Standard Operating Procedure

(SOP)

Band Energetics Measurement

Test ID #PEC-P-7

Rev 1

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Revision History

This page documents the revisions over time to the SOP. The most recent iteration should be listed in the row space, with consecutive versions following.

Date of Revision	Page(s)/Section(s) Revised	Revision Explanation
04/05/2019	All	First Release

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3. Procedures

a. Scope and Applicability – This SOP details procedures for measuring band energetics of semiconductors using XPS measurements.

b. Summary of Method – XPS spectra are taken of semiconductors. Fitting of valence electrons are used to identify the band positions of these semiconductors.

c. Definitions –

- XPS – X-Ray photoelectron spectroscopy
- VBM – Valence band maximum
- FWHM – Full-width half-maximum
- Band edge positions (BES) – conduction band (CB) minimum or valence band (VB) maximum vs. reference potential in a specific electrolyte (pH, solvent, cations and anions)
- CLBE – core-level binding energy

d. Health & Safety Warning – X-Rays present both acute and chronic exposure hazards to all tissues. Users should be properly trained in X-ray safety. Proper X-ray shielding must be in place to ensure that exposure does not occur.

e. Cautions – Ideally, samples should be prepared inside an Ar-purged glovebox to minimize oxygen exposure. Samples should be mounted and transferred quickly to minimize this exposure. Typically, 15-30 minutes of exposure is the maximum allowable exposure.

f. Interferences – Formation of oxides on the semiconductor surface due to oxygen exposure can significantly impact the accuracy of the XPS measurements.

g. Personnel Qualifications / Responsibilities – Personnel must be trained in XPS safety and use.

h. Equipment and Supplies –

1. XPS
2. Potentiostat with electrochemical impedance capability
3. Photoelectrode
4. Cell components: electrolyte (pH, cations, anions), reference electrode, counter electrode

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization – Calibrate binding energy axis using either a standard with a known fermi level (e.g. Au by using its Fermi edge) or adventitious carbon (e.g. 284.8 eV)

- Sample Collection – Not applicable for this SOP.

- Sample Handling and Preservation – Special attention should be paid while mounting sample on sample holder to ensure good grounding from its surface. This avoids charging issues of samples during XPS data acquisition. Whether or not charge occurs can be validated by XPS valence spectra or adventitious carbon core-level spectra.

- Sample Preparation and Analysis –

    1. Transfer photoelectrode samples into the XPS chamber (See note in Sample Handling and Preparation)
    2. Measure the XPS survey spectrum, taking the average of 5 spectra, typically.
    3. Find the C1s carbon core-level spectrum at ~285 eV. It is generally not recommended to shift the binding energy scale based on C1s core-level spectra, as a means of adjusting the binding energy axis so that the C-C peak is at 284.8 eV, for the purpose of calibrating the binding energy axis.
    4. For the same sample set, switch to UPS mode: measure the UPS spectrum, taking the average of 5 spectra, typically. Make sure He I or II source for UPS is monochromatic.
    5. Take high resolution XPS core-level spectra of each element from which the photoelectrode is composed
       Take the band alignment for Si/TiO_2 heterojunction as an example, for determining the interfacial energetics, the following steps can be taken:
        1) For both Si with a thick TiO_2 overlayer and without overlayer, do XPS and UPS characterization following the aforementioned Steps 1) – 4). XPS measurements allow determination of the energy levels relative to the Fermi level of the material while UPS determines the valence band position and work function. XPS and UPS gives different probing depth. For TiO2, their "leaky" defect cannot be probed by UPS but can be probed by XPS. This step enables the derivation of the energetics of bulk Si and amorphous TiO_2.
           Attention: since Si may easily form a thin oxide layer on surface, so Si^0 peak and Si_{ox} peak should be distinguished; similarly, for TiO_2's O1s peaks, surface Ti-OH and bulk -Ti-O-Ti- should be distinguished.
        2) For Si substrate with stepwise thickness increase for TiO_2 overlayers, do similar XPS and UPS measurement just like Step 1). Shifts in the core-level binding energy (CLBE) and the valence-band maxima (VBM) should be monitored for

both the substrate and the overlayer. Attention: the CLBE of an element is the energy level difference between the Fermi level of the sample and its elemental core-level energy.

