Band Offsets at High-κ Oxide/Semiconductor Interfaces: From Silicon to High-Mobility Channel Materials

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Abstract

Electron barrier heights and band offsets at interfaces of Si and various high-mobility semiconductors with insulating oxides can be most reliably obtained from internal photoemission experiments. The available results are overviewed revealing several general trends in the semiconductor/insulator band alignment.

1. Introduction

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 AlxBe1-x less fortunate than Si in terms of their 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 the permittivity of the insulator, determines the limits for the thickness downscaling. Second, the energy position of the semiconductor bandgap edges within the insulator bandgap directly affects the threshold voltage through the semiconductor/top electrode work function difference. The knowledge of barrier heights is also needed to evaluate quantum-wire and quantum-well (QW) channels and the possibility of realization of resonant tunneling devices.

We will overview the experimental analysis of interface barriers of Ge, Si1-xGe0 (0.28 ≤ x ≤ 0.93) and Ge1-xSn (x ≤ 0.08) alloys as well as a wide spectrum of AixB1-x semiconductors (GaP, InP, GaAs, In0.5Ga0.5As, In0.5Al0.5As, InAs, GaSb, InSb) with different oxide insulators, ranging from the conventional SiO2 and Al2O3 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 corresponding semiconductor conduction (CB) and valence band (VB) edges. On the other hand, comparison between different oxide insulators allowed us to reveal a significant impact of specific interfacial oxide layers on the barrier height. 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 in the semiconductor materials.

2. Internal Photoemission Spectroscopy

Determination of the interface barrier height between a semiconductor and an insulator represents a significant experimental challenge since conventional photoelectron spectroscopy suffers from 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. 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. At the same time, PC measurements provide a verification possibility for IPE as they allow independent determination of the oxide bandgap width, which then can be compared to the value found from the electron and hole IPE.

3. Experimental Results

Interfaces of Silicon with Oxide Insulators

There is a considerable amount of data regarding band offsets at interfaces between silicon and various oxide insulators which allows one to trace several important trends.1-3 Energies of the oxide CB and VB edges are shown in Fig. 1 relative the bandgap edges of Si as functions of the cation radius ri of the corresponding oxide. Open and filled symbols corresponding to amorphous and (poly)crystalline oxide layers, respectively, indicate that the crystallinity may have a profound effect on the oxide CB and VB energies. In the best studied case, i.e., Al2O3, crystallization results in an increase in bandgap from ~6 eV for amorphous alumina to 8.7 eV in the cubic γ-alumina which occurs mostly (~80 %) by the VB shift. By contrast, no effect of the oxide crystallinity is found in the case of “large” cations (ri >0.75 Å). The oxide VB top in these insulators remains approximately at the same energy of 2.5±0.2 eV below the Si VB indicating that the lone-pair O2p electron states may be used as the convenient energy reference (the common anion rule) while the oxide bandgap variations are predominantly reflected in the CB energy.

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Germanium and Ge-based alloys

From the analysis of spectra of electron IPE from the VB of Ge and Si\textsubscript{1-x}Ge\textsubscript{x} alloys into the CB of different oxides (SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, HfO\textsubscript{2}, ZrO\textsubscript{2},...), it is found that the up-shift of the VB top accounts for at least 90 % of the gap narrowing between Si and Ge.\textsuperscript{4,5} The resulting $\geq 0.4$ 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 of Ge\textsubscript{1-x}Sn\textsubscript{x} (x$\leq$0.08) compared to pure Ge suggesting the possibility to use Ge\textsubscript{1-x}Sn\textsubscript{x} as a source/drain stressor rather than as a material for QW-type hole channel.

$A\textsubscript{III}B\textsubscript{V}$ semiconductors

In the case of $A\textsubscript{III}B\textsubscript{V}$ semiconductors, electron IPE from the VB into the CB of amorphous Al\textsubscript{2}O\textsubscript{3} was studied in much detail. The Al oxide CB bottom edge is used as the common reference energy to analyze the behavior of the $A\textsubscript{III}B\textsubscript{V}$ VB top as a function of semiconductor composition. 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.\textsuperscript{4} This means that the semiconductor bandgap narrowing is a matter of the CB bottom edge shift. Furthermore, for the alloys with variable group-III element composition, the CB shift simply corresponds to the bandgap width variation.

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.\textsuperscript{7,8} In the case of phosphides the VB top is downshifted by $\approx 0.6$ eV as compared to arsenides. By contrast, in the antimonides of In and Ga the VB top lies at $\approx 0.4$ eV above that of their corresponding arsenides. These observations indicate the available potential for band edge profile engineering in $A\textsubscript{III}B\textsubscript{V}$ heterojunctions, which may be used in a variety of device structures, e.g. in the tunnel MIS field-effect transistors.

Band offset transitivity

Furthermore, the available experimental data suggest that the band offsets at the interfaces of $A\textsubscript{IV}$ and $A\textsubscript{III}B\textsubscript{V}$ semiconductors do follow the transitivity rule, suggesting absence of significant interface dipoles.\textsuperscript{2,9} As a result, it appears possible to use the VB and CB edge energies measured with respect to a same common reference level, e.g., the CB bottom edge of amorphous Al\textsubscript{2}O\textsubscript{3}, to evaluate the band offsets between two dissimilar semiconductors forming a heterojunction. This possibility may be of particular interest for the evaluation of tunneling barriers in semiconductor and oxide heterojunctions.

4. Conclusions

The overviewed results demonstrate how the spectral analysis of the IPE photocurrents can provide a vast amount of information regarding electron energy band alignment at interfaces of semiconductors with insulator materials. Using the IPE/PC spectroscopy, several general trends in the evolution of electron band offsets have been revealed. These include the common anion rule for the oxides with cations of large ionic radii, absence of significant structure- and composition-sensitive dipoles at semiconductor/oxide interfaces, and the validity of the simple band offset transitivity rule at semiconductor interfaces.

As the final remark it should be added that regarding the metal/oxide interfaces, IPE experiments reveal the presence of a significant additional contribution to the interface barrier stemming from charged electron states in the insulator.\textsuperscript{1,2} The origin of these states depends on the composition of the metal/oxide interfaces, ranging from hydrogen-induced dipoles to electron localization at oxide defects and impurities. In all cases the polarization of the nearby metal surface results in a dipole-like barrier modification. As a result, the effective work function may differ from the vacuum work function by up to 1 eV or even more.\textsuperscript{3,10} Obviously, the use of the vacuum work function when analyzing electrical data will then lead to a significant systematic error.