Standard Operating Procedure

(SOP)

Measurement of Semiconductor Flat Band Potential

Test ID # PEC-P-17

Prepared By: Todd Deutsch, Burton Simpson, James Young	Date
Approved By: Chengxiang Xiang	Date
Approved By: NAME / TITLE	Date

Date: 04/05/2019

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

Outline/Table of Contents

1. Title Page
2. Table of Contents
3. Procedures
    a. Scope and Applicability
    b. Summary of Method
    c. Definitions
    d. Health & Safety Warning
    e. Cautions
    f. Interferences
    g. Personnel Qualifications / Responsibilities
    h. Equipment and Supplies
    i. Step by Step Procedure
        - Instrument or Method Calibration and Standardization
        - Sample Collection
        - Sample Handling and Preservation
        - Sample Preparation and Analysis
        - Troubleshooting
        - Data Acquisition, Calculations & Data Reduction Requirements
        - Computer Hardware & Software
    j. Data and Records Management
4. Quality Control and Quality Assurance Section
5. Reference Section

3. Procedures

a. Scope and Applicability – This SOP details procedures for measuring the flat band potential of n- and p- type semiconductors.

b. Summary of Method – Photoelectrode flat band potentials are measured using illuminated open circuit potential, Mott-Schottky, and/or photocurrent onset techniques. Each technique has inherent shortcomings, and the applicability of each is discussed to aid users select which is most appropriate for their working photoelectrode.

c. Definitions – E_{fb} – flat band potential
HER – Hydrogen evolution reaction
OER – Oxygen evolution reaction
E_g – Band gap
$h\nu$ – Photon energy (in eV)
j-V – Current density - potential
OCP – Open circuit potential
EIS – Electrochemical impedance spectroscopy
M-S – Mott-Schottky
HER – Hydrogen evolution reaction

d. Health & Safety Warning – Light sources that produce UV radiation present both acute and chronic exposure hazards to eyes and skin, and proper PPE should be worn to minimize exposure. Light sources that produce deep UV radiation (xenon) present potential ozone exposure hazards, and engineering controls must be in place to minimize exposure. Light sources that use gas-filled bulbs present explosion hazards if the bulbs overheat, and manufacturer safety guidelines must be followed to prevent injury. Arc lamps emit UV radiation, and thus can cause retinal and corneal damage if viewed directly. Long-term exposure to skin can cause burns similar to sunburn. The arc lamps require high voltage, high current power supplies which present a danger of electrical shock. Furthermore, the bulbs of the arc lamps are above atmospheric pressure when either cold or hot (2-5 atm pressure when cold and ~25 atm when in operation) and can explode during handling or normal operation. The lamp housing is strong enough to withstand a lamp envelope failure (lamp explosion). The chief hazard is during the lamp installation and removal.

e. Cautions – On a short timescale, illuminated OCP analysis is non-destructive, but extended periods of illumination may lead to corrosion of the photoelectrode. Extended illumination may also heat the solution or allow slow adsorption/desorption to cause drift of the measured potentials.

f. Interferences – The illuminated OCP can be used to estimate the E_{fb} if the above-band gap illumination ($h\nu \geq E_g$) is sufficiently intense to completely remove pre-existing band bending at the surface and the material does not have very fast carrier recombination rates.

g. Personnel Qualifications / Responsibilities – Not applicable for this SOP.

h. Equipment and Supplies –

1. Potentiostat (with frequency response analyzer or EIS capabilities)
2. Photoelectrochemistry cell
3. Counter electrode (typically a large area Au or Pt electrode)
4. Reference electrode
5. Calibrated light source
6. Electrolyte solutions containing supporting electrolytes of different pH
7. For photocurrent onset: Electrolyte solution containing supporting electrolyte and a facile redox couple.

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization –
    1. Plan electrode dimensions based on cell openings,

- Sample Collection – Not applicable for this SOP.

- Sample Handling and Preservation –
    1. Never touch the front surface of the semiconductor, especially with bare hands.

- Sample Preparation and Analysis – Follow protocols in the sample preparation SOP for preparation of photoelectrodes for testing.

- Troubleshooting – Not applicable for this SOP.

- Data Acquisition, Calculations & Data Reduction Requirements –

  Illuminated OCP
    1. Set up photoelectrochemical cell in either a two- or three-electrode configuration with the photoelectrode as the working electrode. Ensure that the setup is covered to prevent any stray light reaching the cell.
    2. Measure OCP with NO illumination
    3. Illuminate the semiconductor and measure OCP
    4. If the OCP moves positive under illumination, the material is p-type, and if OCP moves negative under illumination, it is n-type
    5. Step 3 may be repeated with various light intensities to ensure saturation of the open circuit potential has been achieved

6. Steps 1-4 may be repeated across a range of pH values, in which case OCP should shift by -59 mV/pH

Mott-Schottky

1. Set up photoelectrochemical cell in either a two- or three-electrode configuration with the photoelectrode as the working electrode. Ensure that the setup is covered to prevent any stray light reaching the cell.
2. Sparge the electrolyte solution with the gaseous product of the photoelectrode (H_2 for p-type photocathodes and O_2 for n-type photoanodes) to produce a well-defined redox potential and consistent Schottky barrier height.
3. Perform M-S measurements in the dark at a single frequency over a range of potentials (at least 5) to determine the voltage dependence of the space charge capacitance.
4. Perform M-S measurements in the dark over a range of frequencies (at least 5) appropriate for the material (avoiding multiples of line frequencies for electrical equipment such as 60 Hz in the USA).
5. Perform M-S illuminated measurements across the appropriate frequency range under reverse bias potentials relative to the expected E_{fb} (determined from illuminated OCP). Scan potentials where no Faradaic reactions occur, starting at few hundred mV reverse bias, going toward OCP, and back.
6. If linear M-S plots are obtained, repeat steps 1-5 in electrolyte solutions of different pH
7. If the software does not automatically make a M-S plot, fit the EIS data to an R-C equivalent circuit where C_{SC} is the dominant contribution. Plot $1/C_{SC}^2$ as a function of potential. Fit this plot to a linear function. The x-intercept of this function equals $E_{fb} + kT/e$, and the slope gives dopant density by substituting into the equation:

$$N_D(cm^{-3}) = \frac{1.41 \times 10^{32}(cm \times F^{-2} \times V^{-1})}{\varepsilon_r \times A^2(cm^4) \times slope(F^{-2} \times V^{-1})}$$

Photocurrent Onset

1. Set up photoelectrochemical cell in either a two- or three-electrode configuration with the photoelectrode as the working electrode. Ensure that the setup is covered to prevent any stray light reaching the cell.
2. Turn on the lamp to allow the lamp spectrum to stabilize, but do not illuminate the sample.
3. Sparge the electrolyte solution with an inert gas (N_2 or Ar).
4. Perform a linear sweep voltammogram WITHOUT illumination starting close to the E_{fb} (determined by the illuminated OCP method described above) and moving toward reverse bias. The

scan should be stopped once an appreciable amount of dark current is observed.

5. Perform a linear sweep voltammogram WITH illumination starting close to the E_{fb} (determined by the illuminated OCP method described above) and moving toward reverse bias.
6. The photocurrent onset potential (where the current changes signs) provides an estimate of E_{fb}

- Computer Hardware & Software – Computer to record data for each technique and data analysis software capable of fitting nonlinear data.

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

4. Quality Control and Quality Assurance Section

5. Reference Section