Controlling the thickness of Josephson tunnel barriers with atomic layer deposition

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Abstract— Atomic Layer Deposition (ALD) is a promising technique for producing Josephson junctions (JJs) with lower defect densities for qubit applications. A key problem with using ALD for JJs is the interfacial layer (IL) that develops underneath the tunnel barrier. An IL up to 2 nm forms between ALD Al₂O₃ and Al. However, the IL thickness is unknown for ALD films < 1 nm. In this work, Nb-Al/ALD-Al₂O₃/Nb trilayers with tunnel barriers from 0.6 – 1.6 nm were grown in situ. Nb-Al/Al₂O₃/Nb JJs with thermally oxidized tunnel barrier were produced for reference. R₀ was obtained using a four-point method at 300 K. Jc, and its dependence on barrier thickness, was calculated from the Ambegaokar-Baratoff formula. The Al surface was modeled using ab initio molecular dynamics to study the nucleation of Al₂O₃ on Al. Current voltage characteristics were taken at 4 K to corroborate the room temperature measurements. Together, these results suggest that ALD may be used to grow an ultrathin, uniform tunnel barrier with controllable tunnel resistance and Jc, but a thin IL develops during the nucleation stage of ALD growth that may disqualify Al as a suitable wetting layer for ALD JJ based qubits.

Index Terms— Ab-initio molecular dynamics, atomic layer deposition, in situ deposition, Josephson junctions, quantum computing.

I. INTRODUCTION

The Josephson Junction (JJ), a superconductor-insulator-superconductor (SIS) tunnel junction, is a strong candidate for the implementation of quantum bits (qubits) due to its compatibility with modern semiconductor processing technology. This tunnel barrier (1 layer) must be ultrathin (~1 nm) in order to maintain phase coherence across the superconducting electrodes, and because the critical current Jc of the JJ decays exponentially with tunnel barrier thickness [1]. Producing an ultrathin, uniform, and leak-free tunnel barrier is difficult on metal substrates due to the naturally formed native oxides on most metals. However, traditional JJ fabrication techniques have cleverly used the easy of oxidation of Al to produce the tunnel barrier by thermally oxidizing a thin (~5 nm) “wetting layer” of Al to form Nb-Al/Al₂O₃/Nb JJs. This thermal oxidation scheme has been used to create high quality JJs for commercial applications such as SQUIDs and voltage standards. However, when JJs are employed for qubits, a more stringent requirement for lower noise arises to avoid superconducting phase decoherence, which makes meaningful quantum computation impossible. One major source of noise is two-level fluctuators (TLFs) in the insulating films of the qubit circuit [2]. Defects in the tunnel barrier arise from the process of thermally oxidizing aluminum and are a primary cause of TLFs [3]. While efforts to shield JJ qubit circuits from environmental noise to increase coherence times have met success [4], the root cause of the decoherence, and thus its ultimate solution, lies in the insulating materials used to in the circuit, primarily the tunnel barrier. Because thermal oxidation is the primary source of defects in the tunnel barrier, it is imperative to find novel methods of ultrathin tunnel barrier fabrication.

Atomic Layer Deposition (ALD) is a promising and unexplored alternative to thermal oxidation. Depicted schematically in Fig. 1, ALD is a chemical vapor growth method that uses self-limited surface reactions to grow films one molecular layer at a time, yielding subnanometer thickness control [5, 6]. Using Al₂O₃ as an example, alternating pulses of H₂O and trimethylaluminum (TMA) are brought to substrates heated to ~200 °C by an inert carrier gas, usually N₂. The pulses are separated by a flush of N₂ to assure the two chemicals never meet in the gaseous state. In this way, the following reactions take place cyclically

\[ \text{AlOH}^* + \text{Al(CH₃)₃} \rightarrow \text{AlOAl(CH₃)₃}^* + \text{CH₄} \]  
\[ \text{AlCH₃}^* + \text{H₂O} \rightarrow \text{AlOH}^* + \text{CH₄} \]

where asterisks denote surface species. On some substrates, such as SiO₂, the surface is naturally hydroxylated (Fig. 1a). Otherwise, the sample may become hydroxylated upon the first pulse of H₂O (Fig. 1b). The chamber is then flushed with N₂, and TMA is introduced (Fig 1c). Ligand exchange occurs between the surface hydroxyl groups and the gaseous TMA. Because TMA only reacts with the surface hydroxyl groups and not itself, only one layer of Al(CH₃)₃ is deposited. Another flush occurs, and H₂O is reintroduced (Fig 1d). One molecular layer, or 1.2 Å, of Al₂O₃ is grown per cycle.

