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Design Guidelines for True Green LEDs and High Efficiency Photovoltaics Using ZnSe/GaAs Digital Alloys

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In the fields of solid state lighting and high efficiency solar photovoltaics (PV), a need still exists for a material system that can target the 2.3-2.5eV energy range. The ZnSe/GaAs system is shown to have great potential. The digital alloy approach can be utilized as a well-ordered design alternative to the disordered alloyed systems. The effective band-gap of the ZnSe/GaAs(001) superlattice has been studied, as a function of the constituent monolayers using tight binding. The possibility of engineering a range of band-gaps with the same material system, to achieve the optimum value for solar PV and LED applications, has been proposed.

INTRODUCTION AND APPROACH

Why ZnSe/GaAs? The solar cell story. Currently, no material system is well tuned for the conversion of high energy photons in the range of 2.3 to 2.5eV. as depicted in Fig.1. In the field of multijunction, or tandem stack, solar cell design, this high energy range is of crucial importance for reaching a combined cell efficiency greater than 50%. In particular, a material system with an energy gap of 2.4eV would be ideal for the top-most cell in a vertically integrated multijunction stack[1, 2]. Additionally, the need still exists for a highly efficient true green light emitting diode (LED) in the wavelength range of 555 to 560nm. InGaN is able to achieve high brightness in green/blue-green LEDs (around 532nm), while GaP and AlGaInP work best in the yellow-green range (around 567nm), leaving a gap in between (the so-called "green gap"). Most work being conducted in this area is with InGaN. However, indium-rich compositions suffer severely from phase separation of InN[3], resulting in detuning from the desired spectral range. In addition, all existing InGaN growth processes result in defect densities that are too high for efficient solar cells. As an alternative, the system between GaAs and ZnSe is particularly appealing for investigation. Given that they are both direct band gap and lattice matched (within 0.27%) semiconductors, the possibility exists of engineering materials both in physical and/or digital alloy form over the full range of band gaps from 1.42eV (GaAs) to 2.7eV (ZnSe). Shen et. al have previously shown calculations on this superlattice (SL) system, though no details were given on our targeted range of band gaps[4]. Our work seeks to guide the experimentalist to engineer ZnSe/GaAs digital alloys (DAs) based on barrier and well thickness.

Digital Alloys vs. Physical Alloys From a materials engineering perspective, there are two possible methods for fabricating materials with band gaps between that of GaAs and ZnSe 1)physical alloying and 2)digital alloying using a SL. It might be indicated that the DA technique has an advantage because of the fact that the density of states for a quantum well like structure has a stair-case form which translates into a non-zero value of density of states even at the minimum(maximum) energy for the conduction(valence) band[5]. In this paper, we investigate the DA technique[6] to provide a well-ordered design alternative to the disordered physical alloyed systems. Due to their miscibility, ZnSe and GaAs could be formed as a physical quaternary alloy. However, the use of a DA is preferable given the heterovalency of the ZnSe/GaAs alloy. As zinc and selenium will each dope GaAs, as well as the reverse case with gallium and arsenic in ZnSe being true, maintaining control on doping densities in the quaternary would be difficult. However, given that one can maintain control in doping pure ZnSe and GaAs, the ability to fabricate doped DAs of ZnSe/GaAs is possible. Given that ZnSe is lattice matched to GaAs, periodic structures on the monolayer scale can be grown using molecular beam epitaxy (MBE). Previous work by Qian et al has shown the ability to create

ZnSe/GaAs interfaces with low defect densities[7]. Additionally, Kobayashi et al have demonstrated ZnSe/GaAs SLs grown by migration-enhanced epitaxy (MEE) as an alternative growth method [8, 9]. **We do note, however, that growth of GaAs on ZnSe does present a difficulty due to growth temperatures, but experiments can be done using low-temperature-grown GaAs[10].**

