Giant Electro-optical Anisotropy in Type-II Heterostructures

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The quantum confined Pockels effect has been observed in type-II ZnSe/BeTe quantum well structures. In order to describe the in-plane optical anisotropy induced by the electric field in type-II heterostructures, a theoretical approach has been developed which is based on the representation of optical matrix elements in the microscopical tight-binding model. It is shown that polarized light spectroscopy allows one to obtain microscopic information on interfaces in heterostructures, especially on the orientation of chemical bonds.

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A single heterojunction grown along the [001] crystallographic direction and composed from semiconductors with a zinc-blende lattice (e.g., GaAs/AlAs, InAs/AlSb, ZnSe/BeTe) has the low point-group symmetry C_{2v}. This symmetry allows an in-plane anisotropy of the system due to the tetrahedral orientation of chemical bonds along the $\langle 111 \rangle$ directions. An ideal quantum well (QW) structure with equivalent interfaces has the higher symmetry D_{2d} and is uniaxially isotropic. In QWs the chemical bonds at the opposite interfaces lie in mutually orthogonal planes $(1\bar{1}0)$, (110) and both contributions to the anisotropy compensate each other. The in-plane anisotropy inherently exists in QW structures with nonequivalent interfaces as has been realized on heteropairs with no-common atom [1,2]. An external or built-in electric field can also modify the balance between normal- and inverted-interface contributions in a QW structure and induce the in-plane anisotropy.

Up to now, the in-plane optical anisotropy in QW structures induced by normally applied electric fields, known as the quantum confined Pockels effect (QCPE), has been observed for two heterosystems with a type-I band alignment. Kwok *et al.* [3] analyzed the photoluminescence (PL) of biased GaAs/AlGaAs multiple QWs (MQWs). No noticeable anisotropy was found for allowed interband transitions, whereas the nominally forbidden PL peak $e2$-$hh1$ showed a substantial difference between $[1\bar{1}0]$ and [110] polarizations reaching 20%–30%. Krebs *et al.* [4] reported the observation of a dichroism up to 11% in InGaAs/InP MQWs inserted into a p-i-n diode. By using the so-called HBF model [1] they suggested an explanation of the in-plane anisotropy observed in Refs. [3,4] by interface-induced mixing of heavy- and light-hole states due to the reduced point symmetry C_{2v} of an ideal (001) interface. Recently the QCPE in type-I heterostructures has been described [2] in terms of the generalized envelope function approximation [5,6].

Semiconductor heterostructures with a type-II band alignment, where electrons and holes are separated spatially in the alternating layers, have obvious advantages for the optical study of interface-related phenomena. In type-I QWs, the overlap between electron and hole wave functions extends over the whole QW layer. This averages and considerably reduces the effect of interface-induced and electric-field affected heavy-light hole mixing. On the contrary, in type-II structures the spatially indirect transitions arise due to the electron-hole wave function overlap only within an extremely narrow region adjacent to the interface. Therefore, the transition oscillator strength has to be strongly correlated with an anisotropic orientation of the interface chemical bonds. This is confirmed by observations of strong linear polarization of the PL in unbiased InAs/AlSb heterostructures [7].

We have recently found a pronounced linear polarization in ZnSe/BeTe heterostructures [8]. This combination is interesting because of its close lattice-match resulting in high crystallographic perfection as determined by high resolution transmission electron microscopy [9], and the combination of a highly covalent (BeTe) and an ionic (ZnSe) chemical bond [10]. In this Letter, we report a very pronounced QCPE in type-II ZnSe/BeTe double-barrier structures (DBS). The effect has been found experimentally and analyzed theoretically. Modification of the band structure under applied external electric fields allows one to detect signals from an individual interface and to determine the orientation of chemical bonds from the field induced optical anisotropy effect.

A set of resonant tunneling ZnSe/BeTe DBS's were grown on GaAs:Si(001) substrates by molecular-beam epitaxy (for growth details, see Ref. [11]). The layer sequence is symmetric and comprises lattice matched BeZnSe:I (300 nm) contact layers, undoped ZnSe (25 nm) spacer layers, which act as electron emitters under applied bias voltage, and the BeTe/ZnSe/BeTe (4 nm/5 nm/4 nm) DBS (see inset in Fig. 1). In sample B the central layer consisted of pure ZnSe, while in sample A it was substituted by a $Zn_{0.9}Mn_{0.1}Se$ (5 nm) layer. We note here that semimagnetic nature of the QW layer is insignificant for the effects discussed in this paper. For both structures

