Effectiveness of Grown Poly(methyl methacrylate)/PMMA Brush as a Masking Agent

NNCI REU Student: Jonathan L. Chang, School of Chemical and Biomolecular Engineering, University of Maryland, College Park

NNCI REU Principal Investigator: Professor Michael A. Filler, School of Chemical and Biomolecular Engineering, Georgia Institute of Technology

NNCI REU Mentor: Amar T. Mohabir, School of Chemical and Biomolecular Engineering, Georgia Institute of Technology

Abstract & Introduction

In the field of nanoscale fabrication, there is an interest in developing entirely bottom-up fabrication methods for the development of functioning nanoelectronics from 3D nanostructures. One process in development for this goal is Selective CoAxial Lithography via Etching of Surfaces (SCALES)[1] where a polymer brush is grown or polymerized from the surface of a nanostructure and subsequently etched to create a polymer mask, patterning the surface to enable area-selective atomic layer deposition (AS-ALD). The focus of this project was to analyze and investigate the effectiveness of grown poly(methyl methacrylate) (PMMA) as a masking agent for the AS-ALD process. This work will help in the continuing development of the SCALES process as well as demonstrate its viability for making functional nanodevices. Grown PMMA brushes were run through ALD processes along with bare silicon. These samples were analyzed with X-ray photoelectron spectroscopy (XPS) to determine chemical changes and quantify deposition amounts on each substrate. The ALD temperature, ALD purge time, and ALD precursors were varied to determine optimal ALD process conditions for the grown PMMA to act as a mask. Following this, an investigation was conducted to find a method which would selectively etch off the PMMA brush while keeping the deposited material intact.
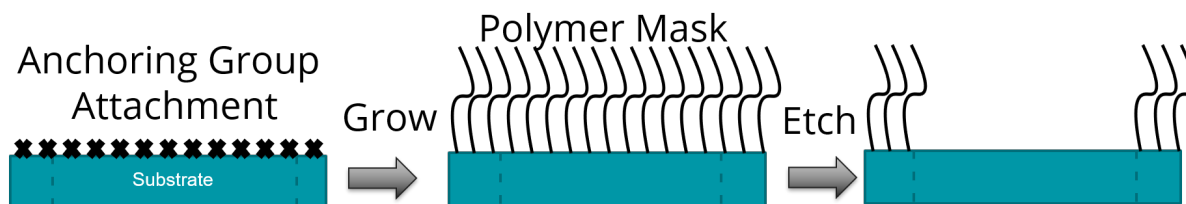
Fig. 1: Illustration of SCALES process

Materials and Methods

PMMA samples were grown on bare silicon using atom transfer radical polymerization (ATRP). To simulate AS-ALD with a SCALES grown PMMA pattern, a bare silicon(111) wafer and a silicon(111) wafer with PMMA grown to approximately 30nm were loaded into the CtrLayer ALD 1 machine for alumina ALD or the Cambridge NanoTech Plasma ALD (Oxide) machine for titanium oxide ALD. These machines were run in a vacuum, and, unless stated, at 100°C with standard purge times as specified by Georgia Tech Institute of Technology and Nanoelectronics

(IEN) staff. For the lift-off process, O_2 plasma was used via the Plasma Etch machine at the Georgia Tech Materials and Characterization Facility (MCF) to test if the PMMA could be selectively removed without significant damage to the deposited oxide. Following these tests, samples were characterized using XPS in the MCF to determine the surface chemistry and relative amounts of chemical species on the sample.

Results and Discussion

During the initial tests of alumina ALD on the samples, aluminum scans with XPS uncovered alumina in the PMMA after ALD, indicating that the process was not selective at all. Aluminum scans with XPS also indicated that while changing the temperature and purge times of ALD did affect the amount of alumina in the PMMA, there was still alumina in the ALD which meant the process was not selective on the PMMA.
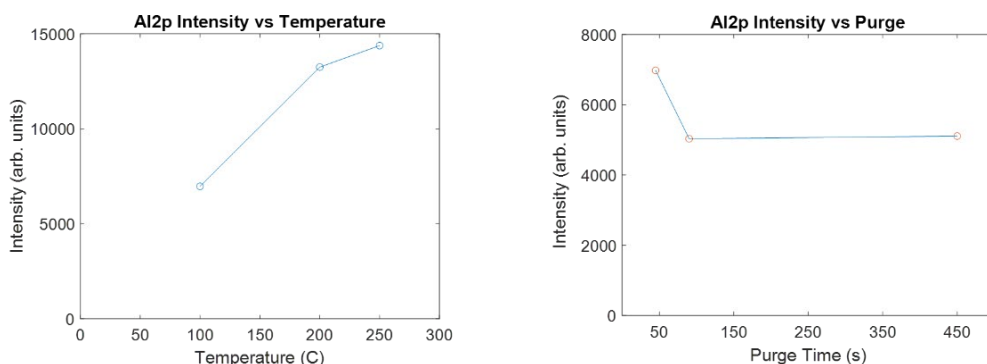

Fig. 2: Plot of aluminum intensity/amount from XPS scans on PMMA after ALD at the specified temperature or purge time.

