Interaction of Localized Electronic States with the Conduction Band: Band Anticrossing in II-VI Semiconductor Ternaries

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We report a strongly nonlinear pressure dependence of the band gaps and large downward shifts of the conduction band edges as functions of composition in ZnS_xTe_{1-x} and $ZnSe_yTe_{1-y}$ alloys. The dependencies are explained by an interaction between localized A_1 symmetry states of S or Se atoms and the extended states of the ZnTe matrix. These results, combined with previous studies of III-N-V materials define a new, broad class of semiconductor alloys in which the introduction of highly electronegative atoms leads to dramatic modifications of the conduction band structure. The modifications are well described by the recently introduced band anticrossing model.

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The compositional dependencies of the band gaps of III-V and II-VI ternaries currently generate intense interest from the point of view of the electronic band structure of semiconductors, issues related to band offsets, and lattice matching in heterostructures. About two decades ago, Hjalmarson *et al.* [1] proposed that highly localized levels are generated in the course of the sp^3 hybridization associated with a substitutional impurity in the tetrahedrally coordinated semiconductors. Consider, for example, a group V element in a III-V compound replaced by a different group V element such as in GaN_xAs_{1-x}. It has been shown that depending on the band structure of the host semiconductor, substitutional N atoms produce resonant states within the conduction band or deep levels in the band gap [2]. Striking evidence demonstrating the effect of such localized levels was reported recently by Shan *et al.* [3] in an investigation of the hydrostatic pressure dependence of the band gap of $Ga_{1-y}In_yN_xAs_{1-x}$. They observed two spectral signatures (E_- and E_+) which evolve as a function of pressure and attributed them to the hybridization of the A_1 state with the conduction band minimum at Γ point. They observed that the effect of the interaction increases as the conduction band minimum approaches the localized state. The nonlinear pressure dependence of the two signatures is characteristic of level repulsion between states of identical symmetry as they approach each other energetically; we refer to it as the band anticrossing (BAC) behavior [3,4]. It is relevant to note here that the relative location in energy of the band extrema in the electronic band structure of a semiconductor can be manipulated by application of hydrostatic pressure [5] or by the composition of a ternary alloy. For example, the Γ conduction band minimum in a direct gap semiconductor increases in energy approaching the A_1 level which is expected to be less sensitive to hydrostatic pressure and thus produces level crossing.

It is useful to note here that a large number of ternary alloys (AB_xC_{1-x}) exhibit a composition dependence of their band gaps that only slightly deviates from the linear interpolation between the band gaps of the end point compounds, e.g., as in $Cd_xZn_{1-x}Te$. This behavior is customarily understood in the framework of the virtual crystal approximation (VCA). But there are many examples in which the variation of the band gap from one end member to the other first shows a significant decrease before increasing finally to the band gap of the other end member. This behavior is referred to as band gap bowing. A typical semiconductor of this type is $ZnSe_xTe_{1-x}$. The band gap bowing has been attributed partly to the nonlinearity of the electronic band structure associated with the matrix elements of the VCA potential and partly to disorder [6]. An alternate point of view has been advanced recently based on the argument that the large bowing observed in highly mismatched alloys originates predominantly from structural relaxation and charge exchange [7,8]. The recently discovered BAC model offers a different approach to consider the same effect. The extent to which the model can explain the apparent band gap bowing in group II-VI based alloys is clearly of considerable interest and is indeed a part of the motivation of the current work.

To date the BAC model has been used to explain the electronic properties of III-N-V alloys where a very large bowing of the band gap is observed [3,4]. In the context of this work it is of interest to inquire if the interaction is not an isolated effect but occurs also in other systems with large band gap bowing parameters. The most important feature of the III-N-V alloys is that the highly

electronegative N atoms introduce low-lying A_1 levels located close to the conduction band edges of III-V compounds. An interaction of these levels with the extended states strongly affects the electronic states that determine the basic electrical and optical properties of the alloys. Most notably the interaction produces a downward shift of the lowest conduction band edge, which is observed as a large bowing of the fundamental band gap. Motivated by this observation we have studied the BAC interaction in ZnS_xTe_{1-x} and $ZnSe_yTe_{1-y}$ where similar effects are expected as metallic Te atoms are partially replaced by much more electronegative S or Se atoms.

