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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 (PVs), a need still exists for a material system that can target the 2.3–2.5 eV 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 bandgap 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 bandgaps with the same material system, to achieve the optimum value for solar PV and light emitting diode (LED) applications, has been proposed.
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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 2.3–2.5 eV, 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 2.4 eV would be ideal for the topmost 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 555–560 nm. InGaN is able to achieve high brightness in green/blue-green LEDs (around 532 nm), whereas GaP and AlGaInP work best in the yellow-green range (around 567 nm), 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 bandgap and lattice-matched (within 0.27%) semiconductors, the possibility exists for engineering materials both in physical and digital alloy (DA) form over the full range of bandgaps from 1.42 eV (GaAs) to 2.7 eV (ZnSe). Shen et al. previously showed calculations on this superlattice (SL) system, although no details were given on our targeted range of bandgaps.[4] Our work seeks to guide the experimentalist to engineer ZnSe/GaAs DAs based on barrier and well thickness.

DAs vs Physical Alloys

From a materials engineering perspective, there are two possible methods for fabricating materials with bandgaps between that of GaAs and ZnSe: (*i*) physical alloying and (*ii*) digital alloying using an SL. It might be indicated that the DA technique has an advantage because the density of states for a quantum-well-like structure has a staircase form that translates into a nonzero value of density of states even at the minimum (maximum) energy for the conduction (valence) band.[5] In this article, we investigate the DA technique[6] to provide a well-ordered design alternative to the disordered physical alloyed systems. Because of 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 each dopes 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. Previous work by Qian et al. has shown the ability to create ZnSe/GaAs interfaces with low defect densities.[7] Additionally, Kobayashi and Horikoshi[8] and Ramesh et al.[9] demonstrated ZnSe/GaAs SLs grown by migration-enhanced epitaxy as an alternative growth method. However, the growth of GaAs on ZnSe is difficult 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. Figure 2 shows each of these devices in configurations that could be used for incorporation of the ZnSe/GaAs SL in each. These designs 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 500 nm[11] and for pure GaAs around 1500 nm.[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 nonparabolicities 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 nonparabolicities, material variations, and confinement are readily captured in multiband tight-binding models. In this article we em-

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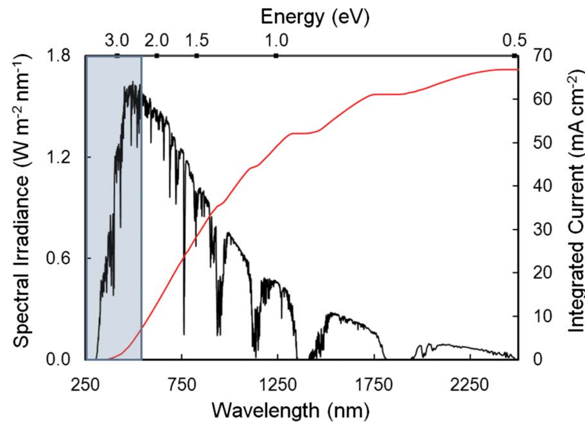

Figure 1. (Color online) AM 1.5 solar spectrum with the shaded region indicating photons absorbed by a 2.4 eV solar cell (constituting 21.1% of total irradiance and 7.5 mA/cm^2 total current density).

Table I. Nearest-neighbor sp^3s^* ZnSe parameters (eV). Labels denote matrix elements. *E*, on site; *V*, coupling; and λ, spin-orbit coupling. Subscripts denote the basis. s, p, x, and y are orbital symmetries. a and c is an anion or a cation.[16]

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

ploy 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. Because 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.

Methodology Experimental

Hamiltonian construction and boundary conditions.— The nearest-neighbor tight-binding Hamiltonian was constructed with the well region (GaAs) surrounded by the barrier region (ZnSe) on either side. Further periodic boundary conditions were 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] are inaccurate. In addition, the Vogl parameters fit the low temperature gaps, whereas we needed to model room-temperature gaps. Finally, the Vogl[16] parameter sets did not incorporate spin-orbit coupling, which is essential to model the imaginary band linking the light-hole and conduction band.[17] We reparametrized the Vogl ZnSe parameter set (Table I) based on the Landolt–Börnstein tables using the analytical expressions for effective masses in Ref. 17. For GaAs the sp^3s^* parameters from Boykin et al.[17] were used. These parameter sets assumed the valence band for both ZnSe and GaAs to be at 0 eV. Various authors had 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 X-ray photoelectron spectroscopy[21,22] measurements put the VBO at 0.9–1.1 eV for ZnSe/GaAs(110) and 0.7–0.9 eV for ZnSe/GaAs(001) heterojunctions. We assumed it to be close to 0.96 eV.[23] This led us to the band diagram depicted in Fig. 3. We also verified that by using the Vogl parameters for both ZnSe and 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 CBO is constructed such that the ZnSe and GaAs conduction band edges are at 2.68 and 2.38 eV (1.42 + 0.96 eV), 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 2.68 eV (2.38 eV), 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 (2.38 eV) for low ZnSe content and gradually increases until the thickness of ZnSe is enough such that the eigenstates 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 en-

