

TOP VALENCE BANDS IN ZnSe-BASED TERNARIES: BULK, 001-SURFACES AND QUANTUM WELLS

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Abstract

We present a band structure calculation of ternary alloys of II-VI wide-gap semiconductors, starting from ZnSe as reference and changing systematically in it: 1) Cation Zn through Cd to obtain the common anion ternaries (Cd,Zn)Se and 2) Anion Se through S to get common cation ternaries type Zn(S,Se). We use the standard tight-binding method but including spin-orbit coupling. In order to account the effects of the alloy in the change of the band gap value, we use the Virtual Crystal Approximation (VCA). Besides that we analyse the band mixing near Γ point in order to get information about the optical properties in these direct gap semiconductors. With the purpose of describing the surfaces [001] we represent the bulk material grown in [001] as alternating cationic and anionic layers. Each principal layer is constituted of anion (Se) layer and a cation (Zn) layer with a width, which is dependent on concentration because the lattice constant of the alloy is also changing with concentration. We study both cases: i) disorder in the anion sublattice (Zn,Cd)Se, ii) disorder in the cation sublattice Zn(S,Se). We detect two new surface states, one in the band-gap of all materials and the other under the top of valence band. All the studied alloys present the same behaviour with the new surface-states shifting in energy according to composition. Since the role played by these states in heterostructures and quantum wells is fundamental in order to gain information about the energies of electrons and holes forming excitons, we calculate in addition the in-plane band mixing near the top of valence band in quantum wells of (Cd,Zn)Se/ZnSe.

Keywords: Semiconductors, Ternaries, Bulk, Surfaces, New States.

Introduction

Zn(S,Se)-based materials are becoming an attractive prospect for utilization in green-blue light emission. In spite of the efforts in technological applications, little background knowledge is available in the literature for the system [1]. Diode laser operation at shorter wavelengths in pseudomorphic (Cd,Zn)Se/Zn(S,Se) [2] and (Zn,Cd)Se/(Zn,Mg)Se [3] QW heterostructures has also been achieved, with a later extending the wavelength deeper into the blue. For the type-I (Zn,Cd)Se/ZnSe quantum well system, however, it has been demonstrated that the quasi-two-dimensional confinement of electron-hole pairs leads to an enhancement of the exciton oscillator strength as well as its binding energy (E_b). The usual model is based on the assumption that both the electron and the hole are confined each one in a finite well with a depth that is varied until the binding energy fits well with the one obtained from experiment. The lack of information about the ground state of electron and hole and its composition in terms of atomic orbitals makes important to have a detailed electronic band-structure. In this work we approach the materials from the electronic structure in order to have values for the valence and conduction bands positions near the Γ point, its mixing at both edges and its dispersion. This is important information for the understanding of the optical properties of these heterostructures. In this paper we combine an empirical tight-binding method with Green's function to obtain the density of states in bulk and in the 001 surface and take advantage of the gained

information to extend the calculation to quantum wells and study dispersion relations near the Γ point.

1. Method

We use a Green's function method starting from tight-binding hamiltonian, which includes description of the electronic structure of each bulk material first as a tridimensional crystal viewed as a stack of layers grown in the 001 direction, so that we can cut at any layer and have the corresponding surface. The Layer Greens's Function is calculated by inverting a tridiagonal matrix as is explained in reference [4]. For each alloy was necessary to obtain the optimized parameters using the same basis as for ZnSe, ZnS and CdSe and comparing with the published experimental data. A surface is a perturbation in the tridimensional crystal and so we use a Green's function based model in the sense of Surface Green's Function Method (SGFM) Theory [5]. The parametrization is done in the framework of Voegl's sp^3s^* tight-binding model including the spin-orbit effect, which is important in II-VI compounds. s^* is a virtual orbital added in order to improve the description in the conduction bands. We assume that there are no overlap between orbitals and only nearest neighbors interactions are considered in the Slater-Koster approximation. In table I are listed the 15 parameters in eV that describe the microscopic interactions in all three basic materials. Energy bands dispersion $E(k)$ along the principal symmetry directions in the Brillouin zone