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cycles of growth, which act substrates interfacial layer hydrogen terminated Si (H satisfied by residual H studied on SiO species, such a ALD Al interfacial layers (ILs). The chemical reactions of ALD (e.g. critically on the nucleation phase prime candidate for fabricating next generation JJ qubits with epitaxial techniques single cryst... Furthermore, while thermal oxidation limits material selection contrast, ALD's self produce the targeted critical current density (produce fewer point defects and TLFs. Also, thermal oxidation requires precise control over oxygen partial pressure and time to consistently produce the targeted critical current density \(J_C\) [1, 7]. In contrast, ALD’s self-limiting growth mechanism allows substantial leeway in processing conditions while still yielding highly reproducible, subnanometer thickness control. Furthermore, while thermal oxidation limits material selection to \(\text{AlO}_x\), many dielectric materials can be grown via ALD, including \(\text{Al}_2\text{O}_3\), \(\text{HfO}_2\), \(\text{MgO}\), and \(\text{ZnO}\) (see reference [6] for a complete list). Some of these films, such as \(\text{HfO}_2\) grow polycrystalline phases, which could be used to produce a single crystal tunnel barrier without laborious and expensive epitaxial techniques [6, 8]. These advantages make ALD a prime candidate for fabricating next generation JJ qubits with lower defect densities and higher coherence times.

However, the quality of ALD JJ tunnel barriers depends critically on the nucleation phase and the presence of interfacial layers (ILs). The chemical reactions of ALD (e.g. ALD \(\text{Al}_2\text{O}_3\) given in eqns. 1-2) require the existence of surface species, such as \(\text{OH}^+\) and \(\text{CH}_3^+\). This problem has been well studied on \(\text{SiO}_2\), where the requirement is automatically satisfied by residual \(\text{H}_2\text{O}\) on the surface (Fig. 1a), and hydrogen terminated Si (H-Si) substrates, where surface activation is necessary to avoid a \(~1\) nm thick silicate interfacial layer [9, 10]. Similarly to \(\text{SiO}_2\) and H-Si, metallic substrates have either reactive surfaces, such as Al and Cu, or inert surfaces, such as Pt and Au. In the latter case, nucleation of ALD films can be completely frustrated for the first 30-50 cycles of growth, which act as an incubation period to physorsb the ALD precursors onto the surface [8]. For reactive metals, such as Al, even in situ deposited films can acquire an IL up to \(~2\) nm thick when as little as 20 ALD cycles are performed [11, 12]. This IL is suspected to be caused by thermal oxidation of the Al substrate when it is exposed to \(\text{H}_2\text{O}\) at 200 °C [11]. For example, in the ideal case of ALD occurring in a clean UHV chamber, the Al hydroxyl groups may not exist in abundance on the Al surface (Fig. 1c). Upon the first exposure to \(\text{H}_2\text{O}\) the surface will become hydroxylated, and oxygen will likely diffuse into the body of the Al film (Fig. 1f). The penetration depth depends on the temperature of the sample, the pressure of oxygen, and the amount of time this oxygen pressure is maintained. When TMA is pulsed into the chamber (Fig. 1g), it reacts only at the surface of the sample according to eqns. 1 and 2. Finally, when water is pulsed into the chamber again (Fig. 1h), not only do the surface reactions in eqns. 1 and 2 take place, but more oxygen may diffuse into the Al film if the total oxide thickness is insufficient to act as a diffusion barrier.

