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Roles of F and O Radicals and Positive Ions in a SF_6/O_2 Plasma in Forming Deep Via Structures

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The roles of F and O radicals and of various positive ions in forming very high-aspect-ratio anisotropic via structures from Si have been investigated in SF_6/O_2 plasma with the help of analytical techniques using optical emission spectroscopy and X-ray photoelectron spectroscopy. The formation of the sidewall passivation layer was found to be greatly affected by both the horizontal and the vertical etching properties as a limited amount of F radicals was available inside deep via structures. Furthermore, an excessive amount of O radicals in the SF_6/O_2 plasma enhanced the formation of unwanted passivation layers on the bottoms of the vias. We also found that positive ions in the SF_6/O_2 plasma, *e.g.*, SF_x^+, F^+ and O^+, were likely to be responsible for horizontal etching.

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I. INTRODUCTION

The plasma etching technique to form deep vias in Si has been broadly used for microelectromechanical system (MEMS) applications and is currently implemented for 3D interconnection using through-via-holes so as to realize systems in a package (SiP) [1–3]. Especially, anisotropic etching to attain high-aspect-ratio via profiles becomes important as the feature size of semiconductor devices continues to decrease rapidly [4].

The Bosch process patented by Laemer and Schip [5] is a common method for forming Si deep via structures. It can attain deep via structures from alternating multiple steps, which consist of an etching step using SF_6 and a passivation step using C_4F_8 on a sidewall with polymer deposition. This Bosch process is believed to have industrial applications due to its feasibility to realize vertical sidewalls and a high-aspect-ratio [6, 7]. However, some drawbacks exist in the Bosch process: low etching rate from alternating multiple steps, reactor contamination due to polymers generated from the passivation step and formation of scallops on the sidewalls. Meanwhile, it is known that a plasma etching technique using SF_6/O_2 (commonly referred to as the non-Bosch process) without alternating steps can also give rise to high-aspect-ratio anisotropic profiles [8]. With this process, however, it is difficult to attain a vertical sidewall, because the sidewall profile changes sensitively to small variations in the etching process parameters, although it has advantages over the Bosch process in its high etching rate and lack of contamination of the reactors from polymers.

A low temperature etching technique using liquid N_2 has been investigated in recent years to overcome the processing issue of the SF_6/O_2 etching process [9,10]. It is understood that the formation of high-aspect-ratio via structures is made possible by a longer surface residence time and/or a higher sticking coefficient of the plasma species, consisting of a sidewall passivation layer at a lower wafer chuck temperature compared to room temperature. The low-temperature process, however, has drawbacks in realizing vertical via structures and in obtaining reproducible profiles due to the temperature sensitivity of the etching process.

The isotropic profile of via structures is known to become more conspicuous with increasing substrate temperature because the sidewall passivation layer cannot be formed properly or because it is ruptured likely due to chemical etching of F radicals, assisted by physical ion bombardment of non-vertically incident positive ions [11]. Here, we think that it is important to understand the roles of the F and O radicals and of the positive ions, which are responsible for the formation of via structures, related to the properties of thin passivation layer.

This work addresses the roles of the F and O radi-

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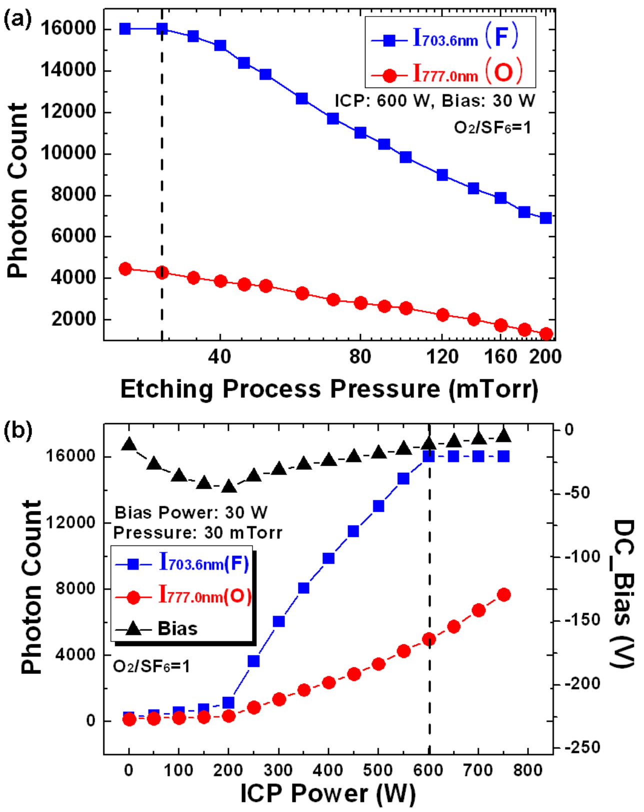


