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Highly Mismatched Semiconductor Alloys: From Atoms to Devices

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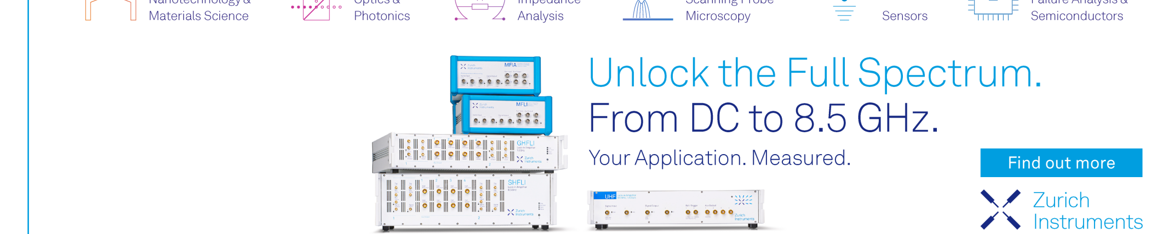

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I. BACKGROUND

Alloying is one of the most powerful methods to broaden the range of application of semiconductors. It has been successfully used to tailor the material properties such as bandgaps, band offsets, and lattice parameters for specific applications. For example, growth of lattice-matched AlGaAs on GaAs allowed for a precise control of the conduction band offsets and a successful realization of the concept of modulation or remotely doped heterostructures with electron mobilities in excess of $10^7\,cm^2/V\,s$[1] and new concepts for high-speed electronic devices. Progress in the growth of GaInP alloys with the bandgap of 1.9 eV and lattice matched to GaAs was critical for the development of high efficiency multijunction solar cells.[2] In one of the most impactful advancements, mastering of the synthesis of group III-nitride alloys led to the development of light emitters that revolutionized the solid state lighting technology.[3] In all of these instances, the alloying is achieved by the substitution of atoms with similar properties facilitating the alloying process that can be conducted near thermodynamic equilibrium. Also, the properties of such "matched" alloys can be reasonably well approximated by linear extrapolations of the end point materials.

Rapid progress in materials synthesis has enabled the preparation of alloys under nonequilibrium conditions by preventing the phase separation of highly incompatible materials. This greatly expands the range of available semiconductor material alloys with prospects for novel practical applications. In a seminal work published more than 25 years ago, Weyers *et al.*[4] have shown that modifications of epitaxial growth conditions allow the incorporation of a considerable amount of N into GaAs. The resulting dilute nitride alloy, GaN_xAs_{1-x}, exhibited interesting and unexpected properties. Most notably, the incorporation of N resulted in a large reduction of the bandgap of close to 100 meV per percentage of N. These developments generated a lot of interest and opened a new field of semiconductor research, as the alloys offered a potential for practical device applications. Thus, it has been shown that the new alloys can be used to make laser diodes in technologically important spectral ranges.[5] Similarly, a $Ga_{1-y}In_yAs_{1-x}N_x$ alloy lattice matched to GaAs was actively pursued as the long sought 1 eV bandgap semiconductor for a fourth junction in high efficiency multijunction solar cells.[6]

The experimental work rapidly expanded the range of group III-V compounds containing small—but impactful—amounts of N and the so-called "dilute nitrides" became a new, distinct class of semiconductor alloys. The experimental efforts were complemented with theoretical attempts to explain the origin of the unusually strong effects of N incorporation on the electronic band structure. Initial *ab initio* band structure calculations encountered a serious computational problem with the large size of the supercell required for alloys with small N contents.[7,8] Also, new experiments demonstrated that, in addition to reducing the bandgap, the incorporation of N modifies the electronic structure of the conduction band at higher energies.[9,10] This led to the development of the Band Anticrossing (BAC) model, which considered an interaction between highly localized states of substitutional nitrogen and the extended states of GaAs.[10] The model led to a definition of highly mismatched alloys (HMAs), in which host atoms are partially replaced with atoms of distinctly different electronegativity and/or ionic radius. The definition expanded the range of possible HMAs to include group II-VI based dilute oxides. In both dilute nitrides and dilute oxides, metallic atoms are replaced with highly electronegative nitrogen and oxygen, and the BAC interaction mostly affects the conduction band. However, it was also shown that a replacement of highly electronegative host atoms with more metallic atoms results in a BAC that mostly

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affect the valence band structure. In the past several years since the synthesis of the first highly mismatched alloys, a large variety of materials has been synthesized and studied. Innovative methods have been developed to control phase separation and broaden the range of possible alloy compositions. Splitting of the conduction band was observed in dilute group III-V nitrides as well as in dilute group II-VI oxides, which led to extensive efforts to design and practically realize the concept of the intermediate band solar cells.