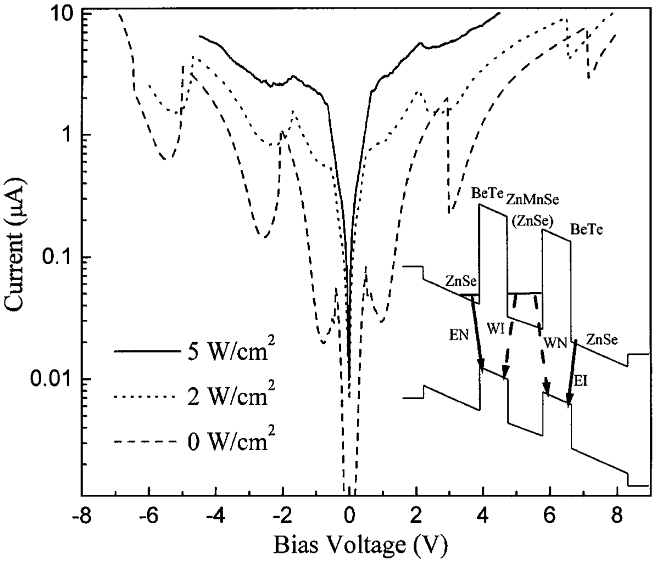

FIG. 1. I-V curves of the double-barrier resonant-tunneling structure BeTe/ZnMnSe/BeTe 40 Å/50 Å/40 Å in dark and for two different illumination intensities. The inset shows the band diagram of the biased sample. $T = 1.6$ K.

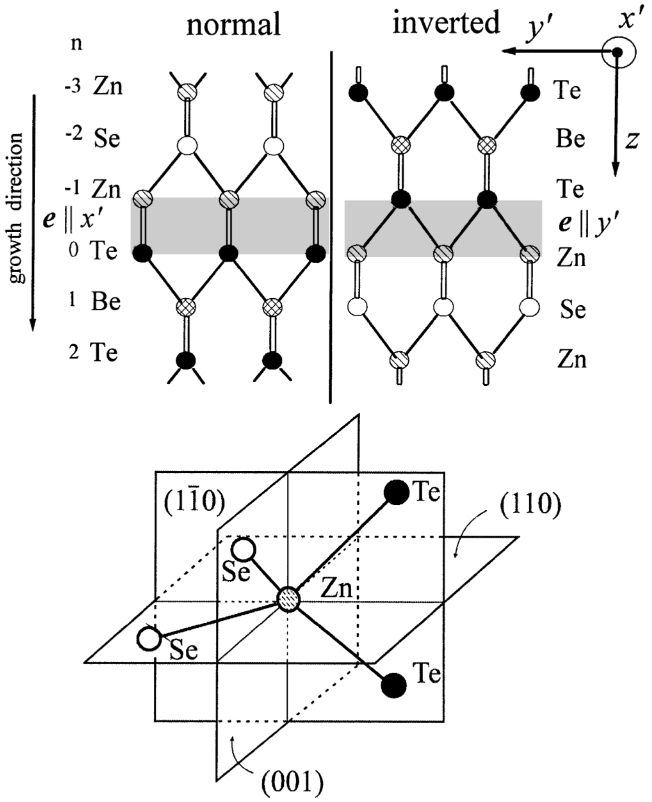

FIG. 2. The sequence of atomic planes near the normal Zn-Te interface in the ZnSe/BeTe heterostructure, the numbers of shown planes with $n = 0$ assigned to the interface Te plane, and the polarization of the corresponding interatomic optical transitions. The in-plane axes x' and y' are parallel to $[1\bar{1}0]$ and [110], respectively.

the *normal* (BeTe on ZnSe) and *inverted* (ZnSe on BeTe) interfaces are grown, respectively, under Zn and Te termination; they contain the Zn-Te chemical bonds (Fig. 2). The PL signal excited by UV lines of an Ar-ion laser was collected from the surface of the mesas and the polarization characteristics of this signal at low temperatures (1.6–50 K) were analyzed.

The tunneling current was measured as a function of applied voltage under the conditions of optical experiments in order to control the electric field in the DBS. Figure 1 presents the I-V characteristics of the BeTe/$Zn_{0.9}Mn_{0.1}Se$/BeTe structure measured for different levels of the laser illumination. The characteristics exhibit a set of strong features related to electron resonance tunneling between the contact layers through the DBS (the resonant tunneling aspects in these structures have been reported in [11] in more detail). Under illumination, i.e., in the condition in which the PL spectra were detected, the features become less pronounced and are shifted. We would like to stress here that the I-V characteristics are quite symmetrical for direct and reverse biases which evidence high symmetry of the structure, in particular small values of built-in electric fields.

