Selective Atomic Layer Deposition of TiO$_2$ on Silicon/Copper-patterned Substrates

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As microelectronic devices shrink, thinner diffusion barrier layers are needed to separate the copper and silicon substrates while leaving the copper vias open for conduction. Selective atomic layer deposition (ALD) of titanium dioxide (TiO$_2$), a good barrier layer, onto silicon was studied by minimizing the exposure time to air of these substrates immediately before deposition. The minimized exposure time mimicked industrial conditions, where waiting before deposition is costly. Tetrakis(diethylamido)titanium (TDEAT) was used as the precursor, and water was the oxidizing agent. TDEAT was first deposited on silicon wafers using ALD to verify a steady, linear growth rate reported in the literature, and the measured rate of 0.9 ± 0.1 Å/cycle is consistent with values previously reported. Minimized exposure to air had no effect on the growth rate of TiO$_2$ on silicon, and the effect on copper has yet to be determined.

Keywords: selective atomic layer deposition, TDEAT, diffusion barrier layer, hot-wall reactor

Introduction

The demand for smaller and faster microelectronic devices necessitates thinner diffusion barrier layers between the silicon semiconductor and copper conductor layers to prevent them from diffusing into each other and increasing resistivity along conducting pathways. To avoid the blurred silicon/copper interface, transition metals such as titanium and hafnium are being studied as ultrathin conductive barrier layers.  

Titanium dioxide has a high dielectric constant and can be deposited in ultrathin films on silicon without diffusing into it as copper does, making it an ideal candidate for this application.$^{1,2}$

However, the copper vias in these devices must remain open to facilitate conduction between the different levels of electronic components. Therefore, it is important to selectively deposit titanium on only the silicon and to ensure that the copper conducting pathways remain open and available to stack, as seen in Figure 1:

To achieve a desired diffusion barrier layer thickness, barrier layers may be deposited using atomic layer deposition (ALD), a highly-controlled method of depositing a layer on a substrate. In this four-step process, a precursor complex introduces the metal to be deposited on the substrate, and the metal binds to the hydroxyl groups of the native oxide on the substrate. An inert carrier gas purges the excess precursor, bubbles an oxidizing agent (usually water or ozone) through to react with the chemisorbed precursor ligands, and purges the excess oxidizer. ALD is self-limiting and it allows reactions according to the feed species sequencing; it is a reliable method of conformally attaining a layer of a specific thickness.$^{3-5}$

As per the first step in ALD, there needs to be a layer of oxide on the substrate in order for the barrier layer to attach to the substrate. Both copper and silicon oxidize in air, forming a layer of native oxide, but copper oxidizes more quickly than silicon does; after 24 hours of exposure to air, 1 nm of native oxide formed on a copper-coated silicon wafer, while a negligible amount of native oxide
formed on a plain silicon wafer, as measured using a spectral ellipsometer. In order to encourage the barrier layer metal to selectively deposit on silicon and not copper, the native copper oxide must be minimized. Chemical reductions using ethanol, formic acid, and hydrogen plasma have been proven to reduce native copper oxides. Recent studies done by Lee et al. and Tao et al. have indicated that vacuum transportation of the samples and minimizing the number of ALD cycles are two effective ways to physically postpone deposition on copper. Although Tao et al. found that TiO$_2$ films did not grow on copper until after at least 50 ALD cycles, the samples used in that experiment were exposed to air for 24 hours prior to deposition, an impractical constraint for industrial fabrication.

It is important to remark that in this experiment, the exposure time to air of silicon/copper substrates was minimized to better simulate realistic conditions, where waiting for 24 hours is a costly option, and the effect of reduced air exposure on the selectivity of TiO$_2$ deposition was studied. Tetrakis(diethylamido)titanium (TDEAT) was used as the precursor for the deposition of a TiO$_2$ film, nitrogen gas was used as the carrier gas, and water was used as the oxidizing agent. The thicknesses and growth rates of the deposited layers were analyzed and compared to those of layers deposited after 24-hour air exposure to determine the effect of minimizing air exposure of the samples before ALD.

**Experiment**

Prior to TiO$_2$ deposition on silicon/copper wafers, TiO$_2$ was deposited onto pure silicon wafers to investigate the linear growth rate established in the literature. Silicon wafers were prepared for deposition with a deionized water rinse and nitrogen drying. They were then loaded into the ALD reaction chamber, one at a time. Figure 2 shows a schematic of the custom-built ALD setup:

Nitrogen served as both the purge gas as well as the carrying gas for the precursor and the oxidizer. Water served as the oxidizer and was kept in an ice bath that was refilled daily to ensure that each pulse contained the same amount of oxidizer. The TDEAT precursor vessel, which was in precursor position A, was kept at 65 °C, the reactor temperature was 200 °C, and the reactor resting pressure was 0.178 torr. The precursor pulse time was 6 plugs, the first purge duration was 10 seconds, the water pulse was 50 milliseconds, and the second purge duration was 20 seconds. These times were previously determined to be most effective in providing the appropriate amount of precursor, nitrogen, and water without leaving extra reactants in the system. The number of ALD cycles varied from 10 to 75 cycles, and the deposition layer thickness was measured using a spectral ellipsometer (J.A. Woollam Col, Inc., model M-44, Lincoln, Nebraska, USA), taking measurements at four different locations on each sample. A constant growth rate at each number of cycles tested was achieved. These conditions apply to all results discussed below.

