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Heterojunction Approaches to Light Emitters: The Role of Band Offsets

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Heterojunctions provide a promising approach for obtaining visible II-VI light emitters. We examine dopability, band offsets, and lattice match for various heterojunctions involving II-VI semiconductors and identify some target combinations for further exploration. We find that the p-ZnTe/n-ZnSe, p-diamond/n-ZnSe, n-AlSb/p-ZnTe and n-CdSe/p-ZnTe heterojunctions appear attractive. Experimental data on these important heterojunctions are presented with an eye to assessing their usefulness for fabricating light emitters.

1. Introduction

Solid–state visible light emitters have been a subject of widespread research since the first light emitting devices were produced in the late 1950's[1]. Much of this effort has been directed towards the fabrication of light emitters in various II–VI material systems, due to the availability of II–VI materials with band gaps spanning the entire visible spectrum. At present, however, there are no II–VI–based visible light emitting diodes (LED's) in production; commercially available visible LED's emit light in the red and yellow–green regions of the spectrum, and are based on GaAsP and GaP.

One of the major difficulties encountered in early efforts to fabricate II–VI–based light emitters was the inability to control doping in these materials; none of the binary II–VI materials with band gaps at visible wavelengths can be doped both p–type and n–type, obviating the possibility of producing visible LED's based on simple p–n homojunctions. The development of high–quality epitaxial growth techniques such as molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), however, has provided myriad new possibilities for overcoming these previously encountered problems, and has sparked a renewed interest in II–VI material systems. In particular, these new growth techniques provide greater flexibility in direct doping of II–VI materials, and also allow highly controllable fabrication of heterojunctions.

In this abstract, we discuss possible heterojunction approaches to the fabrication of II–VI–based LED's, with emphasis on the role of band offsets in determining the viability of these approaches. Using dopability, band offset values, and lattice match as the principal criteria, we identify heterojunctions that show the greatest promise for application in LED structures, and we also review recent experimental data on some of the most important of these heterojunction systems.

2. Band Offsets, Band Gaps, and Lattice Constants

Figs. 1 and 2 show the positions, referenced to the valence band edge of GaAs, of the conduction and valence band edges (indicated by upward–pointing and downward–pointing triangles, respectively) of several semiconductors of interest, plotted as a function of lattice constant. For each material, the position of the band gap is indicated by the solid line connecting the conduction and valence band edges. A solid symbol for the conduction (valence) band edge indicates that the material can be doped n–type (p–type) by conventional means; an open symbol denotes lack of dopability. Assuming transitivity of band offset values, the conduction (valence) band offset for a heterojunction system is given simply by the separation of the conduction (valence) band edges of the constituent materials on the absolute energy scale given in the figures. In Fig. 1 we have used the predictions of Harrison[2] to place these materials on a common energy scale; Fig. 2 is based on the predictions of Harrison and Tersoff[3].

As shown in these figures, each of the wide–gap

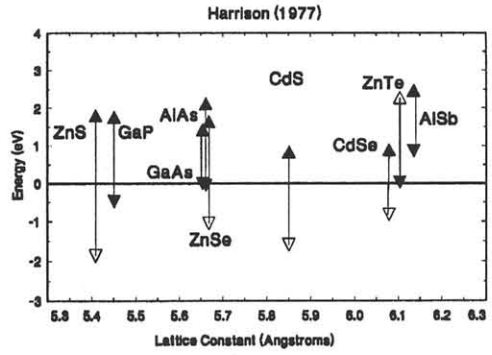

Fig. 1: Conduction and valence band edge positions and dopability versus lattice constant for selected semiconductor materials. Band edge positions were determined using the predictions of Harrison (Ref. [2]).

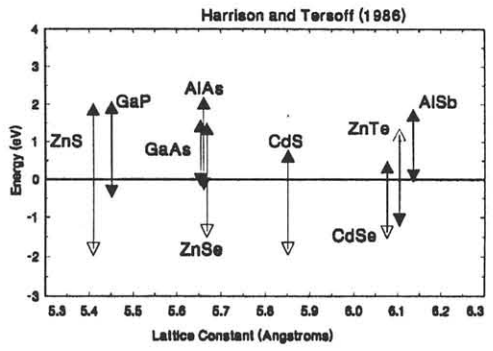

Fig. 2: Conduction and valence band edge positions and dopability versus lattice constant for selected semiconductor materials. Band edge positions were determined using the predictions of Harrison and Tersoff (Ref. [3]).