Fig. 1. Photon counts from F*, O* and DC biases in a SF_6/O_2 plasma discharge as functions of (a) pressure and (b) ICP power.

cals and of the positive ions present in a SF_6/O_2 plasma in affecting via formation. Optical emission spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS) were used to explore the densities of those components and to identify the chemical bonds present in the sidewall passivation layer formed in the SF_6/O_2 plasma. In addition, Ar, which is expected to generate a large amount of positive ions, was incorporated into SF_6/O_2 for the purpose of simulating the role of other positive ions.

II. EXPERIMENTAL SETUP

Si etching was performed using SF_6, O_2 and Ar in an inductively coupled plasma (ICP) with a source power frequency of 13.56 MHz and a wafer bias power frequency of 12.50 MHz. The distance between the ICP dielectric and the wafer chuck was fixed at 8 cm. Various sized via patterns for SiP applications were formed in photoresists deposited onto p-type (100) Si substrates.

An optical emission spectrometer was used to estimate the relative densities of F, O and Ar radicals (F*, O*, Ar* where * denotes radicals in a plasma) as functions of power, pressure and gas composition by counting the photons detected at wavelengths of 703.6 nm for F*, 777.0 nm for O* and 419.6 nm for Ar*. The detector of the OES was set up parallel to, but 1 cm higher than, the wafer surface. We used the OES results in Figure 1 to find an optimized etching condition at which the maximum photon emission could be generated. The baseline recipe determined by Figure 1 (a source power of 600 W and a pressure of 30 mTorr) was also used in another work [12]. The via profiles obtained after etching were analyzed by using scanning electron microscope (SEM). In addition, X-ray photoelectron spectroscopy (XPS) was performed on the top surface of the Si wafer at a source power of 600 W without applying a wafer bias power, under the assumption that the surfaces of the via sidewalls were similar in ion bombardment and radical reaction at a source power of 600 W and a wafer bias power of 30 W.

III. RESULT AND DISCUSSION

1. Roles of F and O in Si Via Formation

Figure 2 shows photon counts from F* and O* and SEM cross-sectional images of via profiles at four different O_2/SF_6 ratios. In our previous study [13], photon counts were measured for F* at 703.6 nm and for O* at 777.0 nm by using OES. Figures 3(a) and 3(b) represent the horizontal etching rates and the vertical etching rates for via widths of 5, 10 and 20 um. Here, the horizontal etching rate is defined as the etching rate at the sidewall location showing the maximum side etching, as illustrated in the inset of Figure 3(a). As in Figure 3(a), the horizontal etching rate decreased with increasing O_2/SF_6 ratio for all the tested via diameters of 5, 10 and 20 um whereas in Figure 3(b), the vertical etching rate increased with increasing O_2/SF_6 ratio up to 0.5 and decreased drastically for $O_2/SF_6 > 0.5$.

The results of Figure 3(a) can be interpreted with the help of the results in Figure 2, where the photon count ratio of O*/F* increased with increasing O_2 flow rate. It is understood that the increase in the O_2 gas flow increases the amount of O* participating in the via etching process while it changes F* little, particularly in the formation of a sidewall passivation layer. A similar interpretation can be applied to Figure 3(b) in that the vertical etching rate decreased with increasing O_2/SF_6 ratio for O_2/SF_6 ratio >0.5. This result is understood as the bottom of via structures being subjected to ion bombardment, which can impede the formation of a passivation layer for low O_2/SF_6 ratios; the vertical etching rate increases with increasing O_2/SF_6 ratio for O_2/SF_6 ratio <0.5 because the passivation layer was formed only on the sidewall; therefore, more available F* participated in the vertical etching occurring at the bottoms of the via structures. This can also be explained by differential etching of F* between the sidewalls and the bottoms of the vias: F* has a low reactivity with the sidewall

