

Investigation of surface polymerization on silicon exposed to C₄F₈ helicon wave plasmas

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Abstract

Polymer layers formed on silicon wafer during silicon oxide overetching using C₄F₈ helicon wave plasmas and their properties were investigated using spectroscopic ellipsometry, X-ray photoelectron spectroscopy, and secondary ion mass spectrometry. The degree of overetching and d.c. self-bias voltage were varied to investigate the effects on the characteristics of the polymers remaining on the overetched silicon surface. The increase of bias voltage from -80 V to -120 V increased the C/F ratio and carbon bonds such as C–C, C–CF_x, and C–Si in the polymer while reducing the thickness of the polymer layer. However, prolongation of the overetch time from 50% to 100% did not change the chemical composition of the polymer layer and the carbon binding states in the polymer layer remained the same even though the polymer thickness was increased. The polymer layer formed at the higher d.c. self-bias voltage was more difficult to remove by the subsequent post-etch treatments compared to that formed at longer overetch time. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Helicon wave plasmas; Surface polymerization

1. Introduction

Dry etching of contact oxides for ultra-large-scale integrated (ULSI) circuits requires high aspect ratio, high etch rate, high etch selectivity to mask layers and underlayer, and low damage and contamination on the plasma-exposed silicon surface during the overetch period [1]. To achieve the above goals, helicon wave plasma sources in addition to other high density plasma sources such as electron cyclotron resonance plasma (ECR) and inductively coupled plasma (ICP) are being investigated with high C/F ratio gases. The use of high C/F ratio gases such as C₄F₈, C₄F₆, etc. with high density plasma sources results in highly selective oxide etching under high ion bombardment of high density plasmas. However, the use of high density plasma sources with high C/F ratio gas compositions often generates a thick polymer layer and physical damage on the exposed silicon surface during the overetch period [2–7]. Therefore, the control of characteristics of the formed polymer layers, which is a main factor in obtaining high selectivity to silicon and also a main source of the contamination at the etched silicon surface, is one of the important key issues in contact

oxide etching using high density plasma sources. In this study, the characteristics of the polymer layers formed on the silicon surface overetched using C₄F₈ helicon wave plasmas were studied as a function of overetch percentage and bias voltage.

2. Experiments

In this study, a helicon wave plasma etcher with a Nagoya type antenna was used for the highly selective contact oxide etching. C₄F₈ gas was used to etch 1 μm thick phosphosilicate glass (PSG) deposited on n-type silicon wafers. 1.5 kW source power was applied to the antenna while the operating pressure was kept at 0.2 Pa and the total flow rate at 30 sccm. Separate r.f. bias power connected to the substrate was varied to achieve -80 V or -120 V of d.c. self-bias voltage on the substrates; 50% and 100% overetch periods of 1 μm thick phosphosilicate glass (PSG) etch time were used for the oxide overetch time. The overetched silicon wafers were treated using piranha cleaning (H₂SO₄:H₂O₂ = 4:1, at 90°C for 10 min), O₂ plasma cleaning using a microwave plasma asher (ASTEX Co.) at 200 W and 67 Pa with various ashing times (10–40 min), or furnace annealing at (450 and 600°C in N₂ for 30 min) followed by the oxygen plasma cleaning. The annealed wafers were dipped in

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Table 1

The atomic percentages of the components in the polymer layer, the thickness of the polymer layer, and C/F ratios of the polymer layers; 1 μm thick PSG-deposited silicon wafers were overetched (50%, 100%) at different bias voltages (–80 V, –120 V) using C_4F_8 helicon wave plasmas at 1.5 kW source power and 0.2 Pa operational pressure

Bias voltage (V)/ overetch time (%)	Thickness	Si	C	F	O	C/F
–80/50	44	17	36	36	11	1.00
–80/100	48	19	36	35	10	1.02
–120/50	36	30	37	19	14	1.94

diluted HF (HF:H₂O = 1:100) for 30 s after the annealing. To characterize the polymer layers remaining on the etched silicon surfaces before and after the post-etch treatments, spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectrometry (SIMS) were applied.