II–VI materials (ZnTe, CdS, ZnSe, and ZnS) can be doped either p–type (for ZnTe) or n–type (for CdS, ZnSe, and ZnS), but not both. These limitations naturally lead one to consider the possibility of injecting carriers into these materials using a suitable heterojunction.

The feasibility of such a heterojunction approach depends on three criteria. First, one of the constituent materials must be n–type, the other p–type. Second, the band offsets must be small enough to allow injection of the desired carriers into the wide–gap II–VI material; blocking of the other carrier type by a favorable band offset can be advantageous, but is less critical. Third, the materials must be approximately lattice–matched to allow the fabrication of high–quality, dislocation–free interfaces.

For injection of holes into p–type ZnSe, the number of suitable heterojunctions is small; most of the work on ZnSe–based heterojunctions has focused on the ZnSe/ZnTe system[5, 6]. Fig. 3 shows band offset values predicted by Harrison, Harrison and Tersoff, and several other theories for the ZnSe/ZnTe heterojunction. The wide range of predicted values renders them of little use in determining the viability of this approach, and makes apparent the need for reliable experimental band offset values.

Another possibility for injecting holes into n–type ZnSe is diamond. The valence band edge of diamond is predicted to be far below that of ZnSe, facilitating injection of holes from diamond into ZnSe, and diamond can easily be doped p–type. The lattice match between diamond and ZnSe is extremely poor, however, making the fabrication of high–quality heterojunctions difficult.

Possibilities for injecting electrons into p–type ZnTe appear to be more promising. As shown in Figs. 1 and 2, the most attractive candidates for formation of a heterojunction appear to be AlSb[4] and CdSe, both of which can be doped n–type and are closely lattice–matched to ZnTe. Figs. 4 and 5 show several predicted band offset values (indicated by the dotted lines) for the AlSb/ZnTe and CdSe/ZnTe heterojunction systems, respectively. As with the ZnSe/ZnTe heterojunction, the range of predicted band offset values is too large to permit a useful determination of the feasibility of electron injection into ZnTe. Several predictions for the AlSb/ZnTe heterojunction, however, indicate that injection of electrons from n–type AlSb into p–type ZnTe should be feasible.

3. Measurements of Band Offsets

Because of the large discrepancies among the predicted band offset values for these heterojunction systems, we have tried to determine band offsets for these heterojunctions based on experimental data. For ZnSe/ZnTe, we have examined data from optical experiments of Kobayashi et al.[5], and interpreted their data using superlattice theory. Our analysis [7] yields a valence band offset of 0.98 ± 0.10 eV, corresponding to a conduction band offset of ~ 0.4 eV. These values indicate that injection of holes from ZnTe into ZnSe would be quite difficult, but that injection of electrons from ZnSe into ZnTe might be feasible.

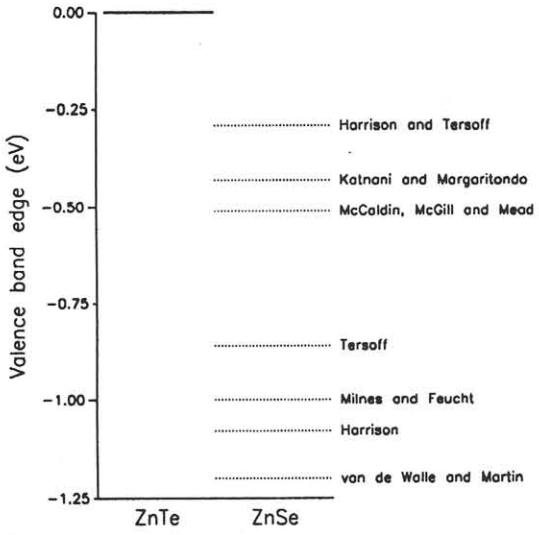

Fig. 3: Valence band offsets predicted by various theories for the ZnSe/ZnTe heterojunction system. The dotted lines indicate that these values are predictions rather than direct experimental measurements.

