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Sacrificial Hardmask ALD with Hydrogen Peroxide: Comparative Study of Low Temperature Growth and Film Characteristics for TiO_2 and Al_2O_3

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ABSTRACT

Continued reliance on 193nm immersion lithography with multiple patterning is becoming much more difficult as line widths decrease. With the use of Self-Aligned Quadruple patterning and related patterning schemes, it is critical to minimize variability, where high quality films must be deposited and etch rates must be very precise. To this end, a better understanding of spacer material properties must be obtained. Initial work has been performed to examine the resulting film properties for TiO_2 and Al_2O_3 spacer materials deposited by low temperature ALD with the use of various oxidants (H_2O_2, H_2O, O_3). Improved film quality has been demonstrated for films deposited with H_2O/H_2O_2 mixtures used as the oxidant. Key to advanced patterning applications is that improved etch resistance is achieved for both Metal Oxide materials. Also significant with regard to multiple patterning is that higher growth rates are obtained at reduced temperatures, enabling lower process temperatures for underlying sensitive materials. The all thermal nature of these deposition methods points toward improved film conformality on 3-Dimensional structures. Improved etch rates and improved electrical properties reflect overall improvements in Metal Oxide dielectric film quality with the use of Hydrogen Peroxide.

Keywords: Multiple Patterning, Hydrogen Peroxide, ALD, Hardmask, Spacer, TiO_2, Al_2O_3, Area Selective Deposition

1. BACKGROUND AND INTRODUCTION

Emerging memory and logic devices require precise lithography definition in order to achieve high storage density as well as decreased line widths. This presents a challenge to optical lithography, which does not have the resolution to meet critical dimension requirements. Double (SADP, SDDP) and Quadruple (SAQP) patterning technologies are being developed to meet the sub 10nm critical dimension requirements.[1] (Figure 1) Key to success of these approaches is deposition of sacrificial spacers and hard masks (TiO_2, SiN, SiO_2, Al_2O_3), where precise etch rates of materials must be intrinsically engineered into the deposited film. Atomic Layer Deposition (ALD) is particularly suited for material fabrication because it allows the formation of ultra-thin films with angstrom level resolution via cyclical layer-by-layer deposition. Control of ALD parameters and use of novel precursors is instrumental in defining feature size and material properties.[2]

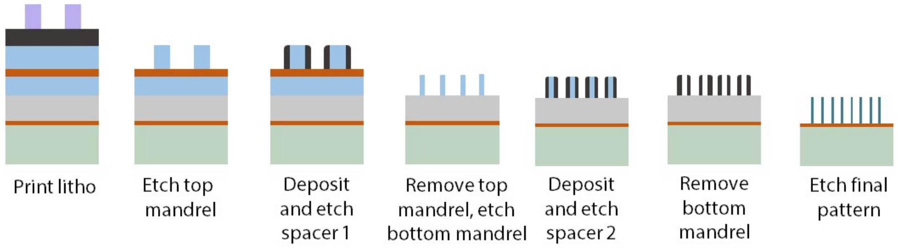

Figure 1. Scheme depicting general SAQP patterning approach.

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One challenge is that low temperature ALD is required. This is due to material properties of underlying layers such as photoresist or other carbon materials which may decompose or undergo irreversible property changes at temperatures above 200° C. Problematic is the fact that ALD is typically a slow process, therefore throughput is a concern if this approach is to be viable for high volume manufacturing. Recent development efforts to overcome these constraints have focused on use of low temperature plasma ALD. In some instances, plasma species have been shown to damage the underlying surface.[3] In other instances, plasma approaches suffer from non-conformal deposition on 3-Dimensional surfaces.[4]

Our study focuses on thermal ALD with high reactivity hydrogen peroxide as an oxidant. Thermal ALD leads to improved film uniformity as gas phase materials are diffusion controlled rather than directionally limited as in the case of some plasma approaches.[4] The use of hydrogen peroxide may allow for higher deposition rates at low temperature and improved film properties when compared to other oxidants such as water or ozone.

2. EXPERIMENTAL

Atomic layer deposition (ALD) was carried out on a home-built deposition system. (Figure 2) A tube furnace was modified with the addition of a proper gas delivery system to allow for precursor pulses and ALD. A Peroxidizer 3.0 (H_2O_2/H_2O) gas delivery system was obtained from RASIRC, Inc. (San Diego, CA, USA) and used to deliver the H_2O_2/H_2O oxidant mixture. Tetrakis dimethylamido Titanium (TDMAT) (Tri Chemical Laboratories, Yamanashi, Japan) was used as the metal TiO_2 precursor. Trimethyl Aluminium (TMA) (Ube Industries, Minato, Tokyo, Japan) was used as the metal Al_2O_3 precursor. Ozone was delivered at 6% concentration with the use of a model SG-01A-PSA4 O3 generator (Sumitomo Precision Products, Amagasaki, Hyogo, Japan). ALD experiments were carried out in the temperature range of 100-350C. The total chamber pressure was kept constant at 10 torr for all precursor materials.

