

The Optical Band Gap of Silicon Quantum Dots: The Influence of Surface Passivation

S. K. Ghoshal, G. A. Desalegn, E. A. Abebe

Department of Physics, Addis Ababa University, Arat Kilo
P.O. Box – 1176, Ethiopia, Email: lordshib@gmail. Com

H. S. Tewari and P.K. Bajpai

Department of Pure and Applied Physics,
Guru Ghasidas Vishwavidyalaya, Bilaspur-459 009
E-mail: bajpai.pk1@gmail.com

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Abstract: To investigate the mechanism of the photoluminescence from silicon nanostructures, we perform computer simulation using tight-binding scheme and empirical pseudo-potential Hamiltonian. The optical and electron correlation effects on confinement and the influence of surface states on gap energy is studied for silicon quantum dots. We examined the variation of the band gap as a function of sizes of small silicon quantum dots with hydrogen and oxygen passivation at the surface (Si_nH_m , and Si_nO_m). It is observed that the gap decreases with increasing dot size in pure clusters. Furthermore, the band gap increases on passivating the surface of the dot with hydrogen and oxygen respectively. Both quantum confinement and surface passivation determine the optical and electronic properties of silicon nanoclusters. Further, the oxygen passivated surface possess a wider energy gap than the hydrogenated surface. The room temperature visible luminescence is due to radiative recombination of electrons and holes in quantum confined nanostructures in which the localized surface states play a pivotal role. The entire energy spectrum starting from the very low lying ground states to the very high lying excited states for silicon dots having 3 to 44 atoms per dot are computed. The role of surface states on the gap energy, HOMO-LUMO states as well as the effect of passivation on the confinement has also been examined. The results are compared and in conformity with other model calculations and experimental observations.

Keywords: Nanoclusters; Confinement; Passivation; Radiative Recombination; Pseudo-potential; HOMO-LUMO States.

1. Introduction

The discovery of visible photoluminescence from silicon nanostructures has focused interest in these nanoclusters, as well as in small semiconductor particles^{1,2}. The most exciting perspective is that light emitting devices based on this effect appear feasible within the well established silicon technology for optoelectronic applications. The knowledge of band structures for these nano-silicon structures is essential to understand the effect. In the last decade, substantial efforts have been made to examine whether silicon can become intrinsically a direct semiconductor in nanocrystalline clusters. It is established that quantum confinement can modify the energy gap such that visible luminescence is produced as observed^{3,4} experimentally.

The quantum efficiency of such systems is increased to 1-10% as opposed to 10^{-4} % in bulk silicon. Efficient emission of visible light has been observed from the silicon nanostructure when exposed to ultraviolet light. It has been surmised that these nanostructures and the porous form of the silicon have a direct band gap and emit light from violet to red depending upon the size of nanostructures. With a large surface-to-volume ratio in nano and porous structures, the surface effects become more pronounced. Surface effects as well as the quantum confinement effects control the optical and electronic properties of these materials. It is possible that the luminescence properties may be related to different silicon compounds such as a – Si:H, polysilane, SiH_x , Si_nO_m and surface defect states possessing a different mechanism from usual radiative recombination. There is an ambiguity whether the observed visible luminescence is due to quantum confinement or due to some extrinsic effect because of the presence of siloxene-like compounds⁵⁻⁸.

In spite of intensive experimental and theoretical studies, no conclusive evidences has been given on the mechanism of the efficient light emission from porous silicon and related materials⁸⁻²⁰. Many issues like size dependent oscillator strength, density of states, radiative recombination rate, absorption coefficient and dielectric function, and the influence of surface passivation on optical properties are still not clearly addressed. One of the explanations for the blue-shifted photoluminescence (PL) from porous silicon is that the microstructure consists of islands of isolated quantum dots each experiencing quantum confinement³.

In this paper, we, therefore, investigated the effect of quantum confinement on the energy gap in silicon dots of different sizes and geometry as well as the role of hydrogen and oxygen passivation therein.