The samples used in this study are single crystals of ZnS_xTe_{1-x} with $0 < x < 0.15$ and $ZnSe_yTe_{1-y}$ with $0 < y < 0.17$ [9,10]. The crystals were grown by the vertical gradient freezing technique. The details of the growth conditions and the methods used to determine the alloy composition are given elsewhere [10]. A detection system consisting of a 0.5-m single-grating monochromator and an UV enhanced Si photodiode was used for optical absorption measurements. The pressure-dependent measurements were carried out using diamond anvil cells (DAC). In order to accommodate the dimensions of the DAC, samples were mechanically polished to a thickness of 8–10 μm and then cut into small sample chips with sizes of $\sim 200 \times 200$ μm^2 to be loaded into the DAC. The applied pressures were determined by the standard method of monitoring the shift of the ruby R1 line. All the measurements were performed at room temperature (295 K).

Figure 1 shows absorption spectra of $ZnTe_{0.9}S_{0.1}$ at several selected pressures. The fundamental absorption edge was determined at the point of the absorption curves where the steeply rising portion sharply bends over and saturates. A remarkable feature of the data shown in Fig. 1 is a strongly nonlinear shift of the absorption edge with increasing pressure that clearly resembles the pressure dependence of the fundamental band gap previously observed in GaInNAs alloys [3,11].

It has been shown in the case of III-N-V alloys that the localized, N-derived A_1 states interact primarily with the conduction band [3,4,11]. The valence band states experience only the gradual shift expected from a linear interpolation between end point compounds. Since the available III-N-V alloys are limited to very low N concentrations, it has been a good approximation to assume that N does not have any effect on the valence band structure [11]. However, in the alloys studied here having relatively larger S or Se contents, we need to decompose the total shifts of the conduction and the valence band edges into their linear parts given approximately by the VCA, and the nonlinear parts associated with the large bowing. The linear contributions to the band edge shifts are calculated from the known valence band edge offsets, $\Delta E_v(\mathrm{ZnTe/ZnS}) \approx 1.2$ eV and $\Delta E_v(\mathrm{ZnTe/ZnSe}) \approx 0.8$ eV [12].

With the known locations of $E_v(x)$ and $E_v(y)$ we can determine the composition dependent energy of the conduction band edge from the relations $E_c(x) = E_g(x) + E_v(\mathrm{ZnTe}) - 1.2x$ (eV) and $E_c(y) = E_g(y) + E_v(\mathrm{ZnTe}) - 0.8y$ (eV) where $E_g(x)$ and $E_g(y)$ are the measured energy gaps in the respective alloys. Figure 2 shows the energies of the conduction band edges, relative to $E_v(\mathrm{ZnTe})$ at $P = 0$, as functions of pressure for a few different alloy compositions. In good agreement with existing data [13] the pressure dependence of E_c in the ZnTe matrix can be well described by the relation $E_c(P) =$

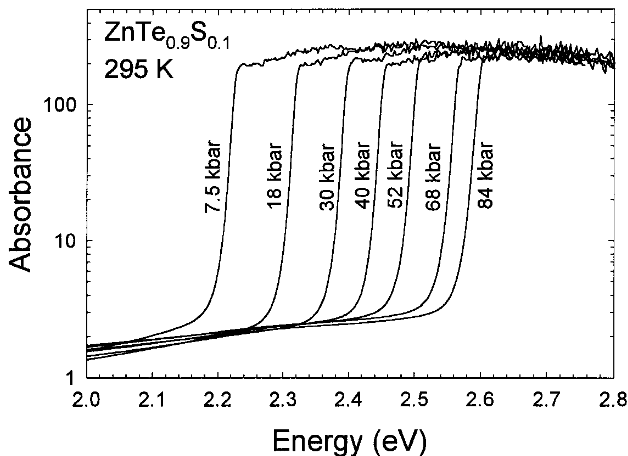

FIG. 1. Representative spectra of dimensionless absorbance (αd) in the vicinity of fundamental absorption edges in $ZnS_{0.1}Te_{0.9}$ measured at different hydrostatic pressures.

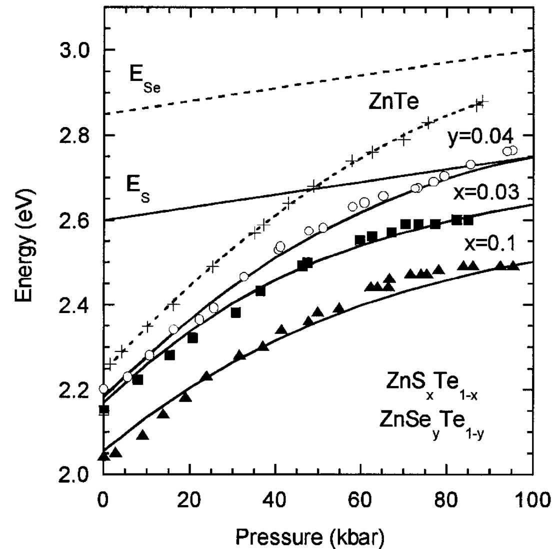

FIG. 2. Dependence of the conduction band edge in ZnSTe and ZnSeTe on pressure. The solid lines represent the dependencies calculated using the BAC model as explained in the text. The energies of the localized S-derived (E_S) and Se-derived (E_{Se}) A_1 states are also shown. All the energies are relative to $E_v(\mathrm{ZnTe})$ at ambient pressure.