show that they are coherent with experimental data available

Table I. Tight-binding parameters used in the calculation

| | ZnSe | ZnS | CdSe |
|-------------|----------|------------|----------|
| ESA | -12.4273 | -10.44842 | -10.1674 |
| ESC | 0.0473 | 2.07151 | 1.2067 |
| EPA | 1.7824 | 0.7842 | 1.0340 |
| EPC | 5.5203 | 6.27886 | 7.6465 |
| VSS | -1.6255 | -6.58933/4 | -0.7231 |
| VXX | 0.8272 | 3.63229/4 | 0.7533 |
| VXY | 1.3530 | 6.34679/4 | 1.4326 |
| VSAC | 0.2842 | 5.18403/4 | 0.5401 |
| VSCA | 1.4506 | 5.87772/4 | 1.4139 |
| VSSAC | 0.4675 | 8.69781/4 | 0.5291 |
| VSSCA | 0.8166 | 9.27886/4 | 0.5542 |
| ESSA | 7.8499 | 5.46999/4 | 6.0265 |
| ESSC | 8.5203 | 4.30627/4 | 3.9615 |
| λ_a | 0.1937 | 0.02789 | 0.1430 |
| λ_C | 0.0194 | 0.00558 | 0.0670 |

In order to test if our description of the ZnSe is good enough we compare the calculation with published measurements. There is new data about this material that we use to fit our parameters. We present in Table II a ten band description where we summarize the eigen-values of several valence states at selected high-symmetry points and compare with the results of other theoretical (first principles) calculations and with the experimental determinations. The topmost valence band Γ_{15} is split owing to spin-orbit coupling into a fourfold state Γ_8 and a twofold state Γ_7 ($\Delta_0 = 0.45$ eV). Thus we reproduce very well the main high-symmetry points with our parameters for ZnSe. Particularly the band-gap of 2.8 eV measured by Petroff et.al. [12] in reflectivity experiments. Also for CdSe and ZnS the main symmetry points agree very well with experimental published data. The satisfactory description of the electronic band-structure of these compounds gives us confidence to use them as basis for describing ternaries with common anion such as $Zn_{1-x}Cd_xSe$ and ternaries with common cation as ZnS_xSe_{1-x} .

We also calculate the projected density of states on a bulk layer for all three materials and show the results in Figure 1, where we can observe the main features of the density of states integrated over the whole bidimensional Brillouin zone and drawn near the center of the Brillouin zone from -4 eV to 3 eV, in this range are the two band

extrema: Valence and conduction and covers the direct gap.

Table II. Calculated and experimental eigenvalues for zinc-selenide at the high-symmetry points Γ , X and L. All energies are referred to the top of the valence bands.

| | VLMT0 | Experiment | Present work |
|-------------------|--------|--------------------|--------------|
| Γ_6^V (eV) | -13.18 | -15.2 ^a | -15.20 |
| Γ_7^V (eV) | -0.45 | | -0.45 |
| Γ_8^V (eV) | 0.00 | 0.00 | 0.00 |
| Δ_0 (eV) | 0.45 | 0.43 ^b | 0.45 |
| X_6^V (eV) | -12.32 | -12.5 ^a | -12.5 |
| X_6^V (eV) | -4.90 | -5.6 ^a | -5.302 |
| X_6^V (eV) | -2.24 | | -2.193 |
| X_6^V (eV) | -2.06 | -2.1 ^a | -1.953 |
| L_6^V (eV) | -12.53 | -13.1 ^a | -13.354 |
| L_6^V (eV) | -5.19 | -5.6 ^a | -4.666 |
| L_6^V (eV) | -1.03 | | -1.23 |
| $L_{4,5}^V$ (eV) | -0.75 | -1.3 ^a | -0.952 |

a [6]

b [7]