Several metrology methods were used to characterize the resulting deposited films. Ellipsometry was carried out on a model GES5E Ellipsometer (SEMILAB, USA) at lambda = 632nm. Film composition was determined by X-RAY Photoelectron Spectroscopy (XPS) on a PHI Quanter II (ULVAC-PHI, Chigasaki, Kanagawa, Japan) at a sputter rate of 5nm/min (normalized with SiO2). CV measurements were carried out on a model SSM 495 Mercury Probe CV System (Solid State Measurements, Inc, Pittsburgh, PA, USA). Sample size was 380x380 mm with a film thickness of 0.1 micrometer on a p-type Si substrate (1-100 ohm/cm) where 10 points were taken.

Wet etch rates (Buffered HF resistance) was carried out with the use of 7.14% (BHF) (Morita Chemical Industries, Osaka City, Japan). Dip time was 2 min for TiO_2 and 20 seconds for Al_2O_3. Film thickness was measured by Ellipsometry before and after dip.

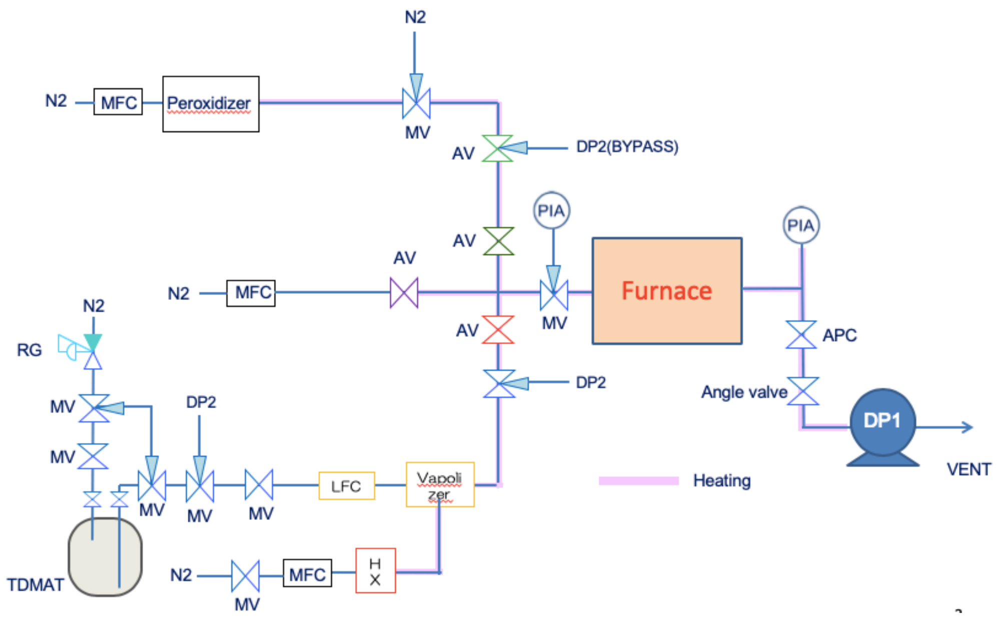


Figure 2. Atomic Layer Deposition System.

3. RESULTS AND DISCUSSION

3.1 Hydrogen Peroxide Delivery System

Hydrogen Peroxide Vapor (HPV) is non-trivial to deliver into typical ALD process chambers. Vaporization of common water/hydrogen peroxide mixtures by common bubbler methods leads to extremely low concentrations (H_2O/H_2O_2 ratio >100:1). This is due to the inherent high vapor pressure of water (20 torr H_2O vs 0.9 torr H_2O_2 at room temperature) where vapor concentrations in the gas headspace are dictated by the mole fraction in the liquid solution multiplied by the inherent vapor pressure of each component (Raoult's Law).[5] Therefore, commonly used 30% H_2O/H_2O_2 liquid bubbler leads to typical gas phase ratios of H_2O/H_2O_2 of 100 or greater.

A new method for gas delivery of high peroxide concentration H_2O/H_2O_2 mixtures has been developed.[6] This method utilizes in situ concentration methods and a membrane delivery system to deliver high concentration H_2O/H_2O_2 gas mixtures of 4:1. Up to 5% hydrogen peroxide concentration can be delivered in a carrier gas which renders this material viable for Atomic Layer Deposition.

