ATOMIC LAYER DEPOSITED ETCH STOP LAYERS FOR HYDROFLUORIC ACID

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ABSTRACT

We report on the evaluation of the etch rate in hydrofluoric acid (HF) for various atomic layer deposited (ALD) thin films. Specifically, the intent is to characterize several films as potential etch stop layers as HF is often used as a release etch for various sacrificial films but most commonly SiO₂. Traditionally in MEMS, SiN has been used as an HF etch stop, and we show that plasma enhanced ALD (PEALD) of SiN at 350°C can achieve similar etch rates to SiN from low pressure chemical vapor deposition (LPCVD) at 850°C. Further, the etch rate of PEALD SiN is drastically reduced when the film contains ~10% AlN as a dopant. Additionally, several metal oxide films are evaluated for their etch characteristics as deposited and as a function of post-deposition anneal temperature. Some of the evaluated metal oxide films showed greater HF etch resistance than PEALD SiN after anneals of moderate temperature (~400°C).

INTRODUCTION

Hydrofluoric acid based release etches of sacrificial silicon oxide layers remains one of the most widely utilized processes in MEMS fabrication. Hydrofluoric acid resistant layers providing an etch stop, enable a wide variety of fabrication processes and device design freedom. Recently, the development of HF etch resistant SiN deposited at low temperature (< 400°C) has been driven by the need for improved insulating spacer layers in advanced CMOS fabrication [1]. The films should be conformal, pinhole free at thicknesses of only a few nm, and of comparable etch rate in dilute aqueous HF to low pressure chemical vapor deposition (LPCVD) SiN. These same properties are of interest to MEMS researchers to provide a robust etch stop layer for HF release etch of sacrificial SiO₂. In this paper we present multiple HF etch resistant thin films deposited by plasma enabled atomic layer deposition (PEALD). The demonstrated films include SiN with incorporation of AlN, HfO₂, ZrO₂, TiO₂, and Al₂O₃.

Films deposited through purely thermal atomic layer deposition as well as PEALD are each explored. Additionally, the effect of post-deposition anneals were evaluated by a treating the ALD thin films rapid thermal anneals (RTA) at various temperatures.

EXPERIMENTAL PROCEDURE

Single crystal (100) silicon wafers were utilized as the starting substrate for all depositions. Substrates were cleaned by the RCA process immediately before deposition. The films deposited for this study were performed in a Fiji F202 (Cambridge Nanotech/Ultratech) hot wall reactor equipped with a remote inductively coupled plasma (ICP) generator which was operated at 300 W at 13.56 MHz at 350°C.

Samples were cleaned by the RCA method and then immediately introduced into the ALD reactor for deposition. After deposition, film thickness was measured with spectroscopic ellipsometry (Woollam M2000). If a post deposition anneal was utilized, it was performed on a piece of the deposited wafer loaded on a carrier wafer. Then the film thickness was re-measured to determine any film thickness change from the anneal process.

For the etch, the samples were etched in aqueous HF (different concentrations were used for different films based on

their relative etch rates). The etch was performed at room temperature in a freshly poured HF bath. After a timed length of etch, the samples were removed and immediately rinsed with DI water. Samples were dried in an N₂ gun, and finally, the film thickness was measured once more to determine the change in thickness and etch rate for each sample.

SILICON NITRIDE

Silicon nitride was deposited by PEALD at 350°C utilizing tris(dimethylamino)silane (3DMAS, Sigma Aldrich) as a precursor and N₂ plasma at 300W. A strong correlation between the density of the SiN film and the HF etch rate was discovered [2]. Two techniques for increased film density and thus low etch rate were identified. One is the duration of N₂ plasma exposure during each deposition cycle, and the second is a post-deposition H₂ plasma anneal also performed in the Fiji 202 reactor without breaking vacuum after the PEALD process. Utilizing these techniques a pure SiN film from PEALD could achieve an etch rate of 6.1 ± 1.0 Å/min in 100:1 dilute HF. This is not statistically significantly different from the etch results attained from a LPCVD sample deposited at 850°C. This result shows that PEALD is a route to high quality SiN HF etch stop layers at temperatures significantly lower than possible LPCVD and on par with PECVD, while surpassing the etch performance typical of PECVD SiN films. Figure 1 shows the etch rates for LPCVD, PECVD, and PEALD SiN films deposited at the Stanford Nanofabrication Facility for this study.