In ZnS (Fig. 1a) and ZnSe (Fig. 1c) we obtain density of states with a maximum of 2 (arbitrary units, a.u.) and the width of the top valence band is quite similar although thinner in ZnSe than in ZnS, which we interpret as a common feature to the DOS in the valence band due to the common cation Zn. Comparing CdSe (Fig. 1b) with ZnSe we notice that the DOS is higher up to 3 a.u. but the width of the top valence band in CdSe is half the one of ZnSe, it should be due to cation different contribution to the top valence band. Our method allows us to discriminate D.O.S. in atomic orbitals contribution and compare this feature of the top valence band.

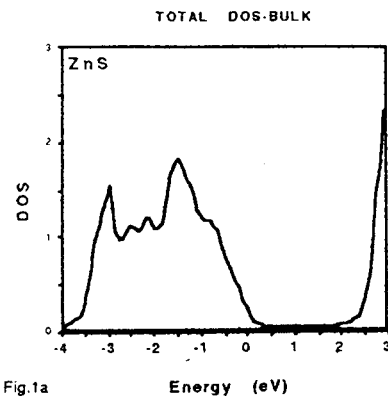


Fig.1a

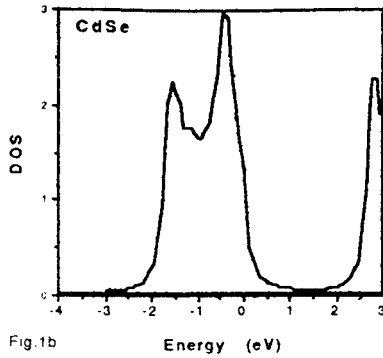


Fig.1b

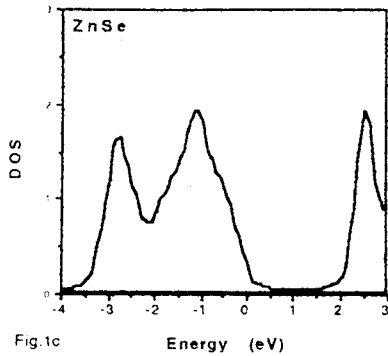


Fig.1c

II. Ternaries

Based on ZnSe, CdSe and ZnS we build up the ternary compounds by finding the tight-binding parameters simply as the concentration weighted average of the constituents:

$$E_{a,b} = x E_{a,b}^{A,B} + (1-x) E_{a,b}^{B,C} \quad (1)$$

Within the VCA we obtain the dependence of energy gap and the lattice constant as function of concentration x , taking into account the variation of the lattice constant $a(x)$ and its effects in the tight-binding parameters. We also calculate the variation of energy gap as function of concentration. The obtained results are in Figure 2.

