The Structural stabilities and Band Gap Engineering of Core-Shell Nanowires

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Abstract. The structural and electronic properties of wurtzite CdSe/CdS and CdS/CdSe CSNWs are predicted with DFT. The geometry optimization and symmetry computation for CdSe/CdS and CdS/CdSe CSNWs based on VASP with GGA-PBE approximation. It is found that CdSe core suffers from the compressive strain in the CdSe/CdS CSNWs and CdS core stretched in the CdS/CdSe CSNWs. A thicker CdS shell can improve the nanowire stability and a thicker CdSe shell decreases their stability. By reducing the size of the NWs the energy gap of the material increase due to strong quantum confinement phenomena. The overall energy gap of the CdS/CdSe CSNWs are increase and decrease for the CdSe/CdS CSNWs due to the difference in their bulk energy gaps. The calculated results were in perfect agreement with that of the red or blue shift of the spectrum in the experimental observations. The electronic structure are discussed in the term of band structure and density of states. Density of states have confirmed that valence orbital p of sulphur and selenium shows the formation of core shell interface. Our results indicate that using core shell composition mechanism the electronic properties can be tuned and the photoemission spectra can be improved.

1. Introduction
Recently, unidirectional nanowires have wide application in the electronic devices. Therefore, more advance technology and new techniques are development to achieve different NWs such as tri-axial, bi-axial, composite and side by side NWs which are composed of different materials. Among them the heterostructure NWs have attracted more attention and industrial interest because of small lattice mismatch at the interface and defect free interfaces [1-3]. The interface formation at the heterojunction between the two isolated materials gives new physical phenomena such band gap opening, improved structural and electronic properties and since extend the application of the pure NWs. The standard lithography have proved that NWs are more interesting and efficient nanostructure materials as compared to the, 3D-bulk, 0D-QDs, 1D-nanotubes etc, because of their high electronic mobility and unique density of states [4]. The special property of the CSNWs are their efficient charge carrier separation and generation of exciton which make them more attractive for the application in more advanced optoelectronic devices [5,6]. A number of reported CSNWs in the literature which are
studied experimentally are found, PbSe/PbS, CdTe/CdS, ZnSe/CdSe, CdS/CdSe, CdSe/CdS and ZnS/CdSe etc [7-17]. Where the CdSe/CdS CSNWs are composed of CdSe (core part) and CdS (shell part) and their core shell nanocrystal systems has been successfully fabricated [19]. The bulk energy gaps for (CdSe= 1.74 eV) and for (CdS=2.42 eV) with the lattice parameter (a=4.1 Å, c=6.714 Å) for CdS (a=4.3 Å, c= 7.03 Å) for CdSe respectively [18, 26]. The CdSe/CdS and CdS/CdSe CSNWs is one of the most widely studied materials experimentally and theoretically as well [6, 21, 22]. Although some computational investigations are found in the literature where CdSe/CdS core/chell nanocrystals have been studied using some theoretical tools. These include the tight-binding model, multi-band K.P model and effective mass model etc [23, 25]. These all theoretical models are using some approximation to deal with such CSNWs and these approximation always gives underestimate properties as has been proven that K.P model and effective mass model have some draw backs when employing it to few monolayer or to QDs [26]. Similarly tight-binding model and other reported models are fails to fully describe the physical properties of CSNWs [24]. However very recently, density functional theory were employed to study the some core shell nanostructures using LDA approximation their consideration were mainly focused on previous some experimental structural models and different alloy interfaces [42]. But we did not found any clear representation of electronic properties of the CSNWs with respect to size and especially composition ratio of core and shell which play crucial role in modulating electronic properties, second, LDA level of theory is not suitable for the theoretical study of such highly correlated system [28, 42]. However the first principles calculations of the composition dependence of physical properties of wurzite CdS-CdSe and CdSe-CdS CSNWs is not studied until now. In the case of CSNWs two materials with different energy gaps and different lattice constants are combined and another new composite material with new energy gap are appeared thus by making core shell heterostructure the electronic energy gap can be tuned. Using first principles calculation the electronic structure of, CdS/ZnS, Si/SiC and AIN/SiC CSNWs has been tuned [29-31]. In addition the structural properties are also very important for manufacturing the optoelectronic devices which still have not found in literature for such CSNWs so here for the first time we are investigating the modulation in the physical properties of the above semiconductor CSNWs using a well-known approach of density functional theory with the GGA approximation. This level of theory is pretty well for the energy gap studies of such type of material reported by literature [32]. In present work we have shaped the wurzite nanocrystal structures of CSNWs; CdSe-CdS & CdS-CdSe in to nanowires geometry with different sizes and core/shell ratio to see the effects on the electronic and structural characteristics of such CSNWs with different core to shell ratio and composition.