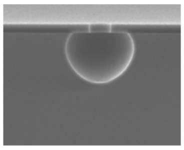
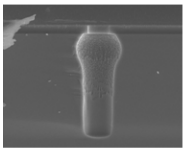
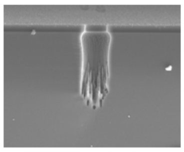
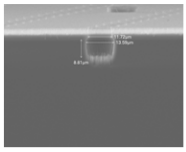
Process #	1	2	3	4
O_2/SF_6 ratio	0	0.5	1	2
Photon counts [11] O* F*	 0 14,000	 2,000 16,000	 5,000 16,000	 10,000 14,200
Photon count ratio of O*/F*	0	0.125	0.313	0.704
Via profile				

Fig. 2. Photon counts from F* and O* and via profiles for various O_2/SF_6 ratios.

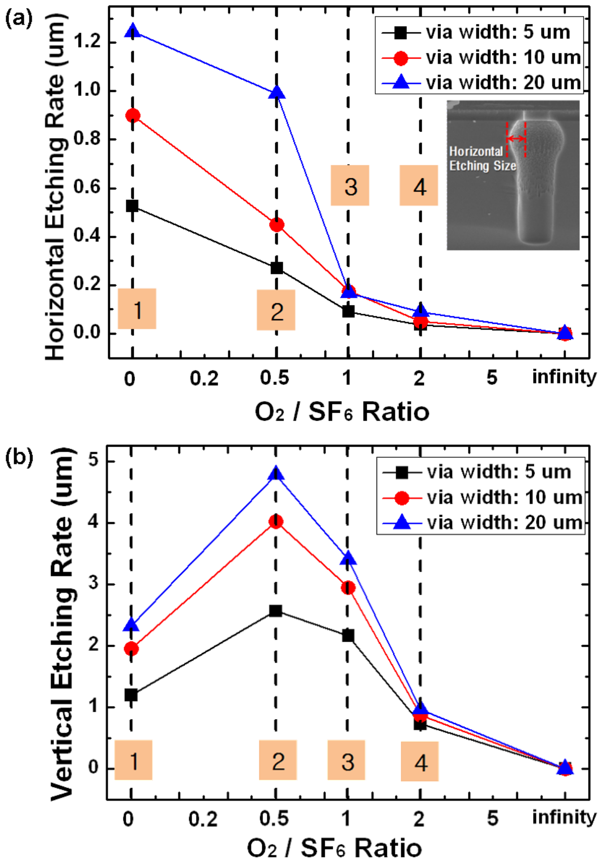


Fig. 3. (a) Horizontal etching rates and (b) vertical etching rates as functions of the O_2/SF_6 ratio for via widths of 5, 10 and 20 um.

passivation layer showing an oxide property, but a high reactivity with the Si exposed at the bottom. However, when an excessive amount of O_2 is introduced into the plasma, the bottom of the via structure is covered by a robust passivation layer, which lowers the vertical etching rate substantially, as shown in Figure 2 and Figure 3(b).

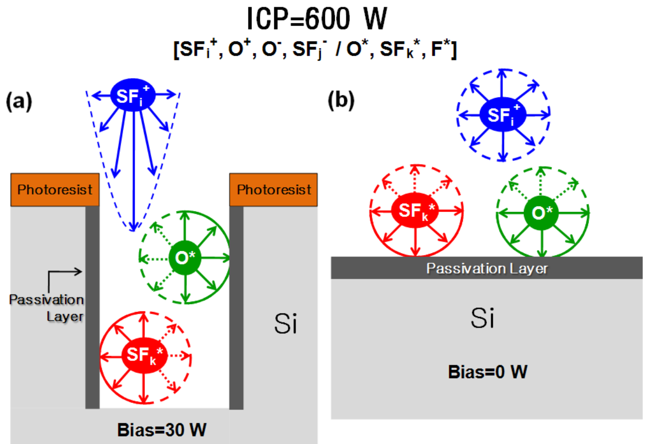


Fig. 4. Schematic diagrams of the energy distribution of radicals and ions, correlated to the reaction with the passivation layer. The passivation layer in (a) is subjected to a similar energy distribution of radicals and ions as that in (b).