This prompted a decision to change the ALD process and move away from alumina ALD. Literature revealed that ALD processes such as HfO_2, Pt, and TiO_2 ALD did not readily deposit material into spin coated PMMA[2]. Due to issues with some of the precursors in the Cambridge NanoTech Plasma machine, it was decided to perform TiO_2 ALD which was revealed through the titanium XPS scans to be more selective due to the presence of TiO_2 on the bare silicon and no significant amount in the PMMA. This was reasoned to be due to the precursor used in ALD since the precursor for alumina ALD (trimethylaluminum) is relatively small and not as sterically hindered as the precursor for TiO_2 ALD (tetrakis(dimethylamido)titanium). It was believed that this difference in size of the precursor influenced its ability to diffuse and react in the PMMA, though other factors related to the chemistry of the precursor itself may also play a role as well.

Following this, it was decided to investigate a way to selectively etch off the PMMA without damaging the deposited material: TiO_2. The best method was found to be oxygen plasma etching which, as indicated by XPS scans, was able to remove the PMMA on the PMMA sample while keeping the TiO_2 deposited on the silicon wafer mostly intact. This is believed to be because of the ability of oxygen plasma to attack and destroy organic materials, which is what the PMMA is comprised of, while leaving metals and oxides relatively untouched.
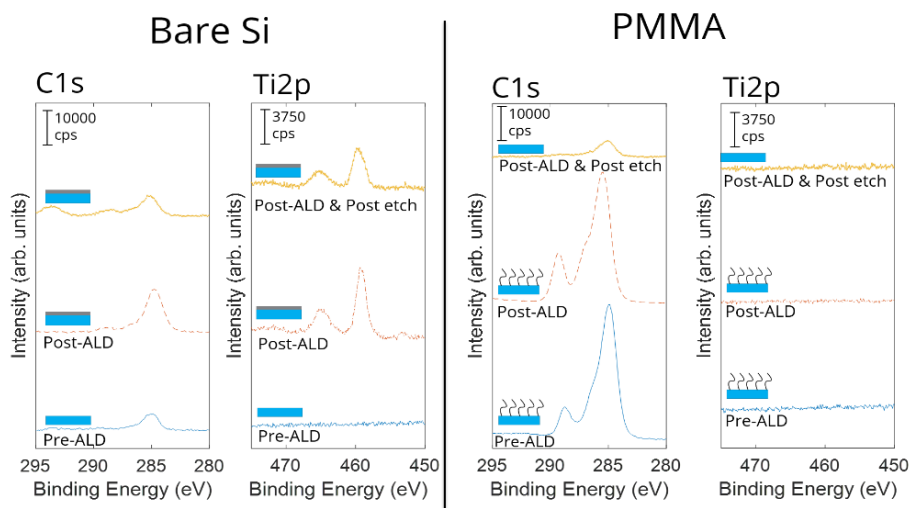
Fig. 3: XPS scans of silicon and PMMA samples pre-ALD, post-ALD and post-ALD & post-O_2 plasma etch

Conclusions and Future Work

Through these experiments, it was found that surface polymerized PMMA via ATRP can be used as an effective masking layer for AS-ALD. The main factor which determined its effectiveness was the precursor used in ALD. It was found that bulkier, more sterically hindered precursors were less likely to diffuse and react with the PMMA; however, other chemistries related to the precursors may play a role as well. Temperature and purge time were found to have a minor effect on the PMMA's effectiveness as a mask. O_2 plasma etching was also discovered to be an effective method at selectively removing the PMMA while keeping the deposited oxide intact.

In the future, the lab hopes to change the precursor for alumina ALD to a bulkier precursor to confirm the current hypothesis regarding the precursor size and improve PMMA selectivity during ALD. The lab also plans to repeat my experiments on nanowires and eventually be able to use this to develop a process for bulk fabrication of functioning 3D nanodevices.

Acknowledgments

References

(1)   Mohabir, A. T.; et. al. *Bottom-Up Masking of Si / Ge Surfaces and Nanowire Heterostructures via Surface Initiated Polymerization and Selective Etching.* **Submitted.** No.2