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Non-linear piezoelectric effect in CdTe and CdZnTe

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Abstract: Strained quantum wells (QWs) grown along the polar axis (111) in a zinc-blende semiconductor exhibit a piezoelectric field. This field strongly modifies the energy of excitons confined in QWs. We have extracted, from optical measurements of excitonic transitions, the piezoelectric field value in a large set of QWs: CdTe/CdZnTe, CdTe/CdMnTe, CdZnTe/CdMnTe. By suitably choosing the composition of alloys, we have obtained different values of strains (compressive or extensive) due to the lattice mismatch between QWs and barriers. The non-linear piezoelectric effect appears clearly when plotting the piezoelectric tensor component e_{14} versus lattice mismatch. For example e_{14} increases from 0.07 C/m² to 0.15 C/m² when the lattice mismatch varies from - 0.3% to - 1.7%.

1. INTRODUCTION.

Strained heterostructures of semiconductors grown along a polar crystallographic axis exhibit a piezoelectric field which deeply modifies their band configuration and their optical properties. Such structures are of particular interest for device applications in non-linear optics, for example to design optical switches. Piezoelectric field in strained heterostructures has been theoretically predicted by Smith and Mailhot [1,2] and then experimentally proved [3,4,5]. Fields in excess of 10⁵ V/cm are experimentally observed in III-V and II-VI [6,7] heterostructures strained by about 1%. A rather surprising result is the observation of a non-linear piezoelectric effect in compressively strained CdTe QWs [8]. In this paper we have extended the study of the piezoelectric effect to QWs under both compressive and extensive strains. The piezoelectric coefficient e_{14} is found to be different from the value in the literature [9,10] and a strong variation of e_{14} with the strain state is again observed which cannot be fully explained by recent theoretical calculations.

2. EXPERIMENTS.

2.1 Samples.

Lattice parameters of CdTe, MnTe and ZnTe are 6.48 Å, 6.33 Å and 6.10 Å respectively [11]. For alloys (Cd_{1-x}Mn_xTe and Cd_{1-x}Zn_xTe) we assume, according to Vegard law, a linear dependence of the lattice parameter "a" on the composition "x". Samples are elaborated by molecular beam epitaxy on a vicinal (111) Cd_{0.96}Zn_{0.04}Te substrate. QWs are coherently grown on a buffer layer (~3 μm), thick enough to be nearly strain-free. Barriers have the same composition as the buffer layer: thus barriers are strain-free and exhibit no piezoelectric field whereas wells are under biaxial strain due to the lattice mismatch. Three types of samples have been grown: CdTe/CdZnTe and CdTe/CdMnTe for which CdTe is always under compressive strain, and CdZnTe/CdMnTe (~ 10% Zn) for which the in plane strain $\epsilon_{//} = (a_{\text{well}} - a_{\text{barrier}}) / a_{\text{well}}$ can be made positive (extensive strains) or nearly equal to zero. By suitably choosing the

composition of alloys, we have obtained fifteen samples for which QWs are under different strain states ranging from $\epsilon_{//} = -1.7\%$ to $\epsilon_{//} = +0.2\%$. Each sample contains at least three QWs of different thicknesses, which allows a direct determination of the internal electric field (section 3.1). Moreover a cap layer of about 3000 Å was used to remove the QWs from the region of surface field (see below).

2.2 Optical experiments

Optical properties of strained QWs were investigated by reflectivity, photoluminescence (PL) and photoluminescence excitation at pumped helium temperature. To avoid any screening of piezoelectric field, the photoluminescence excitation power was kept below 1 W/cm². The alloy composition of the barrier CdZnTe or CdMnTe was determined from optical measurement of its excitonic gap. Applying the Vegard law one deduces its lattice parameter, and thus the in-plane strain $\epsilon_{//}$ in the QWs.