3.2 Material Property Optimization

The etch-resistant properties of TiO_2 make it an attractive candidate for advanced patterning applications.[7,8] Here, low temperature deposition is required (100-250° C). Key required properties of the resultant film include film density and wet etch rate, where low TiO_2 wet etch rates are needed for selective etching of SiO_2 versus TiO_2. Moreover, high growth per ALD cycle (GPC) is needed for increased manufacturing throughput.

For TiO_2 ALD, we began our study with tetrakis(dimethylamino)titanium (TDMAT) precursor. Our initial goal was to compare the growth and film properties of Ozone (O_3) vs Water (H_2O) vs H_2O_2/H_2O mixtures. Initial results show that H_2O_2/H_2O mixtures can be grown at growth rates (GPC) 10-20% higher than H_2O and 20-50% higher than O_3. (Figure 3) More significantly, the H_2O_2/H_2O mixtures generate films with wet etch rates (WER) much lower than traditional oxidants. At 125° C, over 50% reduction in WER was observed for H_2O_2/H_2O vs H_2O and over 70% reduction was observed for H_2O_2/H_2O vs O_3. (Figure 4) Therefore under thermal conditions at low temperature, TiO_2 films grown with the use of H_2O/H_2O_2 mixtures may provide improved etch selectivity and increased manufacturing throughput.

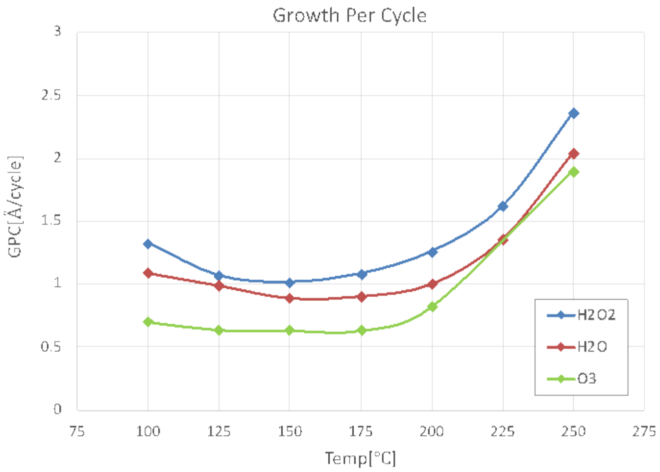


Figure 3. Higher growth per cycle GPC at various temperatures for H_2O_2/H_2O mixtures vs water and ozone.

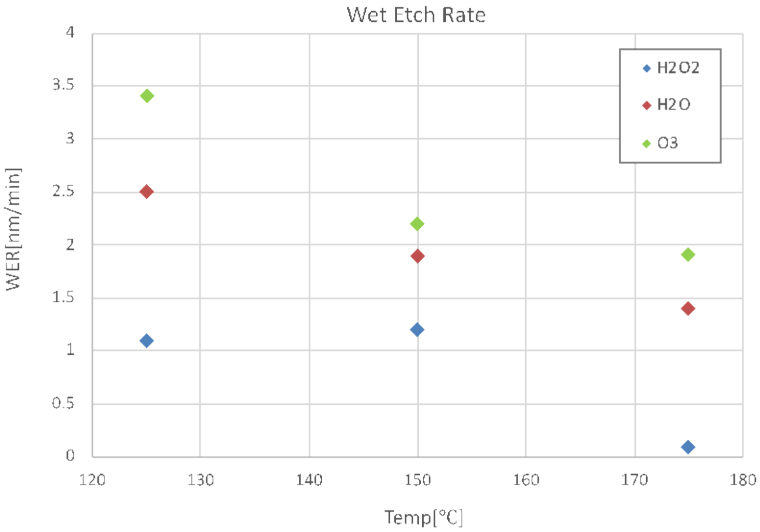
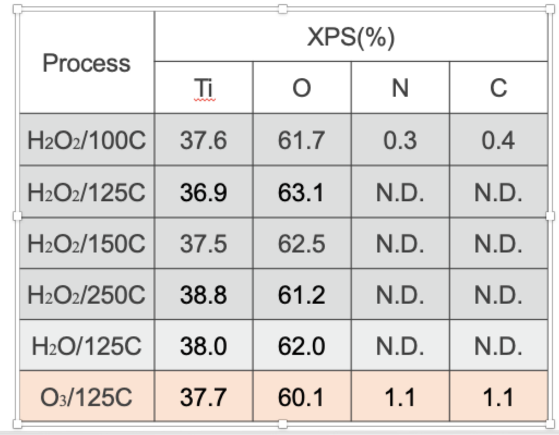


Figure 4. Significantly lower wet etch rates (WER) are observed for films grown with H_2O_2/H_2O mixtures vs water and ozone.

