Observation of interface carrier states in no-common-atom heterostructures ZnSe/BeTe

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Received 13 May 2011, in final form 25 July 2011
Published 16 August 2011
Online at stacks.iop.org/Nano/22/365707

Abstract

The existence of intrinsic carrier interface states in heterostructures with no common atom at the interface (such as ZnSe/BeTe) is shown experimentally by ellipsometry and photoluminescence spectroscopy. These states are located on interfaces and lie inside the effective bandgap of the structure; they are characterized by a high density and a long lifetime.

A tight binding model confirms theoretically the existence of these states in ZnSe/BeTe heterostructures for a ZnTe-type interface, in contrast to the case of the BeSe-type interface for which they do not exist.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The main element of any semiconductor nanostructure (quantum wells, quantum wires, quantum dots) is an interface. Indeed, there are no nanostructures without interfaces; and their influence can become very important as the structure’s size is reduced. The imperfections of the interface limit many basic parameters of the structures. For example, the carrier mobility in high electron mobility transistors (HEMTs) is reduced by interface fluctuations, the quantum efficiency of nanostructures is limited by non-radiative recombination on interfaces and the interfaces are centers for segregation of impurities and defects, etc [1, 2].

There have been many studies of extrinsic carrier states localized at interfaces, for example states at the Si/SiO₂ interfaces in metal oxide semiconductor (MOS) structures or interface dipole states in heterovalent structures AₓBₓ/A₁B₅. But, besides such extrinsic imperfections on interfaces, which can in principle be eliminated, the microscopic structure of ideal interfaces in ideal heterostructures can also strongly influence nanostructure properties.

In 1932 Tamm predicted the existence of carrier states localized at the ideal surface of a semiconductor crystal [3]. Such states (Tamm surface states) are characterized by one-dimensional localization along the direction normal to the surface and by energy levels located inside the bandgap of the bulk semiconductor. These surface states, originating from clean and well-ordered surfaces, are intrinsic. They induce a Fermi level pinning and lead to band bending at the semiconductor surface. Since Tamm’s prediction, many theoretical and experimental studies have shown the strong influence of such surface states on the optical and electrical properties of semiconductors and semiconductor devices, see, for example, [4].

James [5] was the first to suggest that similar states might exist in the vicinity of a sharp interface separating two different semiconductor materials. The analogy between Tamn and interface states is based on the fact that a heterointerface, like the surface, is a strong perturbation of the crystal’s periodic potential, which can lead to carrier localization.

Advances in molecular beam epitaxy with growth control at the monolayer level have catalyzed scientific interest in
research on semiconductor interfaces. There has been recent theoretical work predicting the existence of the intrinsic interface states [2, 6], but until now there have been only a few experimental studies of such states, despite their obvious importance for fundamental science and applications.

One example of the interface states is electron states in HgTe/CdTe superlattices. These structures are heterostructures of type III, in which the bottom of the conduction band in one of the materials lies below the top of the valence band of the contacted material. In such structures, intrinsic interface states appear due to mixing of electron and hole states on the interface [7].

Reference [8] represented another example of indirect experimental observations of interface states. Its authors studied the temperature dependence of the lateral conductivity of quantum wells made of materials with no common atom, namely InAs/AlSb. To explain this dependence they postulated the existence of Tamm-like, localized interface states not associated with defects but due to the strong discontinuity in the periodic potentials on the two sides of the interface.

In the structures with no common atom on the interface, for example AC/BD (here A and B are anions, C and D are cations), the perfect interface is an isoelectronic plane of one of the two possible binaries AD or CB, that is a binary different from the heterostructure components. The absence of a common atom across the interface seems to favor the existence of an additional carrier-confining interface potential, thus promoting the formation of interface states.

Nevertheless interface states could be observed sometimes in systems with a common atom on the interface, either a common anion as in HgTe/CdTe (see [7]) or a common cation as in ZnO/ZnSe [9].

In ZnSe/BeTe quantum wells, another heterostructure with ‘no-common-atom’ interfaces, our investigations of the in-plane optical anisotropy [10] gave some preliminary indications of the possible existence of interface states in the case where the interface is of the ZnTe type.

In the present work we have performed a systematic study of the no-common-atom interface, quantum well structure ZnSe/BeTe by low temperature photoluminescence (PL) spectroscopy and spectrally resolved ellipsometry. In association with a theoretical tight binding study, the experiments have allowed us to answer the following questions. (1) Do intrinsic electron (hole) states similar to the Tamm surface state exist localized on the ideal interface? (2) Are such states always present or are there some limitations on their existence?

We also studied time-resolved photoluminescence in these structures. Our experimental data clearly demonstrate the existence of electronic states strongly localized on heterostructure interfaces.