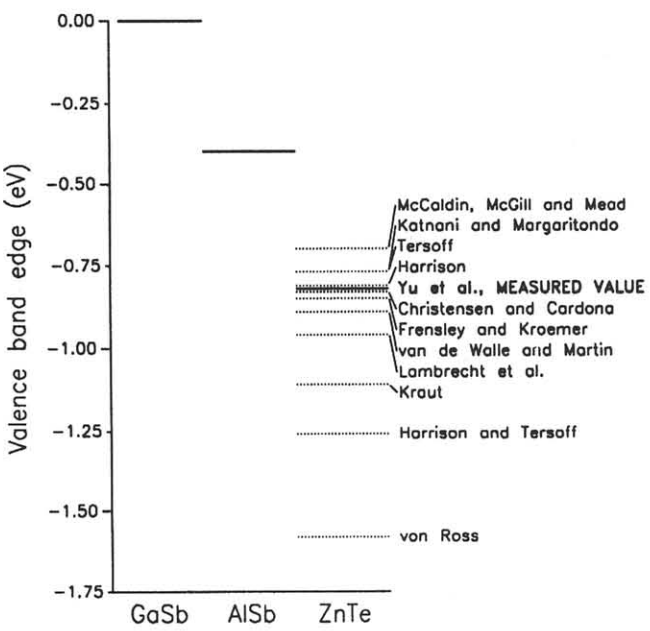

Fig. 4: Valence band offsets for the AlSb/ZnTe system based on the experimentally measured GaSb/AlSb band offset (Ref. [8]) and predicted band offsets for the GaSb/ZnTe heterojunction. Predicted values are shown as dotted lines. Our measured value for the AlSb/ZnTe valence band offset is indicated by a solid line.

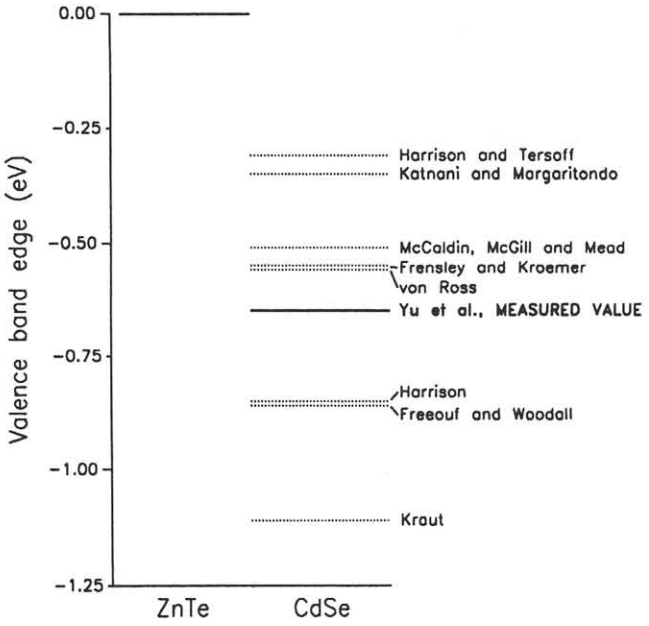

Fig. 5: Valence band offsets for the CdSe/ZnTe system predicted by various theories (dotted lines) and determined from preliminary experimental measurements (solid line).

For the AlSb/ZnTe heterojunction system, we have performed direct measurements of the valence band offset by x-ray photoelectron spectroscopy (XPS)[9], using the method developed by Grant and co-workers [10]. We grew AlSb/ZnTe heterojunctions using a multi-chamber MBE system, with transfer of the samples between growth chambers and into the XPS analytical chamber taking place under ultra-high vacuum conditions. This capability allowed us to grow and characterize the AlSb/ZnTe heterojunctions under highly controllable conditions. Our measurements yielded a valence band offset for the AlSb/ZnTe heterojunction of 0.42 ± 0.07 eV, corresponding to a conduction band offset of 0.21 ± 0.07 eV. Our measured value for the valence band offset is indicated by the solid line in Fig. 4. The conduction band offset of 0.21 eV suggests that injection of electrons from n-AlSb into p-ZnTe should be feasible, provided that the AlSb layer is sufficiently heavily doped.

A close examination of the XPS core level spectra from the AlSb/ZnTe heterojunction, however, reveals evidence of an interfacial reaction between the AlSb and ZnTe layers. As shown in Fig. 6, the Al $2p$ core level spectrum from an AlSb/ZnTe heterojunction contains a chemically shifted peak that is not present in the spectrum from bulk AlSb. A detailed analysis suggests that a layer of Al_2Te_3 is