The PL spectra detected in linear polarizations along $[1\bar{1}0]$ and [110] axes are shown in Fig. 3 for the two studied structures. The emission lines under study originate from the spatially indirect transitions involving electrons from the ZnSe emitters (E) or quantum wells (W) and holes from the BeTe layers. At zero electric field pairs of the *EN* and *EI* PL lines are due to recombination of electrons from the left- and right-hand side emitters and photoholes in BeTe (N and I indicate the normal and inverted interfaces, respectively). Additionally, in sample B a pair of the *WI* and *WN* lines involving electrons from the well layer is observed. Splitting between the *EN* and *EI* lines can be attributed to a small charge asymmetry of the emitters. Positive electric fields push off electrons from the right interface and form a triangular potential near the left interface pushing electrons towards the latter. As a result the relative intensity of the *EN* line contributed by transitions at the Zn-Te interface increases and that for the *EI* line related to the Te-Zn interface vanishes. A field reversal leads to an exchange of the role played by the interfaces. The bias-induced PL intensity variations and energy shifts for the *EN* and *EI* lines in the sample A are presented in Figs. 4a, and 4b. The field-induced optical anisotropy, i.e., the Pockels effect, is visualized in Fig. 4c as a degree of linear polarization $P_l = (I_{1\bar{1}0} - I_{110})/(I_{1\bar{1}0} + I_{110})$, where $I_{1\bar{1}0}, I_{110}$ are the integral intensities of the PL lines measured in the $[1\bar{1}0]$ and $[110]$ polarizer positions. For both directions of the bias voltage the absolute value of P_l rapidly increases, saturates to 0.7–0.8 at the voltage exceeding 0.25 V and is almost constant for higher voltages up to ± 2 V. We found no temperature and magnetic field dependencies of the P_l value. Under the same conditions the linear polarization detected along the axes [100] and [010] was absent. The *WI* and *WN* lines observed in the sample B are polarized similarly to

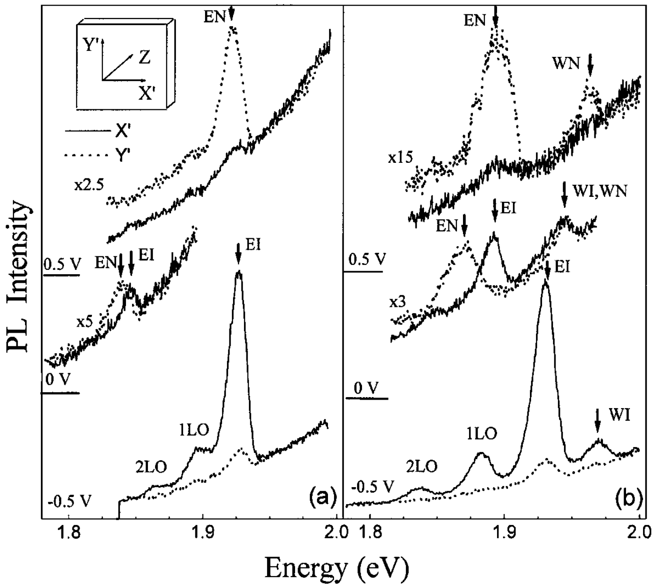

FIG. 3. The polarized PL spectra measured at different bias voltages for the analyzer orientation along the x' and y' axes of the sample A with $Zn_{0.9}Mn_{0.1}Se$ in the middle layer (a) and sample B with the undoped ZnSe middle layer (b). $T = 1.6$ K.

the *EI* and *EN* lines. In the following we propose a model which consistently interprets the experimental findings and suggests a new mechanism of the QCPE realized in type-II heterostructures.

For zinc-blende heterostructures $CA/C'A'$ grown along the [001] principal axis, a single interface is characterized by the reduced point symmetry, C_{2v}, due to perpendicular orientation of the planes (110) and $(1\bar{1}0)$ containing A-C and C-A' chemical bonds at an interface (see Fig. 2). In $C'A'/CA/C'A'$ QW structures with equivalent interfaces C'-A and A-C', say the Zn-Te and Te-Zn interfaces in Fig. 2, the unbiased sample is optically isotropic in the plane perpendicular to the growth direction $z \parallel [001]$: the chemical bonds at the opposite interfaces lie in mutually orthogonal planes and their contributions to the anisotropy cancel each other. In the presence of an electric field the wave functions of free carriers are distorted in the z direction, their values at the opposite interfaces become different, and the balance is disturbed, which results in nonzero PL polarization.