2. Experiment

Type-II ZnSe-based quantum well structures were grown on [100] GaAs substrates as a set of alternating ZnSe and BeTe layers with 20 periods in each sample. Some of the samples studied contained manganese ions in the quantum well with a concentration of about 1% in the ZnSe layers, but we consider that Mn is not concerned in the observation of interface states because of its low concentration and because it is an isoelectronic atom which does not give rise to any impurity levels. We studied about 10 samples with different well widths grown in different conditions. Only two of them contained 1% manganese. We did not observe any essential difference in the optical spectra between the samples with manganese and those without.

In the samples, the width of the BeTe layers was equal to half the width of the ZnSe layers and varied from 10 to 100 Å. The ZnSe and BeTe lattice constants almost coincide, so these layers do not experience any strain [11, 14]. From previous work [10], it was found that the band alignment between ZnSe and BeTe layers is of type II (see figure 1). This was deduced from the observation of an indirect transition (IT) in the PL spectrum corresponding to a spatially indirect recombination of electrons confined in ZnSe layers and holes confined in BeTe layers. Since the barrier heights in the conduction and valence bands are sufficiently large (valence band offset = 9 eV, conduction band offset = 2.6 eV [11, 14]), our samples can be considered as structures of isolated quantum wells even at the minimum layer widths studied. The details of the sample growth and characterization are given in [12].

Two types of interfaces can be realized in such structures depending on the growth conditions. They can be a ZnTe-type interface or a BeSe-type interface, and they have been identified by the observation of a strong optical anisotropy [13]. In our structures it was demonstrated that all interfaces were of the ZnTe type [11, 14].

Studies by means of scanning tunneling microscopy of these A2B6 samples show that the interface roughnesses do
Figure 2. (a) At bottom: solid trace—photoluminescence spectrum from ZnSe/BeTe quantum well structure with 40 Å/20 Å layer thicknesses; dotted trace—PL spectrum for structure with 120 Å/60 Å layer thicknesses. At top: ellipsometry spectrum from the 40 Å/20 Å sample. Line IT corresponds to the spatially indirect exciton transitions, while line IST corresponds to the transitions via symmetric (S) and anti-symmetric (AS) interface states. (b) is for a 100 Å/50 Å ZnSe/BeTe quantum well structure. At bottom: photoluminescence; at top: ellipsometry. Line DT corresponds to the spatially direct exciton in the ZnSe well. The peak intensity of the pulsed optical excitation for this figure was 100 W cm\(^{-2}\).

not exceed two monolayers and are comparable with those of conventional \(A_3B_5\) structures [14]. Optical characterization of these samples [15] confirm these results by showing a localization energy of only 10 meV due to interface roughness.

We performed a comparison of PL spectra and spectrally resolved ellipsometry data. The ellipsometry spectra were recorded in a wide spectral range and at temperatures varying from 10 to 77 K with a laboratory-built ellipsometer like that of [16]. PL was excited by the third harmonic (335 nm wavelength) of a pulsed YAG laser with diode pumping. The pulse duration was 20 ns and repetition rate 1 kHz with maximum average power density of 2 W cm\(^{-2}\). Spectra were dispersed by a single monochromator with linear dispersion of 20 Å mm\(^{-1}\) and recorded by a box-car integrator and photomultiplier.

Time-resolved spectra were obtained by exciting with the second harmonic (at a wavelength of 410 nm) of a Ti:sapphire laser with pulse duration 200 fs and repetition frequency 5 kHz. The traces were recorded with a streak camera with time windows from 1 ns to 1 µs.

Figure 2 shows typical spectra of our ZnSe/BeTe quantum well structures. We present both PL spectra and the spectral dependence of the pseudo-dielectric function extracted from the ellipsometry data.

The ellipsometry and photoluminescence spectra both exhibit three main features: the relatively narrow line at high energy (2.8 eV) labeled DT, which is observed in samples with wide ZnSe layers ([17]), has been identified as due to the spatially direct excitonic optical transition in the ZnSe layers.

The very broad line labeled IT at 2.05 eV corresponds to the indirect recombination of electrons confined in ZnSe layers with holes confined in the BeTe layers.

In addition, a new line labeled IST(S) appears at lower energy in both luminescence and ellipsometry spectra in figure 2. The IST emission is absent in spectra of bulk ZnSe and BeTe. It can be observed in heterostructures only at rather low excitation density. Its considerable intensity in both ellipsometry and PL spectra (which reflect respectively the density of states and the carrier population) indicates a large density of states and a high carrier-capture rate. We connect this line with interface state transitions (ISTs).

The ratio of DT, IT and IST line intensities depends on the ZnSe and BeTe layer widths, namely the intensity of the IST line relative to the intensity of the IT line grows with a decrease of the structure period, while the intensity of the DT line falls.