The "Highly Mismatched Semiconductor Alloys: From Atoms to Devices" Special Topic in *Journal of Applied Physics* presents an extensive collection of papers that cover a broad range of subjects relating to highly mismatched alloys. It covers topics ranging from theoretical calculations of the electronic band structure through crystal growth methods to material properties relevant to potential applications of HMAs. The studied alloys range from inverted band structure semimetallic to very wide gap bandgap insulating materials. The most prominently represented classes of materials are group III-V based HMAs[11–27] followed by group II-VI based HMAs.[28–34] Group IV based HMAs are less represented, reflecting many challenges in the synthesis of these materials. Interestingly, two previously unknown materials, $B_xGa_{1-x}N$[35] and $Ga_2(O_{1-x}S_x)_3$,[36] were identified as new HMAs.

II. GROUP III-V BASED HMAs

A. Bismuth containing alloys

The predominant classes of HMAs represented in the "Highly Mismatched Semiconductor Alloys" Special Topic are materials containing bismuth, which is the heaviest nonradioactive column V element. The incorporation of Bi into standard III-V compounds enables a control of the bandgap, bandgap temperature coefficients, and spin-orbit splitting energy. A large variety of Bi-containing HMAs has been studied ranging from simple ternaries[11,15] to quaternaries[16,21] with a complex interdependence of the incorporation of different species. A special effort has been directed toward the synthesis of Bi-containing low bandgap alloys as they offer potential for the development of mid- to long-wavelength optoelectronic devices. Several papers report on detail studies of the growth parameters affecting Bi incorporation, which is a critical issue for this class of alloys. Thus, it has been shown that the incorporation of Bi and the properties of (Ga,In)(As,Bi) alloys are greatly affected by Bi surface diffusion,[16] and that an increase of the In content suppresses Bi incorporation in (Ga,In)(As,Bi)[17,18] as well as in GaInSbBi alloys.[21]

In simpler ternary Bi-containing HMAs, the incorporation of Bi was found to be related to the growth surface reconstruction,[11] whereas a study of the subbandgap absorption and photoluminescence shows that a slight increase of the substrate temperature results in a significant reduction of band edge broadening. In most instances, effects of Bi incorporation on the electronic structure are reasonably well described by the BAC interaction between the localized Bi level and the extended defects of the host crystal. However, Zhang *et al.*[19,20] noted that a simple version of the valence BAC can underestimate the valence band edge shift at larger Bi contents in which other defects can occur.

Any quantitative analysis of the composition-dependent electronic band structure of HMAs requires reliable information about the end point compounds. Dang *et al.* grew and studied films of InBi on Si.[37]

B. Dilute nitrides and antimonides

In several papers of the "Highly Mismatched Semiconductor Alloys" Special Topic, the authors report on studies of group III-V based dilute nitrides[22,26] and dilute antimonides.[25,27] These alloys were extensively studied for solar power conversion applications either as a component junction for lattice-matched multijunction tandems or as materials with a band structure suitable for intermediate band solar cells. The results presented in Ref. 25 show that thermal annealing greatly improves the performance of GaInNAsSb based n-i-p devices. The improvements have been attributed to a reduction of concentration of charge traps and nonradiative recombination centers. Raman spectroscopy has shown that the incorporation of only 0.6% Sb into GaN leads to a considerable softening of optical phonon modes, whereas a comprehensive micro-Raman investigation of hydrogenated GaAsN shows the evolution of the N-H interaction with increasing H dose.[23]

A systematic study of the effect of the growth conditions on the structural and optical properties of GaAsP based dilute nitrides has shown that a judicious choice of As to P ratio allows for the growth of the alloys with the lattice parameter closely matching Si substrates.[22] Group III-V compounds with very low, impuritylike concentrations of nitrogen are known to produce sharp photoluminescence lines attributed to N-N pairs. In a detailed and systematic study of these PL spectra in GaAs:N, Fluegel *et al.*[24] have shown that the PL line-broadening is associated with an exciton transfer between adjacent N-N pairs. The broadening sets limits on using N-N pairs as coherent quantum computing qubits.