The dependence of energy gaps on the size and geometry of the silicon dots is examined in detail using two different calculations namely empirical pseudo-potential and non-orthogonalized tight-binding (NOTB) approach. Surface passivation of the dot with hydrogen and oxygen atoms is modeled through appropriate pseudo-potential⁵⁻⁹. The TB parameters are also obtained with appropriate fitting to different structures following Liu et al^{11,20}. The findings give a more detailed account for the variation of energy gap, and HOMO-LUMO states as a function of dots size as well as the role of hydrogen and oxygen passivation on surface. These results are utilized to examine how quantum confinement in silicon nanoclusters (quantum dots) can lead to symmetry allowed optical transitions across the gap with energy in the visible range.

2. Methodology

Empirical pseudo-potential plane wave theory is used to study the electronic and optical properties of spherical quantum dots having varying sizes from 3 to 44 atoms in the dot. Usually, a large number of plane-wave basis states are required to describe adequately the electronic wave functions of the silicon dots. Instead, we use the empirical pseudo-potential approximation, which allows the wave functions to be expanded using a much smaller number of plane-wave basis states (approximately 50 states per atom). It is known that most of the physical properties of solids are dependent on the valence electrons to a much greater extent than on the core electrons. This is exploited in the pseudo-potential approximation by removing the core electrons and by replacing them and the strong ionic potential by a weaker pseudo-potential that acts on a set of pseudo wave functions rather than the true valence wave functions⁸.

The interest in the present work is to find the size dependence of the gap energy and the near band gap solutions i.e. the separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the presence of hydrogen and oxygen at the surface of the dots. We then solved the effective single-particle Schrödinger equation for different sizes of the quantum dots.

Following Wang and Zunger⁷⁻⁹ two different forms of the local pseudo-potential for hydrogen and oxygen (in atomic units) are used. An ideal unrelaxed structure with Si-H bond distance of 1.487Å and Si-O bond distance 1.693Å is used for all the cases. We used two different values of cutoff energies ($E_{\text{cutoff}} = 5 \text{ Ry}$ and $E_{\text{cutoff}} = 10 \text{ Ry}$) for the plane wave

expansion and the same cutoff is used for the potential energy too. We solve the effective single-particle Schrödinger equation

$$(1) \quad \hat{H}\psi_i = \varepsilon_i\psi_i,$$

for different sizes of the quantum dot.

The NOTB method is very useful to investigate the emission spectra and the radiative recombination rate of the direct band-to-band recombination process. Before the optical effects are examined, it is necessary to look at the optical gap and density of states using tight-binding approach. Our method is based on realistic structure models and reliable calculation methods for electronic structures to make a quantitative comparison between theoretical results and experimental data. For starting structures, we adopt the continuous random network (CRN) of bulk a-Si generated by Barkema and Mousseau¹⁰. There are two important reasons to use tight-binding model for our computation: (1) the computation speed to calculate the electronic states of each structure model is considerably high, (2) it can well describe the conduction band by evaluating the sum of square matrix elements between the conduction and valence states to examine optical properties.

In tight-binding approach, we need to solve the following equation to determine the electronic structure:

$$(2) \quad H C_\lambda = E_\lambda S C_\lambda,$$

where C_λ is the column vector representing the coefficients of expansion of the wave function ψ_λ with the eigen-energy E_λ in terms of some localized basis set $\varphi_{i\alpha}$. Here i refer to the atomic site and α the orbital at the site i . The Hamiltonian matrix elements H and the overlapping matrix elements S are defined as

$$(3) \quad H_{i\alpha, j\beta} = \int \varphi_{i\alpha}(\mathbf{r}) \hat{H} \varphi_{j\beta}(\mathbf{r}) d\mathbf{r},$$

$$(4) \quad S_{i\alpha, j\beta} = \int \varphi_{i\alpha}(\mathbf{r}) \varphi_{j\beta}(\mathbf{r}) d\mathbf{r}.$$

On the other hand, in the semi-empirical non-orthogonalized TB approach, these matrix elements are treated as parameterized functions of $R_{ij} = R_j - R_i$ with the relevant parameters fitted to experimental results and/or first principles calculations.

