

Selective Atomic Layer Deposition (SALD) of Titanium Dioxide on Silicon and Copper Patterned Substrates

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Atomic Layer Deposition (ALD) of TiO_2 has potential applications in the micro- and nano-electronics industry such as in the formation of copper barrier layers. In this paper, TiO_2 deposition on silicon and copper substrates is studied with a focus on the initial growth and nucleation period on different substrates. Silicon with about 1.5 nm-thick native oxide, silicon with reduced oxide thickness (i.e., < 1 nm-thick), and copper patterned silicon substrates are used for TiO_2 deposition within the ALD temperature window over which the film deposition rate is independent of the substrate temperature. The obtained results are used and discussed in the context of selective TiO_2 deposition on the silicon part of copper-patterned silicon substrates. Selective ALD is found to be possible on the silicon of these substrates by taking advantage of the 15-20 cycle TiO_2 nucleation period on copper, therefore allowing a film ~ 2.5 nm-thick to grow on silicon while less than 1-2 monolayers grow on copper. These findings can be used to further investigate TiO_2 selective deposition on copper patterned silicon substrates.

Introduction

As the microelectronics industry has evolved, chip components and systems have become progressively smaller. In some cases, current fabrication technologies have reached the limits of component materials, and a need has developed for a higher class of materials that can withstand the demands of microscale technology applications and future evolution. A specific example of this can be found in copper barrier layer technology. The International Technology Roadmap for Semiconductors predicted that the standard copper barrier layer would decrease in thickness from 12 nm in 2003 to 2.5 nm in 2016,¹ placing a high demand on researchers to provide manufacturers with materials and processes capable of producing effective ultra-thin barrier layers in this realm. Several materials have emerged as potential candidates for use in barrier layers, such as HfO_2 , Ta_2O_5 , Al_2O_3 , and TiO_2 .²⁻⁴ These materials were chosen based on their high dielectric constants, their long term stability in a variety of conditions, and their ability to bond to a silicon substrate without reacting with or diffusing through it.

A process is also necessary which will deposit these materials in a manner conducive to proper barrier layer function - the deposited barrier layer should have a thickness of about 2.5 nm while still providing full, even coverage over a variety of contours.² Atomic Layer Deposition

provides a viable production method for forming these thin films, as it satisfies these characteristics due to the distinctive nature of the deposition process. ALD is a self-limiting surface reaction process in which the first gaseous precursor, followed by the second, is pulsed over the substrate with a purging session in between pulses. The cycle is repeated many times to deposit a film with the desired thickness. Unlike Chemical Vapor Deposition (CVD), which introduces both precursors together in the vapor phase and may result in undesired side reactions, ALD allows very precise thickness control because the precursors are introduced individually to ensure the formation of identical monolayers at the atomic scale. The limiting factor in most ALD reactions is time, as the process is lengthy compared to other film deposition procedures.

One of the key aspects of film deposition and production is that a film is often desired in certain areas of the substrate. This can be achieved by universally depositing the film, then removing the film from desired areas; however, masking and etching processes are often time consuming, technically challenging, and costly. Recently efforts have been made in order to pattern film deposition, either through self-assembled monolayer (SAM) masking or direct selective growth of the film material on one substrate over another.^{4,5} The latter, known as Selective Atomic Layer Deposition (SALD), allows the desired patterned film deposition to occur and does not require

subsequent etching step(s). Unlike using SAM masking, it does not require any additional materials, and therefore simplifies the post-mask etching process. SALD in this study relies solely on the preference of the growing film material on one substrate over another based on differences in material and surface chemistry along with reaction engineering. Since ALD is a surface reaction, the surface chemistry of the substrate is critical to film growth - a film material may require different induction periods for seed nucleation on particular substrates depending on the surface chemistry. Based on this concept, our studies of SALD have been carried out for the achievement of selective coatings of titanium dioxide on silicon over copper surfaces, for copper patterned silicon substrates. This has potential applications not only for the copper barrier in the semiconductor sector but also in a variety of industries, such as integrated circuit metalization, gate electrodes, and very large scale integration multilevel interconnects.⁶⁻⁸

