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THERMAL STABILITY OF FLUORINATED SiO₂ FILMS: EFFECTS OF HYDRATION AND FILM-SUBSTRATE INTERACTION

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ABSTRACT

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The thermal stability of fluorinated SiO₂ films (SiOF) was found to be dependent on F content and the type of substrate upon which the film was deposited. SiOF films with a range of F concentrations were deposited using an electron cyclotron resonance (ECR) plasma upon Si, Al/Si, TiN/Al/Si, and Al/SiO₂/Si substrates. Following deposition, the films were deliberately hydrated and/or annealed and their stability assessed. Hydration was found to only affect the high F content films. Capacitance changes with annealing in the high F content films were found to occur beginning at 200°C. These changes, which were independent of substrate type, likely occurred due to desorption of H₂O in the films. After annealing of the high F content films up to 400°C, a reduction in F content was found for SiOF films on some substrates. Significant reductions were found for SiOF films on Al/Si substrates, while little or no change was found for films on TiN/Al/Si, Al/SiO₂/Si, or Si substrates. Local chemical analysis of those films which showed F reduction indicated that the F profile was approximately uniform throughout the layer and did not pile-up at the interface. The substrate-dependent thermal instability exhibited by these films suggests the chemical nature or qualities of the substrate may play a role in the F reduction reaction.

INTRODUCTION

Fluorinated SiO₂ (SiOF) films have emerged as a leading candidate to replace SiO₂ as an intermetal dielectric (IMD) for future ultra-large scale integrated microelectronics.[1] It is acknowledged, however, that SiOF films can exhibit instability problems, particularly in their tendency for moisture absorption.[2] The tendency for moisture absorption is very sensitive to the deposition process and deposition conditions. It is generally observed that SiOF films that are deposited using a high density plasma process [e.g. electron cyclotron resonance (ECR) or helicon plasma chemical vapor deposition (CVD)] produce SiOF films with improved degradation resistance, possibly due to preferential elimination of weakly-bonded F.[3] Further improvement is obtained by using an electrical bias between the substrate and plasma[4] and depositing the SiOF films at elevated temperature.[5] Even though these processes lead to significant improvements in degradation resistance, the ultimate stability of these films when integrated with Al interconnects and other microelectronic materials is not fully known. In this study, the thermal stability of SiOF films deposited using ECR CVD with a biased substrate at elevated temperature was examined as a function of both F content and substrate type.

EXPERIMENTAL

The SiOF films were deposited in an ECR plasma reactor using a gas mixture of SiH₄, SiF₄, O₂, and Ar. The F content of the films was controlled by adjusting the ratio of flow rates, SiH₄:SiF₄, from 0:1 to 4.7:1, yielding films with F contents ranging from 11% to approx. 2.5%, respectively (as measured by Rutherford Backscattering Spectroscopy, RBS). The microwave power used to excite the plasma was 1500 W and the RF bias power from substrate to plasma was 2300 W. The substrate temperature was 330°C. These conditions have previously been found to lead to SiOF films with excellent thermal stability on Si.

Four types of substrates were used in this study: high resistivity Si, Al(0.29 to 0.7 μm)/Si,

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TiN(0.05 μm)/Al(0.7 μm)/Si, and Al(1.0 μm)/SiO₂(1.0 μm)/Si. The thick Al layers were sputter deposited at 100°C with an intentional Si-doping of 0.75%. For most of the samples, the SiOF deposited layer was 0.15 to 0.19 μm thick, and all measurements were taken approx. 2 to 14 days after film deposition and unloading (outside the deposition system, the samples were exposed to normal room ambient conditions). For a few samples, identified as "thick SiOF", the SiOF layer was much thicker, 0.8 to 0.9 μm , and the measurements were taken more than 6 mos. after film deposition and unloading.

"Hydration" treatments were performed by boiling the samples in distilled H₂O for one hour (95°C and 690 Torr). All annealing treatments were performed at 400°C, in vacuum (2×10^{-6} Torr), for 30 min., unless otherwise noted. Other annealing ambients (forming gas or Ar) gave similar results to those found for the vacuum anneals. The annealing temperature was chosen to approximate the thermal budget the SiOF films would need to withstand during processing as an IMD.

Electrical characterization was performed on the SiOF layers on the metallized substrates. (High interface state densities and high substrate resistivities prevented accurate determination of the SiOF film capacitance for layers deposited on Si substrates.) Contact was made to the metal layer beneath the SiOF by photoresist masking and reactive ion etching through the SiOF. Shadow mask deposition of circular Ti/Au contacts were made to the top surface of the films with diameters ranging from approx. 200 μm to 1000 μm . Uncertainties in the measurement of film capacitance changes following annealing were greatly reduced by measuring the exact same contacts immediately prior and following the anneal step.