Device Descriptions By utilizing the DA technique for device engineering, one has more freedom in narrowing in on a specific need, such as optimal light absorption in a solar cell or tuned light emission in an LED. Fig.2 shows each of these devices in configurations that could be used for incorporation of the ZnSe/GaAs SL in each. These designs are by no means intended to be novel, but provide a basis from which to build upon. For use in a solar cell, a p-i-n structure would be well suited where primary absorption takes place in the intrinsic SL region. Ideally, one would expect to incorporate the necessary number of SL periods to absorb an adequate number of photons (99%). In pure ZnSe this is around 500nm[11] and around 1500nm for pure GaAs[12]. The experimentalist could estimate from these what may be acceptable for the ZnSe/GaAs SL, taking into account the greater difficulty and time involved in growing thicker SL layers. **From a cost perspective, the increased cost to fabricate such SL-based solar cells may turn out to be worthwhile in the scheme of single or dual-axis concentrator systems.** For an LED, a similar design could be used except for the desire to have doped SL layers on either side of an intrinsic SL layer. Making the intrinsic layer very thin should help promote carrier confinement for increasing radiative recombination. A ZnSe substrate would need to be used for light transmission through the bottom, or a GaAs substrate could be used for growth and then etched off. The p ZnSe needs to be contacted directly due to the insulating nature of ZnSe substrates.

Need for atomistic models: The need to capture properties at the atomic level for device detail that varies at the nanometer level is often not fully appreciated. It has been recognized for several years now that effective mass models cannot treat band non-parabolicities properly. From the point of view of the SL it is imperative that a quantum mechanical approach that includes confinement effects is used. Effects of band non-parabolicities, material variations and confinement are readily captured in multi-band tight binding models. In this paper we employ the sp^3s^* nearest neighbor tight binding scheme to model the SL. The scheme is capable of replicating both the conduction and valence bands close to the Γ valley. Since X-minima are not in the energy range of interest we do not need to model them extremely accurately and we therefore do not include 'd' orbitals or second nearest neighbor interactions in this tight binding approach.

METHODOLOGY

Hamiltonian Construction and Boundary Conditions: The nearest neighbor tight binding hamiltonian is constructed with the well region (GaAs) surrounded by the barrier region (ZnSe) on either side. Further periodic boundary conditions are incorporated to repeat the structure indefinitely.

Parameter sets and Band offset treatment: Based on the experimental data for ZnSe [13–15], the effective masses in the seminal work of Vogl et al.[16] turn out to be inaccurate. In addition to that the Vogl parameters fit the low temperature gaps whereas we need to model room-temperature gaps. Finally the Vogl[16] parameter sets do not incorporate spin-orbit coupling which is essential to model the imaginary band linking the light-hole and conduction band[17]. We re-parametrize the Vogl ZnSe parameter set [Table I] based on the Landolt-Bornstein tables using the analytical expressions for effective masses in [17]. For GaAs the sp^3s^* parameters from Boykin et al.[17] are used. These parameter sets assume the valence band for both ZnSe and GaAs to be at 0eV. Various authors have reported the experimentally measured Valence band offset (VBO) and Conduction Band offset (CBO) for the ZnSe/GaAs(001) and ZnSe/GaAs(110) SLs. Raman Scattering[18], Electrical[19], Optical[20], and XPS[21, 22] measurements put the VBO at 0.9-1.1eV for ZnSe/GaAs(110) and 0.7-0.9eV for ZnSe/GaAs(001) hetero-junctions. We assume it to be close to 0.96eV[23]. This leads us to the band diagram as depicted in Fig. 3. We have also verified that by using the Vogl parameters for both ZnSe/GaAs, similar results are obtained, though electron and hole states have to be treated separately to get the correct band offsets.