2.3 Surface field

A series of samples were grown to estimate the surface electric field effect which could alter the internal piezoelectric field. These samples contained two identical QWs. The first QW was grown deep below the surface (~ 1 µm) and served as a reference. The second QW was grown at different depths (from 170 to 1300 Å) to probe the surface effect. The electric field continuously decreases inside the sample. The experimental results are consistent with a simple model [12] assuming a depletion region of width 2500 Å and a constant impurities density of $4 \cdot 10^{15}$ cm⁻³. Within this model the maximum electric field was found to be about 0.2 mV/Å at the surface and it vanishes at a depth of 2500 Å. A piezoelectric QW is a very good probe for this study because its fundamental energy level is sensitive to first order to little variations of the electric field whereas the same variations will affect a square QW only to second order.

3. RESULTS AND DISCUSSION

3.1 Determination of the electric field

The energy levels in piezoelectric QWs have been calculated within the envelope function approximation, assuming a flat band configuration for the barriers. Figure 1 shows a fit for a sample containing four QWs of different thicknesses. Since these QWs were grown on the same buffer layer they experience the same in plane-strain $\epsilon_{//}$ and therefore the same piezoelectric field. This reduces the number of free parameters for the fit to one (the field F). Figure 2 shows a plot of the measured fields in QWs under compressive and extensive strain. For comparison, we have plotted the piezoelectric field expected from linear elasticity and piezoelectricity:

$$F = \frac{2\sqrt{3}}{\epsilon\epsilon_0} \frac{c_{11}+2c_{12}}{c_{11}+2c_{12}+4c_{44}} e_{14} \epsilon_{//} \quad (1)$$

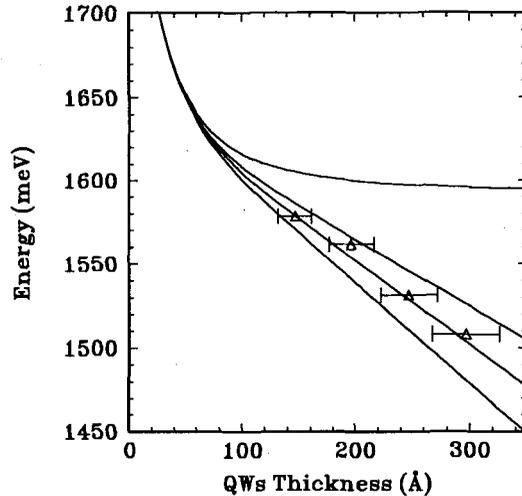


Figure 1: Photoluminescence energy of four piezoelectric QWs CdTe/Cd_{0.87}Mn_{0.13}Te (triangles) of different thicknesses (all other parameters being equal) and calculated curves corresponding, in order of decreasing energy, to $F=0, 0.4, 0.5$ and 0.6 mV/Å.

c_{ij} are elasticity tensor components and $\epsilon\epsilon_0$ is the permittivity of the material. Taken into account c_{ij} values from references [14,15,16] and the bulk value of e_{14} determined by piezoelectrically active shear waves [9,10] ($e_{14}=0.0335$ C/m²), F should follow the dash line on figure 2. Clearly other effects than linear piezoelectricity are involved, such as interface charges or a non linear piezoelectric effect. Charges at (111) interfaces are not ruled out by symmetry, but they are calculated to be very small in GaAs/AlAs [17]. Moreover the measured field does not depend on the nature of the barriers (CdMnTe or CdZnTe). Hence, in the following, we make the hypothesis of a non-linear piezoelectric effect.

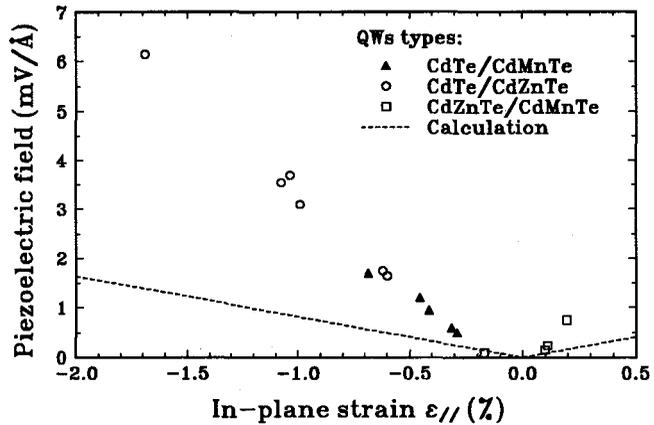


Figure 2: The piezoelectric field (absolute value) extracted from optical measurements, on a large set of samples, could not be fitted by equation (1) and parameters taken in the literature (dashed line).

