Journal of the Korean Physical Society, Vol. 54, No. 2, February 2009, pp. 616∼620

Application of the Black Silicon Phenomenon to Forming High-Aspect-Ratio Deep Vias

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(Received 10 September 2008)

A Si deep via formation technique applying the black Si phenomenon was investigated using an inductively coupled plasma of SF_6/O_2 for various O_2/SF_6 ratios and Si substrate temperatures. The properties of the Si via profiles, *e.g.*, the undercut and the local bowing, were investigated to correlate them to the black Si phenomenon, because these properties pose difficulties in subsequent via filling. We found that the extents of undercut and local bowing were greatly reduced in certain processing ranges of the O_2/SF_6 gas ratio and the Si substrate temperature that result in black Si. In addition, the mechanisms responsible for Si deep via formation during cryogenic etching were studied. We found that cryogenic etching gave rise to higher etching rates than room-temperature etching, while reducing the undercut and the local bowing.

PACS numbers: 52.70.Kz, 52.75.Rx
Keywords: SF_6, O_2, Plasma, Via, Silicon, Cryogenic, Undercut, Local bowing, Black silicon, SiO_xF_y, Passivation layer

I. INTRODUCTION

The formation of deep vias is known to be a critical processing step because it has become a key process to micro- and nano- fabrication, *e.g.*, MEMS device fabrication. In particular, stacking of different chips or wafers by using through-silicon vias (TSVs) for accomplishing 3-dimensional (3-D) interconnects is receiving significant attention because this technology can realize short vertical interconnections between chips or wafers [1,2] and 3-D interconnects can realize small-sized packages, simple electric circuits and high-speed operation.

Plasma technologies such as the Bosch process [3] and the cryogenic etching process [4] are well known to be required to form small-sized, high-aspect-ratio TSV structures. The Bosch process is a process that consists of two steps: an etching step using a SF_6 plasma and a deposition step using a C_4F_8 plasma. Carbon polymers deposited on the via sidewall contribute to the suppression of the undercut and the local bowing. However, sidewall scalloping and carbon polymer contamination are known to be the major drawbacks of the Bosch process [3,5]. The cryogenic etching process is performed to form Si vias by using a SF_6/O_2 plasma for a Si substrate at cryogenic temperature. A passivation layer of silicon oxyfluoride, SiO_xF_y, is formed on the inside surfaces of the vias, the SiO_xF_y layer is understood to be effective in suppressing local bowing without contaminating the plasma reactor, but the Si via profile is sensitively changed as a function of the O_2/SF_6 ratio or the Si substrate temperature due to variations in the SiO_xF_y layer's properties. Therefore, Si via formation by using a cryogenic etching process requires fine control of the O_2/SF_6 ratio and the Si substrate temperature for the formation of an optimum SiO_xF_y layer [6,7].

It is interesting to note that Si via profiles with reduced undercut and local bowing can be attained when Si via etching results in black Si. Therefore, it is possible to identify optimum processing conditions to attain high-aspect-ratio vias by using bare Si samples instead of patterned Si samples. The black Si phenomenon observed during the formation of deep vias was mentioned in Jansen *et al.*'s work [8,9].

The following three research topics are addressed in this study: the effects of the O_2/SF_6 ratio and the Si substrate temperature on the occurrence of the black Si phenomenon, the correlations of undercut and local bowing of deep Si vias to the black Si phenomenon and the etching mechanism of the cryogenic etching process used for Si deep via formation.

II. EXPERIMENTAL SETUP

Figure 1 is a schematic diagram of the experimental setup. Si via etching in a SF_6/O_2 plasma was carried out by using an inductively coupled plasma (ICP) power source and a chuck bias power source. The ICP source at

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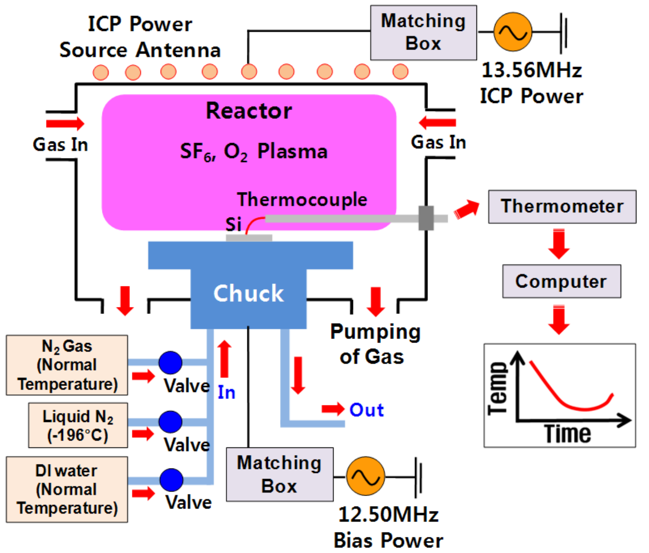

Fig. 1. Schematic diagram of the experimental setup.

