Reactive ion etching of Ta–Si–N diffusion barriers in CF$_4$+O$_2$

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(Received 22 February 1994; accepted 24 May 1994)

Ta$_3$N$_5$Si$_3$N$_{10}$ amorphous layers were reactive ion etched in CF$_4$+O$_2$ plasmas. The etch depth was determined as a function of gas composition, pressure, and cathode power. Adding small amounts of O$_2$ to CF$_4$ increased the etch rates up to approximately 15% O$_2$ concentration, with etch rates then decreasing with further addition of O$_2$. Etch rates increased with both pressure and power. Etching proceeded only after an initial delay time which depended upon gas composition and power. The delay is probably caused by a surface native oxide which must be removed before etching can commence. The presence of a surface oxide was observed from Auger electron spectroscopy intensity depth profile measurements and is estimated to be 2 nm thick. Under optimal conditions, the etch rate of Ta$_3$N$_5$Si$_3$N$_{10}$ is about seven times higher than for SiO$_2$, thus providing a high degree of selectivity for integrated circuit processing.

I. INTRODUCTION

Ta–Si–N is an amorphous conducting alloy with a high crystallization temperature and strong chemical stability. This material has been shown to be an excellent diffusion barrier in silicon metallizations$^{1-4}$ as well as an excellent encapsulant for III–V semiconductors.$^{5,6}$ As a requisite for incorporation into high-density integrated circuit processing, Ta–Si–N must be patternable into small structures, preferably by dry etching. Plasma etching of both TaSi$_2$(Ref. 7) and Si$_3$N$_4$(Refs. 8–10) in CF$_4$+O$_2$ mixtures has been previously demonstrated. We report here results obtained on reactive ion etching (RIE) of Ta$_3$N$_5$Si$_3$N$_{10}$ amorphous buffer layers in similar CF$_4$+O$_2$ mixtures.

II. EXPERIMENT

Thin films of Ta$_3$N$_5$Si$_3$N$_{10}$ were deposited onto (100) Si substrates by rf sputtering of a Ta$_3$Si$_3$ target in an Ar:N$_2$ discharge as detailed elsewhere.$^1$ Etching of 150 nm thick films in CF$_4$+O$_2$ was performed in a PlasmaLab u Etch RIE system with a 24 cm diameter water-cooled cathode driven by a 13.56 MHz power supply. The film samples were patterned with AZ5214 photoresist, and etch depths were determined from Deukit profilometer measurements. Gas mixture composition was adjusted by varying the amount of gas flow through the CF$_4$ and O$_2$ flow meters. For comparative purposes, the etch rates of thermally grown SiO$_2$ were also measured under similar conditions. SiO$_2$ is a common passivation material in integrated circuits, and thus a high degree of selectivity in etching Ta–Si–N over SiO$_2$ is desirable. Auger electron spectroscopy (AES) intensity depth profiles were measured in a Perkin Elmer PHI 660 scanning Auger microscope using a 10 kV electron beam with a 4 kV Ar$^+$ ion beam for sputtering.

An etch rate dependence on chamber condition and history is sometimes observed with a CF$_4$+O$_2$ plasma.$^{11}$ This dependence can be attributed to the presence of a polymer coating on the chamber walls which can affect plasma chemistry. For our experiments, this effect was more evident at the lower O$_2$/CF$_4$ ratios, and several etch runs sometimes had to be performed for a given set of etching parameters in order to “condition” the chamber and obtain reproducible results.

III. RESULTS AND DISCUSSION

Fluorine atoms are created in a CF$_4$ plasma and produce volatile SiF$_4$(Ref. 8) and Ta-fluoride (Ref. 12) etch products. When oxygen is added to a CF$_4$ plasma, it reacts with carbon species to form molecules such as CO$_2$, CO, and COF$_2$, limiting the recombination of F atoms and freeing them for the etching process. The net result is an increase in etch rate as O$_2$ is added to CF$_4$. However, sufficiently high O$_2$ concentrations will ultimately reduce the etch rate due to a dilution effect, and therefore, an O$_2$ concentration can usually be found which will produce the maximum etch rate.

Figure 1 shows Ta$_3$N$_5$Si$_3$N$_{10}$ and SiO$_2$ etch depths as a function of O$_2$ concentration in a CF$_4$+O$_2$ plasma for a 1 min etch duration and fixed pressure and cathode power. The etch depth of Ta$_3$N$_5$Si$_3$N$_{10}$ is a maximum at approximately 15% O$_2$ concentration. Harshberger et al.$^{13}$ measured the optical emission intensity from atomic F as a function of O$_2$ concentration in a CF$_4$+O$_2$ plasma and reported a similar dependency with a maximum intensity at about the same 15% O$_2$ concentration. The results of Fig. 1 indicate the expected correlation between the Ta–Si–N etch rate and F atom concentration. Sun et al.$^{17}$ reported a similar reactive ion etch rate curve for amorphous sputtered TaSi$_2$ etched in CF$_4$+O$_2$, which had a maximum etch rate for 4% O$_2$ concentration. Figure 1 also shows that the etching of SiO$_2$ exhibits little dependence on gas composition, with lower etch rates than Ta–Si–N. Consequently, the CF$_4$+O$_2$ mixture satisfies selectivity requirements for many integrated circuit processes.