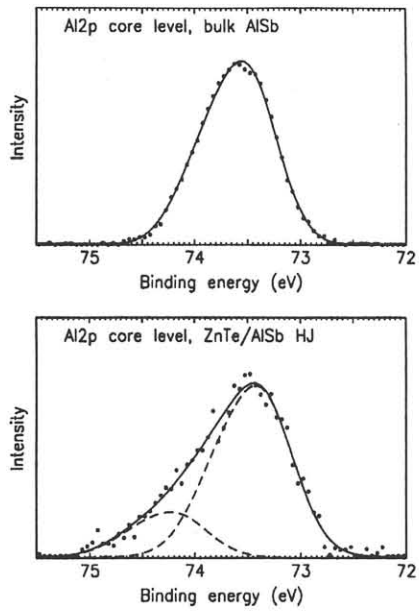

Fig. 6: Al $2p$ core level XPS spectra from bulk AlSb (upper spectrum) and a ZnTe/AlSb heterojunction (lower spectrum). The heterojunction spectrum contains a chemically shifted component, indicating the presence of a reacted interface layer in the heterojunction.

formed at the AlSb/ZnTe interface; reactions of this type have also been observed in other III–V/II–VI heterojunctions[11]. The presence of this intermediate layer, in addition to possible effects on the band offset value, could introduce a large number of non–radiative recombination centers that would adversely affect the performance of AlSb/ZnTe–based LED structures.

We have also carried out preliminary investigations on the CdSe/ZnTe heterojunction system. ZnTe, cubic CdSe, and CdSe/ZnTe heterojunctions have been grown by MBE, and XPS measurements have been performed. Results of these preliminary studies yield a valence band offset value of ~ 0.65 eV, corresponding to a conduction band offset of ~ 1.16 eV. Evidence of an interfacial reaction between CdSe and ZnTe has not been detected, suggesting that the CdSe/ZnTe interfaces should be of reasonably high quality.

4. Conclusions

We have presented an analysis of several heterojunction systems containing wide–gap II–VI materials to determine their suitability for use in heterojunction–based II–VI LED structures. Our analysis, using dopability, band offsets, and lattice match as the principal criteria, suggests that ZnTe/ZnSe, diamond/ZnSe, AlSb/ZnTe, and CdSe/ZnTe are especially promising systems for fabricating visible electroluminescent devices. The feasibility of these structures, however, is quite sensitive to the exact values of the heterojunction band offsets, and the large discrepancies among values predicted by different theories renders these theories of little use in analyzing device structures. We have measured band offsets directly for the AlSb/ZnTe and CdSe/ZnTe material systems, and have also obtained a band offset for the ZnSe/ZnTe heterojunction based on an analysis of experimental data. Our results for these systems have provided a much sounder basis for determining the attractiveness of these heterojunction systems for LED structures. The XPS measurements have also provided information about interface reactions in these heterojunctions, which could have a strong influence on the performance of heterojunction–based electroluminescent devices. Our data indicate that a substantial reacted layer forms at the AlSb/ZnTe interface, but that the CdSe/ZnTe interface should be of reasonably high quality.

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References

[1] E. E. Loebner, *Proc. IEEE* **61**, 837 (1973).
[2] W. A. Harrison, *J. Vac. Sci. Technol.* **14**, 1016 (1977).
[3] W. A. Harrison and J. Tersoff, *J. Vac. Sci. Technol. B* **4**, 1068 (1986).
[4] J. O. McCaldin and T. C. McGill, *J. Vac. Sci. Technol. B* **6**, 1360 (1988).
[5] M. Kobayashi, N. Mino, H. Katagiri, R. Kimura, M. Konagai, and K. Takahashi, *Appl. Phys. Lett.* **48**, 296 (1986).
[6] Y. H. Wu, H. Yang, A. Ishida, H. Fujiyasu, S. Nakashima, and K. Tahara, *Appl. Phys. Lett.* **54**, 239 (1989).
[7] Y. Rajakarunanayake, R. H. Miles, G. Y. Wu, and T. C. McGill, *Phys. Rev. B* **37**, 10212 (1988).
[8] G. J. Gualtieri, G. P. Schwartz, R. G. Nuzzo, and W. A. Sunder, *Appl. Phys. Lett.* **49**, 1037 (1986).
[9] E. T. Yu, E. T. Croke, D. H. Chow, D. A. Collins, M. C. Phillips, T. C. McGill, and J. O. McCaldin, to appear in *J. Vac. Sci. Technol. B* , July/August 1990.
[10] E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, *Phys. Rev. Lett.***44**, 1620 (1980).
[11] W. G. Wilke and K. Horn, *J. Vac. Sci. Technol. B* **6**, 1211 (1988); D.–W. Tu and A. Kahn, *J. Vac. Sci. Technol. A* **3**, 922 (1985).