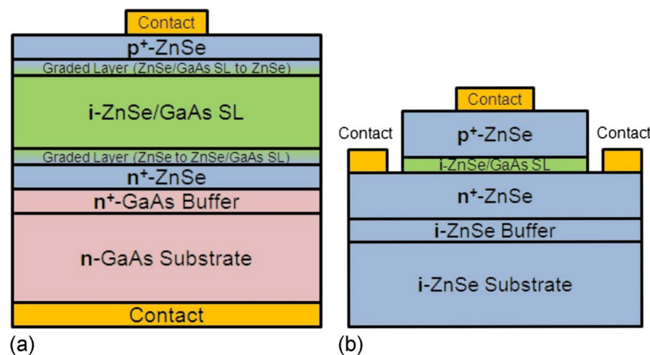

Figure 2. (Color online) General concepts for incorporating the ZnSe/GaAs SL.

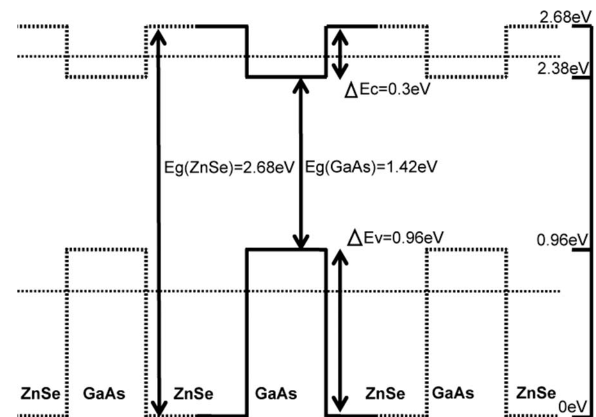

Figure 3. Band diagram of the ZnSe/GaAs SL: The band offsets have been indicated with arrows. The dashed band edge indicates that the structure is periodic. The dotted lines indicate confined states that penetrate into the barrier region.

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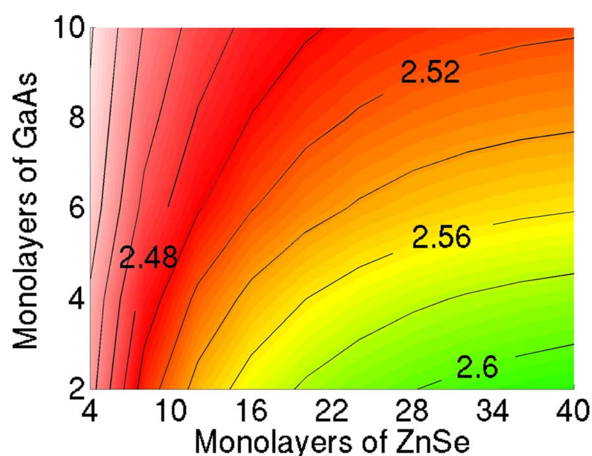

Figure 4. (Color online) Ground state energy in eV of the states formed in the conduction band well for different monolayers of ZnSe and GaAs.

ergy of the lower bonding state increases and that of the higher antibonding state decreases. The plot for the effective valence bands shows equivalent trends and can be explained using similar arguments.

Effective bandgap of the SL.— Finally, in Fig. 5, the effective bandgap 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.

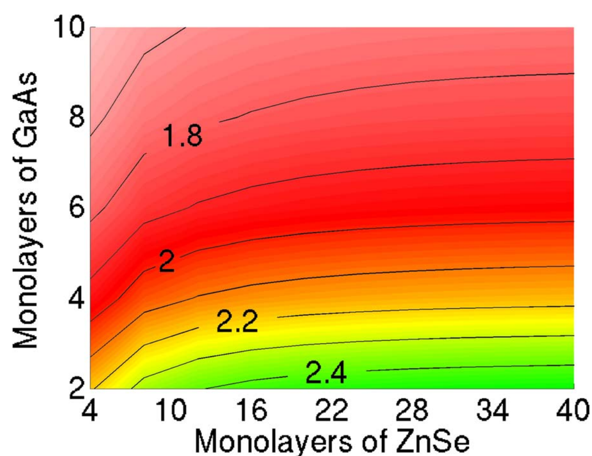

Figure 5. (Color online) Difference in the ground state energy in the conduction band well and the highest state in the valence band barrier in eV for different monolayers of ZnSe and GaAs.

Conclusion

Range of bandgaps can be fabricated.— We have used the tight-binding technique to predict the effective bandgap of the ZnSe/GaAs SL. The calculation potentially paves the way for obtaining bandgaps ranging from 1.7 to 2.5 eV in the same material system using DAs. A bandgap slightly greater than 2.4 eV can be achieved with 20 monolayers of ZnSe interspersed with 2 monolayers of GaAs. This will enable the solar cell to target the spectrum around 2.3–2.5 eV 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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