Figure 1: Wet etch rate in 100:1 dilute HF for silicon nitride films deposited by various methods. Note that PEALD at 350°C can achieve WER similar to LPCVD at 850°C.

We found that the etch rate can be further reduced by the incorporation of AlN into the PEALD SiN. This introduction of controlled levels of AlN into SiN is straightforward to achieve because of the cyclic, layer-by-layer nature of ALD. Cycles of SiN PEALD were intermixed with cycles of AlN from trimethylaluminum (TMA, Sigma Aldrich) and N₂ plasma during the deposition. Figure 2 shows the relationship between incorporated AlN and the etch rate of the film in 100:1 dilute HF. For films with more than 12% Al content as measure by X-Ray photoemission spectroscopy, the etch rate is negligible, verifying

an optimal etch stop. This level of AlN incorporation relates to roughly 1 cycle of AlN for every 19 cycles of SiN.

Figure 2: Wet etch rate in 100:1 dilute HF for intermixed films of SiN and AlN deposited by PEALD at 350°C as a function of Al concentration.

ALUMINUM OXIDE

Aluminum oxide (Al_2O_3) films were prepared by thermal ALD utilizing alternating precursor pulses of TMA and DI H_2O and by PEALD utilizing alternating precursors pulses of TMA and O_2 plasma at 300W. Deposition was performed at 200°C and the etch was performed in 20:1 BOE for 20 sec. Figure 3 contains the etch rate as a function of post-deposition anneal for both thermal and plasma ALD of Al_2O_3 . The rapid thermal anneals were all performed for a duration of 4 minutes with a 20 second ramp time under N_2 atmosphere. While the etch rate of the PEALD sample remains relatively constant under the various anneals, the thermal ALD film has a transition to lower etch rate occurring around 700°C.

From the thickness measurements before and after annealing, we can see change in the thermal films at roughly the same temperature, while the plasma films remain more consistent in thickness change (Figure 4). This provides an indication for film densification within that temperature range which would contribute to the lowered etch rate. This will ultimately need to be established as a definite film densification through a more direct test of film density such as X-Ray reflection refractometry or nano-indentation.

Figure 3: Etch rate of thermal ALD and PEALD Al_2O_3 as a function of post-deposition anneal temperature. The anneals were 4 min in duration and the etch was performed in 20:1 BOE.

Figure 4: Change in film thickness from the post-deposition anneal for thermal ALD and PEALD of Al_2O_3 . A decrease in thickness is an indication of film densification.

HAFNIUM OXIDE

Hafnium oxide (HfO_2) films were prepared by thermal ALD utilizing alternating precursor pulses of tris[dimethylamido]hafnium (TDMA-Hf) and DI H_2O and by PEALD utilizing alternating precursors pulses of TDMA-Hf and O_2 plasma at 300W. Deposition was performed at 200°C and the etch was performed in 20:1 BOE for 600 sec (thermal ALD) and 180 sec (PEALD). Figure 5 contains the etch rate as a function of post-deposition anneal for both thermal and plasma ALD of HfO_2 . The rapid thermal anneals were all performed for a duration of 4 minutes with a 20 second ramp time under N_2 atmosphere. For HfO_2 , the etch rates are significantly lower than Al_2O_3 or SiN and are negligible above 400°C for thermal ALD and above 600°C for PEALD.

The film thickness change under anneal again shows an indication of densification at the approximate temperatures at which the etch rate drops significantly (Figure 6). However, unlike in Al_2O_3 , the thickness change is not monotonic with anneal temperature indicating a more complex film response.

Figure 5: Etch rate of thermal ALD and PEALD HfO_2 as a function of post-deposition anneal temperature. The anneals were 4 min in duration and the etch was performed in 20:1 BOE.

Figure 6: Change in film thickness from the post-deposition anneal for thermal ALD and PEALD of HfO₂.

TITANIUM OXIDE

Titanium oxide (TiO₂) films were prepared by thermal ALD utilizing alternating precursor pulses of tris[dimethylamido]titanium (TDMA-Ti) and DI H₂O and by PEALD utilizing alternating precursors pulses of TDMA-Ti and O₂ plasma at 300W. Deposition was performed at 200°C and the etch was performed in 20:1 BOE for 180 sec (thermal ALD) and 600 sec (PEALD). Figure 7 contains the etch rate as a function of post-deposition anneal for both thermal and plasma ALD of TiO₂. The rapid thermal anneals were all performed for a duration of 4 minutes with a 20 second ramp time under N₂ atmosphere. Titanium oxide has comparable etch rates to HfO₂ but achieves a negligible etch rate at even lower anneal temperatures.