The orbital energies used in the calculation are $\varepsilon_s(\text{Si}) = -13.55$ eV, $\varepsilon_p(\text{Si}) = -6.52$ eV, $\varepsilon_s(\text{H}) = -8.67$ eV and $\varepsilon_s(\text{O}) = -10.54$ eV. For the hydrogen passivated Si clusters, the parameters characterizing the Si-H interactions within the NOTB formulation were obtained by fitting to the bond length of

Si-H and the molecular orbital energy of SiH_4 . Similarly, for the oxygen passivated Si clusters, the parameters characterizing the Si-O interactions within the NOTB formulation were obtained by fitting to the bond length of Si-O and the molecular orbital energy of SiO_2 .

The TB parameters are carefully chosen to include an appropriate number of atomic bases for the reliability of statistics¹¹. We used the $\text{sp}^3\text{d}^5\text{s}^*$ TB scheme proposed by Jancu¹² and others^{13,14}. In case of amorphous Si nano-structures the surface dangling states are usually terminated in order to sweep out the surface states from the band gap. The full-geometry optimization of silicon nanoclusters of different sizes is necessary for the calculation of electronic density of states of stable configuration¹³⁻¹⁵. For the hydrogen and oxygen passivated Si clusters, the parameters characterizing the Si-H and Si-O interactions within the TB formulation are obtained by fitting to the bond length of Si-H and Si-O and the molecular orbital energy of SiH_4 and SiO_4 . For complete understanding of the passivation, a local analysis of the electronic structure for the un-relaxed Si as well as the un-relaxed Si_nH_m clusters is carried out.

The eigen-value equation (Eq-3) is used for the analysis. Within the framework of the TB treatment, the electronic density of states can be expressed as the TB Hamiltonian for this study is developed in a sp^3 framework. For the un-relaxed Si_n cluster, there are $4n$ possible states. Subtracting n_1 dangling bond states, there are $4n - n_1 = n_2$ states with half of them i.e. $n_2/2 = n_3$ being the bonding states and the other half anti-bonding states. In the mean time, there are $4n$ valence electrons in Si_n and they occupy the lowest $2n$ states. Out of these $2n$ states, n_3 are the bonding states. This means that the remaining $2n - n_3 = n_4$ states must come from the n_1 dangling bond states, leaving the other n_4 dangling bond states unoccupied.

Three-dimensionally confined silicon particles have symmetry allowed optical transitions across the gap. It is important to mention that we consider nano-crystals that have small dimensions in all three directions called quantum dot. The intrinsic properties of such clusters are expected to be obtainable from the most symmetric class of such clusters, disregarding any lattice contractions. As an idealization, we consider spherical dots with no relaxation of the bulk lattice⁷. There are two kinds of such clusters with T_d symmetry for silicon, one with a silicon atom at the center and the other with a tetrahedral interstitial at the center. Since our interest is in states around the band gap, saturation of all dangling bonds at the surface is essential; otherwise the gap would be completely masked by the dangling bond states. Saturation of the dangling bonds removes the corresponding

localized surface states from the energy range near the Fermi energy. Physically the dangling bonds would suppress the luminescence.

3. Results and Discussions

Figure 1 shows the variation of HOMO-LUMO gap energy as a function of number of atoms in the dots i.e. dot size using empirical pseudo-potential calculation.