3. Results and discussion

The compositions of the polymers remaining on the silicon surfaces during overetching of 1 μm thick PSG deposited silicon wafers with C_4F_8 helicon wave plasma (1.5 kW, 0.2 Pa) were measured using X-ray photoelectron spectro-

scopy and are shown in Table 1. Effects of different overetching at –80 V d.c. self-bias voltage and different d.c. self-bias voltages for 50% overetching are shown. The measured elements in the polymer layers formed on the overetched silicon surfaces consisted of carbon, fluorine, and oxygen. Furthermore, no differences in the composition of the polymer layers were found when the overetch percentage was increased from 50% to 100% as shown in Table 1. However, the increase of the d.c. bias voltage from –80 V to –120 V changed the composition of the polymer layer.

Table 1 also shows the thickness of the polymer layers measured by an ellipsometer and C/F ratios of the polymer layers calculated from the atomic percentages of carbon and fluorine in them. As shown in Table 1, the increase of d.c. bias voltage drastically decreased the concentration of the fluorine component in the polymer layer, therefore, a carbon-rich polymer with a high C/F ratio was formed. The increase of d.c. self-bias voltage also decreased the thickness of the polymer measured by the ellipsometer. The decrease of the polymer thickness was also confirmed by the increase of the silicon (2p) peak intensity measured by X-ray photoelectron spectroscopy. The decrease in the polymer thickness and the change of the composition to carbon rich with the increase of the bias voltage appeared to be related to the enhanced physical sputtering and the selective removal of more volatile fluorine containing species by the increased incident ion energy. The change of the characteristics of the polymer layer with the increase of bias voltage obtained in the experiment was similar to the results on the change of polymer composition by the increase of incident ion density by other researchers [7,9,10].

To investigate the characteristics of the polymer layers in detail, carbon binding states in the polymer layers were measured using narrow scan X-ray photoelectron spectroscopy. Fig. 1 shows the narrow scan XPS spectra of carbon (1s) for the conditions shown in Table 1. When the spectra shown in Fig. 1 were deconvoluted, the C–CF_x binding state turned out to be the most abundant bonding state for all of the polymer layers. The increase of overetch percentage did not change the carbon binding states significantly, therefore, similar properties between the polymer layers could be maintained. However, the higher d.c. self-bias voltage increased less volatile carbon binding states such as C–CF_x, C–C, and C–Si bondings while decreasing C–F_x (x = 1, 2, 3) bondings. Especially, a much higher percentage of chemically stable and strongly bonded C–Si bonds was formed by increasing the bias voltage.

During the overetch period, species in the plasmas could not only form a polymer layer on the exposed silicon, but also could be implanted into silicon. Fig. 2 shows SIMS depth profiles of carbon and fluorine implanted into silicon for the conditions shown in Table 1. As comparison, SIMS depth profiles of a non-etched control silicon wafer are included. Exact implanted depths of the species for different overetching conditions were difficult to measure, possibly

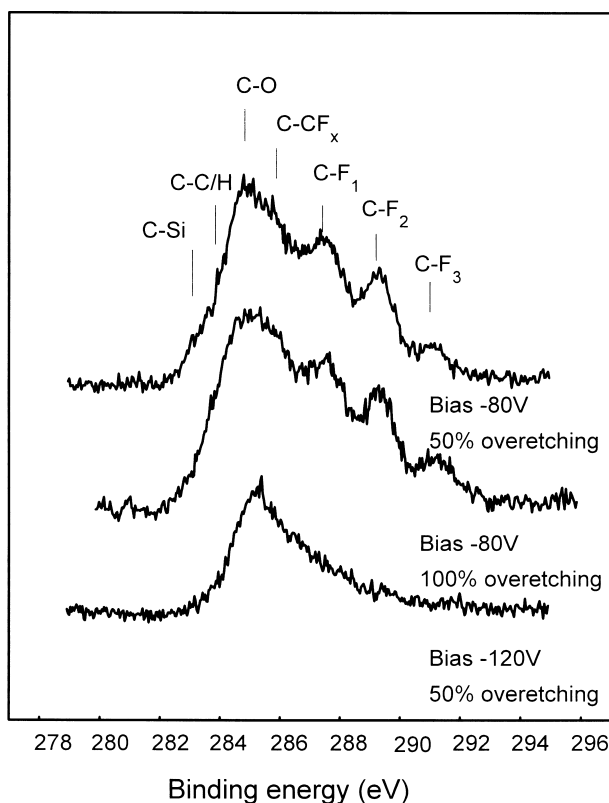


Fig. 1. Narrow scan XPS data of carbon (1s) for the silicon surfaces shown in Table 1.