\textit{Ab-initio} molecular dynamics (AIMD) simulations were used to study the changes in Al surface chemistry that occur after an \(\text{H}_2\text{O}\) pulse, and the results are given in Fig. 2. The AIMD simulations adopted the Bohn-Oppenheimer molecular dynamics implemented in VASP [13, 14] and used a 2x2 supercell of FCC Al under constant equilibrium volume and temperature (473 K). To simulate the initial Al surface, one \(\text{H}_2\text{O}\) molecule was placed on the supercell to simulate the expected traces of \(\text{H}_2\text{O}\) in the ALD chamber (Fig. 2a). After 6 ps of simulation time, no dissociation of \(\text{H}_2\text{O}\) into OH was observed (Fig 2b). However, when multiple \(\text{H}_2\text{O}\) molecules were placed on the surface to simulate an \(\text{H}_2\text{O}\) pulse (Fig. 2c), dissociation occurred almost immediately. After only 3 ps of simulation time, the \(\text{H}_2\text{O}\) molecules dissociated into \(\text{OH}^+\) (Fig. 2d). We note the main mechanism of \(\text{OH}^+\) formation during this initial period of AIMD simulation appears to be proton transfer between molecules, forming \(\text{H}_2\text{O}^+\), which almost instantly dissociates into \(\text{H}_2\text{O}_{ad}\) and \(\text{H}^+_{ad}\). These simulations suggest the formation of \(\text{Al}_2\text{O}_3\) becomes thermodynamically favorable under typical ALD processing conditions and that nucleation of ALD \(\text{Al}_2\text{O}_3\) films is key and more importantly, can be controlled by the initial \(\text{H}_2\text{O}\) exposure. Work to model the penetration of oxygen into the Al film is ongoing.
For JJ tunnel barriers, less than 10 ALD cycles are required for a thickness of ~1 nm. In this thickness regime, it is unknown whether AlOₓ or Al-ALD-Al₂O₃ dominates the film. Furthermore, at the end of ALD growth the surface is populated with either hydroxyl or methyl groups, and our AIMD simulations suggest a high hydrogen mobility on the Al surface. The hydrogen in these surface groups may act as TLFs [15] or charge scattering centers [16], which could cause poor coherence in qubit applications or decrease the tunneling current through the JJ. The key challenges in the use of ALD for JJ tunnel barriers are to minimize the thickness of the AlOₓ IL and to produce a pristine Al₂O₃ top surface.

There are several possible ways to minimize the thickness of the IL and to clean the top surface of the ALD films, such as ion milling or processing condition optimization. However, we must first understand the influences on JJ performance before designing a solution. In this work, ALD was performed in situ to produce Nb-Al/ALD-Al₂O₃/Nb trilayers, which were then patterned into JJs. By varying the number of ALD cycles performed, extracting the projected \( J_C \) and extrapolating the trend to 0 ALD cycles, we have found evidence that a thin AlOₓ IL forms even in this thickness regime. Low temperature measurements were used to corroborate these conclusions.

II. EXPERIMENTAL

Nb-Al/ALD-Al₂O₃/Nb trilayers were fabricated in a homemade deposition system, which integrates UHV sputtering and ALD in situ [16, 17]. For comparison, traditional thermally oxidized Nb-Al/AlOₓ/Nb trilayers were also fabricated with a target \( J_C = 50 \text{ A/cm}^2 \). The Nb films were sputtered onto a water-cooled sample stage at 1.7 nm/s to minimize the formation of NbOₓ from trace oxygen. The bottom Nb was 150 nm, and the top Nb was 50 nm. The 7 nm Al wetting layers were sputtered at 0.5 nm/s. For trilayers with ALD tunnel barriers, 5 – 13 cycles (0.6 – 1.6 nm) of ALD-Al₂O₃ growth occurred at 200 °C with TMA and H₂O. For the trilayer with a thermally oxidized tunnel barrier, the Al wetting layer was exposed to 100 Torr O₂ for 3.5 hours.

The trilayers were patterned into JJ arrays using advanced lithography and etching techniques. Nominal JJ dimensions ranged from 7 – 10 µm, but profilometry was used to measure the actual dimensions, which were reduced by ~1.5 µm by etching. UV Photolithography was used to define the main wiring of the circuit, which includes four electrical leads for each of the 12 JJs on the circuit. The Nb films were etched using reactive ion etching in 15 mTorr SF₆ at 0.4 W/in². The Al₂O₃, AlOₓ and Al films were wet etched in 8% H₃PO₄. Electron Beam Lithography was used to define the junction area and the top wiring leads. The junctions were insulated by sputtered SiO₂. The tops of the junctions were cleaned in Ar plasma before the top Nb wiring was sputtered.

The completed devices were characterized at room temperature and low temperature using a four-point configuration. At room temperature, current-voltage curves (IVCs) were taken using a semiconductor device analyzer (Agilent B5015A) with 25 µm tungsten probes. The room temperature resistances \( (R_N) \) were extracted from the slope of the IVCs. The samples were then cooled to 4 K using a physical properties measurement system (PPMS) from Quantum Designs. Current voltage characteristics were obtained using a custom, battery-operated measurement system independent of the PPMS.