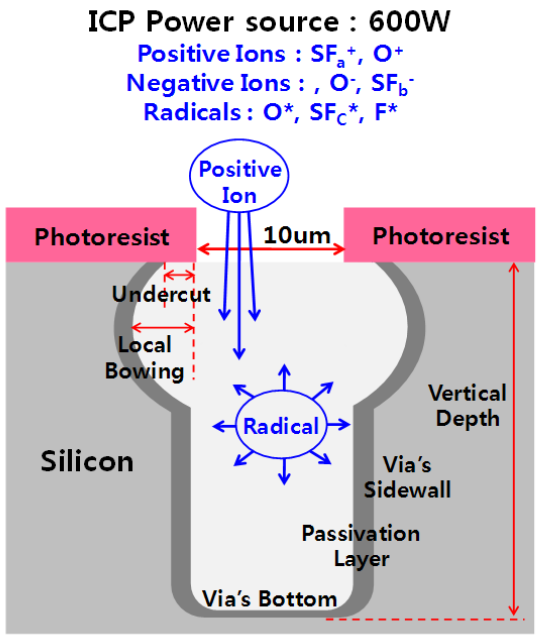

Fig. 2. Schematic model for Si via formation by using a SF_6/O_2 plasma.

13.56 MHz could generate up to 1500 W and the chuck bias power source at 12.50 MHz could generate up to 500 W. The distance between the ICP antenna and the wafer chuck could be controlled, but it was fixed at 8 cm in this work. SF_6 and O_2 gases were injected into the reactor through mass-flow controllers. The pressure of the reactor was adjusted by using a throttle valve located in the middle of the gas pumping line. Various via patterns were formed on p-type (100) Si substrates. In this work, 10 um- diameter vias were mainly investigated. All the Si samples were etched for 750 s.

For the control of the Si substrate temperature, the chuck temperature was controlled because the Si substrates and the chuck could be thermally connected by thermal paste. De-ionized water and liquid N_2 lines, which were linked up to the cooling line of the chuck, could help adjust the chuck from room temperature to cryogenic temperature. A temperature sensor located at the end of a thermocouple was in contact with the Si substrate so as to measure the surface temperature and the results were monitored using a computer. A field- emission scanning electron microscope (FE-SEM) was used to obtain the images of the Si via profiles. Some parts of the patterned photoresist mask cracked at cryogenic temperature [10]. A schematic of a typical etching profile of Si vias is shown in Figure 2. An UV-visible spectrometer was used to determine the reflectivity of the plasma-etched samples in the wavelength range of UV and visible light.

III. RESULT AND DISCUSSION

1. Black Si Phenomenon

Figure 3 shows that the black Si phenomenon depends on the O_2/SF_6 ratio and the Si substrate temperature. Also, the results show a correlation between the Si via profiles and the black Si phenomenon. At room temperature, the black Si phenomenon is not observed when the O_2/SF_6 ratio is 0 $\sim$ 1.5 while it is observed when the O_2/SF_6 ratio is 2 $\sim$ 2.5. When the O_2/SF_6 ratio increases to >3, it is no longer observed. On the other hand, when the Si substrate temperature is –50 °C, the black Si phenomenon is not observed when the O_2/SF_6 ratio is 0 $\sim$ 0.4 while it is observed when the O_2/SF_6 ratio is 0.5 $\sim$ 2. Again, when O_2/SF_6 ratio is >3, it is no longer observed. This phenomenon can be understood by interpreting the role of O^* (* means a radical state in a plasma), which contributes to the formation of passivation layers. During the stage of Si via formation, O^* reacts with Si and F^* so as to help form passivation layers, which are understood to be SiO_xF_y. At room temperature, when the O_2/SF_6 ratio is 2 $\sim$ 2.5, the Si surface is partially covered with SiO_xF_y layers, which obstruct subsequent chemical reactions with F^*, giving rise to a micro-masking effect. This results in a nano-pillar structure on the bare Si substrate, as shown in image B of Figure 3 [11]. This nano-pillar structure absorbs most of incident light, so the Si surface turns black. However, when the O_2/SF_6 ratio is >3, the Si surface is completely covered with SiO_xF_y, which prevents chemical reactions with F^* from occurring. As a result, black Si is not observed from image A in Figure 3. The same interpretation can be made for the results obtained for Si substrate at cryogenic temperature.