In type-I QWs the envelope function theory [2] predicts that the degree of linear polarization of the PL should change continuously with increasing field and, in moderate electric fields, can amount to a value up to 10%. For the PL due to weak optical transitions $e2 \rightarrow hh1$ in GaAs/AlGaAs MQWs, the linear polarization also changes continuously, reaches a maximum, and then decreases with increasing electric field [3]. These results are at variance with the experiment on ZnSe/BeTe resonant tunneling structures demonstrating very high linear polarization and its insensitivity to the electric field for each ZnSe emitter-BeTe transition.

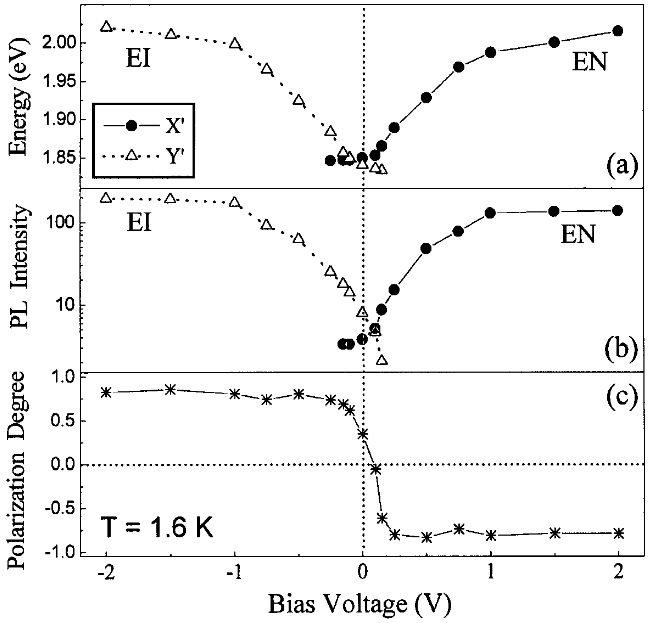

FIG. 4. Effect of an electric field on the position, intensity, and polarization of the PL lines due to optical transitions from the ZnSe emitter to the adjacent BeTe layer in the sample A. (a) Peak position vs bias voltage for the peaks polarized predominately along the x' (triangles) and y' axes (circles) and related to transitions, respectively, at the rightmost and leftmost interfaces. (b) The bias-voltage dependence of the PL intensity integrated over the main resonance range. Triangles represent the PL signal measured in the x' polarization and related to the left-hand interface, whereas circles correspond to the y' polarization and the right-hand interface. (c) The degree of linear polarization calculated by using the integral PL intensity components polarized along x' and y'.

In the ZnSe/BeTe system the conduction- and valence-band offsets amount to 2 and 1 eV, respectively, and the penetration depth of the electron wave function into the BeTe layer or for a hole into the ZnSe layer is about 3 Å. Therefore in type II direct-gap ZnSe/BeTe heterostructures the wave functions of an electron and a hole participating in the spatially indirect transition overlap substantially only over few atomic planes. In this case the calculation of the interband matrix elements requires the knowledge of microscopic behavior of the wave functions at the interfaces which can be obtained by using pseudopotential or tight-binding models. Let us take into account the D_{2d} point symmetry of a QW structure ZnSe/BeTe/ZnSe with symmetrical interfaces. Then in the tight-binding approach the spinor wave functions of a valence-band electron with zero in-plane wave vector can be written as

$$\begin{aligned} \psi_1 &= \sum_n [\uparrow (C_{nx'}\phi_{nx'} + iC_{ny'}\phi_{ny'}) + \downarrow C_{nz}\phi_{nz}], \\ \psi_2 &= \sum_n [\downarrow (C_{nx'}\phi_{nx'} - iC_{ny'}\phi_{ny'}) - \uparrow C_{nz}\phi_{nz}]. \end{aligned} \tag{1}$$

Here the integer n enumerates anion (for even $n = 2l$) and cation (odd $n = 2l - 1$) atomic planes perpendicular to the growth direction, $\uparrow$ and $\downarrow$ are the spin-up and spin-down columns, ϕ_{nj} ($j = x', y', z$) are the planar atomic orbitals (see, e.g., [6,12]), and we use the orbitals $p_{x'} \parallel [1\bar{1}0]$, $p_{y'} \parallel [110]$.