Initial composition results by XPS (Figure 5a) show that residual carbon and nitrogen for the H_2O_2/H_2O film grown at 125° C are non-detectable vs 1.1% carbon and 1.1% nitrogen for Ozone at 125° C. While all films deposited show oxygen deficiency vs the ideal stoichiometric TiO_2, films deposited with hydrogen peroxide show less deficiency compared to those deposited with H_2O or Ozone. (Figure 5b) In this instance, it is implied that as oxygen content decreases, film density decreases, therefore leading to poor etch resistance. Here the use of hydrogen peroxide helps to increase the Oxygen content in the film and lead to improved etch resistance. (Figure 6)

a)



Process	XPS(%)			
	Ti	O	N	C
H_2O_2/100C	37.6	61.7	0.3	0.4
H_2O_2/125C	36.9	63.1	N.D.	N.D.
H_2O_2/150C	37.5	62.5	N.D.	N.D.
H_2O_2/250C	38.8	61.2	N.D.	N.D.
H_2O/125C	38.0	62.0	N.D.	N.D.
O_3/125C	37.7	60.1	1.1	1.1

b)

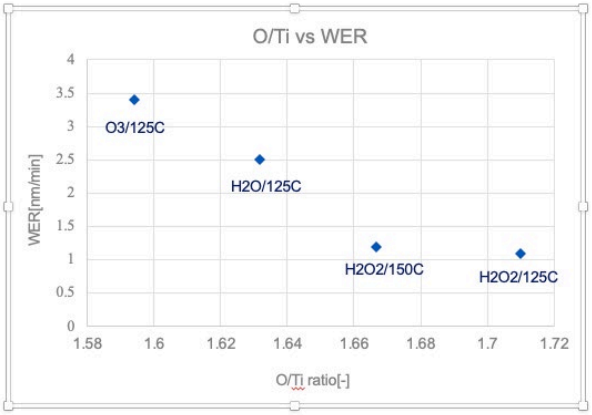


Figure 5. a) Composition of TiO_2 films determined by XPS b) O/Ti Ratio vs Etch Rate, Etch Rate becomes lower as O/Ti ratio increases.

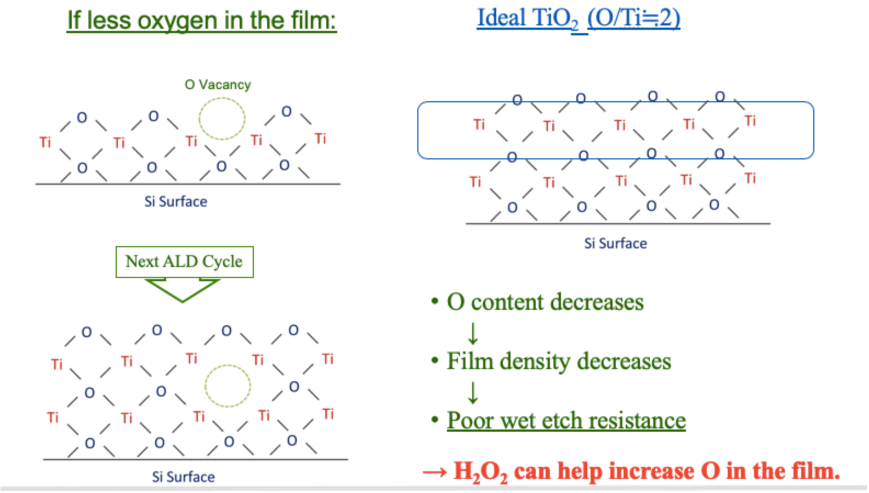


Figure 6. Relationship between TiO_x Oxygen content and Etch Rate.

Deposition studies on Al_2O_3 films have also been conducted with the use of Trimethyl Aluminum (TMA) precursor. Initial comparisons have been made between H_2O/H_2O_2 vs H_2O vs Ozone. Results point towards similar film improvements as observed for TiO_2. Growth rates for H_2O/H_2O_2 are increased over water and ozone. In this instance, the growth rate improvement (Figure 7) over water is not a dramatic as that observed for TiO_2, however ozone remains significantly lower, especially at reduced temperatures. FT-IR for films grown with H_2O/H_2O_2 and H_2O was examined (Figure 8); the measured signal for the hydrogen peroxide films is approximately 20% stronger. Though this measurement is somewhat qualitative, it implies that the films grown with hydrogen peroxide have higher film density.

