Fabricating 2D Silica with Atomic Layer Deposition

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Abstract:

Two-dimensional (2D) materials exhibit exciting new properties that could have applications for next-generation electronic devices. One such material is 2D silica, called silicatene, which is an SiO_2 bilayer that only binds to a surface via van der Waals forces. Previous research has shown that silicatene can be made via evaporation of Si and subsequent annealing in oxygen on a few single-crystalline metal surfaces, including Pd, Pt, and Ru. Atomic layer deposition (ALD) is a thin-film deposition technique used in the manufacturing of a variety of devices. This process repeats two self-limiting reaction steps to deposit a thin film, allowing angstrom-scale control of film thickness. The focus of this project was to investigate the use of ALD to deposit silicatene on several metal substrates. The metal films were deposited on silicon wafers via electron-beam assisted evaporation, and silica films were deposited with ALD. Post-deposition characterization of deposited film includes ellipsometry, contact angle, and x-ray photoelectron spectroscopy (XPS).

Introduction and Goals:

The thinnest stoichiometric arrangement of silica is a bilayer of silicon dioxide, known as silicatene. This material adheres to its substrate through van der Waals forces (see Figure 1). Silicatene has been fabricated on single crystal palladium (Pd), platinum (Pt), and ruthenium (Ru).

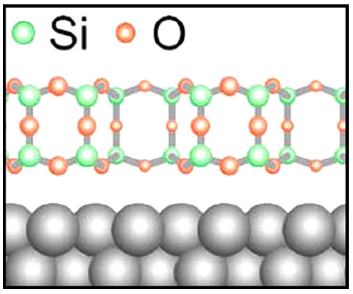


Figure 1: Figure adapted from ref. [1], the structure of silicatene. It consists of a bilayer of SiO_2 molecules attached to a metal substrate via van der Waals forces.

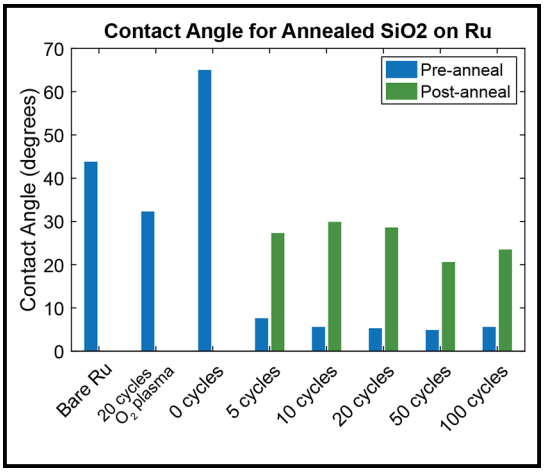
Silicon (Si) was evaporated onto the metal substrate with an electron-beam assisted evaporator, then the films are annealed near 800°C and 10^{-6} mbar in an oxygen-rich environment [1].

Atomic layer deposition (ALD) is a thin-film deposition technique in which two self-limiting reactions are repeated, forming a film, atomic layer-by-atomic layer. This method allows low-temperature deposition of highly conformal, uniform films [2]. This research aimed to fabricate silicatene using ALD.

Methods:

We chose Pd, Pt, and Ru as metal films for SiO_2 ALD. These metals were deposited on p-type silicon using an electron beam-assisted evaporator. Each metal film was 150Å thick, and the Pt film was deposited on a 100Å thick Ti adhesion layer on Si. Metal films were characterized with contact angle and ellipsometry. SiO_2 films were deposited with ALD, using tris(dimethylaminosilane) (3DMAS) precursor and O_2 plasma as a co-reactant. Before the precursor was introduced, substrates were reduced in a H_2 plasma.

Films were deposited at 200°C, with 5, 10, 20, 50, and 100 cycles of ALD. In addition, a "0 cycle" sample was created, which was not exposed to the Si precursor or the O_2 plasma, and a "20 second-half cycle" sample was created, which was not exposed to the 3DMAS, but did undergo 20 cycles of the O_2 plasma co-reactant. Samples



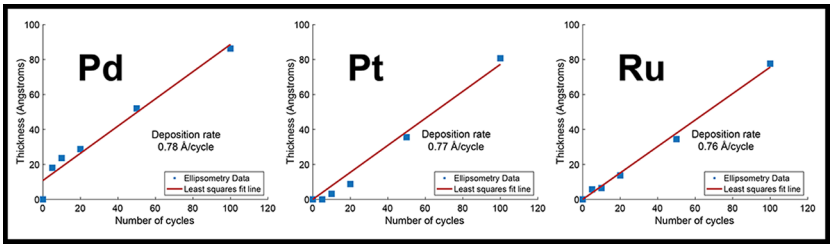


Figure 2, left: *Contact angle data before and after annealing Before annealing, contact angle is high without the introduction of Si precursor. When the Si precursor is introduced, the contact angle is consistently low. After annealing, the contact angle increases.* ***Figure 3, above:*** *Ellipsometry data before annealing. All metals show a linear increase in thickness with number of ALD cycles.*

were annealed in an oxygen environment at 800°C for 10 minutes at atmospheric pressure, then were allowed to cool to 300°C. Samples were characterized with contact angle, ellipsometry, x-ray photoelectron spectroscopy (XPS), and angle-resolved XPS (ARXPS) before and after annealing.

Results:

Contact angle showed high angles of water contact for the samples that were not exposed to the Si precursor (bare metal, 0 cycles, and 20 second-half cycles). The contact angles for the pre-annealed samples that were exposed to the Si precursor were uniform and low. This data shows that the exposure to the Si precursor caused a change on the sample surface, suggesting that SiO_2 was deposited.

After annealing, contact angles were high, which is inconsistent with the expectation for silicatene. This trend (summarized in Figure 2) was observed for all three. Ellipsometry data shows a linear increase in thickness with the number of ALD cycles for all metal substrates, as seen in Figure 3. This suggests that we observed normal ALD behavior, as the formation of silicatene would have led to an asymptote in the film thickness because it is unlikely the complete bilayer would have reacted with additional precursor due to the lack of dangling bonds.

Ellipsometry data for the annealed samples was different than that of the pre-annealed samples, and it could not be fit to the expected models. XPS confirmed that the amount and thickness of SiO_2 increased with the number of ALD cycles. ARXPS showed that before annealing, our sample consisted of a thin film of SiO_2 on a buried Ru substrate. After annealing, ARXPS still showed a layer of SiO_2 on top of the sample but the morphology of Ru was inconclusive.

Conclusions:

XPS and ellipsometry suggest that silicatene was not produced. It is likely that during annealing, the SiO_2 combined with the metal to form metal silicides. This is supported by the change in contact angle after annealing and a study showing that Si will diffuse into metals, forming silicides [3]. This would also change the optical constants of the film, which caused the failure of the ellipsometry models.

Future Work:

Successful silicatene fabrication involved single crystal metal substrates [1], whereas our metal films were amorphous due to their evaporation. As a result, we would like to replicate this experiment on single-crystalline metal substrates.

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References:

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