2. XPS Analysis on Passivation Layers

We conducted an XPS analysis on the passivation layers formed during SF_6/O_2 plasma etching. It is a plausible assumption that the passivation layer contains Si and O as O* helps their formation, as shown in Figures 2 and 3(b). Here, we performed XPS analysis on the top surface of the Si wafer formed at a source power of 600 W without applying a wafer bias power because the surface of the via sidewall was assumed to be similar to that for weak ion bombardment induced from the baseline process at a source power of 600 W and a wafer bias power of 30 W. The proposed concept for this experiment is described in Figure 4, where the ion bombardment on the Si flat surface without bias power is similar

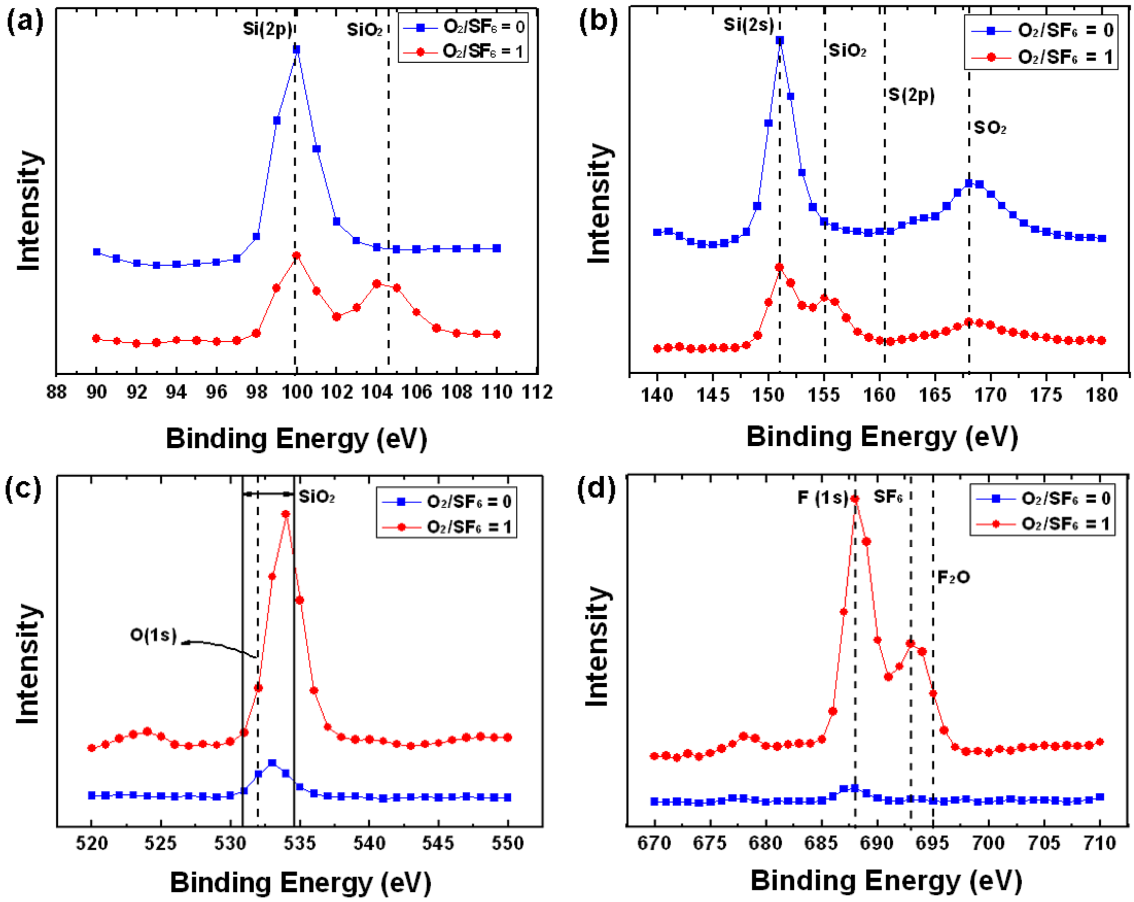


Fig. 5. XPS analyses on the passivation layers as functions of the binding energy in the range of (a) 90 – 110 eV, (b) 140 – 180 eV, (c) 520 – 550 eV and (d) 670 – 710 eV.

to that on the via sidewall when a bias power is applied, *e.g.*, 30 W, because positively charged ions are responsible for ion bombardment, but they affect only vertical etching, while the kinetic energies of neutral radicals are the same, independent of the direction and the surface morphology.

