Development of a High and Low Frequency Recipe for PECVD and Characterization of Silicon Dioxide Films Produced in the UC Berkeley Marvell Nanofabrication Lab

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Abstract:

A high and low frequency (HiLo) recipe for electric field dominant plasma enhanced chemical vapor deposition (PECVD) was developed that produced a comparable purity to thermal oxide. Four other types of oxide films, using various deposition methods, were also characterized in order to compare different properties of the films to each other and the new PECVD recipe. These other methods included thermal growth (in tystar3), Low Temperature (in tystar12), High Temperature (in tystar17), and Electron Cyclotron Resonance magnetic field dominant PECVD (in the PQECR). In this study, the comparative properties included the index of refraction, oxide charge, surface roughness, stress, and etch rate. A conclusive ranking of the different oxides was determined for each property, and an optimal HiLo recipe was developed through various trial recipes, taking into account film uniformity and the index of refraction.

I. INTRODUCTION

Silicon dioxide is a very important component of electronic devices, functioning as an insulator in the metal oxide semiconductor. Oxide is also a very versatile film in the semiconductor industry, with many uses in a nanofabrication lab; thus, its properties and characteristics are important to understand. Wet oxidation atmospheric furnaces commonly produce some of the best quality oxides, running at 1050 °C and atmospheric pressure. Unfortunately, many device technologies cannot withstand such high temperatures; plasma enhanced chemical vapor deposition (PECVD) is a viable alternative.

The Plasmalab 80 Plus (referred to as Oxford2 in the lab) PECVD machine has a common PECVD set up[1], with a parallel plate capacitor and low and high frequency generators. Unlike some other PECVD processes, this one is electric field dominated instead of magnetic field dominated. The neutral gases are flowed from the top electrode plate and the reaction happens between the two plates, depositing a film on a substrate on the bottom plate. The benefit of this machine is that it deposits oxide at 350 °C, which is more reasonable for many device technologies. However, the reaction of SiH_4 and N_2O results in unwanted hydroxyl groups in the oxide that interrupt the silicon oxygen network.[2] In order to remedy this impurity, the user has an

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[1] R. Curley, T. McCormack, and M. Phipps, *Low-pressure CVD and Plasma-Enhanced CVD.*
[2] B. Diaz, C. Dominguez, A. Llobera, M. Riera, J. A. Rodriguez. Journal of Applied Physics. 93, 5125 (2003).

option to introduce a low frequency (LF) conduction current to alternate with the high frequency (HF) deposition plasma. The LF conduction current has a low enough frequency to overcome the inertia of large atoms, such as argon, and has the capacity to move them. With the argon now mobile, it collides with the layer of silicon dioxide deposited on the wafer, ideally knocking the H or OH off in order to free up an oxygen or silicon atom to form more pure silicon dioxide.[3] The reaction happening between the SiOH and argon is:

$$2SiOH_{(s)} + Ar^{+} \rightarrow Si\text{-}O\text{-}Si_{(s)} + H_2O + Ar^{+}$$

The property used to determine the film's purity was its index of refraction. Since the index of refraction is a material specific property, it is a good indicator for what material is being measured. The index was measured on an ellipsometer and was used to strategically determine the various trial recipes in this study.

In addition, in order to get a more comprehensive characterization of this PECVD film, 4 other films from various deposition methods were characterized for comparison purposes. These films were thermal oxide, low temperature oxide (LTO), high temperature oxide (HTO), and electron cyclotron resonance magnetic field dominated PECVD oxide.

II. EXPERIMENTAL

A. Oxford2

In order to determine the recipe that would deposit an oxide comparable to a thermal oxide, the standard oxide recipe with no low frequency conduction current was deposited for baseline purposes. When looking through the various recipes already created in the Oxford2 memory, one was found with a "HiLo" label. Based upon these preliminary numbers, a starting HiLo recipe was created to begin the study.

After analysis of both the standard and starting oxides, with the most focus on the index of refraction, the recipe was changed. If the index was lower, the assumption was that there were hydroxyl groups within the oxide, which warrants a longer low frequency period to knock off more impurities. If the index was higher, the assumption was that larger atoms, such as extra silicon or argon, were being incorporated into the oxide, which warrants a decrease in the low frequency time to incorporate less argon.