SALD of HfO_2 on silicon (100) substrates patterned with copper has been studied previously.⁴ The e-beam was provided with a 10 kV voltage having 175 mA current resulting in 0.24 nm/sec copper deposition. In this manner, a ~ 200 nm-thick copper coating was deposited on the patterned substrates over a portion of the silicon substrate whereas the other portion (about one-half of the silicon substrate) was masked during the evaporation process in order to prepare the partially copper coated silicon substrates; next, approximately 3 nm-thick HfO_2 was deposited on the silicon portion without any trace amount of HfO_2 on the copper surfaces of the copper patterned silicon substrate. In that study, the nucleation period for HfO_2 on copper was found to be approximately the first 25 ALD cycles, which enabled the deposition of about 3 nm of HfO_2 on silicon with a growth rate from 0.11-0.12 nm/cycle.

In the present study, the early growth period and selective deposition potential of TiO_2 is investigated with the goal of introducing new feasible materials and processes into the microelectronics industry. Different surface treatment methods were employed, and findings were applied to achieve the desired selective deposition of TiO_2 on the silicon portion of copper patterned silicon substrates.

Because the copper barrier layer necessitates a thickness of ≤ 2.5 nm,¹ the nucleation period of early film growth is of utmost concern. Typically, the period of early growth is not commented on, perhaps because the later constant growth period has been of interest. However, in order to achieve selective deposition, one must focus on and study the initial growth and film nucleation period.

Materials and Methods

This research hinges on the ability to test deposition on substrates with different surface chemistries, so the

successful fabrication of such substrates was imperative. Three different substrates were used: silicon (100) with native oxide, silicon (100) with reduced oxide, and a copper patterned silicon substrate with likely native oxides on both surfaces.

Silicon (100) substrates with approximately 1.5 nm-thick native oxide were prepared by rinsing with DI water and drying with nitrogen gas.

Silicon (100) substrates with reduced/negligible oxide were prepared by using an RCA-1 clean followed by a 2% HF etch for 20 seconds, rinsing with DI water and drying with nitrogen gas. The oxide present from re-oxidation was less than 1 nm-thick. This is an estimated value, because the oxide thickness was below the resolution level of the Spectral Ellipsometer (SE) normally used to measure film thickness. Etched substrates are hydrophobic and the water rolls off of the surface, whereas un-etched substrates are hydrophilic and water has to be blown off of the surface with nitrogen. It was assumed etching was complete if the substrate was hydrophobic after 20 s. Later, it was found that much of the re-oxidation was a result of storing the substrates in DI water in between etching and deposition (a period of no more than a few hours). Omitting the DI water rinse and storage would result in a significantly smaller oxide layer from the oxygen/humidity in the ambient air.

Patterned substrates were produced by etching a silicon wafer in a 2% HF solution for 20 seconds, rinsing with DI water and drying with nitrogen gas. One half of the substrate was then covered with a scrap piece of silicon and taped in place with thermal tape. The copper pattern was created using an electron-beam evaporation procedure described earlier,⁴ which produced a copper film approximately 200 nm-thick on the uncovered half of the silicon substrate. The native oxide layer on the patterned substrates was approximately 1.5 nm-thick on silicon and 2 nm-thick on copper. Prior to ALD, the patterned substrates were rinsed with DI water and dried with nitrogen gas.

The ALD reactor setup consisted of a hot-walled reactor, three metal precursors and DI water in an ice bath to provide water vapor as the oxidizing precursor. Nitrogen was supplied as both purging and carrier gas, and

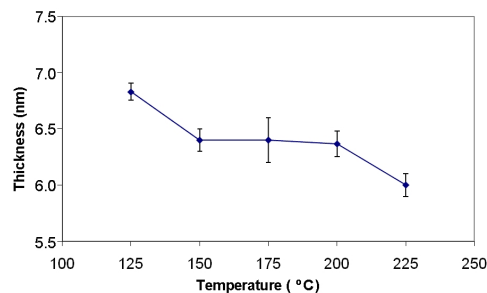


FIG. 1: Temperature dependence of TiO_2 films grown on silicon substrates after 50 cycles at 0.18 torr.

a vacuum pump evacuated the ALD chamber down to 0.01 torr before deposition in order to remove any gas or moisture residues left in the chamber. Further details of the setup can be found elsewhere.⁹ The titanium precursor used was tetrakis-diethyl(amino) titanium (TDEAT) provided by Air Liquide. At least one test sample of TiO₂ on silicon (100) with native oxide was taken every day before experimental runs to ensure the proper operation of the reactor and to flush out any possible contaminants accrued during the night.