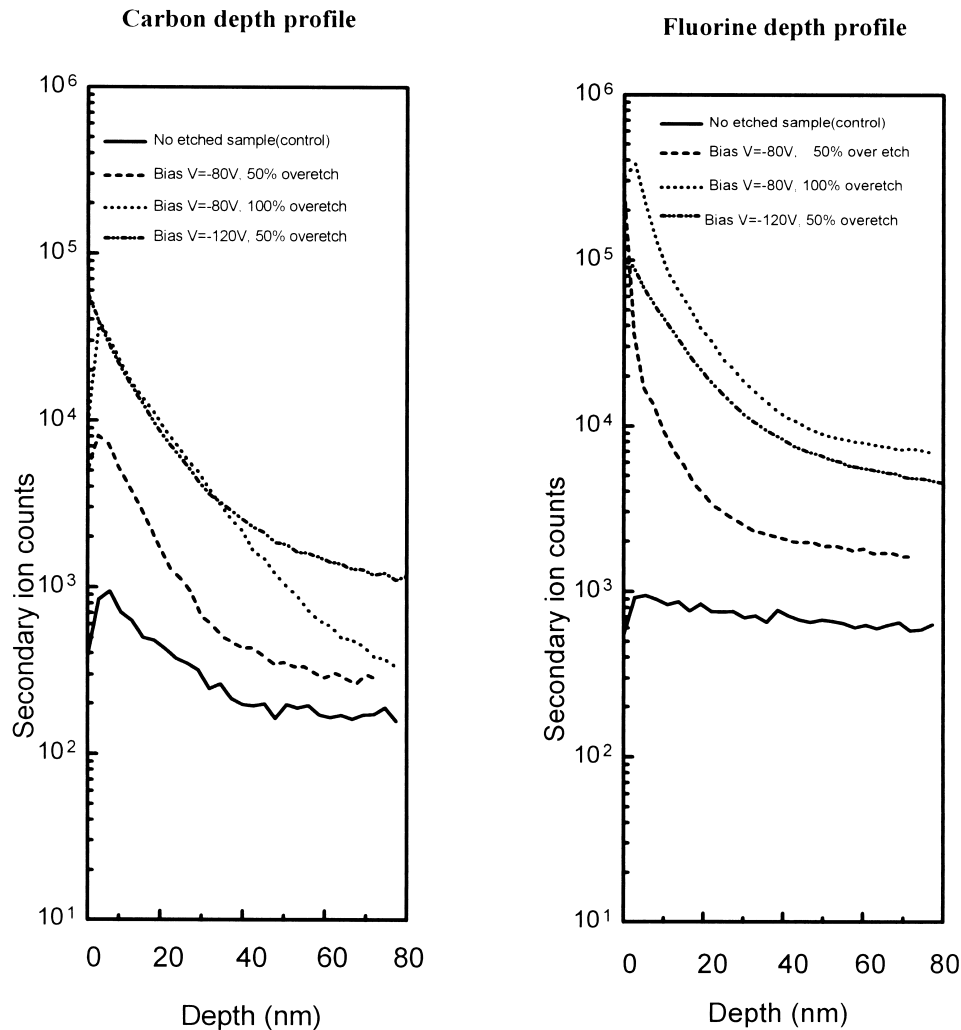


Fig. 2. SIMS depth profile of carbon and fluorine implanted into silicon for the conditions shown in Table 1.

due to the trace remaining during the SIMS analysis. In general, the increase of overetch time and bias voltage seems to increase the depth of the implantation. The increase of the implantation depth by increasing d.c. self-bias voltage might be explained by the increase of the incident reactive ion energy, however, with the range of ion energy used in the experiment, this deep implantation cannot be accomplished. Also, the increase of the implantation depth by the increase of overetch time at a constant ion energy also cannot be explained. Some kind of diffusion appears to happen during the etching to increase the depth of the impurities in silicon.