$2.24 + 10.9 \times 10^{-3}P - 4.25 \times 10^{-5}P^2$ (eV), where P is the pressure in kbar. The nonlinear term originates from the pressure dependence of the bulk modulus in ZnTe.

It is quite evident from the data shown in Fig. 2 that alloying of ZnTe with both ZnS or ZnSe considerably affects the pressure dependence of the conduction band edge. This is especially visible in ZnS_xTe_{1-x} where $E_c(P)$ curves tend towards a near zero slope at very high pressures. It should be emphasized that the quadratic term in the pressure dependence of the band gaps of ZnS and ZnSe is about 3 times smaller than that of ZnTe. Therefore the observed highly nonlinear pressure dependence of the band gaps cannot be attributed to the pressure dependence of the bulk modulus in the alloys. In fact, the results in Fig. 2 closely resemble the pressure dependence of the band gap previously observed in $Ga_{1-y}In_yN_xAs_{1-x}$ alloys [3,11] where it has been explained in terms of an interaction between localized N states and the extended states of the $Ga_{1-y}In_yAs$ matrix [3,4,14]. To apply the same theoretical model to ZnS_xTe_{1-x} and $ZnSe_yTe_{1-y}$ alloys we consider an interaction between localized S-derived or Se-derived A_1 states and the extended states of the ZnS_xTe_{1-x} or $ZnSe_yTe_{1-y}$ matrix. The parameters of the semiconductor matrices are given by a linear interpolation between parameters of the end point compounds. According to the BAC model the interaction splits the conduction band into two subbands with the dispersion relations given by [3,4]

$$E_{\pm}(k) = \frac{1}{2}\{[E_M(k) + E_L] \pm \sqrt{[E_M(k) - E_L]^2 + 4xC_{LM}^2}\}, \qquad (1)$$

where E_L is the energy of the localized S or Se level, $E_M(k)$ is the k wave vector dependent energy of the conduction band states of the ZnSTe or ZnSeTe matrix, and C_{LM} is the matrix element coupling the localized and extended states. It is worth noting that the strength of the anticrossing interaction depends on the composition x and is given by $C_{LM}x^{1/2}$.

The lines in Fig. 2 represent calculations of the conduction band edge $E_-(0)$ for samples with different x and y. In the calculations the pressure coefficients of the conduction band edge of the matrix $E_M(0)$ were obtained by linear interpolation of the pressure coefficients for the end point compounds. It should be emphasized, however, that the small variations in the pressure coefficients do not have any significant effect on the calculated results. The best fit to experiment was obtained by assuming that the locations of both the S and the Se levels depend slightly on pressure and are given by $E_L = E_{L0} + 1.5 \times 10^{-3}P$ (eV), where E_{L0} is the energy of the S or Se level at ambient pressure. It should be noted that this is exactly the same pressure dependence as the one found for the N level in III-N-V alloys [3,11]. As is seen in Fig. 2, for both ZnS_xTe_{1-x} samples, good agreement between the calculations and the experiment is obtained by setting $E_S = 2.6$ eV and $C_{SM} \cong 1$ eV. The same value of the coupling parameter $C_{SeM} = 1$ eV but a larger energy of the Se-derived level $E_{Se} = 2.85$ eV provides the best fit for the pressure dependence of the conduction band edge in $ZnSe_{0.04}Te_{0.96}$. The value of the coupling parameter is significantly smaller than $C_{NM} = 2.7$ eV used previously to describe the interaction between the N levels and the extended states in GaN_xAs_{1-x} alloys [4,11]. This is not surprising, however, since the electronegativity difference between N and As ($\Delta X = 1$) is more than 2 times larger than between S and Te ($\Delta X = 0.4$) or Se and Te ($\Delta X = 0.3$) [15].