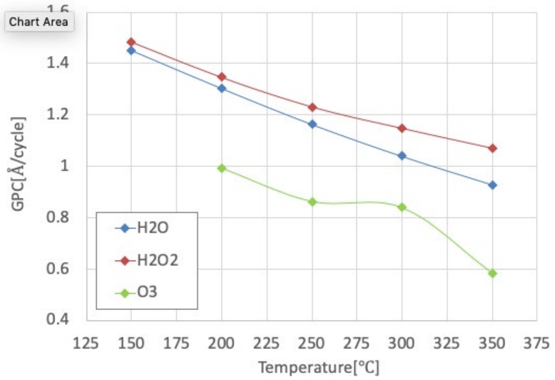
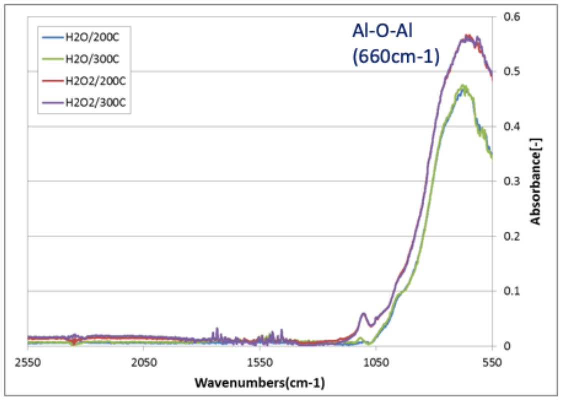


Figure 7. Growth rates for Al_2O_3, H_2O_2>H_2O>>O_3.



- **Film Density : H2O2＞H2O**

Figure 8. FT-IR of Al_2O_3 films grown with H_2O_2/H_2O vs H_2O, strong signal for hydrogen peroxide films implies higher density. Spectra are normalized with film thickness.

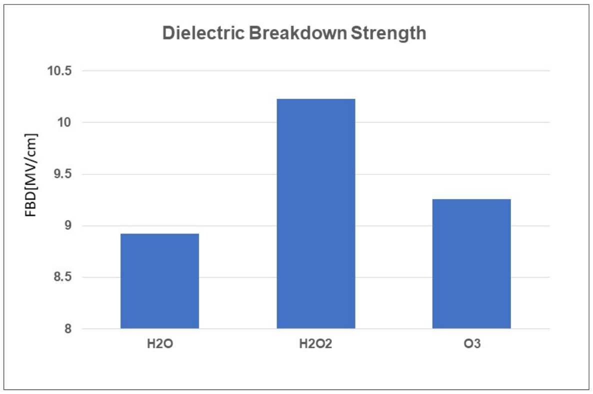


Figure 9. Dielectric Breakdown Strength measurement comparing films grown by all three oxidants. Hydrogen peroxide based film shows a significant increase in this electrical property where $H_2O/H_2O_2 > O_3 > H_2O$.

Composition of films grown by all three oxidant methods was measured by XPS, all films have stoichiometric Al_2O_3 composition, within the experimental error of the instrument. Initial wet etch rate studies were performed on H_2O/H_2O_2 and H_2O films grown at 200° C. In this instance, the hydrogen peroxide film has an etch rate of 69.9nm/min vs 81.5nm/min for water which is a 15% improvement in etch resistance. Our initial work with Al_2O_3 has included the study of electrical properties. (Figure 9) For films grown at 300C, Dielectric Breakdown Strength was measured. Here, the film grown with hydrogen peroxide was significantly greater than both water and ozone grown films. In general, electrical properties reflect overall film quality with regard to density, mechanical strength, stress, and etch resistance.

4. CONCLUSIONS

Continuing to rely on 193nm immersion lithography with multiple patterning is becoming much more difficult as line widths decrease. With the use of Self-Aligned Quadruple patterning and related patterning schemes, it is critical to minimize variability, where high quality films must be deposited and etch rates must be very precise. Initial work has been performed to examine the resulting film properties for TiO_2 and Al_2O_3 spacer materials deposited by low temperature ALD with the use of various oxidants. Improved film quality has been demonstrated for films deposited with H_2O/H_2O_2 used as the oxidant. Key to multiple patterning applications is that improved etch resistance is achieved for both dielectric materials. Also significant with regard to multiple patterning is that higher growth rates are obtained at reduced temperatures, enabling lower process temperatures for sensitive materials. The all thermal nature of these deposition methods points toward improved film conformality on 3-Dimensional structures. Improved etch rates and improved electrical properties reflect overall improvements in dielectric film quality.

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