3.2 Non-linearities.

There are three possible sources for non-linearity in equation (1): ϵ , c_{ij} and e_{14} . The fields involved in this study are rather small (a few mV/Å), so the linear regime should be appropriate for the dielectric constant ϵ [18]. Non-linearity of elastic constants have been investigated under high hydrostatic pressure by Maheswaranathan et al. [16]. According to their results, in the range of strains in our QWs, non-linearity of c_{ij} is about 2% and may be neglected. Ab-initio calculation of c_{ij} [18] leads to the same conclusion. So, non-linearity of the electric field could only be attributed to the piezoelectricity tensor component e_{14} . Equation (1) has been used to extract e_{14} from the measured electric field and the result is shown in figure 3. Since the sign of F cannot be measured in our experiments, we have arbitrarily chosen the sign of e_{14} to get a smooth variation when going from negative to positive strain. Not only e_{14} value is different from the value obtained in bulk materials by ultrasonic waves determination [9,10], but it also largely depends on strain.

Piezoelectricity in zinc-blende materials has been theoretically investigated by Martin [19] and Hübner [20]. In their models, the piezoelectric constant involves an ionic contribution, related to the internal displacement, and an electronic contribution. In CdTe, these contributions are almost equal in magnitude but opposite in sign. This situation is particularly favourable to non linear effects. A recent work by Dal Corso et al. [18] provides an interesting ab-initio calculation of e_{14} for CdTe using the density functional theory. They report that non linear piezoelectricity in CdTe is mainly a volume effect and obtain a linear variation of e_{14} with the change of volume. In (111) strained QWs the change of volume can be expressed in terms of the in-plane strain $\epsilon_{//}$:

$$\frac{\delta V}{V} = \frac{12 C_{44}}{C_{11} + 2C_{12} + 4C_{44}} \epsilon_{//}$$

Using this relation we have compared our results to the calculation of Dal Corso et al. The predicted variation of e_{14} is too weak to account for the strong increase we observed for

$|\mathcal{E}_{//}| < 0.5\%$. On the other hand, the experimental e_{14} seems to follow the predicted linear dependence for $\mathcal{E}_{//} < -0.5\%$.

CONCLUSION

We have observed a strong dependence of e_{14} with strains due to lattice mismatch in (111) oriented QWs. This is due to the fact that e_{14} results from two contributions (ionic and electronic) of opposite sign which nearly cancel in CdTe. The non linearity of piezoelectricity is not fully explained by the volume effect mentioned in recent ab-initio calculations. Further investigations under high hydrostatic pressure are planned.

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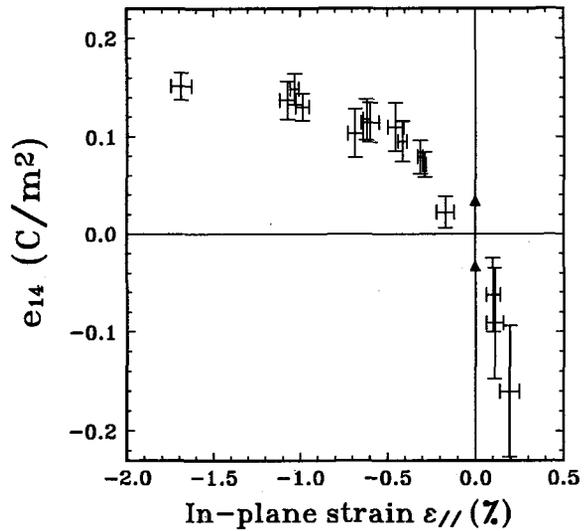


Figure 3: Piezoelectricity tensor component e_{14} extracted from piezoelectric QWs under different strain states. Triangles are the absolute value of e_{14} taken in the literature [9,10].