2. Methodology
An electronic structure calculation code VASP (Vienna Ab-initio Simulation Package) based on DFT (density functional theory) are used to perform the calculation in present work [33], with the GGA-PBE approximation suggested by perdew, Becke and Emzerhof [34]. An energy cutoff of (360 eV) are considered for the plane wave basis set. In Monkhorst–Pack scheme we select K-points (1×1×3) for the integration of Brillouin zone [35]. The force criteria was set to (2 × 10-2 eV/Å) and the criteria for energy is (10^−4 eV). We employed 15Å vacuum between to the NWs to avoid the interactions between the periodic repetitions of NWs. Although bulk CdSe and bulk CdS can crystalize as cubic (zinc blende) and hexagonal (wurzite) structure, however, experimental work shows that these materials often grows in wurzite form [36]. Thus, we built CdSe/CdS and CdS/CdSe CSNWs from the bulk wurzite CdSe and CdS. If NCore and NShell represent number of atoms of core and shell regions of the CSNWs respectively. Then we can write the quantity of atoms in core and in shell part as: x=NCore/NCore+NShell.

3. Calculation Results
The structure parameters were studied in the term of lattice constant c and size d of CdSe/CdS and CdS/CdSe CSNWs and the results are given in Figure 1(a) &3(b). Figure 1(a) shows the change in lattice parameter c for CdSe/CdS and CdS/CdSe CSNWs with respect to concentration x. The lattice constant c increases with increasing the quantity of atoms in the core for CdSe-CdS, while it
decreasing for the case of CdS/CdSe CSNWs. Figure 1(b) shows that with the increasing of concentration x the size of the CdSe/CdS CSNWs increases and it decreases for the CdS/CdSe CSNWs for the same concentration. The variation in lattice constant and diameter shows a non-linear trends which are not in line with the Vegard’s law, since such CSNWs are not obeying Vegard’s law for the linearity characteristics in structure parameters [37].

Figure 1. (a) Shows the relationship of c (lattice constant) Vs x (concentration) of CdSe-CdS and CdS-CdSe CSNWs (b) Shows the relationship of size d with the composition x of CdSe-CdS and CdS-CdSe CSNWs.

To find the energetic stability the $E_b$ (binding energy) of both CSNWs are calculated according to the below formula [38].

$$E_b = N_{Cd}E_{Cd} + N_{Se}E_{Se} + N_{H}E_{H} - E_{Tot}/N_{Cd} + N_{Se} + N_{H}$$

Where $E_{Cd}$, $E_{Se}$, $E_{H}$ are per atom energy with their corresponding atoms are given in the subscript. Cd, Se and H, $E_{Tot}$ is relaxation energy of the nanowire and $N_{Cd}$, $N_{Se}$, $N_{H}$ indicates the amount of atoms such as; Cd, Se, S and H respectively in the NWs, and $N=N_{Cd} + N_{Se} + N_{H}$ are the overall atoms in the system. The calculated $E_b$ (binding energy) (Figure 2) shows a decreasing trend for CdSe/CdS CSNWs with enlarging the core atoms. Where, increasing the size of wire and CSNWs the $E_b$ become larger and larger i.e the binding energy is higher for NWs and CSNWs containing 190 atoms/unit cell and it becomes lower for NWs and CSNWs containing 108 atoms/unit cell and become lower for system contains 48 atoms/unit cell. It is concluded that NWs and CSNWs with larger size are much stable then the smaller one. Where the calculated binding energy of the bulk CdSe are lower than the bulk binding energy of CdS and this is the reason that the binding energy are decreasing with increasing the amount of CdSe in the core part.

Figure 2. The figure shows modulation of binding energy with x for CdSe/CdS CSNWs.

Furthermore, we have calculated the electronic structure and energy gaps for all pure and core-shell nanostructures with all the possible composition and studied the composition effect in these composite structures. We have investigated the band gaps from the DOS (density of states), which can be defined
as: the subtraction of highest occupied molecular orbital (HOMO) from unoccupied molecular orbital (LUMO). It is shown that as the diameter decreases the H-L gap of the NWs increase. This elongation in the energy gap due to reduction in size has been studied in experiment and also in theory based on the crystal field theory [43, 44]. The result means that the CdSe/CdS CSNWs with a larger shell would have larger band gap when the diameter is fixed, which is in line with the experimental results that emission maximum of CdSe/CdS CSNWs and nano-rods is blue-shifted with the increasing of shell thickness [6, 19, 40]. Where the amount of CdSe and CdS, drastically affects the electronic structure of CSNWs. The electronic structure depends on the ratio of CdSe and CdS in the core–shell structure. Thus we can tune the band gaps of the CSNWs with modifying the size of the core or shell in the synthesizing process of nanowire materials.

