the intrinsic excitonic transitions consist of a

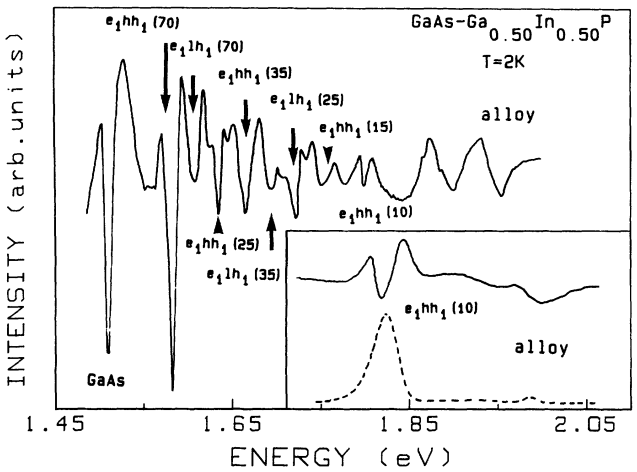

FIG. 1. Photoreflectance spectra taken at 2 K on a series of GaAs wells with respective thicknesses of 70, 35, 25, 15, and 10 Å. Data taken on a second sample are included.

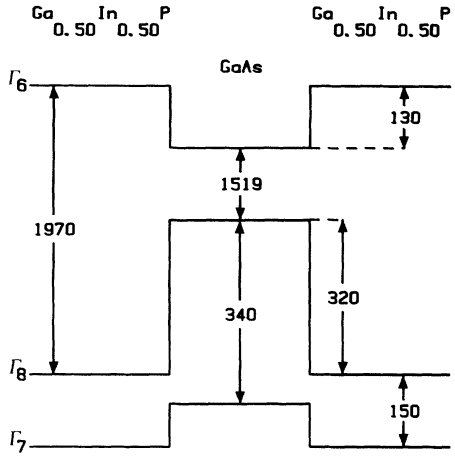

FIG. 2. The band line ups deduced from this photoreflectance investigation, for GaAs-$Ga_{0.5}In_{0.5}P$ quantum wells.

series of sharp structures, some of which correspond to the photoluminescence features observed in similar samples,[11] and allow us to identify the ground-state transition of the different quantum wells. All the wells give a pair of features corresponding to the e_1hh_1 and e_1lh_1 transitions from low to high energy, respectively. Due to the design of the samples, the transitions corresponding to different wells sometimes overlap, but can still be identified. For energies above 1.82 eV, the energy corresponding to e_1hh_1 in the thinnest well, the derivative structures are broad and weak and the light-hole transitions are not clearly resolved. This is not surprising and can be qualitatively explained as follows with the arguments generally invoked: The spreading of the carriers in the barrier layers is important for thin layers. The broadening arises from the fluctuations of the composition sampled by these carriers at the scale of their wave function.

The spectrum obtained on a second sample with a simpler design (a single quantum well) has been included in Fig. 1. The corresponding photoluminescence spectrum was also reported (dashed line). We obtain a nice heavy-hole derivative structure, but do not detect any feature that could be attributed to e_1lh_1. Note the weak photoluminescence signal at 1970 meV, which corresponds to recombination of excitons in the wide (Ga,In)P layers. The occurrence of a feature at this energy, and in the two photoreflectance spectra, gives us the value of the alloy energy gap. The observation of exciton polaritons freely propagating in wide barrier layers already has been reported in GaAs-(Ga,Al)As (Ref. 13) and CdTe-(Cd,Zn)Te (Ref. 19) samples. The energy at which this transition is observed in our samples could indicate the absence of a significant atomic ordering in our (Ga,In)P material, contrary to some previous observations.[20] However, the exciton diameter is too large to state this without reservation. In fact, transmission electron microscope studies performed on our (Ga,In)P material indeed confirmed that it is not ordered.