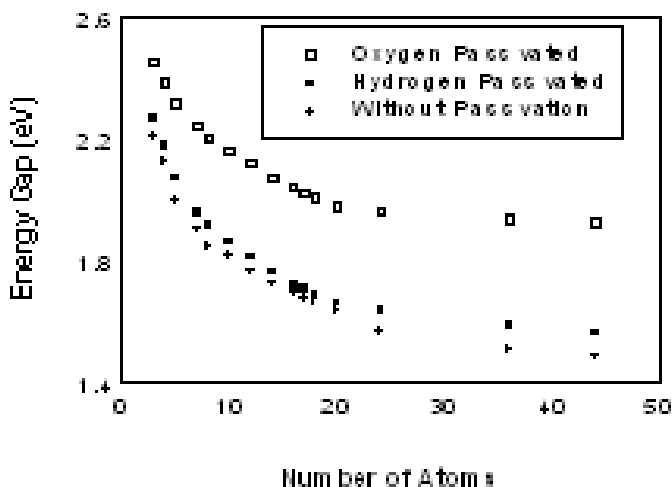


Fig.1 Size dependent gap energy using empirical pseudo potential calculation. Filled circles (bottom) for pure clusters (free surface), filled square (middle) for hydrogenated surface and Open Square (top) for oxygenated surface.

A three-atom dot with tetrahedral arrangements joined by a single bond without and with hydrogen at the surface gave an energy gap ~ 2.213 eV and ~ 2.270 eV respectively. However, in the presence of oxygen the gap increases to ~ 2.454 eV. As we passivated the surface of 3-atom dot with hydrogen i.e. Si_3H_6 and 5-atom dot with hydrogen i.e. Si_5H_{12} and with oxygen i.e. Si_5O_8 , the occupied number of level changes and the emerged value of the gap shows a change. The same happens for larger dots also.

Following a similar procedure, we examined all other dots without and with hydrogen and oxygen atoms at the surface. We found an energy gap ~ 1.483 eV and ~ 1.566 eV for 44 atom dot without and with hydrogen respectively. The value of the gap energy increases due to surface passivation with oxygen to ~ 1.928 eV. There is continuous increment in gap

energy for other dots; with oxygen it's more compared to that of hydrogen passivation.

The value of the gap energy as observed from the energy spectrum decreases as the size of the dot increases implying weaker confinement for larger sizes. As we increase the number of atoms in the dot and change its geometry, the degeneracy's are increasingly lifted. This is because the grouping-up tendency of the energy levels in a single energy value becomes less (effect of de-confinement). For smaller sizes the confinement is more and the degeneracy's are also higher. As we saturate the surface dangling bonds with hydrogen atoms, there is an enhancement of the gap energy ~ 0.057 eV for 3 atom cluster and ~ 0.083 eV for 44 atom dot. On the other hand, if the saturation of the surface dangling bonds take place with oxygen atoms, there is an enhancement of the gap energy ~ 0.241 eV for 3 atom cluster and ~ 0.445 eV for 44 atom dot. The degeneracy's are also lifted as the presence of hydrogen and oxygen at the surface imparts an interaction potential that acts as a perturbation. For relatively larger dot, due to sp^2 and sp^3 hybridization, de-localization of the electron is more and the energy spectrum is more non-degenerate. For smaller dots, this effect of de-localization near the surface is less and hence the degeneracy's are more pronounced.

We present the results of our simulation (Figure 1) for the variation of gap energy for different sizes of the dot without hydrogen-passivation (filled circles), with hydrogen-passivation (filled square) and with oxygen-passivation (unfilled square). The gap energy increases as the number of atoms in the dot decreases that confirm the stronger confinement for the smaller sizes. Higher gap with passivation is due to the localization of electron cloud arising from the sp^3 hybridization of the silicon-dangling bond with the hydrogen atom and with oxygen atoms. These results are in conformity with the earlier observation^{4,9}.

Figure 2 compares our results for the size dependent gap energy to the empirically fitted non-orthogonal tight-binding model where the dot without hydrogen-passivation (filled circles), with hydrogen-passivation (filled square) and with oxygen-passivation (unfilled square). In the NOTB estimate a three atom dot without and with hydrogen at the surface gave an energy gap ~ 2.312 eV and ~ 2.356 eV respectively. However, in the presence of oxygen the gap increases to ~ 2.541 eV. As we passivated the surface of 3-atom dot with hydrogen i.e. Si_3H_6 and 5-atom dot with hydrogen i.e. Si_5H_{12} and with oxygen i.e. Si_5O_8 the occupied number of level changes and the emerged value of the gap also show a change.

