

A comparative study on the CF₄/H₂ and HF/H₂ plasmas for etching of highly hydrogenated SiN films

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Abstract: Dependence of etching characteristics of the PECVD-prepared SiN films on H₂ concentration in the feeding gas mixture of CF₄/H₂ and HF/H₂ plasmas was investigated with a dual-frequency capacitively coupled plasma reactor. Optical emission actinometry was used to estimate relative concentrations of F radicals in the studied plasmas. With increasing H₂ percentage from approximately 5 % to 34 %, the etch rate decreased by ~35 % in the CF₄/H₂ plasma case but only 10 % in the HF/H₂ plasmas. The results from the actinometry show that the F density decreased by ~60 % in the both plasmas. This implies that the F density cannot fully explain the decrease of ER with increasing H₂ in the plasmas. The surface analysis reveals that in the HF/CF₄ plasma the addition of H₂ caused the surface modification by formation of N–H_x bonding which probably led to a higher reaction probability between F radicals and Si dangling bonds. In the CF₄/H₂ plasmas case, the thickness of fluorocarbon layer on the etched surface increased as the H₂ content was increased. The F etchants released from the fluorocarbon deposition layer by ion bombardment upon the plasma discharge can also react with Si, even under a F radical deficient condition. These suggest that the surface modification layer produced by hydrogen-containing plasma is likely to assist the progress of SiN etching.

Keywords: plasma etching, CF₄/H₂, HF, SiN, F radicals

1. Introduction

Dry process plasma etching is one of most critical processes used in fabrication of semiconductor devices. Developing an isotropic etching with controllable material selectivity is one of concerns in the scaled logic transistors as well as 3D NANDs. It has been reported that a high SiN/SiO₂ selectivity can be achieved using gas mixtures such as CF₄/N₂/O₂ or NF₃/O₂ plasmas, due to the effect of NO radicals[1,2]. On the other hand, hydrogen-contained plasmas such as CF₄/H₂ or hydrofluorocarbon gases can be used to improve etch rate and/or the selectivity of SiN/SiO₂ [3-5]. We also reported that the etch rate (ER) of SiN films depended on the hydrogen content inside the films and bonding structures of the films as well as substrate temperatures[6,7]. Recently, selective etching of SiO₂ over Si using anhydrous hydrogen fluoride (HF) vapor has been investigated using computational simulation [8].

In this works, CF₄/H₂ and HF/H₂ based-plasmas with variable gas composition were adopted to etch the PECVD-prepared SiN films. The influence of H₂ on the chemical properties of the plasmas and their effects on the surface structure and ER of the SiN films were discussed.

2. Experimental procedures

A home-made dual-frequency capacitively coupled plasma reactor, equipped with a very high frequency of 100 MHz and a 2 MHz power source at the upper and bottom electrode, respectively, was used for the presented study. The base vacuum was maintained below 4×10^{-4} Pa prior to the process being performed. A mixture of the feeding gases with different ratios of CF₄/H₂ or HF/H₂ was introduced from a showerhead distributor installed in the upper electrode. The SiN films were prepared by a PECVD on a 300-mm Si wafer which were cut to coupons

approximately 20×20 mm². The coupon sample was fixed on a carrier Si wafer using a grease. The carrier wafer was then fixed on an electrostatic chuck with a backside He flowing to improve the thermal conductivity between the wafer and bottom electrode. The bottom electrode was cooled with a circulation of coolant at 20 °C.

The chemical composition of the PECVD-prepared SiN was turned out to be Si_{39.2}N_{41.3}H_{19.5} using an Rutherford back-Scattering spectroscopy/hydrogen forward-scattering spectroscopy. ER was estimated by a real time monitoring of thickness variation during plasma discharge using an in-situ spectroscopic ellipsometry. The atomic fluorine concentration was determined by an optical emission spectroscopy (OES) calibrated by 2 sccm of Ar addition to the gas mixture for actinometry measurement. Surface chemistries of the etched SiN were investigated with an X-ray photoemission spectroscopy (XPS). The thickness of fluorocarbon (FC) layer deposited on top of the etched SiN was estimated by comparing the intensity variation of Si2p spectra using angular resolved XPS. See more details about experimental methods from our recent work [9].

3. Results and Discussions

The dependence of ER on H₂ addition to the gas mixture of CF₄ and HF is illustrated in Fig. 1. For the CF₄/H₂ plasmas discharge the ER decreased monotonically from 4.9 to 3.3 nm/s as the H₂ addition was increased from 6.7 to 33.3 %. In the HF/H₂ case a slight increase of ER, from 3.0 to 3.4 nm (~12 %), was found for the H₂ addition of 4 %. With further increasing H₂ content (from 10 to 34 %), the ER decreased to approximately 2.7 nm/s and then was insensitive to the H₂ addition.

