Electron Band Alignment at Ge/Oxide and A_{III}-B_V/Oxide Interfaces from Internal Photoemission Experiments

Valery V. Afanas'ev, H.-Y. Chou, M. Houssa, and A. Stesmans
University of Leuven, B-3001 Leuven, Belgium

Based on successes in deposition of non-native high-permittivity (high-κ) oxide insulators on silicon, the possibility of realizing functional Metal-Insulator-Semiconductor (MIS) devices on high-mobility materials such as Ge and $A_{III}B_V$, less fortunate than Si in terms of its native oxide electrical properties, comes closer to reality. This brings up the issue of fundamental characterization of electron states at interfaces of these semiconductors with oxide insulators, most of all regarding the interface band alignments determining the electron transport across the interface. Knowledge of the corresponding barrier heights is of utmost importance for a number of reasons. First, a sufficiently high barrier is mandatory for achieving reliable gate insulation, which, together with permittivity of the insulator, determines the limits for the thickness downscaling. Second, the energy position of semiconductor bandgap edges within the insulator bandgap directly affects the threshold voltage through the semiconductor/top electrode work function difference. The information regarding barrier heights is also needed to evaluate the quantum-wire and quantum-well (QW) channel structures as well as the possibility of the realization of resonant tunneling devices.

We will overview the experimental analysis of interface barriers of Ge, $Si_{1-x}Ge_x$ ($0.28 \le x \le 0.93$) and $Ge_{1-x}Sn_x$ ($x \le 0.08$) alloys as well as a wide spectrum of $A_{III}B_V$ semiconductors (GaP, InP, GaAs, $In_{1-x}Ga_xAs$, $In_{1-x}Al_xAs$, InAs, GaSb, In,Sb) with different oxide insulators, ranging from the conventional SiO_2 and Al_2O_3 to complex rare-earth metal oxide insulating stacks. Studied as a function of the semiconductor composition, the barrier heights deliver the most straightforward information about shifts of the semiconductor conduction (CB) and valence band (VB) edges. On the other hand, comparison between different oxide insulators allowed us to reveal significant contributions of specific interfacial oxide layers on the resulting barrier height. From the applied point of view, these results not only expose the limits of interface barrier engineering in the studied material systems, but also demonstrate the possibility to fabricate QW channels for electrons and holes using composition gradients of the semiconductor materials.

Determination of the interface barrier height between a semiconductor and an insulator represents a significant experimental challenge since conventional photoelectron spectroscopy suffers from the charging artifacts when applied to samples with poor electric conduction. In order to obtain reliable information concerning the interface barriers we applied the spectroscopy of internal photoemission (IPE) of electrons and holes from the semiconductor into the oxide in combination with photoconductivity (PC) measurements in MIS structures. The IPE represents a close analog of the conventional external photoemission process, but the final state of the emitted electron now belongs to the insulating oxide CB.[1] Yet, as a bonus, the availability of occupied electron states in the oxide VB also enables IPE of holes, a process which has no analog at the surfaces of solids. In this way, the spectral thresholds of electron and hole IPE directly provide the energy offsets between the CB and VB edges at the semiconductor/insulator interface. This allows one to minimize the influence of insulator charging by applying a constant bias to the metal electrode. The PC measurements provide a valuable verification possibility for IPE as they allow one to determine the oxide bandgap width, which then can be compared to the value found from the electron and hole IPE barriers.

From the analysis of electron IPE spectra from the VB of Ge and $Si_{1-x}Ge_x$ alloys into the CB of different oxides (SiO_2, Al_2O_3, HfO_2, ZrO_2…) it is found that the up-shift of the VB top accounts for ≈90% of the gap narrowing between Si and Ge.[2,3] The resulting ≥0.4 eV VB offset between Si and Ge suggests the possibility of hole confinement inside a Ge-rich QW channel. By contrast, no measurable VB shift is found in the electron IPE spectra from $Ge_{1-x}Sn_x$ ($x \le 0.08$) compared to pure Ge. This would suggest the possibility to use $Ge_{1-x}Sn_x$ as a material for source/drain stressor rather than for a QW-type hole channel.

In the case of $A_{III}B_V$ semiconductors, electron IPE from the VB into the CB of amorphous Al_2O_3 was studied in detail, where the oxide CB bottom edge is used as the common reference energy. These experiments reveal two important trends: First, the change of the group III cation from Ga to In has no measurable influence on the semiconductor VB energy.[4] This means that the semiconductor bandgap narrowing is a matter of the CB bottom edge shift. Second, in varying the group V anion from P to As and further to Sb, a considerable shift of the semiconductor VB top is observed.[5,6] These observations indicate the available potential for band edge profile engineering in $A_{III}B_V$ heterojunctions which may be used in a variety of device structures.

Furthermore, the available experimental data suggest that the band offsets at the interfaces of A_{IV} and $A_{III}B_V$ semiconductors follow the *transitivity rule*.[7] As a result, it appears possible to use the VB and CB edge energies measured with respect to the same common reference level, e.g., the CB bottom edge of amorphous Al_2O_3, to evaluate the band offsets between two dissimilar semiconductors. For the sake of reference, we list in Table I the CB and VB energies of different semiconductors referenced to the CB and VB of (100)Si, respectively. These values can directly be used to evaluate the band offsets in different heterojunctions (strain and confinement effects are not included).

TABLE I. Bandgap width of several semiconductors and their CB and VB offsets ΔE_C and ΔE_V relative to (100)Si as evaluated by IPE at the interfaces with a-Al_2O_3 (±0.05 eV).

sc	E_g(300K)	ΔE_C(Si/sc)	ΔE_V(Si/sc)
Ge	0.67	-0.05	0.40
GaAs	1.42	0.10	-0.20
$In_{0.53}Ga_{0.47}As$	0.74	-0.58	-0.20
InAs	0.35	-0.97	-0.20
$In_{0.52}Al_{0.48}As$	1.52	0	-0.40
GaP	2.26	0.34	-0.80
InP	1.35	-0.57	-0.80
GaSb	0.73	-0.19	0.20

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