3) Noticing that differences between the CLBEs and the VBM are independent of the band bending, so by looking at the respective CLBE shift corresponding to different overlayer thickness, the energy shift of VBM as overlayer thickness increase can be obtained.
4) Concomitant monitoring of the shifts in the secondary electron-emission cutoff (work function) reveal the presence of interfacial dipoles. The contact potential difference between Si and TiO2 has two contributions: 1) band bending; 2) interfacial dipoles. The interfacial dipoles can be measured by work function difference, and is independent to the measured band bending from Steps 5.2) – 5.3).
5) Combining the result above, positions of the band edges as a function of overlayer thickness can be plotted. For Si, its CBM and VBM energy difference is fixed, i.e. Si's band gap. For TiO_2, its CBM and VBM energy difference is TiO_2's band gap.
1) While doing these measurement, comparison to literature and calculation is always necessary. Besides, the two types of measurement errors that exist during XPS measurement should be noticed. One is the error for the absolute peak position, due to the relative change of the absolute binding energy between the several samples; the other error is associated with determination of the relative peak shift of a single sample. The first type of error can be statistically reduced by multiple measurements of samples prepared in the same manner. The latter error of the relative peaks shifts, i.e. the quality of peak fitting, can be reduced statistically in the same manner by improving the signal-to-noise ratio of the measurement.
(If only XPS measurement is done without UPS to determine the work function, then the interface band edge alignment can still be derived, but the complete energetics including contributions of band bending and interfacial dipoles require more information obtained by UPS.)

6. Optional: do (near)ambient-pressure XPS (NAP-XPS). Acquire core-level spectra of elements found on surfaces: Dip sample into electrolyte, vary applied potential of electrode, pull sample out of electrode under applied potential control, and then repeat with a different applied potential. Such measurements directly

measure the surface chemistry of photoelectrode/electrolyte interfaces, band edge position of photoelectrode materials, and the behavior of junction energetics (e.g. conditions of Fermi level unpinning, liquid junction band edge positions, or surface state pinning, etc.)
In most cases, the band edge positions can be obtained from literature. Typically, these energetics were measured by Mott-Schottky analysis using Electrochemical Impedance Spectroscopy (EIS). NAP-XPS will be typically useful for studying the band alignment of new coating materials or new interfaces. Because one may not find their literature counterpart for their band energetics in their semiconductor form, or one may not obtain sound EIS data for the Mott-Schottky analysis. Light-dependent open-circuit photovoltage also provides estimations for flat-band positions, which combined with semiconductor doping and effective density of states at band edges, gives band edge positions.

Appendix: The correlation between carrier concentration (doping density), fermi level, and band edge position:

We shall start with a simple case for intrinsic semiconductors, where no impurity is introduced. The electron number n is the integration of number of states $N(E)$ multiplied by the occupancy *F(E)*, over the conduction band.

$$\mathrm{n} = \int_{Ec}^{\infty} N(E)F(E)dE \quad (1)$$

The density of states can be approximated by density near bottom of conduction band.

$$\mathrm{N(E)} = M_c \frac{\sqrt{2}}{\pi^2} \frac{m_{de}^{\frac{3}{2}}(E-Ec)^{1/2}}{\hbar^3} \quad (2)$$

M_c is the number of equivalent minima in the conduction band and m_{de} is the densityof-state effective mass for electrons.

$$m_{de} = (m_1^* m_2^* m_3^*)^{1/3} \quad (3)$$

$m_1^*,\ m_2^*,\ m_3^*$ are the effective masses along the principal axes of the ellipsoidal energy surface.

The occupancy obeys Fermi–Dirac distribution.

$$\mathrm{F(E)} = \frac{1}{1+\exp\left[(E-E_F)/kT\right]} \quad (4)$$

Here E_F is fermi energy level which can be determined by XPS and UPS measurement.

Plug (2)(3)(4) into (1), it can be estimated as:

$$n = N_C \frac{\sqrt{2}}{\pi^2} F_{\frac{1}{2}}\left(\frac{E_F - E_C}{kT}\right) \quad (5)$$

The N_C is the effective density of states near the conduction band. And it's given by:

$$N_C = 2\left(\frac{2\pi m_{de} kT}{\hbar^2}\right)^{3/2} M_c \quad (6)$$

In Nondegenerate semiconductor:

$$F_{\frac{1}{2}}\left(\frac{E_F - E_C}{kT}\right) = \frac{\sqrt{\pi}}{2} \exp\left(-\frac{E_C - E_F}{kT}\right) \quad (7)$$

So plug (7) in (5), it's easy to get:

$$n = N_C \exp\left(-\frac{E_C - E_F}{kT}\right) \quad (8)$$

$$\text{or } E_C - E_F = kT\, In\left(\frac{N_C}{n}\right) \quad (9)$$

Similar to (8) and (9):

$$p = N_v \exp\left(-\frac{E_F - E_V}{kT}\right) \quad (10)$$

$$\text{or } E_F - E_V = kT\, In\left(\frac{N_V}{P}\right) \quad (11)$$

So, from (9) and (11), once the doping density and fermi level position is known, the CB and VB position can be calculated.