The temperature-independent deposition window for TiO₂ was tested by subjecting silicon (100) samples with native oxide to 50 cycles at temperatures ranging from 125 to 225 °C, in increments of 25 °C. Film thickness was measured with a spectral ellipsometer (J. A. Woolam Co., Inc., model M-44); after a sample is measured, a model is constructed to describe the sample (the model is used to calculate the predicted response from Fresnel's equation which describes each material with thickness and optical constants). For each thickness determination, 3 measurements across the film were made with mean values representing the film thickness. Thin film deposition runs were carried out within the temperature-independent window and a pressure of ~ 0.18 torr.

The reactor was recently modified; therefore, a verification of the long-term growth rate of TiO₂ on silicon was necessary. Silicon (100) with native oxide was deposited for 50, 100, and 150 cycles - after this many cycles, the nucleation time is complete and growth has entered the constant region. The reactor successfully produced TiO₂ films at a rate of ~ 0.11 nm/cycle.

Once it was determined that deposition was proceeding normally, attention shifted to the early growth and nucleation period of TiO₂ on silicon. TiO₂ was deposited on silicon (100) substrates with native oxide and with reduced oxide at 200 °C and tested after 0, 5, 10, 15, 30 and 50 cycles. Film thickness was measured using the spectral ellipsometer (SE), and composition was probed using X-ray Photoelectron Spectroscopy (XPS). Model information for the XPS and SE can be found elsewhere.⁴

Patterned substrates were tested after 15, 20, 25 and 30 cycles of TiO₂ deposition at 175 °C. Copper and silicon portions were measured for each cycle number and compared. SE and XPS were employed to analyze the resulting films.

The SE used one of three computer models to calculate film thickness, depending on which substrate was used for deposition. Films on silicon (100) with native oxide were measured with a model for TiO₂ / SiO₂ / Si (three layers). Films on silicon (100) with very little native oxide were measured using a model for TiO₂ / Si. For the measurement of TiO₂ on substrates consisting of approximately 200 nm of copper on silicon, a specially calibrated Cauchy model (Cauchy/Cu) was required to achieve proper fit. This model was designed to measure films on conductive metal substrates due to the different optical properties of metals from silicon. In this case, the thickness calibration was not capable of distinguishing

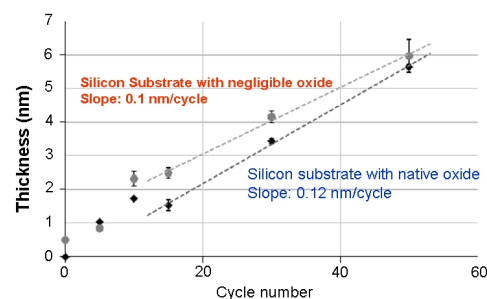


FIG. 2: The early TiO₂ growth period on Si (100) with native oxide and with negligible native oxide is shown.

TiO₂ deposition rates are ~0.11 nm/cycle and 0.10 nm/cycle, respectively, while the nucleation time is negligible for both surfaces. Deposition temperature is 175 °C.

copper oxide from titanium dioxide. This required that the copper oxide be measured before deposition, and the thickness of TiO₂ after ALD was calculated by subtracting the initial oxide thickness from the final total film thickness.

Results and Discussion

The optimum temperature window for TiO₂ deposition is from 150 to 200 °C - in this temperature range, the film deposition rate is independent of reactor/substrate temperature (Fig. 1). Temperatures below 150 °C result in a larger growth rate due to likely excess precursor adsorption onto the surface. Substrate temperatures above 200 °C result in a lower growth rate perhaps because chemical bonds are unstable at those higher temperatures, causing re-evaporation of the precursors from the substrate surface.¹⁰

ALD of TiO₂ on silicon (100) substrates with native oxide resulted in an average growth of 0.11 nm/cycle, while no nucleation time was observed (Fig. 2). Similarly, silicon (100) substrates with reduced oxide produced films at a rate of 0.10 nm/cycle and no observed nucleation time. The difference in initial growth between silicon (100) with native oxide and with reduced oxide is within the experimental uncertainty of the experiments. At very low cycle numbers (film thickness less than 1 nm-thick, i.e., after about 5-10 cycles), the SE results alone could not be effectively used for analysis, because the measurements were near the detectability of the SE. Indeed, the data points from 0 to 10 cycles in Fig. 2 may not represent the actual film thickness and growth rates and are therefore concluded from data for 15 - 50 cycles.

