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13. ABSTRACT (Maximum 200 words)

The purpose of the research was to explore the microscopic mechanisms that determine interface parameters in semiconductor heterojunctions and develop new methods to tune such interface parameters. We found that while in most isovalent heterojunctions the interface parameters are primarily dependent on the properties of the bulk semiconductor constituents, in heterovalent heterojunctions with polar orientation the interface parameters can be controlled by modifying the local interface environment. Changes in the relative abundance of the different elemental constituents at the interface, for example, produced unprecedented changes in the band alignment across the interface. Even in isovalent heterojunctions, we succeeded in modifying the band offsets through fabrication of thin heterovalent interface layers within the interface region. The resulting system of inequivalent, neutral heterovalent interfaces can be used to control the band alignment across the overall structure. Among the systems of interest for which we have obtained unprecedented modifications of the interface parameters, we mention AlAs/GaAs, CdTe/GaAs, and ZnSe/GaAs heterostructures, all of which have important applications in optoelectronic devices ranging from lasers to light emitting diodes and photodetectors.

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FINAL REPORT

A. Statement of the problem studied

Semiconductor heterojunctions are fundamental components of most modern solid state electronic and optoelectronic devices. Characteristic interface parameters of semiconductor heterojunctions include the composition profile, the valence and conduction band discontinuities, and the position of the Fermi level at the interface. Such parameters control carrier injection and confinement in devices ranging from MOSFET's and MESFET's, to lasers and light emitting diodes. The goal of our program was to characterize heterojunction parameters for a number of semiconductor heterostructures, and control the offsets by means of dipole layers created at the interface during growth. We focused on a number of compound semiconductor heterostructures relevant to optoelectronic technology, including AlAs/GaAs, CdTe/GaAs and ZnSe/GaAs, all fabricated by molecular beam epitaxy (MBE) and characterized in-situ by electron diffraction and photoemission spectroscopy (XPS) techniques, and ex-situ by transmission electron microscopy (TEM) and x-ray diffraction.

B. Summary of the most important results

Theoretical calculations and our experiments^{2,7} studies generally indicate that while for isovalent heterojunctions, such as II-VI/II-VI (HgTe-CdTe) and III-V/III-V (AlAs-GaAs) systems, the band offsets depend mainly on the bulk properties of the two semiconductors comprising the junction, at polar interfaces between heterovalent semiconductors (such as ZnSe-GaAs or Si-GaAs) the offsets also depend strongly on the microscopic detail of the interface. This makes this class of interfaces an ideal candidate for microscopic tuning of heterojunction parameters.

AlGaAs/GaAs heterojunctions, which are crucial elements of MODFET's, MESFET's as well as infrared lasers, belong to the class of isovalent heterojunctions, i.e. heterojunctions in which the band offset should not depend on the local interface environment. However, we succeeded in modifying the band offsets through fabrication of thin Si or Ge interface layers in the interface region. This transforms the isovalent heterostructure in a system containing two heterovalent - i.e. tunable - interfaces. Our experimental results for AlAs-Si-GaAs(100) and GaAs-Si-AlAs(100) heterostructures have consistently shown that Si layers grown in the interface regions of AlAs-GaAs heterostructures give rise to a local dipole of up to 0.38eV. Depending on the growth sequence and Si concentration, the dipole can be exploited to continuously tune the valence band offset in the 0.02-0.78eV range. The observed dipole is consistent in sign and order of magnitude with that expected from an extrapolation of the theoretical predictions, but the Si coverage dependence of the dipole is markedly different from that expected on the basis of the same analysis.

For lattice-matched Ge layers within AlAs-GaAs heterostructures, our results showed that a Ge-induced local dipole can be added to, or subtracted from the natural band offset depending on the growth sequence to tune the band offsets throughout the 0-0.82eV range. Comparison of results for the lattice-matched AlAs-Ge-GaAs system with our results for AlAs-Si-GaAs, shows qualitative similarities but important quantitative differences. If one defines for simplicity the total dipole as the modification of the band offsets resulting from the presence of the group IV

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layer, and the specific dipole as the offset modification per group IV atom, then Ge exhibits a maximum total dipole identical, within experimental uncertainty, to that of Si (0.4eV), but a specific dipole about three times as large as that of Si.

Such trends challenge present theoretical models of interface dipole formation. In a simple and stimulating picture, recent calculations predict that abrupt group IV bilayers at AlAs-GaAs heterojunctions would be uniformly distributed over two consecutive atomic layers at all coverages to ensure local charge neutrality and give rise to a maximum total dipole of 1.3eV for Ge and 1.4eV for Si, at a coverage of two monolayers. We observed, instead, an identical maximum dipole of about 0.4eV at coverages of 0.15 and 0.5ML, respectively, for Ge and Si. This value of the maximum dipole is compellingly similar to that observed by McKinley et al. during studies of As-Ga and Ga-As interface double layers in Ge-Ge homojunctions. Band offsets of 0.35-0.45eV and opposite sign for "Ga-first" versus "As-first" growth sequences were reported by these authors.

The existence of a maximum interface dipole of identical magnitude for AlAs-Ge-GaAs, GaAs-Ge-AlAs, Ge-GaAs-Ge, Ge-AsGa-Ge, AlAs-Si-GaAs and GaAs-Si-AlAs, with quite different interface layer thicknesses, represents the most stringent criterion to date for the validity of theoretical models of interface dipole formation. Many of the mechanisms that one can devise to explain the local dipole saturation (strain induced interface chemical roughness, antisite defect formation, δ -doping effects, transition from cation to anion initiated III-V overlayer growth, Si or Ge thermally activated diffusion, etc.) fail to meet this test. We have proposed that the answer may come from new models incorporating cation or anion swaps across the interface to counteract the effect of a critical group IV-induced interface electrostatic field, that reaches values of $2\text{-}3 \times 10^7 \text{V/cm}$ at the maximum dipole for all of the heterostructures examined.