7. EIS (Mott–Schottky method) can be used to obtain flat band potentials of semiconductor/ liquid interface.
   Once an n-type semiconductor is brought into contact with an electrolyte, where E_F is higher in energy compared to $E_{F(redox)}$, an equilibrium will be established by forming a space charge region on the semiconductor side and a sheet charge on the electrolyte side.
   By using a potentiostat we can change the voltage of semiconductor which causes the semiconductor and redox couple Fermi levels to separate, and hence the level of band bending owing to charge depletion (e.g. free and mobile

electrons in n-type semiconductors) will be changed depending on the applied voltage. When the applied voltage is such that there is no band bending, then the semiconductor is at its flat-band potential V_{fb}.
From Mott–Schottky equation:

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 A^2 e N_d}\left(V - V_{fb} - \frac{k_B T}{e}\right) \quad (12)$$

Here C and A are the interfacial capacitance and area, respectively, N_d the number of donors, V the applied voltage, k_B is Boltzmann's constant, T the absolute temperature, and e is the electronic charge. Therefore, a plot of $\frac{1}{C^2}$ against V should yield a straight line from which V_{fb} can be determined from the intercept on the V axis. The value of N_d can also be conveniently found from the slope knowing ε and A.

Below is the step procedure to determine flat band potential, and then determine the band edge positions with respect to liquid potentials:

1) Immerse the semiconductor electrode in the electrolyte, with desired Reference and counter electrode.
2) Start impedance measurement, which is to apply a small amplitude sinusoidal ac voltage, V(t), and then measure the amplitude and phase angle (relative to the applied voltage) of the resulting current, I(t).

   $$\mathrm{V(t)} = V_0 + V_m \sin(\omega t) \quad (13)$$
   $$\mathrm{I(t)} = I_0 + I_m \sin(\omega t + \theta) \quad (14)$$

   According to ohm's law,

   $$|\mathrm{Z}(\omega)| = \frac{\mathrm{V(t)}}{\mathrm{I(t)}} \quad (15)$$

   For each applied potential value, impedance $\mathrm{Z}(\omega)$ is measured in a wide range of frequency ω, this can give a circle-like impedance spectrum. So, based on the circuit, we can get the interfacial capacitance value C in a certain applied potential.

3) Plot the value of $\frac{1}{C^2}$ as the function of applied voltage, then we get Mott–Schottky plot and flat band potential by fitting the data and obtain the intersect at the potential axis.
4) The flat band potential is vs. reference electrode.

5) The CBM and VBM vs. reference electrode can be calculated according to Equation (9). If we know the redox potential, such as $E(H^+/H_2)$ or $E(O_2/H_2O)$ vs. reference electrode, we can obtain CBM and VBM band edge positions with respect to these redox potentials.

8. Combine solid/coating(solid/solid) interface energetics from Steps 1) – 5), and coating/liquid (solid/liquid) interface energetics from Step 6, or with semiconductors/coating/liquid interface energetics from Step 7 (flat-band potential of semiconductors not coating), one can obtain the holistic picture for the band alignment for such complex interfaces.

- Troubleshooting – Not applicable for this SOP
  - Data Acquisition, Calculations & Data Reduction Requirements –

    1. Subtract baselines from the high resolution spectra
    2. Fit the high resolution spectra of the valence orbitals to Gaussian curves
    3. Record the position of the FWHM for the Gaussian fits
    4. Determine the E_{VBM} using a linear fit of the leading edge of the spectrum
    5. Once the known peaks for the crystalline material have been fit, remaining peaks can be assigned as defect peaks.

  - Computer Hardware & Software – Computer with software to control XPS and CasaXPS for spectra analysis.

j. Data and Records Management – Not applicable for this SOP.

4. Quality Control and Quality Assurance Section

Data and Records Management – Not applicable for this SOP.

5. Reference Section

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