XPS results for all samples showed Ti 2p orbitals with the standard line separation of 5.7 eV, corresponding to titanium in the Ti⁴⁺ oxidation state. This shows formation of TiO₂ films.

The deposition of TiO₂ on patterned substrates showed

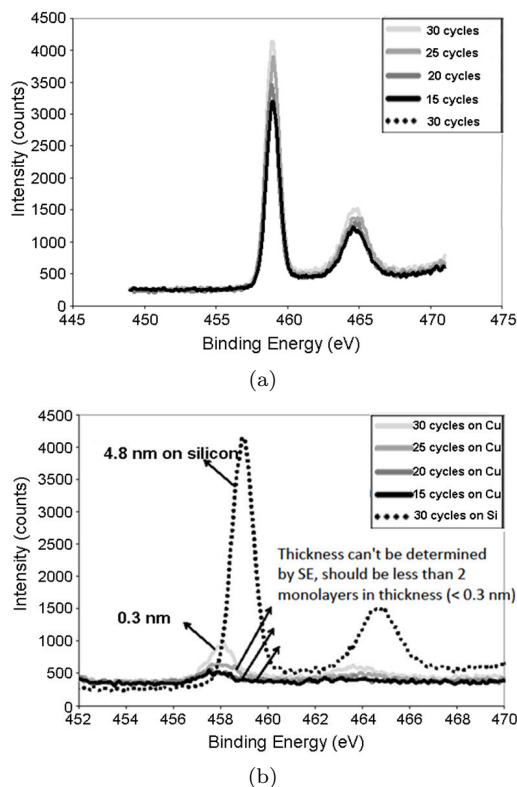


FIG. 3: a) XP spectra of Ti 2p on the silicon portion of the copper-patterned silicon substrate are shown. The signal is indicative of Ti^{4+} , showing successful formation of TiO_2 . The signal steadily increases with the number of cycles, showing the increasing growth of film on the silicon portion of the substrate. Deposition temperature is 175 °C; b) Ti 2p XP spectra on the copper side of the patterned silicon substrate. These also indicate TiO_2 formation. However, the signal is very small and it does not change between 15 and 20 cycles. The Ti 2p signal after 30 cycles on silicon is included for magnitude comparison. The horizontal shift in signal is due to the different substrates. Deposition temperature is 175 °C.

preferential deposition on silicon and not on copper for the first 15-20 cycles - a very thin layer of TiO_2 was de-

tected by XPS after 15 cycles on copper, but was too thin to be detected by the SE and was likely less than 1-2 monolayers thick (Fig. 3). The XPS signal did not increase between 15 and 20 cycles, indicating the nucleation period on copper is approximately 15-20 ALD cycles. In contrast, the TiO_2 film on the silicon portion of the substrates was approximately 2.5 nm thick after 15 cycles. Selective deposition of TiO_2 on silicon over copper was indeed achieved at the conditions used in this study. This degree of selective growth could likely satisfy the requirement set forth for the copper barrier layer.

Conclusions

Based on results from ellipsometry and XPS, the nucleation time for growing TiO_2 by ALD on silicon (100) is negligible, regardless of the presence of native oxide. The initial growth rates are ~ 0.11 nm/cycle on silicon with native oxide and 0.10 nm/cycle on silicon with negligible native oxide. Selective deposition of TiO_2 thin films on copper patterned silicon substrates with preference on silicon over copper was achieved. This selective ALD occurs for the first 15-20 cycles of deposition, however - after that, a film begins to grow on copper. During the first 15-20 cycles, a minute amount of TiO_2 may form on copper, with a thickness of less than 1-2 monolayers (< 0.3 nm-thick).

Future experiments will involve probing the patterned substrate surfaces with Scanning Electron Microscopy (SEM) and applying effective surface treatments to substrates in order to completely remove the oxide layer while minimizing reoxidation. A greater degree of selectivity may be expected by applying the proper surface treatment prior to deposition.

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