III. GROUP II-VI BASED HMAS

A significant number of the Special Topic papers are devoted to studies of group II-VI based HMA oxides.[28,34] This is a very active research area as many of these alloys retain a multicrystalline structure in the wide composition range even when synthesized with simple material deposition methods. Alloys with oxygen atoms as a minority[28–31,33,34] and majority[32] components were synthesized and studied. Among group II-VI HMAs, a considerable effort has been devoted to tellurides containing dilute amounts of oxygen, as the electronic structure of these alloys provides a relatively good match for the solar spectrum. A systematic study of the carrier dynamics shows that the electrons photoexcited to the conduction band rapidly recombine into the unoccupied oxygen derived intermediate band.[28] The authors suggest that the recombination rate can be reduced by partial filling of the intermediate band with doping. In fact, this is what has been achieved by Tanaka *et al.*,[34] who have shown that Cl doping of the ZnTeO absorber layer improves the open circuit voltage and short circuit current of the intermediate band solar cell structure.

A study of the optical properties of $Zn_{1-y}Cd_yTe_{1-x}O_x$ alloys allowed for an evaluation of how the relative location of the conduction band edge and the O-level affects the electronic band

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structure of the quaternary alloy.[33] Two papers present results on HMAs with a large minority component content. In the case of $ZnS_{1-x}O_x$, the authors were able to incorporate up to 30% of O.[29] The observed reduction of the bandgap is attributed to a transition from isolated O to pairs and larger clusters. In contrast, the dramatic bandgap reduction observed in $ZnO_{1-x}Te_x$ with up to 34% Te is explained by band anticrossing between localized Te states and the extended states of the ZnO host.[32]

IV. THEORY AND GROUP IV HMAs

The principal interest in alloying group IV materials is to realize a material with a finite direct bandgap. Over the years, a significant effort was directed toward the synthesis of C or Sn containing group IV alloys. It has been recognized, however, that the synthesis of such alloys is difficult and requires nonequilibrium growth conditions because of a strong phase separation. To address this issue, Prucnel *et al.*[39] synthesized and crystallized $Ge_{1-x}Sn_x$ HMA using ion implantation combined with rapid annealing. They were also able to reduce the alloy resistance by coimplanting P donors. In comprehensive theoretical calculations, Broderick *et al.*[38] predict that a $Ge_{1-x}C_x$ alloy will show an interesting evolution of the electronic band structure with a significant disorder of the lowest conduction band states that cannot be accounted for by a simple version of the BAC model.

An interesting alloy of two important compounds, GaN and BN, is considered by Turiansky *et al.*[35] Although the electronegativities of Ga and B are not very different, the alloy can be considered highly mismatched because of the large ionic radius difference. Detail first-principles calculations show a very large composition-dependent bowing parameter for the direct gap of the alloy. This resembles the situation in standard HMAs in which composition dependence of the bandgap was routinely described by a composition depended bowing parameter.

V. CONCLUSIONS

In recent years, highly mismatched alloys have become increasingly important, both scientifically and technologically, with progress resulting from advances in growth, characterization, and theory. The papers in the “Highly Mismatched Semiconductor Alloys: From Atoms to Devices” Special Topic show an evolution and expansion of the field from original group III-V dilute nitrides to a large variety of alloys with a much wider composition range and the band anticrossing observed in both the conduction and the valence bands. The current applications of HMAs focus on dilute nitrides and dilute oxides for intermediate band solar cells and Bi-based alloys for far infrared optoelectronic devices. The demonstrated flexibility of independently controlling the bandgap and band offsets of highly mismatched alloys offers an interesting potential of using these materials as energy selective contacts for thin film solar cells and active components of photoelectrochemical devices.

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