The calculation of the electronic structure of these samples has been made in the context of a multiband envelope function approach, including the complex structure of the valence band in order to quantify the eventual influence of the spin-orbit split-off states. The spin-orbit splitting is important (~340 meV) for GaAs, and is smaller for $(Ga_{0.5},In_{0.5})P$ [~150 meV (Ref. 21)]. A nice agreement between the experimental results and the envelope function approach is obtained with band offsets such that $\Delta E_c = 0.4\Delta E_v$. Figure 2 illustrates the corresponding potential profiles in the GaAs-(Ga,In)P quantum well. We wish to emphasize the fact that we fit both ground-state transitions as well as excited state transitions. The effect of the coupling between the light-hole and the spin-orbit split-off hole is to reduce the light-hole confinement energies. The physics of the effect was addressed in Refs. 22 and 23 for (Ga,In)As-(Ga,Al)As quantum wells and superlattices. Figure 3 shows the difference between the cal-

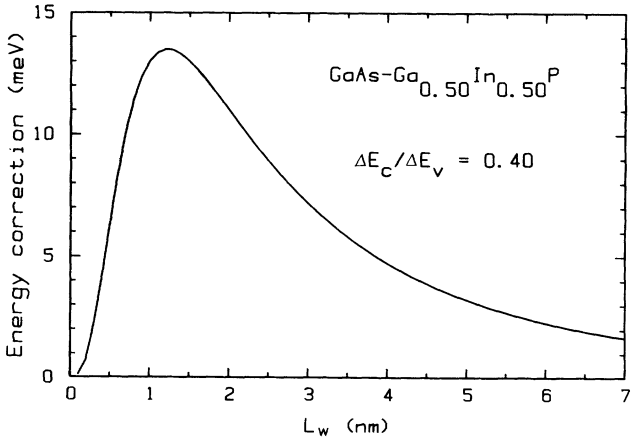

FIG. 3. The reduction of the light-hole confinement energy resulting of the interaction between the light-hole and spin-orbit split-off hole valence-band states. The result of the calculation shows that the effect is maximum for GaAs wells of small thicknesses (~3–4 monolayers).

culation which takes this interaction into account and the calculation which ignores it. The maximum coupling occurs for well widths close to 1.3 nm. The smaller deviation observed for GaAs thicknesses smaller than 1 nm ($\sim$3–4 monolayers) is explained as follows: In the one-dimensional finite quantum well calculation, one always gets at least one confined state. In the limit of narrow wells, when L_w tends to zero, when the $n=1$ value resides extremely close to the top of the well, a saturation of the dependence of the confinement energy with changes of the well width is observed. This is also obtained from a two-band calculation. For finite wells, the difference between the two calculations diminishes when L_w tends to zero.

The band lineups deduced from this study are in very good agreement with the calculation of Ref. 10. However, as already mentioned, there is a large spread among the experimental values reported for the system GaAs-(Ga,In)P. One possible explanation for that is the dependence of the band lineups on the interface chemical bonding for a heterostructure between two semiconductor materials which share neither a common anion nor a common cation. A recent determination by photoelectron spectroscopy on InP-(Ga,In)As heterostructures grown by MOMBE (Ref. 24) has shown an asymmetry of $\sim$180 meV associated with the chemical asymmetry of the direct and inverse interfaces, thus confirming the important role of interface bonding in the buildup of the band offsets in these systems. Ordering effects, already observed in (Ga,In)P,[20] may also play role in the formation of the band offsets, although the band-gap difference for ordered and disordered alloys is only of the 50 meV (a smaller gap exists for ordered alloys).

In summary, we have studied the optical properties of a series of GaAs-$Ga_{0.5}In_{0.5}P$ quantum wells by photoreflectance spectroscopy, and calculated their electronic structure using a two-band envelope function approach. We found a valence-band offset value of 320 meV, corresponding to the ratio $\Delta E_c/\Delta E_v = 0.4$. We have evaluated the implication of the interaction between the light-hole and spin-orbit split-off hole on the light-hole confinement energy and gave its dependence with the thickness of the GaAs layer.

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