The film thickness change under anneal again shows an indication of densification at the approximate temperatures at which the etch rate drops significantly (Figure 8), but again shows a more complex relationship to anneal than Al₂O₃.

Figure 7: Etch rate of thermal ALD and PEALD TiO₂ as a function of post-deposition anneal temperature. The anneals were 4 min in duration and the etch was performed in 20:1 BOE.

Figure 8: Change in film thickness from the post-deposition anneal for thermal ALD and PEALD of TiO₂.

ZIRCONIUM OXIDE

Zirconium oxide (ZrO₂) films were prepared by thermal ALD utilizing alternating precursor pulses of tris[dimethylamido]zirconium (TDMA-Zr) and DI H₂O and by PEALD utilizing alternating precursors pulses of TDMA-Zr and O₂ plasma at 300W. Deposition was performed at 200°C and the etch was performed in 20:1 BOE for 300 sec. Figure 9 contains the etch rate as a function of post-deposition anneal for both thermal and plasma ALD of ZrO₂. The rapid thermal anneals were all performed for a duration of 4 minutes with a 20 second ramp time under N₂ atmosphere. Zirconium oxide has comparable etch rates to HfO₂ but achieves a negligible etch rate at even lower anneal temperatures.

The film thickness change under anneal again shows an indication of densification at the approximate temperatures at which the etch rate drops significantly (Figure 10), but again shows a more complex relationship to anneal than Al₂O₃.

Figure 9: Etch rate of thermal ALD and PEALD ZrO₂ as a function of post-deposition anneal temperature. The anneals were 4 min in duration and the etch was performed in 20:1 BOE.

Figure 10: Change in film thickness from the post-deposition anneal for thermal ALD and PEALD of ZrO₂.

SILICON OXIDE

As a comparison we measured etch rates of PEALD SiO₂ as well this is the most likely sacrificial material which might utilize the etch stops demonstrated. Silicon oxide (SiO₂) films were prepared by PEALD utilizing alternating precursor pulses of tris(dimethylamino)silane (3DMAS) and O₂ plasma at 300W. Deposition was performed at 200°C and the etch was performed in 50:1 Hf for 10 sec. Figure 11 contains the etch rate as a function of post-deposition anneal for PEALD of SiO₂. Note that a lower concentration of HF is utilized than in the other oxide films. The rapid thermal anneals were all performed for a duration of 4 minutes with a 20 second ramp time under N₂ atmosphere. Silicon oxide has etch rates several orders of magnitude over HfO₂, TiO₂, or ZrO₂, and significantly higher than Al₂O₃ and SiN.

The film thickness change for SiO₂ shows a monotonic thickness decrease with increasing anneal temperature matching the monotonic decrease in etch rate (Figure 12).

Figure 11: Etch rate of PEALD SiO₂ as a function of post-deposition anneal temperature. The anneals were 4 min in duration and the etch was performed in 50:1 HF.

Figure 12: Change in film thickness from the post-deposition anneal for PEALD of SiO₂.

VAPOR HF ETCHES

All of the above characterization has been performed with aqueous HF mixtures. However, it is becoming increasingly common to perform vapor phase releases of MEMS and NEMS devices. The chemical role of water in the etching mechanisms for these films should not be overlooked. Testing Al₂O₃ and HfO₂ PEALD films in an anhydrous HF etch system (Primaxx μ Etch System), we found negligible etch rates for each film as deposited at 200°C. This extreme selectivity in vapor etches also demonstrates the importance of ALD metal oxide films as HF etch stops.

SUMMARY

Evaluation several thermal ALD and PEALD films for HF etch resistance shows several candidates for etch stops or etch barriers. SiN doped with AlN, ZrO₂, TiO₂, and thermal HfO₂ can all achieve negligible etch rates in aqueous HF with a total thermal budget of deposition and anneal of < 400°C. This low temperature process capability allows compatibility with a wide array of materials and post-CMOS fabrication. Further the precise thickness control, highly conformal, and pinhole free nature of ALD means these films integrate well with the unique topologies of MEMS processes.

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