Measurement of the Energy-Band Relations of Stabilized Si Photoanodes Using Operando Ambient Pressure X-ray Photoelectron Spectroscopy

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The energy-band relations and electronic properties for the light-absorber/protection-layer stack of TiO₂-stabilized Si photoanodes have been determined by ambient pressure x-ray synchrotron radiation photoelectron spectroscopy under an applied potential (*operando*), from single core-level emission lines. The experiments have also been complemented with laboratory-based monochromatic XPS data. Electrochemical parameters are additionally derived directly from x-ray photoemission data, and a method is presented to derive interface-state densities from such *operando* data.

Introduction

The electrochemical potential at semiconductor/liquid, semiconductor/metal, and semiconductor/semiconductor junctions equilibrates by charge transfer across the interface between the two contacting phases. This charge transfer consequently produces band bending, (partial) Fermi level (E_F) pinning at interface states, and the formation of interface dipoles (1,2). The energy-band alignment also affects the electronic properties and performance of the resulting photoelectrochemical cell. Typically, the energy-band alignment is determined experimentally by a combination of x-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) during the step-wise growth of a contacting phase on top of the substrate of interest (3,4).

This approach does not, however, consider the integral nature of photoemission spectroscopy, and is not feasible for *operando* investigation of solid-liquid interfaces.

We describe herein the use of ambient pressure photoelectron spectroscopy (AP-PES) (5,6) and standard x-ray photoelectron spectroscopy (XPS) to analyze the energetics of light-absorber/protection-layer stacks (7-9). Specifically, the integral nature of PES and the large inelastic mean-free path (IMFP, λ) of tender X-Rays for *in-situ* PES has been used to determine the electrostatic (Galvani) potential of semiconductor junctions by x-ray photoelectron spectroscopy. All of the required parameters have been determined experimentally from single core-level emission-line profiles at each applied potential, U . For the *ex-situ* XPS experiment, this method has been applied to the growth by atomic-layer deposition (ALD) of a TiO₂ protection layer on a Si surface.

Experimentation

Deposition of TiO₂ was performed by ALD on degenerate, p-type boron ($4 \times 10^{19} \text{ cm}^{-3}$) and n-type arsenic doped ($3 \times 10^{19} \text{ cm}^{-3}$) Si(100) substrates (7). Silicon wafers were cleaned with an RCA SC-1 procedure by immersion in a 3:1 (by volume) “piranha” solution of $\sim 18.4 \text{ M H}_2\text{SO}_4$ and $\sim 11 \text{ M H}_2\text{O}_2$ for 10 min, followed by a 10 s etch in 10 % by volume of hydrofluoric (HF) acid, and finally, an RCA SC-2 etch of 5:1:1 (by volume) solution of H₂O, 11.6 M hydrochloric acid, and $\sim 11 \text{ M H}_2\text{O}_2$ for 10 min at 75 °C. TiO₂ was then deposited by ALD from a tetrakis(dimethylamido)titanium (TDMAT) precursor. A 0.1 s pulse of TDMAT was followed by a 15 s purge of N₂ at 20 sccm, followed by a 0.015 s pulse of water and another 15 s N₂ purge. The layer growth rate was determined to be 0.04 nm per cycle (7).

Operando (in-situ) ambient pressure x-ray photoelectron spectroscopy data were collected on a Scienta R4000 HiPP-2 system, with the photoelectron collection cone aligned to the beamline x-ray spot at a distance of $\sim 300 \mu\text{m}$. The system used differential pumping supplied by four turbo pumps, backed by rough pumps that were protected by liquid-nitrogen cold traps, to maintain a pressure of $\sim 5 \times 10^{-7} \text{ mbar}$ at the detector while allowing a stable pressure of 27 mbar at the sampling position. Beamline 9.3.1 at the Advanced Light Source was used to provide “tender” x-rays with an energy of $h\nu = 4000 \text{ eV}$. The potential, U , was applied to the substrate (working electrode) in a three-electrode potentiostatic configuration (6).