Individual isolated Ge/III-V and III-V/Ge interfaces, that cannot be charged, were also synthesized by growing the desired overlayer on suitably thick buffer layers. The band offsets of such individual isolated IV/III-V interfaces exhibited substantial deviations from the commutativity rule. Using the measured valence band offsets for individual neutral interfaces to estimate the behavior of III-V/IV/III-V structures, we obtained deviations from the transitivity rule in good agreement with our direct measurements. We therefore concluded that the observed changes in band offsets in III-V/IV/III-V structures, that can be interpreted as deviations from the transitivity rule, are due to the establishment of inequivalent neutral IV/III-V interfaces rather than to the presence of charged interfaces. Comparison with the results of first principle calculations incorporating different types of point defects suggest that the formation of antisite defects during Ge growth on III-V substrates and a mixed Ge/As interface during III-V growth on Ge are some of the possible mechanisms that may lead to neutral interfaces exhibiting the observed offsets.

An other important result with technological implications concerned the ZnSe-GaAs heterojunction system. The wide band gap of ZnSe makes it a promising material for optoelectronic device technology in the blue region of the visible spectrum. Very recently pulsed operation at 77K with 20% quantum efficiency of a blue-green laser comprised of a ZnSe-CdZnSe-ZnSe quantum well structure grown by MBE on GaAs has been demonstrated. The large valence band offset found for ZnSe-GaAs heterojunctions, however, hinders hole injection from GaAs substrates into ZnSe epitaxial layers.

High resolution synchrotron radiation photoemission studies of the valence band discontinuity for ZnSe/GaAs(110) heterojunctions indicated that the natural (unmodified) valence band offset was $1.10 \pm 0.05 \text{ eV}$. The effect of ultrathin Ge interface layers on the band offsets as determined by XPS was to decrease monotonically the ZnSe-GaAs valence band offset with increasing Ge coverage in the 0.3-6ML range. While Ge and Si interface layers are known to give rise to local dipoles in III-V/III-V heterojunctions and homojunctions, this was the first evidence of a group IV-induced dipole at an heterovalent heterojunction (II-VI/III-V). The dependence of the magnitude of the dipole on interface layer thickness was markedly different from that observed for AlAs-Si-GaAs and AlAs-Ge-GaAs, and suggests that the corresponding microscopic mechanisms may be different.

For ZnSe/GaAs interfaces with (001) orientation, first principles calculations suggest that a 1-eV wide range of band offsets might be achieved by varying the local atomic configuration at the interface. Experimentally we found that the Zn/Se beam pressure ratio (BPR) employed in the early stage of MBE fabrication of the heterostructure determines the local composition of the interface. High BPR's produce a Zn-rich interface composition, while low BPR's yield a Se-rich interface composition. The excess Zn or Se at the interface is of the order of one monolayer, and TEM studies suggest that it may occupy substitutional positions without the formation of a second phase with structure different than ZnSe. Our photoemission studies of the band offsets indicated that valence band offsets as low as 0.6eV can be achieved at the interface for Se-rich compositions, while valence band offsets as high as 1.2eV can be obtained for Zn-rich compositions. Such a wide range of tunability of the interface parameters could be exploited to substantially increase hole collection efficiency in blue LEDs and lasers.

The CdTe-GaAs heterojunction is the initial building block of many mercury-cadmium-telluride based infrared devices. It is probably the most studied II-VI/III-V semiconductor heterostructure, but surprisingly little direct experimental information was available on heterojunction parameters prior to our studies. We conducted the first in-situ photoemission investigation of the CdTe-GaAs(110) heterojunction, which was also the first study of the temperature dependence of the CdTe-GaAs valence band offset, and the first demonstration that a synchrotron radiation induced saturation photovoltage can be used to measure heterojunction parameters in ideal, flat-band conditions. We found for CdTe-GaAs(110) a valence band offset $\Delta E_v = 0.21 \pm 0.05 \text{ eV}$, and therefore a conduction band offset $\Delta E_c = 0.07 \pm 0.05 \text{ eV}$, and no detectable interdiffusion across the interface (ideally abrupt composition profile) at room temperature.

An especially exciting methodological result of our study was the experimental evidence that cooling the samples at 35K under synchrotron radiation illumination yields flat band conditions. This is the result of the low temperature surface photovoltage effect theoretically analyzed by Hecht and co-workers. The mechanism involves electron-hole pairs excited by the radiation which are separated by the built-in field at a surface or interface. The resulting photovoltage is enhanced at low temperature due to the increased junction resistance, so that a saturation photovoltage can be obtained to induce flat band conditions. We used this effect to greatly simplify the measurement of heterojunction parameters.

For the CdTe/GaAs heterojunctions we also examined the effect of interface orientation and strain on the band offsets by fabricating monocrystalline CdTe overlayers with (111) and (001) orientation on GaAs(001) substrates. CdTe(001)-

GaAs(001) heterostructures were found to be fully relaxed even at the lowest overlayer thicknesses explored through the formation of a misfit dislocation network. Correspondingly, the valence band maximum in the CdTe(001) overlayer was found 0.07-0.09eV *below* that of GaAs(001). In CdTe(111)-GaAs(001) heterostructures, the residual strain appeared gradually accommodated within a 200Å-thick CdTe layer near the interface. The average position of the valence band maximum in CdTe(111) was 0.09-0.11eV *above* that of GaAs(001) at the interface. We found that the difference in valence band discontinuity for the two interfaces is qualitatively consistent with that expected from the effect of the residual strain on the valence band maximum of CdTe(111).

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