The recipe was altered with high frequency pulse time to low frequency pulse time ratios of 26:6, 26:12, 26:18, 26:13, 18:8, 21:10, and 52:24 (secs). For all of the recipes, the HF and LF power were set to 25 W, temperature to 350 °C, pressure to 0.9 Torr, and time to 20 minutes. After every deposition, the oxides were measured for their indexes of refraction, oxide charge, surface roughness, and stress; an ellipsometer, surface charge analyzer, white light interferometer system, and thin film stress measurement system were used to measure these properties,

[3] E. S. Adil, S. M. Han. Journal of Vacuum Science and Technology A. 14, 2062 (1996).

respectively. To determine the etch rate of the oxides, 5:1 buffered HF and deionized water were used. Portions of the wafer were submerged in the HF for 5-16 seconds, in various steps with varying times, and measured for film thickness on the ellipsometer.

B. Other Oxides in the Lab

To aid in the characterization of the new PECVD oxide, it was compared to the others in the lab. A thermal oxide was grown in an atmospheric non-MOS dry/wet oxidation and anneal tystar furnace at 1050 °C and atmospheric pressure (760 Torr). LTO was deposited with a non-MOS LPCVD tystar furnace dedicated to undoped and phosphorus doped low temperature oxides at 450 °C and 300 mTorr. HTO was deposited with a non-MOS LPCVD tystar furnace dedicated to low stress nitride and high temperature oxide at 920 °C and 400 mTorr. The backs of these wafers (those with furnace oxide) were dry etched with SF_6 and O_2, in order to get the most accurate stress measurement; by removing most of the oxide on the back of the wafer, only the oxide on the front would put stress on the wafer. The oxide made with Electron Cyclotron Resonance PECVD was deposited with a recipe of 36 sccm of O_2 flow, 142 sccm of SiH_4, and 129 sccm of argon at 19 °C and 32 mTorr. All four of these oxides were measured for the same properties as the PECVD oxide, using the same tools and methods.

III. RESULTS AND DISCUSSION

A. Oxford2

Based on the results of the study, alternating high and low frequency pulses do seem to be effective in creating more pure films. The standard oxide recipe produced a film with an index of 1.322 and the first HiLo recipe, with a high frequency pulse of 26 seconds and a low frequency pulse of 6 seconds, produced an oxide with an index of 1.4197. This increase in index, in the direction towards the standard thermal oxide's 1.4622, indicated that less hydrogen was being incorporated into the film, and thus the oxide was more pure. In addition, the index still being lower than that of thermal oxide indicated that more hydrogen needed to be removed (essentially with the argon "hammer" at low frequency), so the low frequency pulse needed to be increased.

The next recipe, with a HF pulse of 26 seconds and a LF pulse of 12 seconds, produced an oxide with an index of 1.4562. Although it is worthy to note that the accepted index of stoichiometric silicon dioxide is 1.4570, the new recipe's value was still shy of the thermal oxide's and therefore the low frequency pulse had to be increased again. With a HF pulse of 26 seconds and a LF pulse of 18 seconds, the recipe produced a film with an index of 1.4843. Assuming a linear relationship with the index being a function of the LF value, the LF value was calculated for an index of 1.4622 and resulted in 12.9, so the next recipe had a HF pulse of 26 seconds and a LF pulse of 13 seconds. Unfortunately, the index was 1.4732.

With the PECVD machine taking only whole numbers for the pulse times, the next step was to adjust both values, keeping a ratio of 26:12. The recipe with a HF pulse of 18 seconds and a LF pulse of 8 seconds was tried twice, but both times resulted in an incomplete deposition, with films only 1000-3000 A thick. With such a low HF pulse time, it is hypothesized that the high frequency plasma did not have enough time to stabilize after the transition from the low frequency. By the time that the plasma was out of the transient state, the HF pulse was almost over. In attempts to remedy this issue, the HF pulse was increased to 21 seconds and the LF pulse to 10 seconds, but still resulted in a nonuniform film. A recipe with a HF pulse of 52 seconds and a LF pulse of 24 seconds was also deposited, but resulted in a nonuniform film as well. It is hypothesized that this nonuniformity is due to the extended LF pulse, which would have allowed too much time for the argon ions to knock into the film; instead of merely removing the impurities, the argon may have become incorporated in the film, causing the nonuniformity.

