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Orientation of chemical bonds at type-II heterointerfaces probed by polarized optical spectroscopy

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Time-resolved and cw photoluminescence (PL) spectra are studied in type-II ZnSe/BeTe multiple quantum wells. Samples with nonequivalent interfaces exhibit a strong in-plane linear polarization of the PL along a $\langle 110 \rangle$ axis. The polarization is stable with respect to an increase in the excitation intensity by many orders of magnitude, to a raising of the temperature up to 300 K and not influenced by applied electric or magnetic fields. The experimental data are discussed in the framework of a tight-binding model taking into account a type-II band alignment and lack of common atom in the ZnSe/BeTe heterosystem.

Polarized optical spectroscopy is a potentially efficient diagnostic technique to probe semiconductor heterointerfaces with practically no limits on the penetration depth. To study the interface-induced in-plane anisotropy in single heterojuctions, quantum-well (QW) structures and superlattices (SL's), various spectroscopic methods have been applied, such as three-wave mixing [ZnSe/GaAs (Ref. 1)], ellipsometry and reflectance difference spectroscopy [InAs/AlSb (Ref. 2)], optical transmission [$\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As/InP}$ (Ref. 3)] and polarized photoluminescence (PL) [GaAs/AlAs (Ref. 4), $\mathrm{In}_x\mathrm{Al}_{1-x}\mathrm{As/InP}$ (Refs. 5 and 6), InAs/AlSb (Ref. 7), ZnSe/BeTe (Ref. 8)].

For a single zinc-blende-based heterojunction grown along [001], an in-plane anisotropy is allowed due to the low point-group symmetry C_{2v} of the heterojunction, and related to a tetrahedral orientation of chemical bonds along the $\langle 111 \rangle$ directions. An ideal QW structure with equivalent interfaces has the higher symmetry D_{2d} and is uniaxially isotropic: the chemical bonds at the opposite interfaces lie in mutually orthogonal planes $(1\bar{1}0)$, (110) and both contributions to the anisotropy cancel each other. In the quantum confined Pockels effect,[3,9] an external electric field applied along the growth direction shifts the free carrier wave function away from one interface towards the opposite one, removing the equivalence of the physical properties along the [110] and $[1\bar{1}0]$ axes. In-plane anisotropy inherently exists in QW structures with nonequivalent normal and inverted interfaces as has been realized on heteropairs with nocommon atom.[9,10] Interface roughness in the form of islands, steps, etc., and material intermixing can also lead to an anisotropy, even in nominally symmetrical QW's and SL's, if the disorder differs at the normal and inverted interfaces.[2,4]

In type-II heterostructures with large band offsets, the radiative recombination is indirect in real space. The transition matrix element arises due to electron-hole overlap within an extremely narrow region containing the interface and, therefore, the transition oscillator strength will be strongly affected by an anisotropic orientation of interface chemical bonds. This is supported by observations of high linear polarization of the PL in unbiased InAs/AlSb and ZnSe/BeTe multiple QW's (MQW's).[7,8] In this paper, we study the temperature- and incident-power dependencies of the in-plane polarization of the PL in ZnSe/BeTe MQW's in order to clarify whether the observed polarization is induced by localization of carriers at anisotropic defects and interface imperfections, or whether it is an intrinsic property of the heterostructure, which is retained under delocalization of carriers.

ZnSe/BeTe is a novel material system with a type-II band alignment.[11,12] Its main specific feature is a large conduction and valence band offset which results in a very small penetration of the carrier wave functions into the neighboring layers. This property makes the transition matrix element extremely ''interface sensitive.'' The samples were grown by MBE on (001)-oriented GaAs substrates. Most results reported here were obtained on a structure containing 20 periods of alternating 100-Å-thick ZnSe and 50-Å-thick BeTe layers. However, the data were always verified on several samples. For this particular structure, all interfaces were grown under cation termination which results in formation of Zn-Te chemical bonds at normal interfaces (BeTe on ZnSe) and Be-Se chemical bonds at inverted interfaces (ZnSe on BeTe). Another sample type is a 10-period 200-Å/100-Å ZnSe/BeTe structure with Be-Se interfacial bonds only. Thus the two structures possess different point-group symmetries,