Once a constant and consistent growth rate was achieved, four silicon/copper samples were prepared. The silicon wafers were washed as before, and then dipped in 1% HF solution for 10 seconds to remove native oxide. Half of each wafer was masked by a silicon piece taped with heat-resistant tape, and the wafers were coated with about 200 nm of copper using electron beam evaporation (Varian model no. NRC3117) as illustrated in Figure 3:

Immediately following the copper coating procedure, the masks were removed, and the samples were loaded into the reactor as before, with the number of cycles varying from 5 to 30. All conditions, including the precursor and reactor temperatures, remained the same. The deposition layer thicknesses were measured with the ellipsometer as before, again taking measurements at four points per sample.
FIG. 4: The growth rate of TiO$_2$ on silicon wafers with negligible native silicon oxide is shown for 10, 25, 50, and 75 cycles under the conditions described in the experimental section above. The error bars represent the variation in thickness in each sample.

Results and Discussion

The results of the TiO$_2$ deposition on pure silicon wafers for 10, 25, 50, and 75 ALD cycles can be seen in Figure 4, which indicates a linear rate of TiO$_2$ growth and a constant growth rate of $0.9 \pm 0.1$ Å/cycle that is independent of the number of cycles run. This growth rate is consistent with prior studies.\(^1,2,7\)

The growth rate of TiO$_2$ on the silicon halves of the silicon/copper wafers is shown in Figure 5. As can be observed, a growth rate of $1.2 \pm 0.2$ Å/cycle is linear with the number of cycles used and this is in general agreement with the data presented in figure 4, indicating that a shorter air exposure period had no significant effect on the process of atomic layer deposition of TiO$_2$ on silicon. This result is significant, for it shows that the desired product, TiO$_2$-covered silicon, is still attainable at the same rate with a shorter waiting time before deposition. Based on our results, the trend line was anchored at the origin. Further, when compared with data reported in the literature, our findings are consistent with previous data on the ALD of TiO$_2$\(^1,2\). Although Tao cites that a nucleation period for 5 cycles or fewer can be observed,\(^1\) no data at less than 5 cycles was obtained during this study. More research is needed on low-cycle studies and nucleation periods. However, once a TiO$_2$ layer begins to deposit, it grows at the ALD rate obtained and reported in the literature.\(^1,2,7\)

Following this set of experiments, the deposition rate of TiO$_2$ on silicon became erratic, eventually resulting in zero deposition. This led to troubleshooting each component of the ALD system, beginning with the simplest aspects to check and progressing to more involved parts:

Temperature. The precursor, valve, leg, and reactor temperatures matched those specified in the Experimental section above. It is important that the temperature increase along the precursors path from the vessel to the valve and through the leg to the reactor to prevent cold spots and precursor condensation. The oxidizer is kept in an ice bath to ensure that a constant amount of water is in each pulse, and the ice is refilled daily.

Pressure. Both the reactor pressure and the gauge on the volumetric flowmeter just upstream of the reactor matched those of the successful experiments. The reactors resting pressure is $23.6 \pm 0.13 Pa$, and the pressure through the flowmeter is 15 standard cubic centimeters per minute.

Purge gas and oxidizer levels. The next aspect of the system to check was the nitrogen and oxidizer levels. However, after replenishing both sources, experiments continued to result in zero deposition of TiO$_2$ on silicon.

Ellipsometer. To eliminate the possibility of the problem lying in the ellipsometer, a previously-measured TiO$_2$/silicon sample was remeasured using the ellipsometer. A matching result to that obtained at the beginning of the experiments verified that the problem was in the reactor.

Reaction condition variables. As a last attempt to solve the problem without taking apart the reactor, the number of precursor plugs was increased to push more precursor through each ALD cycle. The number of cycles was also increased to give more deposition time, and the system temperatures were increased to promote precursor vaporization. Despite these variations, the deposition rate remained at zero.

Precursor. The precursor vessel was removed, and it was determined that the precursor had solidified. However, the problem persisted after replacing the vessel with one filled with liquid TDEAT. The new TDEAT precursor was then replaced with tetrakis(diethylamino)hafnium (TDEAH) to isolate the problem: if there was successful deposition, the problem lay in the TDEAT valve; if not, the problem lay in the line to the reactor. However, after the reaction, strong vapors and rainbow-patterned substrates indicated that...
a high enough pressure in the TDEAH vessel had probably caused excess precursor to push through a blockage in the line. After purging and cleaning the system, the TDEAT precursor was reinstalled in a different position, and efforts are still underway to determine the cause of continuing near-zero deposition.

Summary-Conclusion

Minimizing air exposure time of silicon/copper-patterned substrates prior to ALD deposition of TiO$_2$ thin films does not affect the growth rate of TiO$_2$ on silicon as determined in the literature. The measured value of 0.9 ± 0.1 Å/cycle and the linear relationship between the number of ALD cycles and the film thickness are consistent with previously-reported work for 10 or more cycles. The minimal air exposure just prior to ALD does not jeopardize TiO$_2$ growth on silicon, the desired product, indicates that this process can be an effective way of selectively depositing TiO$_2$ thin films on silicon in an industrial environment, where the stages of microelectronic fabrication take place in rapid succession. Due to the constraints of the system and the extensive troubleshooting of the reactor setup, there is not enough data yet to determine the effect of minimizing air exposure on the growth of TiO$_2$ on copper. Such research is ongoing. Above all, it is important to note the inevitability of experimental design setbacks and the importance of troubleshooting and problem-solving in research.

Further research includes studying the effect of minimizing air exposure on the TiO$_2$ nucleation period that appears to elongate when exposure is minimized. Work in this area could expedite low-cycle depositions as enhance selectivity of deposition. Another path of future research is an in situ reduction of native copper oxide, such as an ethanol pretreatment, that would combine already-known copper oxide reduction methods with ALD to reduce copper oxide as it forms.

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