Ex-situ x-ray photoelectron spectroscopy measurements were performed using a Kratos Axis Ultra system with a base pressure of $< 5 \times 10^{-10} \text{ mbar}$. X-rays were produced by a monochromatic Al K α ($h\nu = 1489.6 \text{ eV}$) source with a power of 150 W.

Figure 1. Model of the light-absorber/protection-layer/catalyst stack used in this investigation, consisting of a silicon substrate (e.g. n-doped Si bulk), the Si space-charge region (Si-SCR), the SiO₂ interface region, a TiO₂ protection layer, and an electrolyte layer for *in-situ* investigation. The expected potential distribution, $U(x)$, is depicted for each layer. An applied potential will drop partially in the silicon space-charge region, in the SiO₂, in the TiO₂ at the interface with the electrolyte, and in the electrolyte double layer. For a highly doped silicon substrate, the potential drop will appear almost exclusively at the TiO₂/electrolyte interface. The thickness of the electrolyte, TiO₂, and SiO₂ layer is specified for both *ex-situ* ($h\nu = 1489.6 \text{ eV}$) and *in-situ* ($h\nu = 4000 \text{ eV}$) experiments.

Results and Discussion

A rigorous description and evaluation (data fitting) of the experimental data requires a precise calculation of the potential distribution in the semiconductor. In the Schottky junction model (10), the charge density in the depletion region is considered to be equal to the (spatially constant) acceptor density, N_A (or donor density, N_D), with the charge density assumed to abruptly become zero at the edge of the depletion layer (i.e. the abrupt-junction approximation). In the abrupt-junction approximation, upon approximating the Fermi-Dirac distribution function with a Boltzmann distribution function, the width of the depletion layer, d_{SCR} , is given by the doping concentration, N , of the material in conjunction with a potential drop, U_0 , in the space-charge region (equation 1):

$$d_{SCR} = \sqrt{\frac{2\epsilon_0\epsilon_r U_0}{eN}} \quad [1]$$

Taking the boundary conditions as $U(x=0) = 0$ (surface) and $U(x=d) = U_0$ (bulk), the electrostatic potential, $E_{pot}(x) = -eU(x)$, across the space-charge region is given by equation 2:

$$U(x)|_0^{d_{SCR}} = \frac{2 \cdot U_0}{d_{SCR}^2} \left(d_{SCR} \cdot x - \frac{x^2}{2} \right); \quad U(x)|_{d_{SCR}}^{\infty} = U_0 \quad [2]$$

In the space-charge region with $0 < x < d_{\text{scr}}$, $U(x)$ depends quadratically on x . For $d > d_{\text{scr}}$, the potential is constant and is given by U_0 , i.e. $U(x > d_{\text{scr}}) = U_0$.

However, an exact solution for $U(x)$ is required to cover the full potential range that extends beyond the thermodynamic potentials for the oxidation (U_{OER}) and reduction (U_{HER}) of water, as is needed to describe *operando* AP-PES measurements, and/or to describe the situation for highly or degenerately doped semiconductors. This relationship can be obtained by solving the full Poisson equation with Femi-Dirac statistics, $f(E)$ (equation 3):

$$\frac{\partial^2 U_{\text{pot}}(x)}{\partial x^2} = \frac{q}{\varepsilon} \left[\int_0^\infty D_C(E) - D_V(E) \right] \cdot f(E) \partial E + N_D^+ - N_A^- \quad [3]$$

In equation 3, $D_C(E)$ and $D_V(E)$ are the effective density of states in the conduction band and valence band, respectively, and N_D^+ and N_A^- are the density of ionized donors and acceptors, respectively.

Figure 2 depicts the potential distribution for both of the potential descriptions (equation 2 and 3) at the outer layer of bulk Si. A potential shift of $U = +0.1$ V vs U_{fb} (depletion) was assumed in Figure 2a. The potential distribution was calculated for a moderate doping concentration of $N_D = 1 \times 10^{17} \text{ cm}^{-3}$. For n-type Si and a positive bias ($+U$), downward band bending is produced, in which the difference between E_F and the conduction band edge, E_C , increases towards the surface.