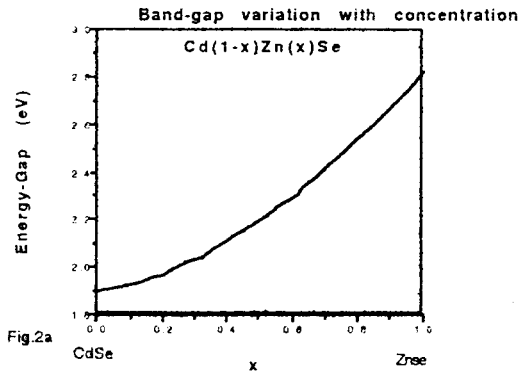


Fig.2a

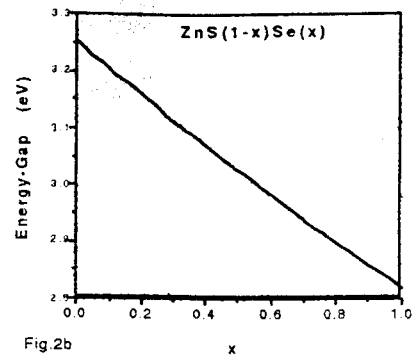


Fig.2b

We obtain a very little bowing as x grows in common cation compounds (Fig.2b) but an observable bowing in the case of common anion (Fig.2a). It is interesting to note that this behaviour arises in a very natural way avoiding a new bowing parameter, but taking into account carefully the correct lattice constant in the tight-binding parameters of the corresponding ternary. Earlier calculations [11] have shown that in ternaries with common cation the bowing parameter is very little. In common cation ternaries both parameters lattice constant and energy-gap vary almost linearly with concentration. On the contrary in common anion semiconductors the bowing is more important. We obtain a remarkable bowing by only introducing the variation of lattice constant in the tight binding parameters.

III. Surfaces

We compare in Figure 3 the DOS for bulk (squares). Surface (001) (solid line) and second layer for a cation terminated surface in all three materials, and find out that a new state appears right in the band-gap.

The corresponding surfaces of CdSe and ZnS are compared with ZnSe in order to follow the behaviour of the surface state. The energy position of this state is closer to the conduction band for ZnS compared with ZnSe, the common feature in these compounds is the common cation. If we observe the new surface states in CdSe compared with ZnSe, it is shifted to the middle of the gap. Then, surface state energy position in the gap depends on the atom, which is substituted. Thus, if we start with ZnSe and change Zn by Cd (cation) the surface state in the middle of the gap, but if we change Se by S (anion) the surface state will shift to the conduction band. In all three cases the width of the surface band is, as expected, thinner than in bulk in the same material due to the loss of the neighbors in the direction 001 as consequence of the lack of translational symmetry.

In order to look at the changes induced by the surface we calculate the difference in the density of states at the surface and in the bulk at Γ point. We present only cation terminated surfaces (Zn and Cd). We have first checked if the Levinson Theorem is satisfied because this guarantees that the number of states is conserved. By integrating the difference in the density of states over all energies we get zero. Taking into account only the

valence band we get -2 which means one state is lacking in valence band (two spin states).

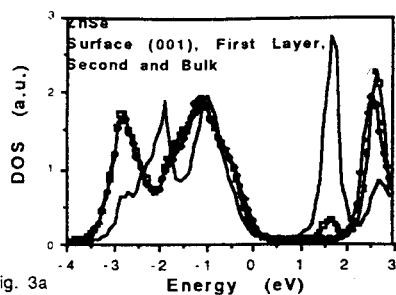


Fig. 3a

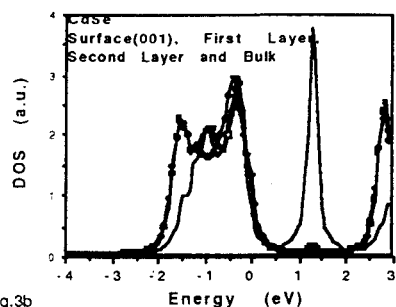


Fig.3b

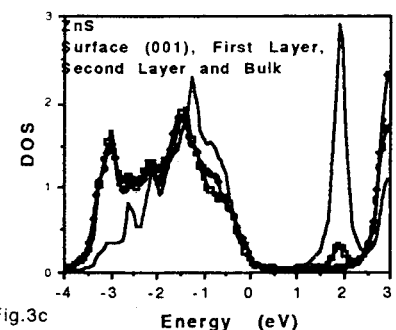


Fig.3c

In Fig.4 we show the Bulk DOS, the Surface DOS and the difference in the density of states Bulk - Surface (solid line) and obtain two negative peaks in all cases: -0.68 eV and 1.32 eV in CdSe and -1.24 eV and 2.04 eV in ZnS, and -1.72 eV and 1.80 eV in ZnSe, which are coming from surface states in energy positions where bulk states are lacking. The lower energy peak is composed from Pz anion orbital (Za) and S cation orbital (Sc), the higher energy one, is built up from Px anion orbital (Xa) and Py anion orbital (Ya). Therefore we conclude that the surface state in the gap comes from valence band and it is occupied at 0K being an donor like state, with anionic origin in all the cation terminated surfaces. In case of anion terminated surfaces the surface state lies closer to valence band but its orbital composition is main coming from S and Pz states, which means conduction band origin and unoccupied state at 0 K or a acceptor like state. These new states are surface states and they are important in making heterostructures, both of them are responsible of bonds at interfaces and they will influence the optical behaviour through their energy and composition.

