Chapter 2

METHODS

This chapter details the experimental and computational methods utilized to generate the data presented and discussed in the following chapters.

2.1 Materials and Chemicals

$(CH_3)_2CO$ (ACS Grade, BDH), CH_3OH (ACS Grade, EMD), H_2SO_4 (ACS Reagent, J. T. Baker), HF (49 %, Semiconductor Grade, Puritan Products), In (99.999 %, Alfa Aesar), Ga (99.999 %, Alfa Aesar), SeO_2 (99.4 %, Alfa Aesar), and TeO_2 (99+ % Sigma-Aldrich) were used as received. H_2O with a resistivity $\geq$ 18.2 MΩ cm (Barnstead Nanopure System) was used throughout. n^+-Si(111) (0.004 – 0.006 Ω cm, As-doped, 400 $\pm$ 15 μm, single-side polished, Addison Engineering) was used as a substrate for deposition. Flash-Dry Silver Paint (SPI Supplies), Double/Bubble Epoxy (Hardman) and nitrocellulose-based nail polish were used to assemble the Si working electrodes.

2.2 Electrode Preparation

One end of a Sn-coated Cu wire (22 AWG) was bent to form a small, flat coil and the wire was then threaded through glass tubing (6 mm O. D.) such that the coil was just outside the tubing. Epoxy was applied to seal the end of the tube from which the coil protruded. Square Si wafer sections (ca. 5 mm by 5 mm) were cut and a eutectic mixture of Ga and In was scratched into the unpolished surfaces with a carbide scribe. The wire coil was then contacted to the unpolished surface and affixed with Ag paint. Nail polish was applied to insulate the unpolished face, as well as the wire-coil contact and the exposed wire between the coil and epoxy seal. Immediately before deposition, the Si surface of each electrode was cleaned with either $(CH_3)_2CO$ alone or sequentially with $(CH_3)_2CO$, CH_3OH, and H_2O, and then the Si section of the electrode was immersed in a 49 wt. % solution of HF(aq) for ~ 10 s, to remove any SiO_x present at the surface from the Si. The electrode was then rinsed with H_2O, and then dried under a stream of $N_2(g)$.

2.3 Electrode Illumination

Illumination for the majority of the photoelectrochemical depositions was provided by narrowband diode (LED) sources (Thorlabs) with respective intensity-weighted λ_{avg} values and spectral bandwidths (FWHM) of 461 nm and 29 nm (M470L2), 630 nm and 18 nm (M625L2 or M625L3), 775 nm and 31 nm (M780L2), and 843 nm and 30 nm (M850L3). Additionally, a HeNe laser (Aerotech LSR5P) emitting at 632.8 nm in a TEM_{00} mode with linear polarization, a broadband diode (LED, Thorlabs MBB1L3) with a relatively flat intensity profile between 500 and 750 nm (λ_{avg} = 646 nm) and a spectral bandwidth (FWHM) of 280 nm, and an ELH-type tungsten-halogen lamp (Phillips 13096) with a λ_{avg} value of 640 nm and a spectral bandwidth (FWHM) of 420 nm, were also used as light sources.

The output of each diode source was collected and collimated with an aspheric condenser lens (Ø30 mm, f = 26.5 mm). The HeNe laser was fitted with a 10x beam expander (Melles-Griot) to create a spot that overfilled the working electrode. A dichroic film polarizer (Thorlabs LPVISE2X2 or LPNIRE200-B) was used to polarize the illumination from all the narrowband diode sources. Illumination from the broadband diode and from the tungsten-halogen lamp was polarized using an ultra-broadband wire-grid polarizer (Thorlabs WP25M-UB). For experiments involving simultaneous illumination with two sources with different λ_{avg} values, a dichroic filter (Edmund Optics #69-900 or #69-219) was utilized to combine the bream outputs. Both sources were incident upon a filter surface at an angle of 45 degrees from the surface normal, generating coaxial output. Similarly, for experiments involving simultaneous illumination with two λ_{avg} = 630 nm sources, a polka dot beamsplitter

(Thor Labs BPD508-G) was utilized in the same geometry to combine the outputs. For experiments involving simultaneous illumination with a $\lambda_{avg} = 630$ nm source along with either a $\lambda_{avg} = 461$ nm or $\lambda_{avg} = 843$ nm source, a single polarizer was placed after the dichroic filter to ensure that all the light that reached the electrode shared a single polarization vector. For experiments involving simultaneous illumination with a $\lambda_{avg} = 630$ nm source along with either another $\lambda_{avg} = 630$ nm source or a $\lambda_{avg} = 775$ nm sources, a polarizer was placed between each source and the appropriate combining optic, to enable independent control of the polarization of each source. No polarizer was used in conjunction with the HeNe laser. For experiments using a series of elliptical polarization states, the output from the HeNe laser was directed at normal incidence through a zero-order $\lambda/4$ plate (Thorlabs WPQ10E-633). The $\lambda/4$ plate was rotated about the optical axis such that the fast axis of the plate was oriented at angles between 0 and 45° clockwise from the polarization axis of the laser. The presence of the $\lambda/4$ plate generated a $\phi = 90°$ phase angle between the orthogonal components of the laser illumination and provided for the generation of defined elliptical polarization. For all experiments, a 1500 grit ground-glass (N-BK7) diffuser was placed immediately in front of the photoelectrochemical cell to ensure spatial homogeneity of the illumination.