In the bulk, i.e. for $x > d_{\text{SCR}}$, U reaches its bias value, and thus the difference between E_F and either E_{CB} or E_{VB} is constant and depends solely on the doping concentration. Hence, for a neutral sample, zero difference in binding energy, ΔE_B , will be produced between the measured core-level emission lines relative to their bulk values. Only when $0 < d < d_{\text{SCR}}$, where U approaches zero, will the Fermi energy shift because of band bending, with $\Delta E_B \neq 0$.

For x-ray photoemission spectroscopy, 95 % of the contribution to the measured core-level emission-line profile arises from an information depth of $3 \cdot \lambda$ (three times the inelastic electron mean free path). Thus, a change in the electric potential, $U(x)$, i.e. the Galvani Potential of the semiconductor, across $0 < d < 3 \cdot \lambda$ will have a strong influence on the position of the core-level emission maximum, as well as on the line shape, because the photoelectrons emitted at different distances from the surface will be exposed to a different potential U , i.e. will have different binding energies. XPS integrates over the different core-level peak signals produced by emission from different depths in the solid, which consequently produces a broadened core-level emission that results in a poorly resolved electronic shift and an apparent band-energy alignment signal. In particular, the maximum core-level emission shift at the interface is, in most cases, underestimated. This behavior occurs because in the presence of a space-charge layer, the observed peak maximum position does not represent the core-level position of the topmost layer, and the emission lines are convoluted in the observed signal due to superposition of the lines from different depths with different weighing factors.

Figure 2. Electrostatic potential for n-Si (a) as calculated by the abrupt junction approximation (Boltzmann, dashed line), and the full Poisson equation (Fermi-Dirac, solid line) for a potential of $U = +0.1$ V (depletion). The change of the core-level binding energy $\Delta E_B(x)$ is $\Delta E_B(x) = -e[U(d) - U(x)]$. The inset in (a) depicts the movement of the conduction-band minimum (CBM) and valence-band maximum (VBM) upon application of a positive potential, U , to the electrode. Due to the assumption of an abrupt junction, the quadratic form of $U(x)$ obtained from Boltzmann statistics shows a kink at d_{SCR} , whereas $U(x)$ obtained assuming Fermi-Dirac statistics is smooth over the complete range of x . In (b), the simulated core-level emission line profile for the neutral sample ($U = 0.0$ V, solid line) and for $U = +0.1$ V (dashed line) are shown, calculated relative to the binding energy signals for the bulk semiconductor. The solid-dashed line shows the additional broadening of the spectra at $U = +0.1$ V with respect to $U = 0.0$ V, obtained as the difference spectrum between the data at the applied potential of interest and the data at the flat-band potential. Due to the broadening, the apparent peak (maximum) shift of the Si $2p_{3/2}$ and Si $2p_{1/2}$ signals for the $U = +0.1$ V spectrum with respect to the $U = 0.0$ V spectrum is $\Delta E_B = -0.07$ eV instead of the expected value of $\Delta E_B = -0.1$ eV. The calculations for obtaining the data of the core-level emission line profile are described in detail in the text.

For a combination of Gaussian and Lorentzian line profiles (also known as pseudo Voigt profile), the core-level emission intensity is a function of the binding energy E_B , electric potential $U(x)$, half-width at half-maximum Γ , a scaling parameter C_1 that is proportional to the peak height, and a shape parameter C_2 (fraction of Lorentz to Gauss peak shape). The observed signal intensity, $I(E)$, can be expressed as an integration over the contribution from each atomic layer at a depth x (equation 4):

$$I(E) = C_1 \cdot \int_0^d e^{-x/\lambda} \cdot \left[(1 - C_2) \cdot e^{-\ln 2 \cdot \left(\frac{E - E_B + qU(x)}{\Gamma} \right)^2} + \frac{C_2}{1 + \left(\frac{E - E_B + qU(x)}{\Gamma} \right)^2} \right] dx \quad [4]$$