RESULTS AND DISCUSSION

Effective Conduction band of the SL: The hamiltonian with the correct conduction band offset is constructed such that the ZnSe and GaAs conduction band edges are at 2.68eV and 2.38eV (1.42eV+0.96eV) respectively. The ground state eigenvalues are found for varying SL periods. As is expected, in Fig. 4, when the ZnSe(GaAs) content is much larger than the GaAs(ZnSe) content, the ground state energy approaches the bulk value of 2.68eV(2.38eV) as shown in Fig.3. For a given thickness of ZnSe as the thickness of GaAs is decreased, an increase in the ground state energy can be seen. This trend is attributed to confinement effects. Alternatively, for a given thickness of GaAs, the ground state energy starts from the bulk value of GaAs(2.38eV) for low ZnSe content and gradually increases until the thickness of ZnSe is enough such that the eigen-states in adjoining quantum wells have no significant effects on each other. This increase can be understood in terms of the coupled quantum well picture. If the coupling between two quantum wells

is reduced by increasing the thickness of the barrier material, the energy of the lower bonding state increases and that of the higher anti-bonding state decreases. The plot for the effective valence bands shows equivalent trends and can be explained using similar arguments.

Effective band gap of the SL: Finally in Fig. 5 the effective band gap of the SL is estimated as the difference in the lowest conduction band and the highest valence band state for different SL periods. The tendency to approach the appropriate bulk value is evident again when the percentage of one material is much greater than the other. **We recognize that as the thickness of the well regions becomes smaller, the effects from the (Ga, Se) compounds at the interfaces[24] may affect these calculations, though including such effects is outside the scope of this work.**

CONCLUSION

Range of band gaps can be fabricated: We have used the tight-binding technique to predict the effective band gap of the ZnSe/GaAs SL. The calculation potentially paves the way for obtaining a range of band gaps from 1.7-2.5eV in the same material system using DAs. A band gap slightly greater than 2.4eV can be achieved with 20 monolayers of ZnSe interspersed with 2 monolayers of GaAs. This will enable solar cell to target the spectrum around 2.3-2.5eV and thus increase efficiency. Though experimental measurements are required to verify the accuracy of these numbers, the variations and trends discussed here will provide a guideline.

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- [1] T. Zdanowicz, T. Rodziejewicz, and M. Zabkowska-Waclawek, *Solar Energy Materials and Solar Cells* **87**, 757 (2005), ISSN 0927-0248, international Conference on Physics, Chemistry and Engineering.
- [2] A. Barnett, C. Honsberg, D. Kirkpatrick, S. Kurtz, D. Moore, D. Salzman, R. Schwartz, J. Gray, S. Bowden, K. Goossen, et al., *Photovoltaic Energy Conversion, Conference Record of the 2006 IEEE 4th World Conference on* **2**, 2560 (2006).
- [3] R. Singh, D. Doppalapudi, T. D. Moustakas, and L. T. Romano, *Applied Physics Letters* **70**, 1089 (1997).
- [4] D. Shen, K. Zhang, and R. Fu, *Applied Physics Letters* **53**, 500 (1988).
- [5] H. Okamoto, *Japanese Journal of Applied Physics* **26**, 315 (1987).
- [6] L. Esaki and R. Tsu, *IBM Journal of Research and Development* **14**, 62 (1970).
- [7] Q.-D. Qian, J. Qiu, M. R. Melloch, J. J. A. Cooper, L. A. Kolodziejski, M. Kobayashi, and R. L. Gunshor, *Applied Physics Letters* **54**, 1359 (1989).
- [8] N. Kobayashi and Y. Horikoshi, *Japanese Journal of Applied Physics* **29**, L236 (1990).
- [9] S. Ramesh, N. Kobayashi, and Y. Horikoshi, *Applied Physics Letters* **57**, 1102 (1990).
- [10] M. R. Melloch, J. M. Woodall, E. S. Harmon, N. Otsuka, F. H. Pollak, D. D. Nolte, R. M. Feenstra, and M. A. Lutz, *Annual Review of Materials Science* **25**, 547 (1995).
- [11] S. Adachi and T. Taguchi, *Phys. Rev. B* **43**, 9569 (1991).
- [12] S. Adachi, *Journal of Applied Physics* **66**, 6030 (1989).
- [13] O. Madelung, ed., *Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology*, vol. 17 a/b of *Group III* (Springer-Verlag, Berlin, 1982).
- [14] O. Madelung, ed., *Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology*, vol. 22a of *Group III* (Springer-Verlag, Berlin, 1987).
- [15] D. Bertho, J.-M. Jancu, and C. Jouanin, *Phys. Rev. B* **48**, 2452 (1993).
- [16] P. Vogl, H. P. Hjalmarson, and J. D. Dow, *Journal of Physics and Chemistry of Solids* **44**, 365 (1983).
- [17] T. B. Boykin, G. Klimeck, R. C. Bowen, and R. Lake, *Phys. Rev. B* **56**, 4102 (1997).
- [18] D. J. Olego, *Phys. Rev. B* **39**, 12743 (1989).
- [19] S. Colak, T. Marshall, and D. Cammack, *Solid-State Electronics* **32**, 647 (1989), ISSN 0038-1101.
- [20] L. Kassel, H. Abad, J. W. Garland, P. M. Raccach, J. E. Potts, M. A. Haase, and H. Cheng, *Applied Physics Letters* **56**, 42 (1990).
- [21] G. Bratina, L. Vanzetti, R. Nicolini, L. Sorba, X. Yu, A. Franciosi, G. Mula, and A. Mura, *Physica B: Condensed Matter* **185**, 557 (1993), ISSN 0921-4526.
- [22] S. P. Kowalczyk, E. A. Kraut, J. R. Waldrop, and R. W. Grant, *Journal of Vacuum Science and Technology* **21**, 482