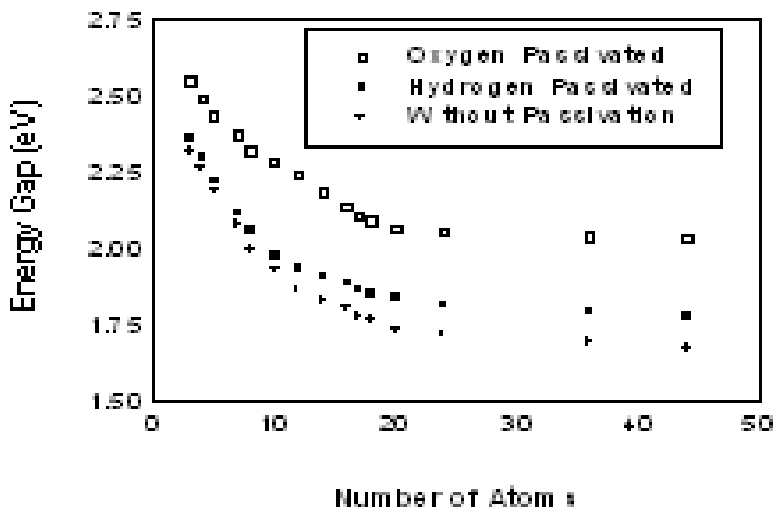


Fig. 2: Size dependent energy gap from NOTB calculation. Filled circles (bottom) for pure clusters (free surface), filled square (middle) for hydrogenated surface and open square (top) for oxygenated surface.

Following a similar procedure, we examined all other dots of varying sizes without and with hydrogen and oxygen atoms at the surface. We found an energy gap $\sim 1.672\text{eV}$ and $\sim 1.773\text{eV}$ for 44-atom dot without and with hydrogen respectively. The value of the gap energy increases due to surface passivation with oxygen to $\sim 2.025\text{eV}$. There is continuous increment for other dots too and with oxygen, it is more compared to that of hydrogen passivation. It is also clear that the NOTB overestimates the gap energy compared to that of pseudo-potential calculation.

The value of the NOTB based gap energy as observed from the energy spectrum decreases as the size of the dot increases implies weaker confinement for larger sizes in a similar way as that of pseudo-potential one. As we increase the number of atoms in the dot and change its geometry, the degeneracy's are increasingly lifted. This is because the grouping-up tendency of the energy levels in a single energy value becomes less (effect of de-confinement). It is observed that for smaller sizes, the confinement is more and the degeneracy's are higher. As we saturate the surface dangling bonds with hydrogen atoms, there is an enhancement of the gap energy $\sim 0.044\text{eV}$ for 3 atom cluster and $\sim 0.101\text{eV}$ for 44 atom dot. On the other hand if the saturation of the surface dangling bonds take place with oxygen atoms, there is an enhancement of the gap energy $\sim 0.229\text{eV}$ for 3 atom cluster and $\sim 0.353\text{eV}$ for 44 atom dot. The degeneracy's are also lifted

because the presence of hydrogen and oxygen at the surface imparts an interaction potential that acts as a perturbation. For relatively larger dot due to sp^2 and sp^3 hybridization de-localization of the electron is more and the energy spectrum is more non-degenerate. For smaller dots this effect of de-localization near the surface is less and hence the degeneracy's are more pronounced.

We further look at the optical properties by calculating the size dependent oscillator strength and absorption coefficient. To do this, we turned our attention to the wave function both for the low-lying states as well as the pair of states near the band gap (HOMO and LUMO states) for different sizes. We calculate the ground state as well as excited state wave function for all dots using periodic boundary conditions. The real part of the ground state wave function has very strong oscillation near the core region, is highly asymmetric and decays to a very small constant value beyond a critical distance equal to the size of the box. The imaginary part of the wave function oscillates and then rapidly goes to zero. We have calculated the wave function for the HOMO and LUMO states as a function of r . Both the bonding and the anti-bonding states show strong oscillation near the core region and are highly asymmetric. The wave function for the HOMO and LUMO states for 3 atoms dot with hydrogen and oxygen at the surface behaves in a different manner. For 5 atom and other higher clusters, the nature of oscillation of the wave functions are different from that of the 3 atom cluster and clearly reflects the effect of geometry of the structure. This result is expected because the bonding and the anti-bonding states are having different symmetry and the effect of passivation is different for the two cases. The surface states contribute differently for the HOMO and LUMO states. The nature of oscillation of the wave functions for higher clusters are also different from that of the 3 and 5 atom cluster and clearly reflects the effect of geometry of the structure. The results show that the HOMO-LUMO states are localized and bulk-like instead of surface-like^{6, 9}.