Figure 3. (a) Band gaps of CdSe/CdS CSNWs. Bulk band gaps are (0.75 eV) & (1.22 eV) for CdSe and CdS respectively; (b) Band gaps of CdS/CdSe CSNWs. Our calculated bulk band gaps for CdSe and CdS are (0.75 eV) & (1.22 eV) respectively not shown in figure.

Furthermore, the partial density of states (PDOS) have been simulated and have investigated the effects of concentration on the PDOS. The calculated PDOS for CdSe/CdS with different core to shell composition are given in Figure 4. The PDOS for the pure CdS NWs shows that the valence band are contributed more from the sulphur s-state whereas Se-s states contribute more to the valance band in case of in CdSe cluster. When the core/shell parts are formed the p states of sulphur and selenium shows major contribution to the valance band. In addition we observe an important effect when core shell interface formed i.e if we see at Figure 4 for x=0.1 and x=0.4 the whole pattern of PDOS is slightly going to compress with the variation of concentration at the composite interface, this compressive stress are observed in many experimental and theoretical work of CdSe/CdS CSNWs where the degenerate states are appearing due to splitting of orbitals [39]. In short, the extension of wave functions on the nanowires surface are due to the strain effects at interface.
4. Conclusion
The structural stabilities and band gap engineering of CdSe/CdS and CdS/CdSe CSNWs has been studied with first principles methods. The composition effects in the term of size \( d \) and lattice constant \( c \) are discussed in detail. Furthermore, we have discussed in detail the compressive strain due to large lattice mismatch which cause a non-linear behaviour in the structural parameters in these CSNWs. For the stability purpose the binding energy has been calculated. From the analysis of binding energy we found that the stability of CdSe/CdS are higher than CdS/CdSe. The study also revealed that thicker CdS shell decrease the NWs stability and thicker CdS shell improves their stability. The blue shift of absorption spectra in these CSNWs are discussed in the term of energy gap modulation. The calculated energy gaps shows that the CSNWs are in strong quantum confinement regime and hence the red and blue shift are discussed in detail. This is very important for the experimental photoluminescence spectra. The partial density of states indicates that the contribution to the VB (valence band) is due to sulphur p-state and Se p and s states and contribution to the CB (conduction band) is due to s-state of Cd for CdSe/CdS CSNWs. Density of states confirmed that valence orbital p of Sulphur and selenium shows the formation of core shell interface.