(1982).

[23] A. Ekpunobi, *Materials Science in Semiconductor Processing* **8**, 472 (2005), ISSN 1369-8001.

[24] D.-W. Tu and A. Kahn, *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films* **3**, 922 (1985).

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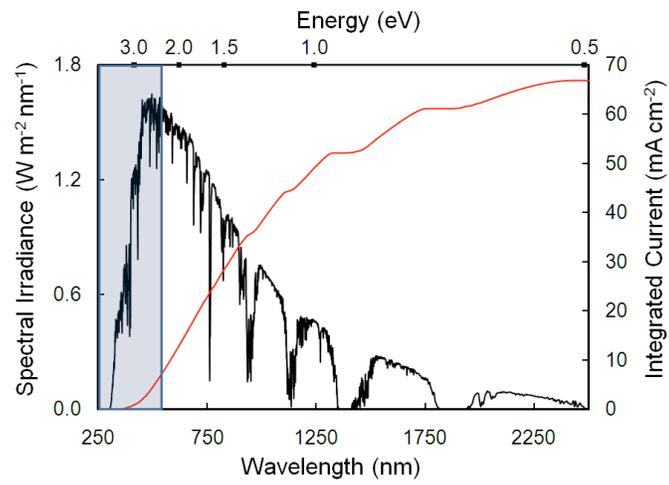


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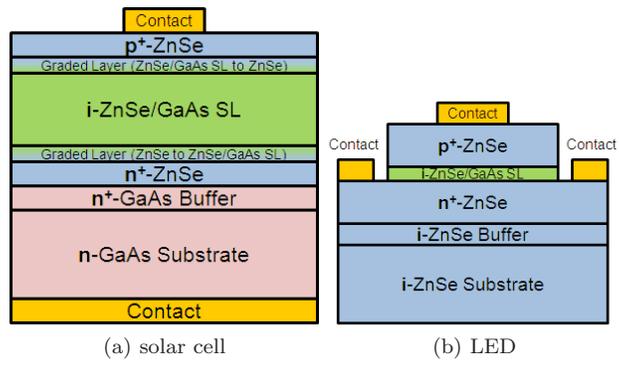