Since Ta-silicide etches more slowly than Si in fluorine-based discharges,$^{14}$ it is reasonable to assume that etching of Ta is the rate limiting process for Ta–Si–N materials. Indeed, TaF$_3$ has a much lower vapor pressure than SiF$_4$.$^{14}$ It has been reported$^7$ that reactive ion etching of TaSi$_2$ in

CF$_4$+O$_2$ plasmas results in the etched surface becoming Ta rich. However, AES depth profile measurements of an etched Ta–Si–N layer reveal no such Ta-rich surface in our case.

The dependence of etch depth on cathode power is exhibited in Fig. 2. As power increases, the plasma density and associated concentration of reactive species (F atoms) should also increase, producing higher etch rates and resultant etch depths for a given etch time. Figure 3 shows that the etch depth also increases with chamber pressure. As pressure is increased, the density of CF$_4$+O$_2$ and the resultant F atom concentration also increase, again producing higher etch rates. The power and pressure dependence of the etch depth indicates that the etch rate is limited by F atom production under the given conditions. Figure 4 shows a scanning electron micrograph of a Ta–Si–N sample patterned with AZ5214 photoresist and etched in CF$_4$+O$_2$. The etched surface is smooth and the sidewalls are sloped due to erosion of the mask edge.

The dependence of etch depth on etching time for several concentrations of O$_2$ in a CF$_4$+O$_2$ plasma is shown in Fig. 5. Etching proceeds only after an initial delay time which depends upon etch gas composition. This delay time varies from about 0.6 min for 40%–50% O$_2$ concentration, down to about 0.3 min for 15% O$_2$ concentration. Figure 6 shows the dependence of etch depth on time for several values of cathode power. Again, a delay in the onset of etching is observed, with the amount of the time delay decreasing as cathode power increased. We speculate that this delay is caused by the presence of a surface oxide which must be removed before etching of the Ta–Si–N can commence. Similar delays have been observed in the etching of GaAs$^{15,16}$ and AlGaAs$^{15–18}$ and have been attributed to the need to etch or sputter away the surface oxide. Since the time delay decreases as power increases and O$_2$ concentration decreases, it seems reasonable to assume that the presence of a surface oxide...
oxide is responsible for the time delay; lower O₂ concentrations in the plasma result in less replenishment of the surface oxide during its removal, while higher powers cause faster removal of the surface oxide due to increased chemical etching and/or sputter etching.

The presence of a native oxide on the surface of an as-grown Ta-Si-N layer is seen from the data of Fig. 7, which shows an AES depth profile of Ta, Si, N, and O as a function of sputtering depth. Upon sputtering, the oxygen signal first increases and then decreases fairly quickly, indicating the presence of an oxide with an estimated thickness of 2 nm. Pokela et al.¹⁹ have demonstrated the capability for growing much thicker oxides on Ta₅S₁₃N₂₀ layers at 650–850 °C temperatures. In addition to the constituent Ta, Si, and N signals, small amounts of carbon and oxygen were detected in the Ta–Si–N layer, and were due to residues of these elements in the sputtering chamber. Since Ta has greater affinity for oxygen than does Si, the existence of a Ta oxide could be the primary cause of this etching time delay. However, Sun et al.²⁰ found no delay in reactive ion etching of a sputtered amorphous TaS₂₃ film in CF₄+O₂, for O₂ concentrations in the range 2%–12%. In any case, it appears that Ta₅S₁₃N₂₀ has a fairly tenacious surface oxide.

Finally, it should be noted that the data of Figs. 1–3 are presented for a given total etch time, including the etching onset delay, and as such are not totally indicative of the dynamic rate of removal of Ta–Si–N material. However, correcting for the delay times will not affect the general etch rate dependencies which allow elucidation of the physical mechanisms underlying the etching process.

**IV. SUMMARY**

Ta₅S₁₃N₂₀ sputtered amorphous layers have been reactive ion etched in CF₄+O₂ plasmas. The maximum etch rate is attained for approximately 15% O₂ concentration, with the etch rate mostly limited by F atom production. For this particular gas mixture, the selectivity of Ta₅S₁₃N₂₀ over SiO₂ is about 7:1. Etching proceeds only after an initial delay time which varies depending upon gas composition and power. The delay time appears to be due to the presence of a native surface oxide which must first be removed before etching of the Ta₅S₁₃N₂₀ can commence.

**ACKNOWLEDGMENTS**

The authors acknowledge A. Deanni for performing the sample patterning. Financial support for a portion of this work was provided by the Army Research Office.

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