Figure 5 shows XPS intensities in various binding energy ranges for the samples obtained from two different plasma conditions: $O_2/SF_6 = 0$ and 1. The result of Figure 5(a) indicates that Si-O bonds are formed, in addition to Si(2p), when O_2 is incorporated into the SF_6 plasma, because only the Si(2p) peak at a binding energy of 100 eV is observed when $O_2/SF_6 = 0$ while the SiO_2 peak at a binding energy of 104 eV is newly observed when $O_2/SF_6 = 1$. Figure 5(b) also supports the formation of SiO_2 from Si(2p). Figure 5(c) supports this conclusion much more clearly than Figures 5(a) and 5(b). The binding energy of O(1s) at 532.9 eV is observed more than two times when the O_2/SF_6 ratio changes from 0 to 1 and this gives rise to a substantial increase in the SiO_2 intensity in the range of 532 ∼ 534 eV. It is interesting to see the result of Figure 5(d) in that the F peak was not observed when O_2/SF_6 was 0, but it was clearly observed when O_2/SF_6 was unity. This indicates that

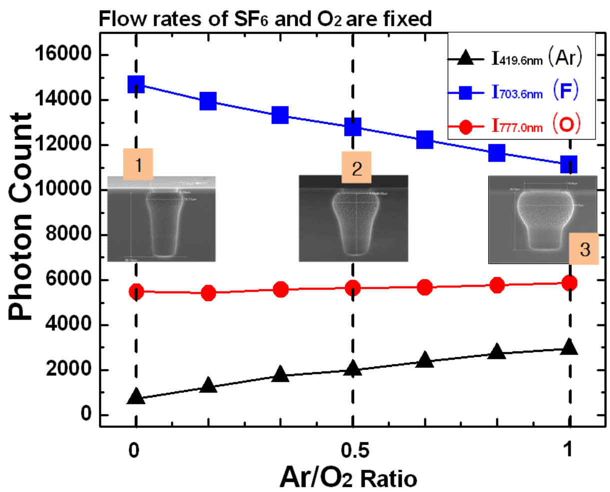


Fig. 6. Photon counts from F*, O* and Ar*, along with via profiles, as functions of the Ar/O_2 ratio.

the passivation layer was not formed when O_2/SF_6 was 0, but was formed when O_2/SF_6 was unity. This result supports the passivation layer thus formed when O_2/SF_6

was unity being SiO_xF_y (silicon oxyfluoride). That is, F contributes to forming a passivation layer as well as to etching Si.

3. Role of Positive Ions in Si Via Formation

To understand the effect of ion bombardment during Si deep etching more clearly, we incorporated Ar into the SF_6/O_2 plasma, as Ar is ionized positively under normal plasma conditions. Figure 6 shows the photon counts of Ar*, O* and F* and via profiles for various amounts of Ar incorporated into the SF_6/O_2 plasma. The results show that the amount of Ar* increased with increasing Ar flow rate. Furthermore, we observed that horizontal etching became active, but vertical etching became suppressed, with increasing Ar flow rate. This indicates that due to the scattering and/or trajectory change in the vias, Ar ions bombard the sidewall passivation layer on which chemical reactions with F* seemed to result in enhanced horizontal etching which induced higher consumption of F* along the sidewall and, in return, reduced vertical etching. We think that, similar to Ar^+, positive ions such as SF_x^+, F^+ and O^+ present in SF_6/O_2 plasmas contribute to horizontal etching.

IV. CONCLUSION

We have investigated the roles of F* and O* and of positive ions in the formation of via structures. O*, which is the main species participating in the formation of the sidewall passivation layer, impedes the chemical reaction of F* with Si. As a result, the horizontal etching of Si is greatly suppressed with increasing O* whereas the vertical etching of Si is greatly enhanced as more F* is available for vertical etching and this helps to accomplish very high-aspect-ratio anisotropic via structures. However, if an excessive amount of O* exists in plasma, a robust passivation layer is formed on the bottoms of the via structures and vertical etching rate is decreased. We found from XPS analysis that O and F exist in the passivation layer formed by using the SF_6/O_2 plasma, which supports the chemical composition of the passivation layer being not SiO_2, but SiO_xF_y. Horizontal etching is enhanced with increasing Ar, from which we conclude that the positive ions in the SF_6/O_2 plasma, *e.g.*, SF_x^+, F^+ and O^+, are responsible for horizontal etching in the via formation process.

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