FIG. 2: General concepts for incorporating the ZnSe/GaAs SL

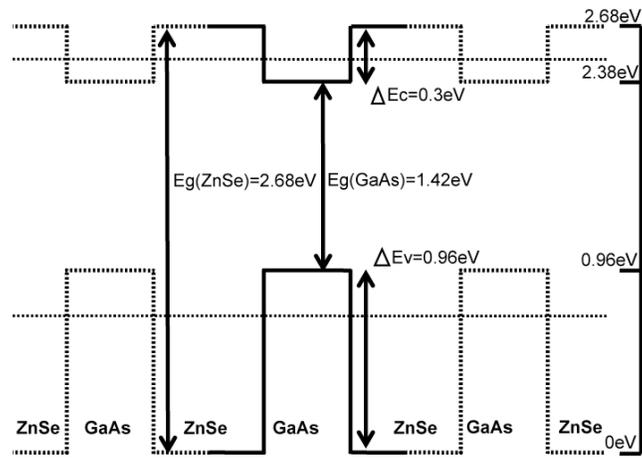


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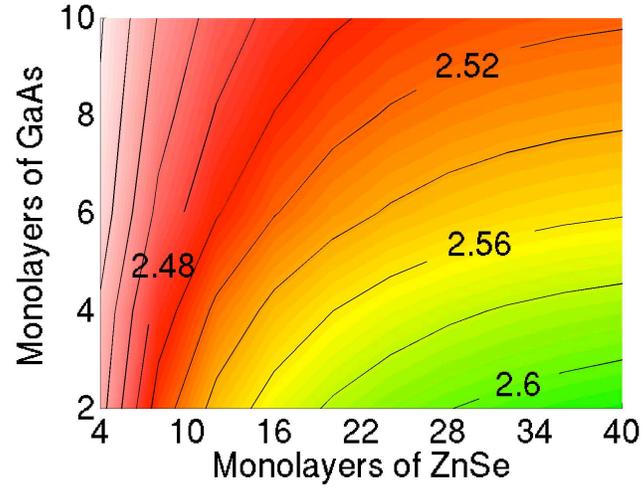


FIG. 4: Ground state energy in eV of the states formed in the conduction band well for different monolayers of ZnSe and GaAs.

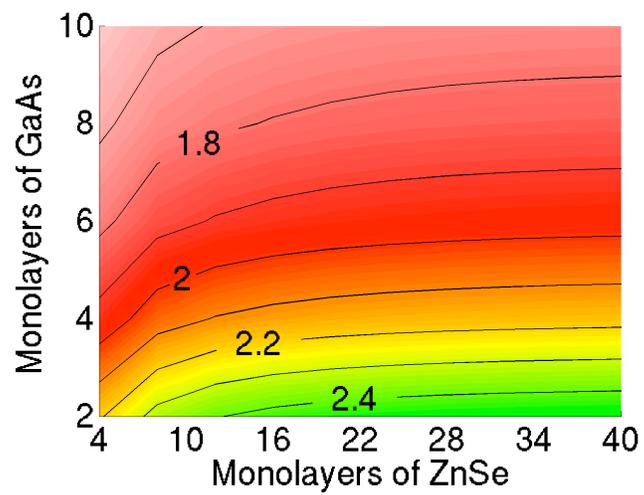


FIG. 5: Difference in the ground state energy in the conduction band well and the highest state in the valence band barrier in eV for different monolayers of ZnSe and GaAs.

E_{sa}	-12.6921	$V_{s,s}$	-6.3967
E_{pa}	1.5072	$V_{x,x}$	3.1784
E_{sc}	0.0183	$V_{x,y}$	5.3489
E_{pc}	6.0298	$V_{sa,pc}$	3.498
E_{s^*a}	7.5872	$V_{sc,pa}$	7.3683
E_{s^*c}	8.9928	$V_{s^*a,pc}$	2.5891
λ_a	0.16	V_{pa,s^*c}	3.9533
λ_c	0.03		

TABLE I: Nearest neighbor sp^3s^* ZnSe parameters(eV). Labels denote matrix elements. E:onsite, V:coupling, λ :spin-orbit coupling. Subscripts denote the basis. s,p,x,y: orbital symmetries. a,c: anion or cation[16]