The intensity of the IST PL line decreases when the excitation density increases, in contrast to the intensities of the direct and indirect exciton PL lines (DT, IT). The PL spectra of these lines are compared in figure 3 for two excitation densities: 2 kW cm\(^{-2}\) and 100 W cm\(^{-2}\).

At high excitation intensities exceeding 1 kW cm\(^{-2}\), spatially separated electrons and holes in the ZnSe and BeTe layers induce strong electric fields inside the QW and giving rise to a strong bending of the conduction and valence bands. This leads to a strong change of the electron and hole wavefunctions in the QWs and to an increase of their overlap at the interface [18]. As a consequence, the IT line intensity increases and its radiative decay time decreases from 50 ns to 100 ps [18, 19].

For the IST line, the decay time is very long (several microseconds) whatever the excitation density. In the inset of figure 3, the decay time for the interface state transition is...
The fact that the IST decay time does not depend on the excitation density indicates that any change in wavefunction overlap induced by the electric field has insignificant effect on the IST recombination time. Instead, the IST optical transition is mainly governed by the internal symmetry of the localized states. The decrease of the IST line intensity (figure 3) as a function of excitation power can be explained by a redistribution of the intensity between IT and IST lines: as recombination via the IT transition becomes more effective, the carrier capture into the interface states should decrease.

We should note that, in previous work [18, 19] with similar heterostructures, the IST line was not observed in PL spectra. However, the minimum excitation densities used in those experiments were higher than our maximum excitation densities. At such high excitation, the IST PL can no longer be observed.

Moreover the decay of the IST PL is almost exponential and independent of the excitation density, in contrast to the decay of the IT PL which is non-exponential and very sensitive to excitation power (from [19] the IT decay time varies from tens of nanoseconds at weak excitation to hundreds of picoseconds at high excitation, as is expected for the indirect recombination in type-II structures). Here, for the same range of excitation conditions, the IST decay time shows no dependence on the excitation intensity and on the structure period. This different behavior of the IT and IST recombinations emphasizes their different nature.

When the temperature increases from 10 to 77 K the intensity of all PL lines decreases by only a factor of about two. This indicates the weak influence of non-radiative centers in these samples.

An other important peculiarity of the IST line is the dependence of transition energy on the heterostructure period. When the structure’s period decreases, the DT and IT lines shift toward higher energies, while the IST(S) line shifts towards lower energies.

Figure 2 compares PL spectra for narrow quantum wells 40 Å/20 Å (solid trace) and wide wells 120 Å/60 Å (dotted trace). One can see clearly that the PL line related to the interface states (IST) shifts to smaller energy with a narrowing of the well. On the other hand, the IT line shifts to higher energy.

The shift to higher energy when the period decreases is typical for any confined state. In contrast, the shift to lower energy for this line IST is very unusual and requires an explanation.

It is well known that electron and hole states confined in a QW increase their energy with decreasing confinement size, according to the uncertainty principle. Hence, the optical transition (absorption or emission) should shift towards higher energies as $1/L^2$, where $L$ is the well width.

Since the IST(S) line behaves in just the opposite way, the corresponding states are apparently not related to quantization of the carriers in the wells.

The IST(S) line shifts down in energy when the interfaces approach each other. The known case for such behavior is realized in double quantum wells, when the pair of states localized in the neighboring wells start to interact and split into symmetric (S) and anti-symmetric (AS) states. In such a case, the energy of the symmetric state decreases, while the energy of the anti-symmetric state increases.

Very similar to the present study, a shift to low energy with decreasing period is known for the interface states in HgTe/CdTe superlattices [2, 7].

3. Discussion

In order to interpret our experimental finding, we use a model similar to that of double quantum wells. We consider that every interface has a state localized in the $Z$ direction with a localization size of several ångströms. To fit the calculations to experimental data we have to assume that the energy level of the interface state is located in the gap nearly 100 meV lower than the bottom of the QW (this value corresponds to the observed energy of the IST transition for the 230 Å width of ZnSe, see figure 4).

Thus, the quantum well acts as a barrier separating these states on the neighboring interfaces (figure 1). When the interfaces approach each other, these states split into symmetric and anti-symmetric states. The symmetric state shifts to lower energy and the anti-symmetric state shifts to higher energy. In the PL spectra we see the symmetric state (S) as a strong line because it is lower in energy. A weak feature on the shoulder of the IT PL line in figure 2 may correspond to the anti-symmetric state (AS). The anti-symmetric state can be observed much more strongly in the ellipsometry spectrum, see figure 2(a).
The energy positions measured for the symmetric and anti-symmetric interface states for different structure periods and the results of the following calculation are shown in figure 4.