Figure 2b depicts the simulated core-level emission-line profile (equation 4) as obtained for the given potential $U(x)$ calculated from the full Poisson equation, using tender X-Ray radiation of $h\nu = 4000$ eV ($\lambda_{Si} = 7.2$ nm (11,12)). As expected from the

underlying approximation of the electrostatic potential, the resulting core-level emission-line profiles are different for different potentials, U . Asymmetric line shapes should be observed for high doping concentrations as well as for large positive applied potentials. Figure 2b includes the additional broadening induced by the potential, depicted as the solid-dashed line in the figure. The peak profile asymmetry and broadening will increase with doping and with applied potential. In this case, the core-level maximum shift is smaller than the applied potential. For the case shown in figure 2, the shift is $\Delta E_B = -0.07$ eV, in contrast to the expected value of $\Delta E_B = -0.1$ eV at $U = +0.1$ V. This behavior is due to integral nature of XPS and $U(x) \neq \text{constant}$. The maximum shift of $\Delta E_B = -eU(d)$ is observed only at the surface ($x = 0$), but core-level emissions with $\Delta E_B = -eU(x < d)$ will also contribute to the XPS signal, resulting in peak broadening and a reduced experimentally observed core-level shift at the emission maximum.

For the potential range used in *operando* AP-PES, a quantitative description over the complete range of U requires use of the full Poisson equation. As the range of applied potential exceeds the band-gap of the semiconductor, the Fermi energy will approach the conduction band, or the valence band, and thus Boltzmann statistics will not be an appropriate description. A quantitative description of the core-level emission-peak profile can be obtained from the actual function $U(x)$ by fitting equation 4 to the experimental PES data. With known $U(x)$ profiles, the energy-band relations can then be obtained for a single bias, as well as over the complete bias range of interest.

Several additional important parameters, such as the flat-band potential (U_{fb}), the valence-band (U_{VB}) and conduction-band (U_{CB}) offsets, and the density of in-gap interface states (N_{IS}), can also be obtained from the experimental core-level emission-line profile. Specifically, at the flat-band potential, a minimum in the FWHM of the corresponding core-level signals is expected. Explicitly considering the dependence of the FWHM on U , at $U = U_{fb}$ the first derivative is zero ($\frac{\partial FWHM}{\partial U} = 0$) and the second derivative is positive ($\frac{\partial^2 FWHM}{\partial U^2} > 0$). Also, at U_{fb} , the binding energy of the core-levels is not a function of depth x , because no space-charge region (band bending) is present. In contrast, at potentials positive or negative of U_{fb} , the actual core-level binding energy depends on x , and consequently an asymmetric peak broadening will be observed in the PES data. Hence the smallest value of FWHM (sharpest core-level emission-line profile) should indicate the position of $U = U_{fb}$.

For potentials energetically close to, and beyond, the values of U_{CB} and U_{VB} the change of the core-level binding energy will be constant, i.e. $\Delta E_B \cong C$. Hence, in this potential range, the band edges will move as the applied potential is changed. At potentials more positive than the VBM ($U > U_{VB}$) or more negative than the CBM ($U < U_{CB}$), the slope of the core-level emission-maximum shift, ΔE_B vs U , will become approximately zero, due to a change from a band-bending regime to a band-edge shifting regime. Hence, in this regime, the difference between E_F and the VBM or CBM will stay approximately constant as E_F approaches either the VBM or CBM. A further shift of the Fermi energy into the conduction band or valence band will not result in a further increase of ΔE_B , i.e. $\frac{\partial \Delta E_B}{\partial U} \cong 0$.

For potentials between U_{CB} and U_{VB} , the difference between the applied potential change and the sum of the binding energy change ΔE_B of each layer can be attributed to a charging or discharging of interface states as the Fermi energy is moving across these states. Specifically, for $U_{VB} > U > U_{CB}$, the difference between overall band bending

(ΔE_B) and the applied potential U (derivative of ΔE_B by U) is related to the density of interface states $N_{IS}(U)$ at that potential.