From the polarization degree of 0.7–0.8 we obtain for the ratio between the indirect-transition matrix elements: $|M_{x'}/M_{y'}| = 2.4\text{–}3$ for one and the inverse value for the other interface. This means a strong in-plane anisotropy for the interband matrix elements of the velocity operator, $\mathbf{v}_{cv}$. We express the matrix elements in terms of the tight-binding parameters by using a representation given by Lew Yan Voon and Ram-Mohan [13]. In the basis of atomlike states $|\mathbf{R}, b, \alpha\rangle$ the tight-binding Hamiltonian is written as $H^{bb'}_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$, where $\mathbf{R}, b, \alpha$ label the atomic position, the atom in a unit cell and the orbital state, respectively. In the same basis the velocity matrix elements are given by $\mathbf{v}^{bb'}_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = (i/\hbar)(\mathbf{R}' - \mathbf{R})H^{bb'}_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$. One can see that in this model the velocity matrix element is parallel to the vector $\mathbf{R}' - \mathbf{R}$ and the intra-atomic transitions are ignored (in this connection, see Sec. IV in Ref. [14]).

In the nearest-neighbor sp^3 model a scalar product of $\mathbf{v}_{cv}$ and the light polarization unit vector $\mathbf{e}$ can be expanded for the electron and hole states with zero in-plane wave vector as

$$\frac{ia_0}{4\hbar}\sum_l [V(sa,pc)C^*_{2l,s}(C_{2l-1,x'}e_{x'} \pm iC_{2l+1,y'}e_{y'}) + V(pa,sc)C^*_{2l-1,s}(C_{2l,x'}e_{x'} \pm iC_{2l-2,y'}e_{y'})]. \tag{2}$$

Here the sign ± corresponds to the transitions from ψ_1, ψ_2 valence-band states to the spin-up and spin-down conduction states, the latter being written in terms of the s-like planar orbitals ϕ_{ns} with the expansion coefficients C_{ns}, a_0 is the lattice constant, $V(sa, pc)$ and $V(pa, sc)$ are the sp-interaction parameters [12]. The terms in the sum (2) describe contributions to the optical matrix element due to particular interatomic optical transitions. They are polarized in the plane containing the chemical bonds between the pair of atoms and, therefore, the transitions $2l \leftrightarrow 2l - 1$ and $2l \leftrightarrow 2l + 1$ are polarized orthogonally. In Fig. 2 we show a sequence of atomic planes at the Zn-Te heterointerface, the plane number assignment and the polarization component contributed by the interatomic transition. The experimental high degree of linear polarization can be understood taking into account that only a finite number of terms in Eq. (2) are important, say those arising due to the Se(s) $\rightarrow$ Zn(p), Zn(s) $\rightarrow$ Te(p), Te(s) $\rightarrow$ Be(p) interatomic transitions, and that the product $C_{-1,s}C_{0,x'}$ corresponding to the Zn-Te transition exceeds $C_{-2,s}C_{-1,y'}$ and $C_{0,s}C_{1,y'}$. In other words, the oscillator strength for the interband radiative recombination is in fact governed by the totally polarized transitions between the Zn and Te interface atomic planes. The studied interface-induced anisotropy should be very sensitive to obviously unpolarized contribution of intra-atomic transitions to the optical matrix elements. Thus the present experiment can serve as an important practical basis for an evaluation of the role played by the inter- and intra-atomic optical transitions in an empirical tight-binding theory. It is clear that monomolecular fluctuations of the QW width retain the character of interfacial chemical bonds and cannot lead to remarkable changes in the polarization. On the other hand, the interfacial disorder connected with admixture of Be-Se bonds or any rearrangement of chemical bonds at the interfaces should be followed by dramatic variation of the polarization.

To conclude, in a resonant tunneling ZnSe/BeTe DBS with a type-II band alignment a very pronounced quantum confined Pockels effect has been demonstrated. The theoretical analysis in the tight-binding model highlights the dominating role of the interface chemical bond alignment in the observed optical anisotropy. The reported effect of optical anisotropy has a potential to became a powerful tool for investigation of the microscopic structure of heterointerfaces with monolayer resolution by means of nondestructive optical methods.

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