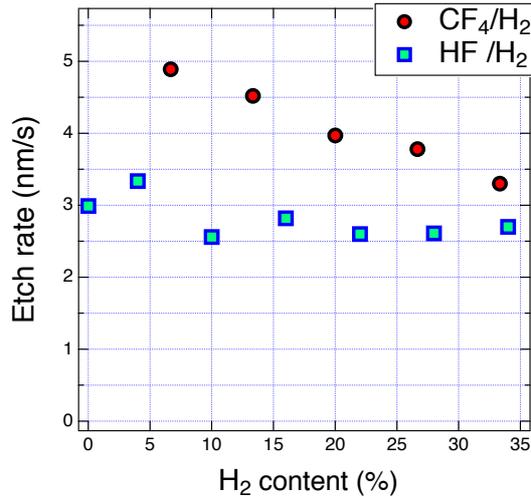


Fig. 1 Dependence of ERs of the SiN films on H₂ content in the CF₄/H₂ and HF/H₂ plasmas.

To correlate the ER variation with the fluorine density, the actinometry measurement based on OES technique using Ar addition was used [10]. By comparing lineshapes from F and Ar produced in the CF₄/H₂ and HF/H₂ plasmas as a function of H₂ concentration, the fluorine density of the plasmas was obtained, as illustrated in Fig. 2. It reveals that the magnitude of F density generated in the CF₄/H₂ plasmas was greater than that in the HF/H₂ plasmas for all gas mixtures. With increasing H₂ concentration in the feeding gases in both CF₄/H₂ and HF/H₂ discharges, the F density decreased monotonically due to the H scavenging of F to form HF molecular.

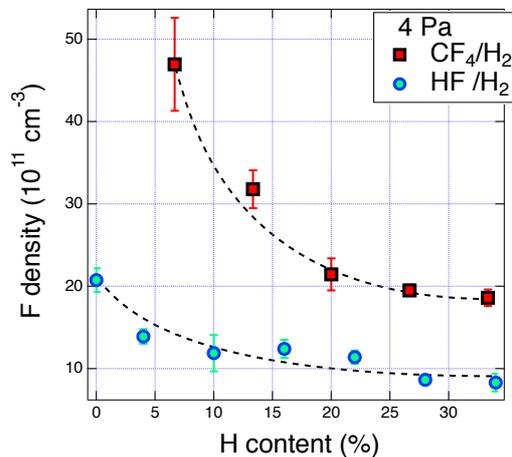


Fig. 2. Dependence of atomic fluorine density on H₂ concentration in the CF₄/H₂ and HF/H₂ plasmas.

By comparing the variation of ER and F density, it reveals that the F density cannot fully explain the studied etching mechanism of the SiN, since the F density decreased by 60 %; in the meanwhile, the decrease of the observed ER in the CF₄/H₂ case was 35 % and, even, in the HF/H₂ case was only 10 %. The surface structure obtained by XPS measurement indicates that for the sample etched by the HF/H₂ plasmas the contribution of the fluorinated Si

peak (Si–F) to the Si 2p spectra increased as the H₂ content in the feedgases was increased. The N1s peak of the samples after plasma treatment shows that the contribution of H–N_x and (NH₄)₂SiF₆ phase increased with increasing H₂ content. This suggests that the hydrogen is likely able to react with N and form H–N bonding, which resulted in the formation Si dangling bond. Hence, F has a higher possibility to react with Si, even though the F density decreased. In the CF₄/H₂ plasma case, the results from the C1s spectra and angular resolved XPS show an increase of FC layer thickness on etched surface. This suggests that F inside the FC layer can also contribute the F etchants which is being released upon plasma exposure. Therefore, even under a condition of F-deficient gas phase, the ER decrease did not match the decrease of F density with increasing H₂ content in the plasmas. Besides, the N1s spectra shows that the contribution of H–N related component increased as the H₂ concentration was increased, which indicates that the surface modification layer was increased due to the increased H ion bombardment. It has been reported that the ammonia salt layers may hinder the etching process in many studies [11,12]. However, in this work we found that the thickness of the ammonia salt layer is not necessarily the main factor which decrease the etch rate, suggesting that the decomposition of the ammonia salt layer may be a key factor for the SiN etching using the hydrogen-contained plasmas.

4. Summary

The effects of H concentration in the CF₄/H₂ and HF/H₂ plasmas on etch rate, plasma chemistries and surface structure of the highly hydrogenated SiN films prepared by PECVD were investigated. In the CF₄/H₂ plasma the ER decreased monotonically with increasing H₂ content; meanwhile, the ER in the HF/H₂ case show less dependent of H₂ content. Due to the expected F scavenging with H atoms, H₂ addition resulted in the decrease of F radical density; however, the magnitude of the decrease in the F density did not match the decrease of ER. Combined with the results from the surface chemical structure analysis, the surface modification produced upon the H₂ plasma exposure is considered to be able to assist the progress of SiN etching instead of etching stopper.

5. References

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