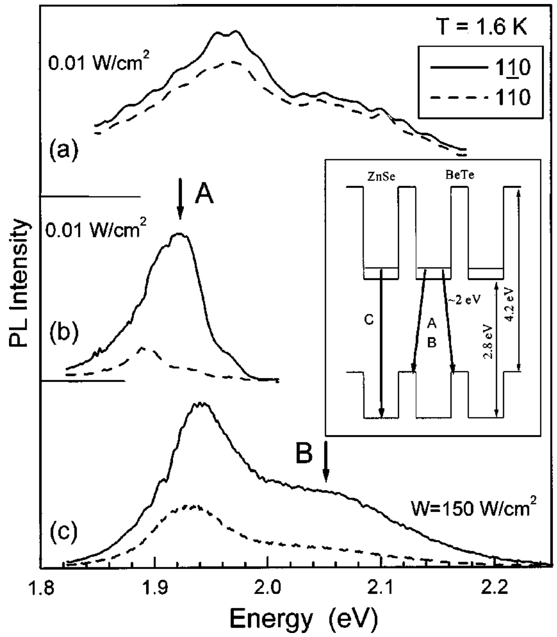

FIG. 1. Polarized PL spectra of ZnSe/BeTe MQW structures with equivalent (a) and nonequivalent (b),(c) interfaces taken under cw excitation.

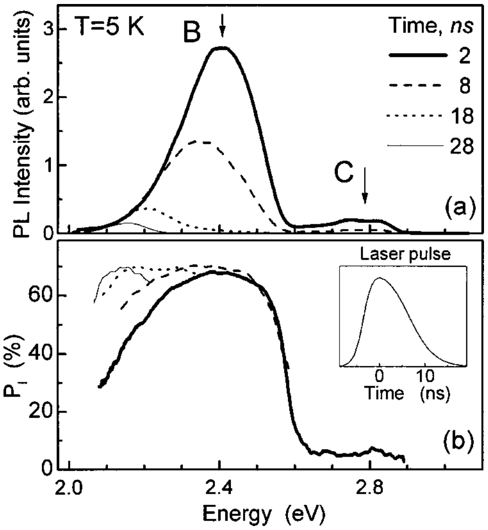

FIG. 2. Time-resolved spectra of the PL intensity and linear polarization P_l measured at different delays in the 100-Å/50-Å ZnSe/BeTe MQW structure with nonequivalent interfaces at $T=5$ K. The inset shows the N_2-laser pulse shape. The excitation density at the laser pulse maximum is 70 kW/cm^2.

namely, C_{2v} and D_{2d}, respectively. The PL was excited either by UV lines of a cw Ar-ion laser or by a pulsed N_2-laser with a pulse duration of 10 ns. The laser light was absorbed in the ZnSe layers only, as the BeTe direct band gap exceeds 4 eV. Polarized time-resolved PL spectra were recorded with a photomultiplier having a temporal resolution of ~ 1 ns. Magnetic fields up to 7 T were applied in the Faraday configuration. Linear polarization of the PL emitted perpendicular to the QW plane, was used to characterize the in-plane anisotropy in the temperature range from 1.6 K up to 300 K, and for photoexcited carrier densities up to 10^{13} cm^{-2}. The degree of PL polarization was insensitive to the orientation of laser polarization (both linear and circular).

At low cw excitation densities and $T<50$ K, an indirect recombination is represented by a PL band centered at 1.93 eV (band A in Fig. 1). This band disappears at $T \approx 70$ K, which indicates that it is related to a recombination of holes weakly localized in the vicinity of interfaces. According to Fig. 1(a) the PL from structures with Be-Se interfacial bonds only has a very small degree of polarization. In contrast, Fig. 1(b) shows that the PL from MQW's with nonequivalent interfaces is highly polarized. The degree of linear polarization $P_l=(I_{1\bar{1}0}-I_{110})/(I_{1\bar{1}0}+I_{110})$ at the maximum of band *A* is about 75%. Here, $I_{1\bar{1}0}$ and I_{110} are the intensities of the PL components polarized along the corresponding directions. With increasing excitation density, *W*, a new band *B* emerges in the spectrum, as can be seen in Fig. 1(c). This band originates from band-to-band, spatially indirect transitions.[13,14] At a laser power $W=150$ W/cm^2 its maximum is centered at ~ 2.05 eV, and the width of about 100 meV indicates a photocarrier density as large as $\sim 10^{12}$ cm^{-2}. It is worthwhile to mention that in the structure with nonequivalent interfaces, the high polarization degree of both bands is only slightly modified when the cw-excitation density increases by four orders of magnitude.