Using the same values for the parameters E_L and C_{LM} we have also calculated the dependence of the conduction band edge energy on the alloy composition in both alloys. The results are shown in Fig. 3. The calculations well reproduce the measured downward shift of the conduction band edge in ZnS_xTe_{1-x} at room temperature as well as previously reported results [9,10] for ZnS_xTe_{1-x} and $ZnSe_yTe_{1-y}$ at 10 K. The fact that we are able to account for both pressure and composition dependence of the conduction band edge strongly supports the notion that the BAC model provides an accurate description of the electronic structure of highly mismatched group II-VI alloys. The previously measured energies of the no-phonon lines [9,10] of the oxygen impurity E_O are also shown in Fig. 3. It is important to note that on this absolute energy scale the energies E_O are to a good approximation constant and equal to about 2 eV in both alloys. The result provides a self-consistency check for our choice of the valence band

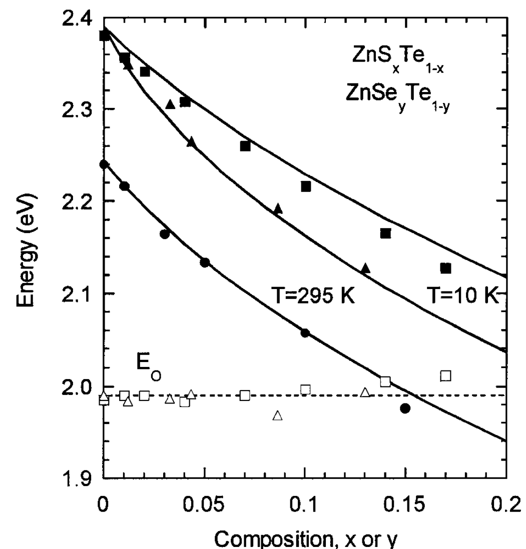

FIG. 3. Composition dependence of the conduction band edge in ZnS_xTe_{1-x} at 10 K (▲) [9] and 295 K (●), and in $ZnSe_yTe_{1-y}$ alloys at 10 K (■) [10]. The lines represent the band edges predicted by the BAC model. Energies of the nonphonon lines E_O in ZnS_xTe_{1-x} (△) and in $ZnSe_yTe_{1-y}$ (□) are also shown. All the energies are measured with respect to E_v(ZnTe).

offsets since it has been shown that highly localized levels can be used as an energy reference to determine the band offsets [16].

The results in Fig. 3 show that similar to the previously considered case of the III-N-V alloys, BAC is also the dominant interaction responsible for the band bowing in ZnSTe and ZnSeTe alloys. This further implies that the other previously proposed bowing mechanisms must be significantly less important. It also explains why the large bowing parameters are observed only in the alloys involving highly electronegative elements (anion alloys) and are conspicuously small when more metallic elements are exchanged (cation alloys). The localized A_1 levels of the metallic atoms have high energy and only very weakly interact with the conduction band edge states. A good example of the later case is ZnMgTe where a negligibly small bowing parameter is found [17] despite a significant electronegativity difference between Zn ($X = 1.5$) and Mg ($X = 1.2$) [15].

Equation (1) for the conduction subbands has been obtained assuming that the highly localized A_1 states of randomly distributed atoms do not interact with each other [4]. This limits the applicability of the present approach to the concentrations x or y small enough so that the average distance between S or Se atoms is larger than the extent of the corresponding A_1 state wave function. Recent tight binding calculations [18] have shown that for N in GaAs the wave function of the A_1 state does not extend much beyond the first nearest member atoms resulting in a value of about 2.5 Å for the effective radius of the A_1 wave function. Adopting a similar localization for the wave function of the A_1 states of S and Se we conclude that the assumption of noninteracting S or Se states is justified for the x and y compositions considered in this work.

It is instructive to examine which of the II-VI compounds would show strongest band anticrossing effects with substitutional S. Since the localized S level lies at about 0.36 eV above the conduction band edge of ZnTe, the compounds with higher lying conduction band edges such as MgTe with $E_c(\mathrm{MgTe}) = E_c(\mathrm{ZnTe}) + 0.4$ eV should exhibit stronger anticrossing effects when alloyed with MgS. Another interesting material system are group II-O-VI alloys in which highly electronegative oxygen ($X_{\mathrm{O}} = 3.5$) [15] partially substitutes other column VI elements. A large BAC effect is expected in this system as it is a direct analog of group III-N-V alloys. Indeed, it is now well established that substitutional oxygen introduces localized states close to the conduction band edge in many II-VI compounds [9,10]. Unfortunately, the preparation of oxygen containing alloys has turned out to be a difficult task and so far the concentrations of O dopants are too low to clearly observe any alloying effects.

In conclusion, we have shown that $\mathrm{ZnS}_x\mathrm{Te}_{1-x}$ and $\mathrm{ZnSe}_y\mathrm{Te}_{1-y}$ belong to a new class of recently discovered highly mismatched semiconductor alloys whose electronic properties are strongly dominated by an anticrossing interaction between localized states of isoelectronic impurities and the extended states of the semiconductor matrix. The results demonstrate the broad applicability of the band anticrossing model extending beyond the previously considered group III-N-V alloys.

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