The recipe that resulted in the best index of 1.4562, with a HF pulse of 26 and a LF pulse of 12, also had an oxide charge of 1.09E12 q/cm^2, a compressive stress of -162 MPa, average surface roughness of 1.44 nm, and an etch rate of 655 Å/s. In relation to the other trial HiLo recipes, this one also had the lowest stress, an average surface roughness, an oxide charge on the higher end (some had charges of E11), and a higher etch rate.

B. Other Oxides in the Lab

The results for all of the properties for the various types of oxide deposition can be found in Table 1. It should be noted that with the exception of the PECVD wafers (from the PQECR and Oxford2), which did not have any oxide deposited on their backs, all other wafer backs had to be dry etched in order to alleviate any stress that a film on the back would add. As a result, the other properties may have been affected by this dry etch through the incorporation or removal of atoms. It should also be noted that there is not an accurate stress measurement for the PQECR film, as the thin film stress measurement system does not measure stresses under 10 MPa. Such a low stress is most likely a result of a low thermal stress due to the small change (a few degrees) in temperature that the wafer experienced.

Table 1

	Index of Refraction	Surface Roughness (nm)	Oxide Charge (q/cm^2)	Stress (MPa)	Etch Rate (Å/s)
Thermal Oxide	1.4622	2.88	-2.37E10	-258	228
HTO	1.4564	1.24	-7.41E10	-110	605
LTO	1.4498	1.40	3.75E11	-85	653

Oxford2 Oxide (Best HiLo Recipe)	1.4562	1.44	1.09E12	-162	655
PQECR Oxide	1.4330	3.41	1.99E12	<10	2223

IV. Summary and Conclusion

A. Oxford2

Based on the results, the hypothesis of adding a low frequency pulse to get the desired hammer effect and a better purity, shown in the index of refraction, is true. Using a PECVD tool, such as the Plasmalab 80 Plus, or as it is known in the Marvell lab, Oxford2, a relatively pure oxide can be created using a combination of high and low frequency pulses. With a high frequency pulse of 26 seconds and a low frequency pulse of 12, an index within 0.05% of the index of stoichiometric silicon dioxide and 0.4% of the index of thermal oxide can be obtained. There are also limitations to what values can be used in this ratio to produce a uniform film. Values lower than 26 and 12 result in nonuniformity due to extra time needed for plasma stabilization in the transient state, while values higher than 26 and 12 also result in nonuniformity due to an extended low frequency period which allows unwanted atom incorporation.

B. Comparing All Oxides in the Lab

In terms of all of the oxides in the lab, now including the improved PECVD one, they all have their stronger and weaker properties relative to one another. Table 2 shows the best deposition method for a particular desired property. The tools cannot be ranked for stress because various stresses are desired depending on individual process needs. In addition, these tools are ranked under the assumption that the index of thermal oxide, the lowest surface roughness, the smallest oxide charge, and the lowest etch rate are desired. Depending on the specific properties desired, this ranking may not be applicable.

Table 2

	Best Tool	2nd Best	3rd Best	4th Best	5th Best
Index of Refraction	Wet Oxide Furnace (tystar3)	HTO Furnace (tystar17)	Oxford2	LTO Furnace (tystar12)	PQECR
Surface Roughness	HTO Furnace	LTO Furnace	Oxford2	Wet Oxide Furnace	PQECR

	(tystar17)	(tystar12)		(tystar3)	
Oxide Charge	Wet Oxide Furnace (tystar3)	HTO Furnace (tystar17)	LTO Furnace (tystar12)	Oxford2	PQECR
Etch Rate	Wet Oxide Furnace (tystar3)	HTO Furnace (tystar17)	LTO Furnace (tystar12)	Oxford2	PQECR

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