In order to achieve even higher photocarrier densities, pulsed excitation was used. Similar to cw experiments, the PL from the 200-Å/100-Å structures with equivalent interfaces reveals a weak polarization, whereas the PL spectra from the structures with nonequivalent interfaces turn out to be strongly polarized. Typical time-resolved PL spectra recorded at $W=70$ kW/cm^2 are shown in Fig. 2(a) for various time delays with respect to the excitation pulse maximum [see inset in Fig. 2(b)]. At small delays, the spectrum consists of two bands: a wide band *B* in the range of 2.2–2.6 eV, which has the same spatially indirect band-to-band origin as band *B* in Fig. 1(c), and band *C* with a maximum near 2.8 eV corresponding to the direct radiative recombination inside the ZnSe layers. The decay time of band *C* is very short (~ 100 ps) and this band is observed only within the pulse duration. In contrast to that, band *B* has a much longer decay time. While decaying, it exhibits a remarkable narrowing and a redshift by more than 300 meV.[13,14] The PL band width reflects a sum of the ZnSe-electron and BeTe-hole quasi-Fermi energies, whereas its spectral position is affected by the electric field induced by a spatial separation of electrons and holes between ZnSe and BeTe layers. This field gives rise to a strong bending of the conduction and valence bands[13] and results in a blueshift of the PL maximum. Under excitation with $W=70$ kW/cm^2, the maximum electron-hole density slightly exceeds a value of 10^{13} cm^{-2}. For longer delays, the carrier density decreases, due to carrier recombination and, in particular, falls to $(4\pm1)\times10^{12}$ cm^{-2} at a delay of 18 ns.

The PL polarization spectra are shown in Fig. 2(b). As expected, band *C* caused by direct recombination inside the ZnSe layer is polarized very weakly. In this case, as for transitions in type-I QW's, the overlap between electron and hole wave functions extends over the whole ZnSe layer and the effect of interface-induced anisotropy is substantially reduced.[3,9] On the other hand, band *B* remains strongly polarized and the polarization at the band maximum of $P_l \approx 65\%$, is almost independent of the delay time. There is

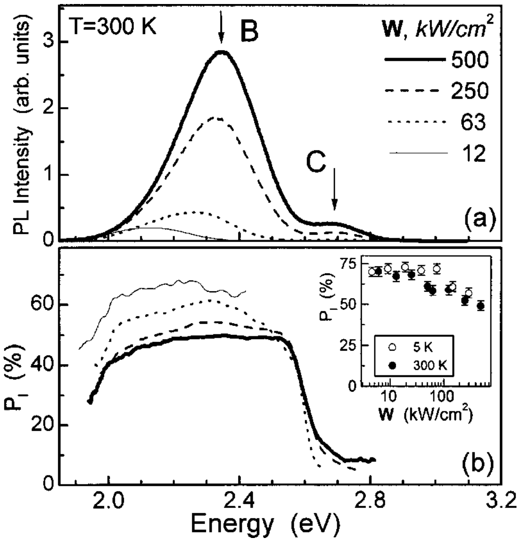

FIG. 3. Time-integrated spectra of the PL intensity and linear polarization P_l measured in the 100-Å/50-Å ZnSe/BeTe MQW structure for different excitation densities at room temperature. The inset shows the excitation density dependence of P_l at the maximum of band B for two different temperatures.

nearly no spectral dependence of the degree of polarization except for some decrease of P_l at the low energy tail. A small decrease in P_l is observed only for $W > 100$ kW/cm^2 as shown in the inset of Fig. 3.

The observed very weak dependence of P_l on the carrier density up to more than 3×10^{13} cm^{-2} excludes any extrinsic mechanisms related to the in-plane anisotropy. It is natural to expect that any built-in electric fields caused by unintentional doping of the investigated structure is screened under such high carrier densities. We can also exclude a significant role of localized states and nonradiative channels in the formation of the in-plane anisotropy, since the high excitation saturates them as well. This statement is supported by measurements of the PL polarization at room temperature, the results are shown in Fig. 3 for excitation densities between 12 and 500 kW/cm^{-2}. The room temperature polarization degree is only slightly smaller than that at $T=5$ K and is nearly independent of the excitation power up to the highest values where the free-electron quasi-Fermi energy exceeds 200 meV. The dependence of the excitation density on P_l is displayed in the inset in Fig. 3(b) for $T=5$ K and 300 K. The two dependencies are very similar. The variation of the degree of polarization in the whole range of temperatures and excitation densities does not exceed 20%.