To calculate the localization energy for the symmetric and anti-symmetric states we solved a one-dimensional Schrödinger equation with a δ-like potential on the interfaces:

$$\frac{\hbar^2}{2m} \frac{d^2\Psi}{dz^2} + U_{QW}(z)\Psi - \gamma [\delta(z+a) + \delta(z-a)]\Psi = E\Psi$$  \(1\)

where \(U_{QW}(z)\) is the rectangular potential of the quantum well, \(2a\) is the quantum well width and \(\gamma > 0\) is the strength of the δ-like potential. Figure 4 shows the result of the calculation with \(\gamma = 9.3\) eV Å.

As follows from these estimates, the splitting of the hole states localized on the neighboring interfaces will be small, due to a large hole mass \((0.7m_0\) in ZnSe \([21]\) and 1.15\(m_0\) in BeTe) and does not explain the significant magnitude observed for the symmetric state’s energy shift. But the energy shift of the electron level, due to the small effective mass of an electron \((0.16m_0\) in ZnSe and 0.25\(m_0\) in BeTe \([22]\)), can reach as much as 100 meV. Thus the energy shift of the IST line observed in the experiment is mainly due to the electron interface states. This conclusion, of course, does not exclude the existence of the hole interface states, but their energy shift with a decrease of the structure period will be significantly smaller than that of the electron states.

To summarize, a new PL line has been found in multiple quantum well ZnSe/BeTe structures, with the following features.

1. It corresponds to a level located inside an effective bandgap at lower energy than the spatially indirect exciton transitions. It is characterized by a high density of states.
2. This line shifts toward low energy with decreasing thickness of the layers in the structures.
3. It disappears at high optical excitation.
4. The decay time of the recombination does not depend on the excitation level and is several orders of magnitude longer than the decay time through indirect exciton recombination (IT) and many orders of magnitude longer than the direct exciton recombination (DT), which is about 100 ps.

All these results clearly indicate that this new line IST corresponds to intrinsic carrier (electron and hole) states localized on the interface, similar to the Tamm states on a crystal surface.

To describe the interface carrier states, a theoretical model has been developed \([23]\) based on the empirical tight binding model. In this model there are two important parameters: \(\beta\) — the overlap energy of the neighboring atoms on the interface and \(\Delta\) — the perturbation of the energy levels of the interface atoms. The numerical calculation shows that interface states for electrons and holes can exist in a wide range of \(\beta\) and \(\Delta\) on the ZnTe-type interface. In contrast, for a BeSe-type interface, the interface states cannot exist at any \(\beta\) and \(\Delta\).

A calculation for the case of GaAs/AlAs heterostructures using the same tight binding model shows the absence of interface states in this system. Indeed, a prerequisite condition for having bound states at the interface is that the heterostructures should have no common atom across the interface: in such cases the strongly confining interface potential for both types of carriers leads to the formation of interfaces states (a detailed theoretical analysis of this problem will be published elsewhere \([24]\)).

4. Conclusion

Studying ellipsometry and photoluminescence spectra from ZnSe/BeTe quantum well structures, we found a new spectral line which we attribute to interface states. This line, IST(S), lies at lower energy than the effective bandgap in these structures. It disappears from the PL spectra at high optical excitation. With increasing confinement, contrary to all other lines, it shifts to lower energies. We explain such a behavior as follows: the states localized on neighboring interfaces form symmetric and anti-symmetric combinations, as in double quantum wells. With decreasing structure period, the symmetric state (S) shifts down in energy while the anti-symmetric state (AS) shifts up. A phenomenological model has been developed to describe the splitting. Calculations in the tight binding model show that the interface states can exist in structures with the ZnTe-type interface and are absent on BeSe-type interfaces.

The interface between ZnSe and BeTe layers in our structures is a giant two-dimensional ZnTe ‘molecule’. The electron states of this molecule are just our interface states. Because of monolayer fluctuations of the QW width and barriers, this two-dimensional ‘molecule’ splits into clusters with different energies of the electron states, which leads to the broadening of the IST and IT lines.

The difference between ZnTe and BeSe interfaces comes from the fact that the intrinsic electron states of the ‘quasi-molecule’ ZnTe lie in the effective bandgap of the ZnSe/BeTe superlattice, but the electron states of the BeSe ‘quasi-molecule’ lie inside allowed bands.

Finally we have to emphasize that the interface states observed in our work are intrinsic to this type of heterostructure and have to be considered for all electronic properties.

Acknowledgments

This work received support from the RFBR, the Presidium RAS, the Department of Physical Sciences RAS and from CNRS grants. We thank M O Nestoklon and A V Platonov for discussions. In particular, we thank Ronald T Cox for help with the preparation of this paper.

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