Surface Modification of Silicon and Indium-Tin Oxide with Phosphonic Acids

Katherine Henry, North Carolina State University, 2011 SURF Fellow
Advisor: Prof. Seth Marder  Graduate Mentor: Sergio Paniagua

Introduction

Surface modification using self-assembled monolayers (SAMs) offers a unique way to change the surface chemistry of a substrate. SAMs have great potential with regard to organic electronics. The surface of a silicon wafer is easily oxidized in air and becomes hydrophilic silica (silicon dioxide). Since organic semiconductors are hydrophobic, delamination readily occurs at the interface from surface energy mismatching. Polarity matching between the substrate and the organic semiconductor may aid in device stability as well as may potentially increase charge transfer.

Experimental Methods

Several methods have been tested and detailed for chemically bonding phosphonic acids with nonpolar tails to the surface of native-oxide silicon. A fluorinated phosphonic acid (FHOPA, see Figure 1) was deposited from solution by the “T-BAG” method (tethering by aggregation and growth), by spin coating, and by an “in-house” method. A combination of experimental design and reproduction of literature procedures was used discern the best method. Samples were measured with X-ray Photoelectron Spectroscopy (XPS) and data was analyzed for both FHOPA coverage and uniformity.

For the T-BAG method, the wafers were first cleaned in boiling (~85°C) “pirhana” (3:1 30% H₂O₂ : 98% H₂SO₄) then in “buzzard” (1:1 30% H₂O₂ : 38% HCl) at 80°C for 45 and 15 minutes respectively. The wafers are then suspended vertically in solution, and the solution is left to evaporate overnight. The wafers are then immediately removed and annealed at 140°C for 2 days, after which they are sonicated in a base bath (K₂CO₃) for 20 minutes. My experimental design included one wafer with no deviation from the protocol, one wafer that was rinsed in THF before annealing, one that received no annealing, and one control.

Spin coating was done on plasma-etched wafers (2 minutes at 60 watts) at 6000RPM for 1 minute. Two nonpolar solvents were used in conjunction with ethanol to deposit a layer of phosphonic acid: 2mM trichloroethylene and 2mM chloroform with 1.5mL ethanol added to each to aid in dissolution.

The “in house” method dissolved a 1mM solution of phosphonic acid in ethanol. Wafers were plasma etched for 2 minutes at 60 watts and then immediately left in solution overnight. Afterwards, the wafers underwent a base bath sonication in 5% v/v triethylamine/ethanol.

Results

The XPS data from 22 samples was analyzed and methods that could be compared were graphed in Excel (see Figure 2).

Discussion and Conclusions

The fluorine content in the chloroform solutions seem to be the highest not only among the spin coat solutions, but also overall. Looking at high-resolution data, the fluorine to carbon ratio is about 1.6, which is the ideal ratio for a monolayer. The calculated thickness was a minimum of 0.5 nanometers, which is evidence of a monolayer, since the FHOPA molecule is 12Å in length. Comparing base baths, the K₂CO₃ seemed to be a little too aggressive, removing most of the FHOPA as compared to the triethylamine. The T-BAG method definitely deposited some fluorine, as evidenced by the fluorine content, but after undergoing a base bath the majority of it was removed. The in-house method deposited so little fluorine as compared to carbon, which is evidence that either the ethanol solvent competed with the phosphate reaction or there was a lot of organic impurities.

The T-BAG method took 3 full days for completion, the in-house method took 2 days, and the spin coat method only took a couple hours. Therefore, based on efficiency and efficacy, the spin coat method with a chloroform solution and a triethylamine base bath seems to be the best.

Acknowledgments

I would like to thank Dr. Seth Marder and the SURF fellowship for making this opportunity possible. A special thank you to Sergio Paniagua for mentoring me throughout the summer, while encouraging me to make this project my own.

References


Hanson, Eric L. et al. “Bonding self-assembled, compact organophosphonate monolayers to the native oxide surface of silicon” J AM CHEM SOC 2003, 125, 16074-16080.