On the overetched silicon wafers, metal deposition or silicide fabrication is generally followed to make an ohmic contact to the exposed silicon surface. From previous studies, it is known that any polymer layer remaining before the deposition of metal or silicide formation can increase the resistance of the ohmic contact and also can affect the formation of stable silicides [6,8]. Therefore, the polymer layer formed during the overetch period should be adequately removed by post-etch treatments after the over-

etching of the PSG and before the deposition of metal or silicide fabrication. Fig. 3 shows the effects of various post-etch cleanings on the removal of the polymer layers formed by the etch conditions in Table 1. The thickness of the remaining polymer layer was measured using the ellipsometer. In general, the polymer layers formed at -80 V (both 50% and 100%) were removed faster than the polymer layer formed at -120 V throughout the various cleanings. In the case of the silicon surfaces overetched at -80 V, after oxygen plasma cleaning for 40 min/ 600°C annealing/HF ($\text{HF} : \text{H}_2\text{O} = 1 : 100$) dipping, almost all of the polymer layers were removed and the polymer thicknesses were about 1 nm with refractive index of 1.45 which is close to the measured value of native oxide on a control sample. However, the polymer layer formed at -120 V was removed more slowly and, after the above final cleaning used in the experiment, a 1.5 nm thick polymer layer remained which is thicker compared to that overetched at -80 V. The reason for the slower removal rate of the polymer formed at -120 V appears to be related to the characteristics of the polymer layer possessing less volatile C–

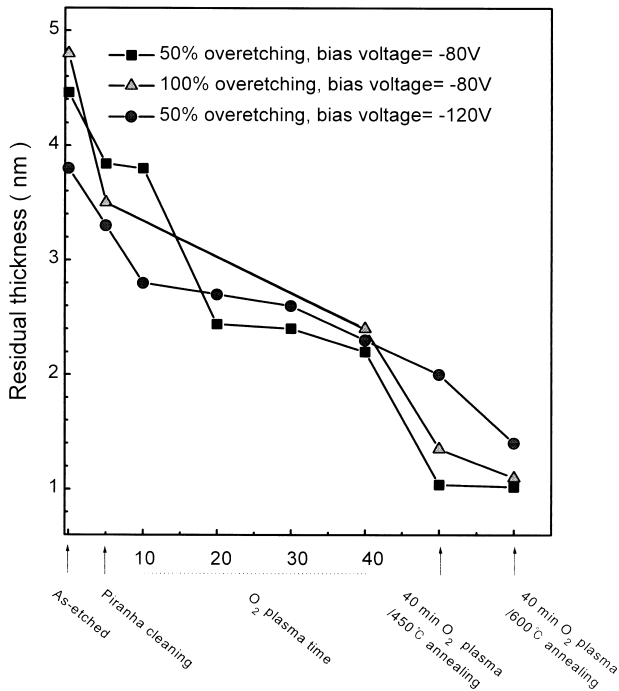


Fig. 3. The effects of various post-etch cleanings on the removal of the polymer layers formed by the etch conditions shown in Table 1.

CF_x , C–C, and C–Si bonds in the polymer as shown in Fig. 1. In addition, the large number of C–Si bonds found on the silicon surface overetched at -120 V could obstruct the formation of stable silicides as discussed by other researchers [8].

4. Conclusions

In this study, the characteristics of the polymer layers formed on the silicon surface during overetching using C_4F_8 helicon wave plasmas were investigated as a function of overetch time and d.c. self-bias voltage. Also, the removal behaviors of the polymer layers by various post-etch treatments were investigated. The polymer layers were composed of carbon, fluorine, and oxygen. The increase of bias voltage from -80 to -120 V increased the C/F ratio

of the polymer while the thickness of the polymer decreased possibly due to the enhanced ion bombardment. The increase of bias voltage also changed the carbon binding states in the polymer to less volatile states such as C–C, C– CF_x , and C–Si. However, the increase of the overetch percentage from 50 to 100% did not change the chemical composition and carbon bonding states of the polymer layers. The penetration depth of the polymer components into the etched silicon surface seems to be increased with the increase of bias voltage and overetch time possibly due to the enhancement of diffusion into silicon. The polymer layer formed on silicon surface at -120 V was not easily removed by various post-etch treatments compared to that formed at -80 V . The difficulty may originate from the characteristics of the polymer layer having less volatile and strongly bonded carbon bonds such as C–C, C– CF_x , and C–Si in the polymer.

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