Optical transitions between the highest occupied and lowest unoccupied orbital are allowed in a cluster of sufficiently low symmetry with surface passivation. In the limit of bulk Si, such transitions are forbidden because of the indirect band gap. Only symmetry breaking by the phonons makes such transitions weakly allowed, which leads to the weak band-gap photoluminescence for bulk Si. One can ask how the dipole-allowed transitions for crystalline nanoclusters are compatible with the dipole forbidden transitions in a bulk silicon lattice. However, this is because of the periodicity, which leads to a k -selection rule. This renders the dipole matrix element from the valence-band top to any linear combination of conduction-

band bottom orbital zero. One should expect that the oscillator strength keep on decreasing by increasing the cluster size. The same trend is retained even in the case of surface passivated cluster. These results are in conformity with the density functional approach by Delley and Steigmeier¹⁷. The results on electronic structure of silicon nano-cluster show that visible photoluminescence for surface passivated clusters are possible due to the effect of quantum confinement and surface effect plays a significant role in optical properties of nanosilicon structures.

4. Conclusion

We have used two different methods viz. empirical pseudo-potential method and non-orthogonalized tight binding (NOTB) method to calculate electronic structure of silicon quantum dots of different sizes ranging from 3 to 44 atoms to examine the quantum size effects on gap energy. In the present treatment, we neglect the role of multi-band coupling. In both cases, results show that the gap energy increases as the size of the dot decreases implying the stronger confinement for smaller dots. The NOTB results differ from pseudo-potential values by a constant shift towards higher side. The result is in conformity with the earlier observation of Wang and Zunger⁹, Proot et al¹⁴, and others¹⁵⁻²⁰. The most interesting and remarkable result is obtained for the HOMO-LUMO gap energy, oscillator strength and absorption coefficient as we vary the size of the dot. It is observed that the change in the energy gap, oscillator strength and absorption coefficient on passivation as a function of the dot size is more prominent for larger dots. The presence of hydrogen and oxygen lifts the degeneracy's of the eigenvalue spectrum and results in an enhancement of the gap energies. The basic characteristics of the quantum dot wave functions pattern indicate that in all cases, the HOMO and LUMO states are localized in the interior of the quantum dot with zero amplitude on the surfaces. Wolkin et al¹⁶ found that the PL characteristics are determined by both quantum confinement and surface passivation, which determined by the electronic states of the silicon quantum dots. Thus, from the results for the oscillator strength we conclude that finely structured silicon appears to be capable of showing a very high luminescence in the visible range, as observed experimentally. Finally, for nanoclusters, excitonic correlations only weakly influence oscillator strength, but shift the energy scale.

The above study indicates that the hydrogen and oxygen passivation contributes surface states near the gap to enhance the gap energy and hence the confinement which is in conformity with the experimental results. The

passivated surface states play an important role as far as the photoluminescence from finite size dots are concerned. The presence of O₂ kinetics during the preparation of the sample can greatly influence the gap energy of Si nanostructures. The enhancement of the gap also depends on the formation of Si-H, Si-O and SiO₂ at the surface of the dot. This enhancement in the band gap may be due to new electronic states appear in the gap for smaller quantum dots when a Si=O bond is formed, is in good agreement with experiments.