III. RESULTS AND DISCUSSION

\( R_N \) was measured at room temperature for samples with 5 – 13 ALD cycle tunnel barriers. \( R_N \), the specific tunnel resistance, was found to be independent of the JJ area, indicating a uniform tunnel barrier had been grown. Fig. 3a shows \( R_NA \) vs. ALD cycles for all the trilayers in this study. The data point at 0 ALD cycles is from Reference [16]. It represents a sample that went through the heating and cooling process in the ALD chamber, but was not exposed to any ALD sources. Its deviation from the trend will be discussed presently. An exponential increase in \( R_NA \) with increasing ALD cycles is observed, indicating \( R_N \), and thus \( J_C \), can be controlled with ALD.

\[
R_N = \frac{\pi \Delta}{2eJ_C} A
\]

where \( J_C \) is the critical current density, \( R_N \) is the normal state resistance, \( A \) is the area of the junction, \( \Delta \) is the superconducting gap energy, and \( e \) is the elementary charge. By fitting \( R_N \) vs. \( 1/A, J_C \) can be extracted from the slope. Fig. 3b shows this calculated \( J_C \) vs. ALD cycles. There is an exponential decrease in \( J_C \) with increasing ALD cycles. The data point at 0 cycles was taken from Reference [16]. \( J_C \) of this sample was measured at 4 K, in contrast to the other data points on the graph. The 0 cycle JJ was not included when fitting the trend to the data. At 0 cycles, the extrapolated \( J_C \sim 1.1 \times 10^3 \text{ A/cm}^2 \). According to the analysis in Reference [1], this \( J_C \) value corresponds to a pinhole free Al surface and an oxidation dose of ~10² Pa-s. This indicates the formation of a thin AlOₓ IL. However, the extrapolated value does not agree

![Graph of specific tunnel resistance vs ALD cycles (a), and projected \( J_C \) vs ALD cycles (B). The data point at 0 is from Reference [16] and was not included in the fits.](image-url)
well with \( J_C \approx 9 \times 10^3 \) A/cm\(^2\) measured on the 0 ALD cycle sample. This indicates an oxidation event occurs in the first few ALD cycles, which has been previously reported for ALD growth on W, Co, and Ta \([19-21]\) and agrees with the AIMD simulations in Fig. 2. This oxidation event could also explain the deviation in Fig. 3a. Therefore, a thermally oxidized IL exists between the Al wetting layer and the ALD tunnel barrier that corresponds to a \( J_C \approx 1.1 \times 10^3 \) A/cm\(^2\). If this IL is sufficiently thick that \( \text{AlO}_x \) dominates the tunnel barrier, pure Al wetting layers may be unsuitable for ALD growth of JJ tunnel barriers due to the presence of point defects in the \( \text{AlO}_x \), and alternative wetting layers may be needed.

In conclusion, Nb-Al/ALD-Al\(_2\)O\(_3\)/Nb trilayers were fabricated in situ. The trilayers were patterned into JJs, which were characterized at room temperature and low temperature. A consistent \( R_N \) indicates the ALD tunnel barriers are uniform across the wafer, and an exponential increase in \( R_N \) with an increasing number of ALD cycles indicates the tunneling properties can be controlled by altering the number of ALD cycles performed. \( R_N \) was extracted from room temperature IVCs, and an exponential increase in \( R_N \) with increasing ALD cycles was observed. Further, extrapolation of this data to 0 ALD cycles indicates a thin \( \text{AlO}_x \) IL was formed during ALD growth. Though this extrapolation does not agree with previous, low temperature measurements, AIMD simulations suggest the nucleation of ALD \( \text{Al}_2\text{O}_3 \) on Al is controlled by \( \text{H}_2\text{O} \) during the first ALD cycle, and that substantial oxidation may occur that would account for the difference. Low temperature measurements corroborated the room temperature data. Together, these results indicate that ALD is a viable method for controlling the thickness of JJ tunnel barriers. However, an \( \text{AlO}_x \) IL develops during the first few cycles of ALD growth, and it may be problematic for JJ qubits. Alternative wetting layer materials that are not susceptible to oxidation at 200 °C may be required to realize JJ qubits with ALD tunnel barriers.
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