Ellipsometry and Fourier Transform Infrared (FTIR) spectroscopy were performed on SiOF layers on Si substrates. RBS and elastic recoil detection (ERD) of hydrogen were performed on samples on all types of substrates. High resolution transmission electron microscopy (HRTEM) and nanoprobe energy dispersive analysis by X-rays (EDAX) were performed on SiOF layers on Al- and TiN-coated substrates. These latter samples were prepared by mounting the samples film surface to film surface, mechanical thinning, and ion milling to electron transparency (< 50 nm thick).

RESULTS AND DISCUSSION

Moisture absorption is known to be a concern in SiOF films.[1-10] In order to quantify this effect in these films, hydration was performed on all films. Fig. 1 shows the effect of hydration on the SiO-H absorbance in low and high F content SiOF layers on Si as measured by FTIR. Hydration was found to increase the absorbance in high F (11% F) content layers while only negligible changes were observed in the middle (6%) to low (2.5%) F content films. Despite the increase in SiO-H absorbance, the total absorbance signal was still very small compared to the dominant vibrational modes ($< 0.5\%$ of the Si-O peak). A slight drop in the Si-F/Si-O ratio of about 3.3% was also observed in the high F content films following hydration, while negligible changes occurred in the low F content films. There was no noticeable increase in absorbance at frequencies associated with the H-OH stretch of water in all films following hydration. The changes which occurred in the film as a result of hydration were not limited to SiOF films on Si. Fig. 2 shows the hydrogen increase in an

Fig. 1. SiO-H absorbance as measured by FTIR before and after hydration for 2.5% and 11% F SiOF films.

11% F content SiOF layer on Al/Si as detected by ERD. ERD measures H from all sources, including Si-OH bonds, Si-H, and trapped H₂O. While the H concentration of the virgin (unhydrated) samples which were analyzed 2 to 14 days after film deposition were all similar, the H content of thick SiOF films deposited > 6 mos. before analysis were higher, being approximately 2% for the low F (2.3% F) films and 3% for high F (11% F) films. This suggests that exposure to room ambient conditions is sufficient to lead to hydration over time. After annealing the hydrated films, no noticeable change in absorption at 3660 cm⁻¹ was found, as shown in Fig. 3. This is consistent with thermal desorption spectra (TDS) for plasma-enhanced CVD SiO₂ films in which no significant changes were observed in the SiO-H absorbance until the anneal temperature exceeded 400°C.[11]

The effect of the moisture-induced instability was determined by measuring capacitance changes in the SiOF layers following annealing. Table I summarizes the capacitance changes for high F content films as a function of substrate type, F content of the film, and anneal temperature. It was found that all high F content films exhibited a decrease in capacitance following annealing independent of substrate type. The capacitance drop was dependent on the F content of the film, however, as shown in the middle section of the table. For low F content films, a slight capacitance increase was observed. Finally, it was observed that the capacitance change following annealing began to show noticeable changes following the 200°C anneal. Since slight thickness changes in the SiOF film could be responsible for the observed capacitance changes, ellipsometry was performed on SiOF layers deposited under identical conditions to those above except on Si substrates. Changes in film thickness following annealing or hydration and annealing were found to be less than 1% (typically a slight decrease was observed, but the changes were close to the estimated uncertainty of the measurement, ~ 0.4%). This is not sufficient to explain the observed capacitance changes, although it might explain part of the capacitance increase for the low F content films. Given that the observed onset for capacitance changes was 200°C, a likely explanation for the capacitance drop is desorption of H₂O in the films. TDS indicates that the only significant desorption species near 200°C for SiOF films is weakly-bound H₂O.[4] Blistering of the metal contacts to the thick 11% F SiOF layer on Al/Si was also found to occur starting after the 200°C anneal. This would also support the desorption of H₂O as the likely mechanism. Due to the blister formation, no accurate measurement of the capacitance reduction of the thick SiOF layers on Al/Si could be obtained. The small capacitance drop observed in the thinner SiOF

Fig. 2. Atomic H concentration in an 11% F SiOF film on Al/Si before and after hydration.

Fig. 3. SiO-H absorbance for hydrated SiOF films before and after annealing.

Table I. Capacitance change following annealing, referenced to unannealed samples, as a function of substrate type, F content, and anneal temperature.

A. Dependence on Substrate		B. Dependence on F Content		C. Dependence on Anneal Temp.	
Sample	Cap. Change	Sample	Cap. Change	Sample	Cap. Change
11% F SiOF/Al/Si	-2.4%	11% F SiOF/Al/SiO ₂ /Si	-3.3%	11% F SiOF/Al/Si annealed 100°C	-0.2%
11% F SiOF/TiN/Al/Si	-2.3%	6% F SiOF/Al/SiO ₂ /Si	-0.3%	11% F SiOF/Al/Si annealed 200°C	-1.1%
11% F SiOF/Al/SiO ₂ /Si	-3.3%	2.5% F SiOF/Al/SiO ₂ /Si	+1.8%	11% F SiOF/Al/Si annealed 300°C	-2.1%
				11% F SiOF/Al/Si annealed 350°C	-2.7%
				11% F SiOF/Al/Si annealed 400°C	-2.7%

films may be a result of either the formation of a void beneath the metal contact of a size too small to be observed as a blister or merely the loss of the highly polarizable, weakly-bound H₂O species from the film. In either case, the electrical measurements support the FTIR and ERD measurements that moisture absorption in the SiOF films increases with increasing F content and that the degree of moisture absorption appears to be independent of substrate type.