Summarizing the experimental findings, in ZnSe/BeTe QW structures with nonequivalent and *only nonequivalent* interfaces, the spatially indirect PL is strongly polarized, up to 75%, along the $\langle 110\rangle$ axes. The most striking point is the stability of polarization P_l against changes of various external and internal conditions, namely, (i) against an increase in the excitation power by more than seven orders of magnitude, resulting in crucial changes in the population of the conduction- and valence-band states and in electric fields appearing due to the photocarrier spatial separation, (ii) against the temperature increase from 1.6 to 300 K, and (iii) in addition, we found no remarkable changes in P_l by application of an external magnetic field up to 7 T. Under such conditions, the PL spectrum exhibits tremendous modifications, its intensity changes by many orders of magnitude, the spectral maximum moves upwards or downwards by 200–400 meV, and the PL band halfwidth varies within wide limits as well. In contrast, the PL linear polarization degree remains stable, varying between the limits of 50% and 75% and is almost constant within the halfwidth of the spectral band. These results are in line with our earlier study of the quantum-confined Pockels effect in n-type doped ZnSe/BeTe double-barrier structures,[15] where we found that under an applied bias voltage the PL band was shifted by 200 meV, but that the polarization of the radiation attributed to a particular interface retained its value between 70% and 80%. At the same time, the polarization changed its sign under electric field reversal. We consider the sum of the presented experimental facts to reflect fundamental properties of type-II interfaces with large band discontinuities. It means that any theoretical interpretation of these facts should be based on intrinsic microscopic properties of a single (001) heterojunction between two semiconductors with a zinc-blende-like lattice.

The framework for a theoretical description of the optical anisotropy in terms of a tight-binding model is presented in Ref. 15, where the interband matrix element of the velocity operator, $\mathbf{v}_{cv}$, is written as a sum of contributions, due to particular interatomic transitions. In the conventional nearest-neighbor sp^3 tight-binding model, the intra-atomic transitions are ignored, the contribution of an interatomic transition to $\mathbf{v}_{cv}$ is nonzero only for neighboring cations and anions and this contribution is directed along the corresponding chemical bond. We recall that in the zinc-blende lattice the chemical bonds are oriented in $\langle 111\rangle$ directions and, under movement along the [001] principal axis, they alternatively change their orientation in the (001) plane from $[1\bar{1}0]$ to [110] and vice versa. For optical transitions between Bloch states in a bulk crystal the contribution of any pair of (001) planes to the matrix element in the x' polarization coincides with that of the neighboring pair in the y' polarization, and as a result, these contributions cancel each other and the optical properties are isotropic.

The observed high and stable polarization of the PL attached to a certain ZnSe/BeTe interface can be understood assuming the main contribution to $\mathbf{v}_{cv}$ comes from the totally polarized transitions between the atoms located at the cation and anion interface planes. Taking into account the interatomic transitions Zn(p)→Se(s), Te(p)→Zn(s), Zn(p)→Te(s), Be(p)→Te(s) for the three corresponding pairs of planes adjacent to the interface, we obtain

$$v_{cv}^{x'}=\frac{ia_0}{4\hbar}(V_{Zn,Te}^{sc,pa}C_{Zn,s}^{c}C_{Te,x'}^{v}+V_{Te,Zn}^{sa,pc}C_{Te,s}^{c}C_{Zn,x'}^{v}), \quad (1)$$

$$v_{cv}^{y'}=\mp\frac{ia_0}{4\hbar}(V_{Se,Zn}^{sa,pc}C_{Se,s}^{c}C_{Zn,j}^{v}+V_{Te,Be}^{sa,pc}C_{Te,s}^{c}C_{Be,j}^{v}). \quad (2)$$

Here, for the sake of convenience, we denote by Be, Te, Zn, Se the planes numbered in Fig. 4(a) as $n=1,0,-1,-2$, respectively, $V_{nn'}^{sa,pc}$ and $V_{nn'}^{sc,pa}$ are the sp-interaction parameters denoted as $V(sa,pc), V(pa,sc)$ in Ref. 16 and as V_{s0p}, V_{s1p} in Ref. 17, $C_{n,s}^{c}$ and $C_{n,j}^{v}$ $(j=x',y')$ are the expansion coefficients in the conduction- and valence-electron wave function expressed in terms of the planar atomic orbitals (see

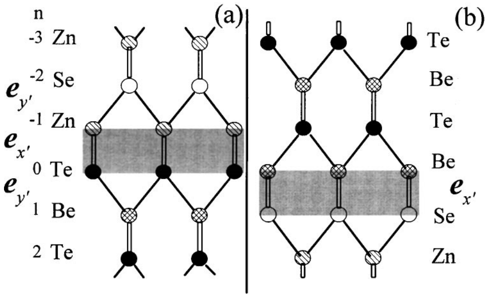

FIG. 4. The sequence of atomic planes near the normal Zn-Te interface (a) and the inverted Be-Se (b) interface. The (001) atomic planes are numbered. The polarization for interatomic transitions is indicated by the nonzero components $e_{x'}$ and $e_{y'}$, where the in-plane axes x' and y' are parallel to $[1\bar{1}0]$ and $[110]$, respectively.