Difference in DOS Bulk - Surface at center of Brillouin zone

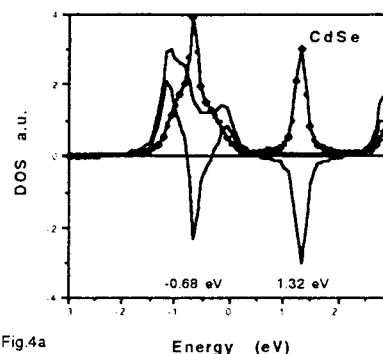


Fig.4a

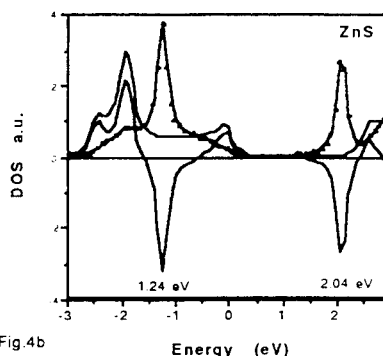


Fig.4b

For the two alloys with equal content of ZnSe: Cd(0.52)Zn(0.48)Se and ZnS(0.52)Se(0.48) we present the same DOS difference Bulk-Surface and see that the main surface peak at the bandgap is very strong in both alloys.

The strongest lower energy peak in Fig.5a is expected because it is a common cation compound and cation terminated surface. In case of common anion the lower peak situated below the top of the valence band is P type, coming from anion p orbitals and because this is a common anion material we expect a weak surface peak, as seen Fig.5b

IV. Quantum Wells

To apply our previous results to quantum wells we construct these heterostructures by building them out as principal layers grown in direction (001) alternating materials: semi-infinite ZnSe layers, N Layers of (Cd,Zn)Se and semi-infinite ZnSe. We transfer the information using the T-Matrix. The only parameter that we do not know is the band-offset. Because our materials are common anion ones and these are the most important states at the top of valence band, we suppose that valence band offset is zero under no-strain condition. Due to strain the top of the valence band splits in heavy hole and light hole, the ground state can be obtained through the difference the lattice constants. We assume that only the material in the well is under strain because the well is built up from only few atomic layers. It has to match the lattice constant of the barrier material. In our case the alloy has a larger lattice constant than ZnSe in the barriers and it has to be compressed to the value of ZnSe.

The heavy hole level shifts to higher energies and the light hole one to lower energies, creating a well for the heavy hole with a depth that we calculate from of deformation potentials for the two semiconductors.

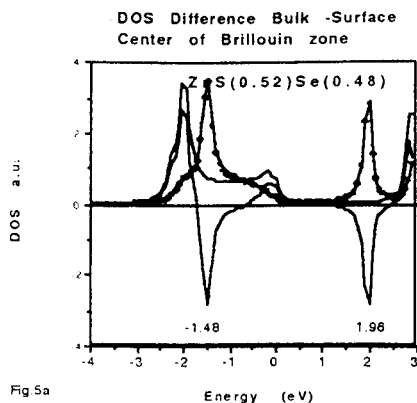


Fig 5a

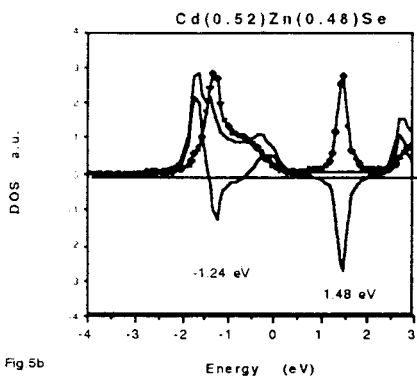


Fig 5b

From our calculated Green's function we obtain the DOS at the energies in the well and thus we follow the states in the well for different k -values in high symmetry direction, to J-point and to K point in the two-dimensional Brillouin zone near the Γ point. In Figure 6 we present an example of the obtained DOS at the middle of the well for a 10 layers quantum well as function of three different values of k .