Although the moisture absorption instability of SiOF films seemed only to depend on the F content of the layer and not on the type of substrate, it was found that there is an instability associated with F loss from the film which does appear to depend on the type of substrate. The F/O ratio in SiOF films was measured by nanoprobe EDAX with a 10 nm spot size. Point composition measurements were taken from the middle of the SiOF layer working towards the SiOF/substrate interface. These composition profiles are shown in Fig. 4. It was observed that there is noticeable loss of F with respect to the oxygen signal for annealed thick SiOF films on Al/Si substrates when compared to the unannealed films [Fig. 4(a)]. This F loss was also found for the thinner SiOF films on the Al/Si substrate [Fig. 4(b)], but no detectable loss was found for the SiOF films on the TiN/Al/Si substrates. RBS confirms these EDAX observations, as indicated in Table II. It does appear that moisture absorption is also important for this reaction to proceed because less F is lost for the 11% F SiOF layer on Al/Si after receiving only an annealing treatment compared to the same film after both a hydration and annealing treatment, see Table II (the thick SiOF films behave as hydrated films following 6 mos. exposure to room ambient conditions). Little or no change in F content was also found for 11% F SiOF layers on Si following hydration and annealing as indicated by measurement of the change in Si-F/Si-O ratio (a decrease of about 5% was found). In summary, the only systems which showed noticeable F reduction were the systems in which there was a high F content SiOF layer on Al/Si. This highlights a potential difficulty when assessing the thermal stability of SiOF layers in contact with Al by only monitoring changes in SiOF layers on Si substrates.

The mechanism for the loss of F from annealed SiOF layers in contact with Al/Si substrates is unclear. It is generally accepted that the F in the SiOF films is directly bonded to the Si, as is supported by theoretical calculations involving small Si_wO_xF_yH_z clusters.[12] Assuming the free energy for bond breakage of the F-Si bond in the SiOF solid is similar to that of bond breakage in the F-SiF₃ molecule, then simple thermodynamic arguments rule out direct reactions between H₂O and SiF₄ to yield SiO₂ [or Si(OH)₄] and HF:[13]

Because Al is more electropositive than Si, stripping of F from Si by Al is possible:

This reaction does not appear operative, however, because the F profile as measured by EDAX showed no significant increase near the SiOF/Al interface. Other possibilities include Al(OH)₃ formation at the SiOF/Al interface due to reaction between Al and H₂O with subsequent release of H₂. H release from the Al layer or catalytic reactions at the Al interface are also possible. Finally,

it is not understood why the F loss from the SiOF layer is different for the Al/Si substrates compared to the Al/SiO₂/Si substrates, as indicated in Table II. This difference could be related to differences in H content between the Al layers in these films, but that difference has not been measured.

In order to reduce the two types of instability problems associated with SiOF films in contact with Al, it is advisable to employ moisture barrier layers, such as F-free SiO₂ layers or Si_xN_y layers on the top surface of the film and use a diffusion barrier, such as TiN, between the SiOF film and the Al interconnect. It is interesting to note that these two approaches, the use of a moisture barrier layer, Si_xN_y, and a Ti barrier layer between the Al and the SiOF, have already been tested experimentally and were found to reduce the degradation observed in Al lines when integrated with SiOF.[8]

CONCLUSIONS

Two types of thermal instability problems were observed for SiOF films. One instability problem is related to moisture absorption which increased with increasing F content and was independent of the type of substrate upon which the SiOF was deposited. The other instability problem was due to the loss of F from the SiOF film for films that were deposited on Al/Si substrates and annealed. It is suggested that the use of a moisture barrier layer and diffusion barrier, such as TiN, should eliminate these instability problems.

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Fig. 4. Measured F/O ratios within SiOF films as determined by EDAX (uncorrected for cross-section differences between F and O) as a function of distance from the metal interface for (a) thick SiOF films on Al/Si and (b) SiOF films on TiN/Al/Si and Al/Si. A reduction in F content is observed for annealed films on Al/Si substrates.

Table II. Percent F reduction in SiOF films as measured by RBS following the specified treatment and referenced to the untreated sample. Reductions of less than approx. 5% are labeled as "small" or "none".

Sample	Treatment	% F Reduction
thick SiOF/Al/Si, 11% F	annealed	25%
thick SiOF/Al/Si, 2.3% F	annealed	none
SiOF/Al/Si, 11% F	hydrated and annealed	18%
SiOF/Al/Si, 11% F	annealed	small to none
SiOF/TiN/Al/Si, 11% F	hydrated and annealed	none
SiOF/Al/SiO ₂ /Si, 11% F	hydrated and annealed	small to none

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