Refs. 9,16–18). Note that the first term in Eq. (1) exceeds the second term, because the Γ_1 conduction-band state is cationlike, $C^c_{Zn,s} > C^c_{Te,s}$, and the Γ_{15} bonding valence states are anionlike, $C^v_{Te,j} > C^v_{Zn,j}$. It is also worthwhile to mention that according to the table of empirical tight-binding matrix elements given by Vogl *et al.*,[16] the parameters $V^{sc,pa}_{Zn,Te}$ and $V^{sa,pc}_{Te,Zn}$ are close to each other and exceed $V^{sa,pc}_{Se,Zn}$ by a factor of 1.7.

The PL polarization is governed by the ratio $|v^{x'}_{cv}/v^{y'}_{cv}|$. Therefore, the stability of P_l implies a weak variability of the ratios $C^c_{Te,s}/C^c_{Zn,s}$, $C^c_{Se,s}/C^c_{Zn,s}$, $C^v_{Zn,j}/C^v_{Te,x'}$ and $C^v_{Be,y'}/C^v_{Te,y'}$ as functions of the $e1$-electron and $hh1$-hole quantum-confinement and in-plane kinetic energies, although absolute values of the coefficients $C^c_{n,s}, C^v_{n,j}$ can vary in rather wide limits. In order to confirm the latter conclusion, we have calculated the coefficients $C^v_{Zn,j}$, $C^v_{Te,j}$, and $C^v_{Be,j}$ under normal incidence of a hole with the wave vector $\mathbf{k} = (0,0,k)$ at a single ZnSe/BeTe interface. For simplicity, we ignored the spin-orbit interaction and, moreover, set the coefficient $C^v_{Se,j} \equiv C^v_{-2,j}$ to be vanishing. Then, by using a procedure similar to that described in Refs. 9 and 18, we find

$$\frac{C^v_{Zn,x'}}{C^v_{Te,x'}} = \frac{\tilde{U}_+}{E - E_{Zn,p}},$$

$$\frac{C^v_{Be,x'}}{C^v_{Te,x'}} = \frac{1}{U_-}\left(E - E_{Te,p} + \frac{\tilde{U}_+^2}{E_{Zn,p} - E}\right). \qquad (3)$$

Here, E is the energy of the incident hole, $E_{Zn,p}$ and $E_{Te,p}$ are the tight-binding diagonal energies for the corresponding atomic orbitals, $U_\pm = (V_{xx} \pm V_{xy})/2$, $\tilde{U}_\pm = (\tilde{V}_{xx} \pm \tilde{V}_{xy})/2$, V_{xx} and V_{xy} are the pp-interaction parameters in BeTe, the tilde marks similar parameters for the Zn-Te interface bond. The ratios of coefficients for the $p_{y'}$ orbitals are obtained from Eq. (3) by the interchange $+ \leftrightarrow -$ of indices. One can also show that, for values of k such as $ka_0/4 \ll 1$, the ratio of $C^v_{Te,y'}$ and $C^v_{Te,x'}$ is given by

$$\frac{C^v_{Te,y'}}{C^v_{Te,x'}} = \frac{(E - E_{Te,p})(E_{Zn,p} - E) + \tilde{U}_+^2 + V_{xx}U_-}{(E - E_{Te,p})(E_{Zn,p} - E) + \tilde{U}_-^2 + V_{xx}U_+}. \qquad (4)$$

It follows then that, while a value of k remains small compared with $4/a_0$, and the hole quantum-confinement energy is small compared with the interband energy gaps, the ratios (3),(4) are fixed, which fixes as well the polarization degree of the PL due to the radiative recombination at an abrupt type-II heterointerface. This result holds also if the condition $C^v_{-2,j} = 0$ is removed and one takes into consideration the nonzero coefficients $C^v_{n,j}$ for the evanescent tail of the valence-band state in the ZnSe layer. We emphasize that no strong PL polarization is expected for structures with smooth type-II heterointerfaces, where the area of the effective electron-hole overlap would extend over several monolayers.

To conclude, the in-plane optical anisotropy is an inherent property of type-II heterostructures with no common atom. The mechanism that rules the anisotropy is based on the orientation of chemical bonds, which is clearly established for ZnSe/BeTe structures. The observed optical phenomenon is proposed as a powerful all-optical, fast and nondestructive method for characterizing interfaces on an interatomic scale (even *in situ*). Other promising candidates for studies of the in-plane anisotropy are ZnTe/CdSe (Ref. 19) and ZnSe/CdS (Ref. 20) material systems.

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