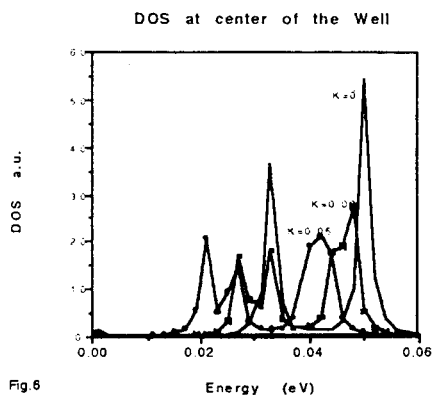


Fig.6

We also plot the DOS as function of k value in two directions and discriminate in the orbitals composition at each peak, thus that we can see how each state is composed and how it develops near the centre of the Brillouin zone (Fig.7).

The ground state is, in both cases, composed from X_a and Y_a orbitals and only the first excited state contains P_z orbital of anion (Z_a), but we also see that the composition of the ground state changes very little compared to the composition of the excited states.

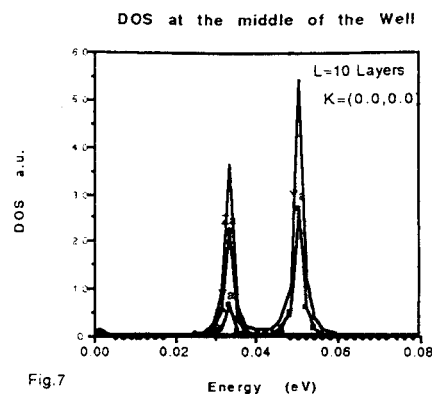


Fig.7

In Figure 8 we show the dispersion of the valence bands near the center of the Brillouin zone by carefully calculating from the DOS the energy position of the peaks as function of k value in two directions, K and J . In the direction K the ground state mixes with Z_a orbital up (0.05, 0.0). In (0.03, 0.0) the ground state broadens indicating a split and mixing with the first excited state to give rise to a new state, whose dispersion is more pronounced than the one from ground state. In the direction to J point the split appears clearly at (0.03,0.03) and we detect four states, the two coming from ground state composed from X_a , Y_a and the two other with a strong Z_a component. Composition is changing very rapid and for (0.05, 0.05) all four states are similar in composition with the strongest component being X_a , Y_a , although Z_a is gaining importance at (0.07, 0.07), and for (0.09, 0.09) is Z_a again so important as in $k=(0,0,0)$

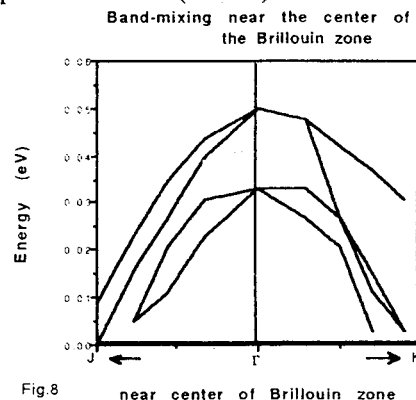


Fig.8

The ground state at Γ -point is pure X_a , Y_a , but it mixes very rapid with Z_a , so that near the center of the Brillouin zone we see a strong contribution of Z_a . The dispersion in the two dimensional Brillouin zone is clearly non parabolic as can be seen in Figure 8, where the energy dependence k is very anisotropic and band composition is also changing with the k values showing a strong band-mixing in this quantum well. We find that contribution of anionic orbitals is the most determining for the composition of the top valence band in this well

also that the heavy hole band is the ground state for the well. We expect that heavy hole would be more important for optical properties of these heterostructures.