The light intensity incident on the electrode was measured by placing a calibrated Si photodiode (Thorlabs FDS100) in the place of an electrode assembly in a photoelectrochemical cell with electrolyte, and measuring the steady-state current response of that Si photodiode. Depositions that utilized a single diode with $\lambda_{avg} = 461$ nm or $\lambda_{avg} = 646$ nm as the illumination source were performed with a light intensity

of 25.0 mW cm^{-2} at the electrode. Depositions with the HeNe laser were performed with a light intensity of 10.0 mW cm^{-2} for the experiment described in Chapter 2 and 13.7 mW cm^{-2} for experiments described in Chapter 4. Depositions with the tungsten-halogen lamp were performed with a light intensity of 50.0 mW cm^{-2}. Depositions using a single λ_{avg} = 630 nm source were performed with a light intensity of 25.0 mW cm^{-2} for the experiments described in Chapter 2 and 13.7 mW cm^{-2} for the experiments described in Chapters 3 and 4. Depositions utilizing a λ_{avg} = 630 nm source in conjunction with a λ_{avg} = 461 source, another λ_{avg} = 630 nm source, a λ_{avg} = 775 nm source, or a λ_{avg} = 843 source, simultaneously were performed with total light intensities of 25.0, 13.7, 30.0, and 50.0 mW cm^{-2}, respectively.

2.4 Photoelectrochemical Deposition

Photoelectrochemical deposition was performed using a Bio-Logic SP-200 potentiostat. Deposition was performed in a single-compartment glass cell with either a pyrex or quartz window. A three-electrode configuration was utilized with a graphite-rod counter electrode (99.999 %, Sigma-Aldrich) and a Ag/AgCl reference electrode (3 M KCl, Bioanalytical Systems). Films were deposited from an aqueous solution of 0.0200 M SeO_2, 0.0100 M TeO_2 and 2.00 M H_2SO_4. Deposition was effected by biasing the illuminated n^+-Si electrode potentiostatically at -0.40 V vs. Ag/AgCl for 5.00 min at room temperature. After deposition, the electrode was immediately removed from the cell, rinsed with H_2O, and then dried under a stream of $N_2(g)$. The Si substrate with a top-facing Se-Te film was mechanically separated from the rest of the electrode assembly. The nitrocellulose-based insulation, as well as the majority of the Ag paint and In-Ga eutectic, were then removed mechanically.

2.5 Scanning-Electron Microscopy

Scanning-electron micrographs (SEMs) were obtained with a FEI Nova NanoSEM 450 at an accelerating voltage of 5.00 kV with a working distance of 5 mm and an in-lens secondary electron detector. Micrographs obtained for quantitative analysis were acquired with a resolution of 172 pixels μm^{-1} over ca. 120 μm^2 areas. Micrographs utilized to produce display figures were acquired with a resolution of 344 pixels μm^{-1} over ca. 8 μm^2 areas.

2.6 Iterative Growth Modeling

      The growths of the photoelectrochemically deposited films were simulated with an iterative growth model wherein electromagnetic simulations were first used to calculate the local photocarrier-generation rates at the film surface. Then, mass addition was simulated via a Monte Carlo method wherein the local photocarrier-generation rate weighted the local rate of mass addition along the film surface.

      Growth simulations began with a bare, semi-infinite planar Si substrate. In the first step, the light-absorption profile under a linearly polarized, plane-wave illumination source was calculated using full-wave finite-difference time-domain (FDTD) simulations ("FDTD Solutions" software package, Lumerical) with perfectly matched layer boundary conditions imposed in the direction normal to the substrate and periodic boundary conditions imposed in the orthogonal direction(s). In the second step, a Monte Carlo simulation was performed in which an amount of mass, equaling that of a 10 nm (for simulations presented in Chapters 2 and 4) or 15 nm (for the simulations presented in Chapter 3) planar layer that covered the simulation area, was added to the upper surface of the structure with a probability F:

$$F(G) = G\prod_{i=1}^{3} \frac{x_i}{r_i} \quad \textbf{(Equation 1)}$$

where G is the spatially dependent photocarrier-generation rate at the deposit/solution interface, x_i is the fraction of ith nearest neighbors occupied in the cubic lattice, and r_i is the distance to the ith nearest neighbor. The multiplicative sum in the definition of this probability (Equation 1) serves to reduce the surface roughness of the film so as to mimic the experimentally observed surface roughness. After the initial Monte Carlo

simulation, the absorbance of the new, structured film was then calculated in the same manner as for the initial planar film, and an additional Monte Carlo simulation of mass addition was performed. This process of absorbance calculation and mass addition was repeated for a total of 30 iterations for the simulations described in Chapters 2 and 3 and for 20 iterations for the simulation described in Chapter 4.

A value of n = 1.33 was used for the refractive index of the electrolyte regardless of wavelength.[63] Previously measured values of the complex index of refraction for Se-Te were utilized.[47] Illumination intensities identical to those used experimentally (see above) were used in the simulations. The electric field vector of the illumination was oriented parallel to the substrate.

2.7 Simulation of Field Amplitude Resulting from Dipole Emitters

The time-averaged field amplitude resulting from two coherent dipole sources was calculated using two-dimensional FDTD simulations ("FDTD Solutions" software package, Lumerical). For simulations representing two illumination sources with different polarizations, the field amplitude profile was rotated about the simulation center and summed with the original field amplitude. A two-dimensional square simulation mesh with a lattice constant of 14 nm was used.

2.8 Simulation of Absorption in Idealized Structures

Three-dimensional FDTD simulations ("FDTD Solutions" software package, Lumerical) were used to calculate the normalized absorption profile of two intersecting idealized lamellar structures. A three-dimensional cubic simulation mesh with a lattice constant of 2 nm was used. The idealized structure, from bottom to top, consisted of a semi-infinite Si substrate, a 100 nm conformal Se-Te layer, and two Se-Te lamellae with hemispherical upper boundaries. The lamellae were either 200 nm or 400 nm tall as indicated in Chapter 4, as measured from the upper boundary of the conformal layer.