References
[1] A. Nduwimana, R.N. Musin, A.M. Smith, X.Q. Wang, Nano Lett. 8, 3341 (2008).
[2] M.E. Pistol, C.E. Pryor, J. Phys. Rev. B 78, 115319 (2008).
[3] S.Y. Yang, D. Prendergast, J.B. Neaton, Nano Lett. 10, 3156 (2010).
[4] T. Mokari, S. E, Habas, M. Zhang, P. Yang, J. Angew. Chem. Int. Ed. 47, 5605–5608 (2008).
[5] T. Sadowski, R. Ramprasad, J. Phys. Chem. C, 114, 1773 (2010).
[6] J.A. Goebl, R.W. Black, J. Puthussery, J. Giblin, T.H. Kosel, M. Kuno, J. Am. Chem. Soc. 130, 14822 (2008).
[7] A. P. Alivisatos, Science 271, 933 (1996).
[8] L. Esaki, IEEE J. Quantum Electron, 22, 1611 (1986).
[9] X. Peng, M. C. Schlamp, A. V. Kadavanich, and A. P. Alivisatos, J. Am.Chem. Soc. 119,
7019 (1997).
[10] M. C. Schlamp, X. Peng, and A. P. Alivisatos, J. Appl. Phys. 82, 583 (1997).
[11] M. A. Hines and P. G. Sionnest, J. Phys. Chem. 100, 468 (1996).
[12] Y. W. Cao and U. Banin, J. Angew. Chem. Int. Ed. 38, 3692 (1999).
[13] S. Kim, B. Fisher, and M. Bawendi, J. Am. Chem. Soc. 125, 11466 (2003).
[14] T. Mokarai, S. E. Habas, M. Zhang, P. Yang J. Angew. Chem. Int. Ed, 47, 5605-5608 (2008).
[15] Shan, Y. Xiao, Z. Chuan, Y. Li, H. Yuan, M. Li, Z. Dou, J. Nonparticle research, 16, 1-11 (2014).
[16] N. Petchsang, L. Shapoval, F. Vietmeyer, Y. Yu, J.H. Hodak, T.H. Kosel, M. Kuno, J. Nano Scale, Art. CN10176E, 1-8 (2011).
[17] A.C. Onicha, L.E. Sink, S.L. Weber-US Patent App. 14/446,313 (2014).
[18] J. Li and L.W. Wang Applied Physics Letters 84, 3648 (2004).
[19] Z. Li, X. Ma, Q. Sun, Z. Wang, J. Liu, Z. Zhu, S.Z. Qiao, G. Lu, A. Mews, Eur. J. Inorg. Chem., 4325-4331 (2010).
[20] R. Banerjee, R. Jayakrishnan, P. Ayyub, J. Phys. Condens. Mater, 12, 10647-10654 (2000).
[21] K. Wu, E. William, R. Cordoba, Z. Liu, T. Lian, J. ascnano.org, 7, 7173-7185 (2013).
[22] D.U. Lee, D.Y. Yun, T.W. Kim, S.H. Park, D. Choi, T.W. Kang, J. App. Phys, 061201 (2015).
[23] D. Schooss, A. Mews, A. Eychmuller, and H. Weller, Phys. Rev. B 49, 17072 (1994).
[24] E. P. Pokatilov, V. A. Fonoberov, V. M. Fomin, and J. T. Devreese, J. Phys. Rev. B 64, 245329 (2001).
[25] S. Pokrant and K. B. Whaley, J. Eur. Phys. D, 6, 255 (1999).
[26] H. X. Fu, L. W. Wang, and A. Zunger, Phys. Rev. B 57, 9971 (1998).
[27] A. Zunger, A. Freeman, J. Phys. Rev. B, 17, 4850-4863 (1978).
[28] A.E. Carlsson, J. Phys. Rev. B, 31, 5178-5182 (1985).
[29] H. Dong, Z. Guo, K. Gilmore, T. Hou, Li, Y. J. iop nanotechnology, 26, 275201 (2015).
[30] Y. Zheng, H. Xing, Y. Huang, Y. Zheng, H. Xing, Y. Huang, Y. Fang, A.Lu, X.Chen J. Nanosci. Nanotechnol, 15, 5851-5855 (2015).
[31] Z. Zhang, Y. Xu, J. Supper lattices and Microstructures, 57, 19-26 (2013).
[32] J.P. Perdew, S. Burke, M. Ernzerhof, J. Phys. Rev. B, 101, 033502 (2007).
[33] Kress, G. Furthmiller, J. Phys. Rev. B, Lett, 54, 11169-11186 (1996).
[34] Perdew, J.P. Burke, K. Enzerhof, J. Phys. Rev. Lett, 77, 3865-3868 (1996).
[35] Monkhorst, H.J. Pack, J. Phys. Rev. B, Lett, 13, 5188-5192 (1996).
[36] D. Guozhang, S. Yang, M. Yan, Q. Wan, Q.Zhang, A. Pan, B. Zou1, J. of Nanomaterials Article ID 427689 (2010).
[37] A. R. Denton, and N. W. Ashcroft, “Vegard’s law,” Physical Review A, 43, 3161-3164 (1991).
[38] H.Z. Xing, H.Y. Zhang, Y. Huang, J. of Nanoscience and Nanotechnology, 12, 2567-2572 (2012).
[39] L. Carbone, C.N. Milena, D.G. Fabio, D. Sala, G. Morello, P. Pompa, M. Hytch, E. Snoeck, Nano Lett, 7, 10 (2007).
[40] H. Shu, X. Chen, X. Zhou, W. Lu, J. Chem. Phys. Lett, 495, 261 (2010).
[41] Z. Zhou, M. Li, P. Wu, L. Guo, J. Adv. Condense. Matter Phys, 2014, (2014)
[42] Kjocevski, et al, J. Sci. rep.5, 10865, doi: 10.1038/srep10865 (2015)
[43] W. H. Zhang and W. D. Zhang, J. Mater. Lett. 98, 5 (2013).
[44] S. Li and G. W. Yang, Appl. Phys. Lett. 95, 073106 (2009).