Our results on the optical absorption strongly suggest that the photo-generation of carriers occurs in the crystalline silicon core with the band gap modified by the quantum confinement effect, while the visible room temperature photoluminescence comes from the near-surface region of crystallites. This study shows that the radiative recombination in the near surface region causes the strong visible photoluminescence at room temperature as observed by others^{18,19}. The blue shift of the absorption edge strongly suggests that the quantum confinement effect plays a key role in the absorption process. This agrees with the experimental results^{18,19}. It is clear that the properties of silicon nano-crystallites in the presence and hydrogen and oxygen at the surface are fundamentally different from those of pure silicon clusters in porous silicon as studied extensively by Daldosso et al¹⁹. Therefore, we conclude that the surface passivation in addition to quantum confinement effect plays active role in deciding optical properties of silicon nanostructures.

Our results demonstrates the theoretical evidence that the emission energy of small spherical nano-crystallites with diameter ranging from 4 to 45 Å⁰ can be tuned in the visible range by controlling the sizes which is in qualitative agreement with the study of Nishio et al¹⁴⁻²⁰. The quantitative nature of difference is due essentially to the use of the different TB parameters used by us. From these investigations, we assert that small size silicon quantum dots are promising candidates for visible, tunable and high quantum yield light-emitting devices as predicted by many experimental findings^{1,2,4,18,19}.

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References

1. L.T. Canham, *Appl. Phys. Lett.*, **57** (1990) 1046-48.
2. V. Lehmann and U. Gosele, *Appl. Phys. Lett.*, **58** (1991) 856-59.
3. Y. Kanemitsu, *Phys. Rep.*, **263** (1995) 1-9.
4. P. Bettoti, M. Cazzanelli, L. Dal Negro, B. Danese, Z. Gaburro, C. J. Oton, G. Vijaya Prakash and L. Pavesi, *J. Phys.: Cond. Mat.*, **14** (2003) 8253-8281.
5. S.K.Ghoshal, Karan Singh Gill, Umesh Gupta and Devendra Mohan, *Asn. Jour. Spect.*, **7(1)** (2003) 49-68.
6. S.K. Ghoshal, K.P. Jain and R.J. Elliott, *J. Meta. Nano. Mat.*, **23** (2005) 129-132.
7. L.W. Wang, *Phys. Rev. B.*, **49** (1994) 10154-10158.
8. L.W. Wang and A. Zunger, *J. Phys. Chem.*, **98** (1994) 2158-2163.
9. A. Zunger and L.W. Wang, *Appl. Surf. Sci.*, **102** (1996) 350-359.
10. G.T. Barkema and N. Mousseau, *Phys. Rev. B.*, **62** (2000) 4985-4993.
11. L. Liu, C.S. Jayanthi and S.Y. Wu, *J. Appl. Phys.*, **90** (2001) 4143-4151.
12. J.M. Jancu, R. Scholz, F. Beltram and F. Bassani, *Phys.Rev. B.*, **57**(1998) 6493-6499.
13. M. Menon and K.R. Subbaswamy, *Phys. Rev. B.*, **55** (1997) 9231-9234.
14. J.P. Proot, C. Delerue and G. Allan, *Appl. Phys. Lett.*, **61**(1992) 1948-1950.
15. L.W. Wang and A. Zunger, *J. Chem. Phys.*, **100** (1994) 2394-2397.
16. M.V. Wolkin, J. Jorne, P.M. Fauchet and C. Delrue, *Phys. Rev. Lett.*, **82** (1999) 197-200.
17. B. Delley and E.F. Steigmeier, *Phys. Rev. B.*, **47** (1993) 1397-1400.
18. Y. Kanemitsu, H. Uto and Y. Masumoto, *Phys. Rev. B.*, **48** (1993) 2827-2830.
19. N. Daldosso, M. Luppi, S. Ossicini, E. Degoli, R. Magri, G. Dalba, P. Fornasini, R.Grisenti, F. Rocca, L. Pavesi, S. Boninelli, F. Priolo, C. Spinella and F. Iagona, *Phys. Rev. B.*, **68** (2003) 85327-1-85327-8.
20. K. Nishio, J. Koga, T. Yamaguchi and F. Yonezawa, *Phys. Rev. B.* **67** (2003) 195304-1-195304-5.