V. CONCLUSIONS

We present an electronic band structure study of three II-VI wide-gap compounds, which are very important in laser applications in the blue-green region: CdSe, ZnSe and ZnS. We calculate also the electronic features of ternaries built up from them by using a simple VCA approximation and extend the study to their (001) surfaces.

We detect two surface states: one of them in the band-gap and other within the valence band. Both states shift with concentration between the corresponding values of the binary materials. The composition of these two states is different. The state in the gap is coming only from anion orbitals: P_x (X_a) and P_y (Y_a) thus it is an occupied state at 0K and the one into the band is composed from anion P_z (Z_a) and cation S orbital (S_c). The behaviour of these two states is very important in the study of optical properties in these materials because they are going to make bonds to other surfaces in heterostructures and quantum wells where interesting optical properties have been detected.

Despite of the inherent alloy broadening, the surface DOS of the alloys considered here retain much of the atomic character of the surface DOS of their individual constituents. We identified the surface state as an anionic state with P_x (X_a) and P_y (Y_a) strong contributions.

Finally we calculate the band-mixing and dispersion in-plane near the Γ point in the valence band for the most important quantum wells based on ZnSe as ZnSe/(Cd,Zn)Se/ZnSe. At Γ point the ground state is pure X_a , Y_a but near Γ point the ground state is constituted by X_a , Y_a and Z_a almost in equal proportions. Also the assumed parabolicity usual in

many theoretical works is not valid. The ground heavy hole state is coming from anionic P orbitals. This is also the composition of the main surface state found in the bandgap in our calculation.

We conclude that in ternary common anion surfaces P orbitals are most important for new bonds in heterostructures and quantum wells.

References

- [1]. J.Ding, H.Jeon, T.Ishihara, M.Hagerott, A.V.Nurmikko, H.Luo, N.Samarthand, and J.Furdyna, *Phys.Rev.Lett.* 69,1707(1992).
- [2]. H.Jeon, J.Ding, A.V.Nurmikko, W.Xie, D.C.Grillo, M.Kowayashi, and R.L.Gunshor, *Appl.Phys.lett.* 60,2045 (1992).
- [3]. H.Okuyama, T.Miyajima, Y.Morinaga, F.Hiei, M.Ozawa, and K.Akimoto, *Electron. Lett.* 28, 1798 (1992)
- [4]. F. J. Rodriguez, A. Camacho and L. Quiroga, *Solid State Comm.* 77, 623 (1991).
- [5]. R.Baquero, V.R.Velasco and F.Garcia-Moliner, *Physic Scripta* 38, 742(1988)
- [6]. Ley L., Pollak R.A., McFeely F.R., Kowalczyk S.P. and Shirley D.A., *Phys.Rev.B* 9,600,(1994).
- [7]. M.Cardona *J.Appl.Phys.* 32,2151(1961)
- [8]. K.Ichino, K.Iwami, Y.Kawakami, S.Z.Fujita and S.G.Fujita, *J.Electron.Mater.* 22,445 (1993)
- [9]. Gun-Do Lee, M.H.Lee and Jisoon Ihm, *Phys.Rev.B* 52,No3,1459 (1995-1)
- [10]. *Physics of II-VI and I-VII Compounds, Semimagnetic Semiconductors*, edited by K.H. Hellwege and O. Madelung, Landolt Boernstein, New Series, Group III, Vol.17, Pt. b (Springer, New York, 1982) and *ibid.* Vol.22.
- [11]. D.Olguin, R.de Coss and R.Baquero, to be published.
- [12]. Y.Petroff, M.Balkanski, J.P.Walter and M.L. Cohen, *Solid State Comm.* 7,459 (1966).