The varied information contained in the line shape of the core-level emission signal allows for the identification of the flat-band potential, usually extracted from Mott-Schottky analysis, and also allows for the determination of the band gap from the core-level AP-PES signals.

Figure 3. Experimental values of the FWHM for the respective core-level emissions of *ex-situ* Si/SiO₂/TiO₂ (a) and *in-situ* Si/SiO₂/TiO₂/electrolyte (b) stacks. Panel (a) presents the FWHM of the Si 2p_{3/2} and Ti 2p_{3/2} signals on n⁺-Si and p⁺-Si substrates. Panel (b) presents the FWHM of the O 1s-TiO₂ and O 1s-H₂O core-level emission. The FWHM of the O 1s-TiO₂ signals showed a minimum at $U = -0.9$ V, whereas the FWHM of the O 1s signal due to the electrolyte stayed nearly constant. The black lines are linear fits to the data.

Figure 3 shows the FWHM values of the (a) *ex-situ* and (b) *in-situ* core-level emission-line profiles of (a) the Si/SiO₂/TiO₂ and (b) the Si/SiO₂/TiO₂/electrolyte stack. For the growth of TiO₂ on p⁺-Si or n⁺-Si, a change was observed in the FWHM of the Si 2p_{3/2} and Ti 2p_{3/2} core-level emissions. As described above, a minimum in the value of the FWHM is expected at the flat-band condition, and an increase in FWHM should occur for depletion or accumulation conditions. Hence, a decrease of the FWHM with increased cycles of ALD indicated a trend toward flat-band conditions as the number of ALD cycles was increased. Thus, for the growth of TiO₂ by ALD (figure 3a), the FWHM trend of the Ti 2p_{3/2} signal indicated that the TiO₂ layer approached the flat-band condition, for both, n⁺-Si and p⁺-Si. The trend of the Si 2p_{3/2} FWHM indicated an approach to flat-band for p⁺-Si (decrease of the FWHM) but the formation of a depletion layer for n⁺-Si (increase of the FWHM), as confirmed by the observed shift of the core-level emission maximum towards lower binding energies. In addition, the ongoing change of the FWHM as the number of ALD cycles increased demonstrated the dynamic formation of a complex Si/TiO₂ interface.

For the TiO₂/electrolyte interface (figure 3b) on a highly doped p⁺-Si substrate, the FWHM of the O 1s core-level emission arising from the electrolyte was constant over the complete potential range. In contrast, the FWHM of the O 1s core-level emission of TiO₂ displayed a minimum at $U = -0.9$ V. This behavior indicates that the applied potential dropped essentially completely in the semiconductor, which exhibited a flat-band

potential of $U_{fb} = -0.9$ V vs. Ag/AgCl. In addition, for depletion and accumulation, a difference in the slope (back line, figure 3b) is expected because the potential drop is limited to a smaller depth d for accumulation, i.e. sharper core-level emission, as compared to a depletion condition, for the same magnitude of $|U|$.

Conclusion

A single core-level emission-line profile of each respective layer contains all of the parameters required to describe the complete energy-band relations in this layer, and consequently of semiconductor/heterojunction and semiconductor/liquid junction structures at an applied potential or during ad-layer growth. For *operando* AP-PES, this method provides a powerful tool to describe the complete system at each potential, where layer-by-layer growth of a contacting material and/or depth-profiling techniques are not either feasible or possible. In particular, for *operando* AP-PES, in addition to accessing the electrochemical parameters directly from core-level emissions, e.g. U_{fb} , the conduction-band offset U_{CB} , valence-band offset U_{VB} , the energy gap ($U_{BG} = U_{VB} - U_{CB}$), and the density of interface states, N_{IS} , can be determined.

Single core-level energy-band relations have been used recently to describe a highly stable photoanode, covering the complete potential range beyond the thermodynamic limits of water splitting. Further use of *tender* AP-PES and the single core-level method will enable detailed investigation of the electrolyte double-layer structure in a variety of electrode systems of interest.

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