Meanwhile, the black Si phenomenon is also observed to depend on the Si substrate temperature. The onset O_2/SF_6 ratio of black Si decreases with decreasing Si

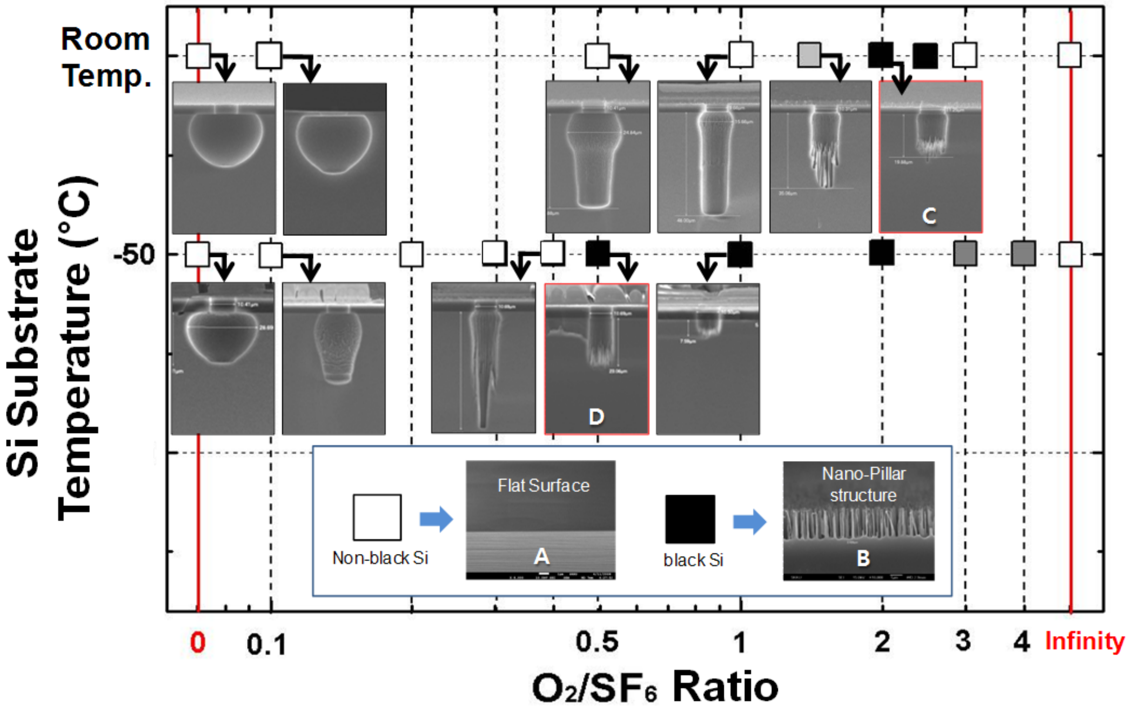

Fig. 3. Black Si maps and Si via profiles as a function of O_2/SF_6 ratio and Si substrate temperature.

Table 1. Gibbs free energy (ΔG) for various Si compounds.

Formula	Gibbs free energy (KJ/mol) at 298.2 K
SiO	–126.4
SiO_2	–853.5
SiF	–24.3
SiF_2	–627.6
SiF_4	–1572.7
SiF_6^{2-}	–2199.5

substrate temperature. (The onset O_2/SF_6 ratio of black Si is 2 at room temperature whereas it is 0.5 at cryogenic temperature). This phenomenon may be explained from the viewpoint of the thermal properties of SiO_xF_y, *e.g.*, the boiling point and the Gibbs free energy. The boiling point of one kind of silicon oxyfluoride (Si_2OF_6) is known to be –23.3 °C while those of other kinds of silicon oxyfluorides are not known [12]. This implies that solid-state SiO_xF_y passivation layers are formed more stably at cryogenic temperature than at room temperature, as these are not evaporated at temperature <–23.3 °C. This can also be supported by the relation $\Delta G = -RT \ln K$, where ΔG is the Gibbs free energy change and K is the equilibrium constant. We understand that the forward reaction occurs more favorably than the reverse reaction when ΔG is negative. Table 1 shows that most silicon oxides and silicon fluorides have negative ΔG. This suggests that the silicon oxyfluorides are very likely to be easier to form at lower temperatures [12].

According to the analysis of via profiles based on the black Si phenomenon, three interesting features are observed: (1) Minimum undercut and local bowing occur for conditions resulting in black Si, independent of the Si substrate temperature. (2) Perpendicular etching is suppressed with increasing O_2/SF_6 ratio for conditions where black Si is observed. It is understood that a SiO_xF_y layer can cover the via's bottom, as well as the via's sidewall when the O_2/SF_6 ratio is high. (3) The anisotropic property of via profiles taken near the onset point of black Si becomes more conspicuous with decreasing Si substrate temperature. Images C and D in Figure 3 support this fact. This is understood by analyzing the thermal properties and the spatial location of the SiO_xF_y layer in the vias. Though the SiO_xF_y layer in image D is thinner than that in image C, the SiO_xF_y layer in image D is thick enough to suppress the undercut and local bowing because the cryogenic temperature applied to the Si substrate is effective in suppressing the etching at spots thinly covered. However, the SiO_xF_y layer formed on the via's bottom in image D is less effective than that in image C. As a result, the via profile in image D is more anisotropic than the via profile in image C.

Figure 4 shows the reflectance versus wavelength results obtained for bare Si plasma-etched at different O_2/SF_6 ratios. These results support the results of Figure 3. The results of Figure 4(a) were obtained for a Si substrate at room temperature: black Si is observed when the O_2/SF_6 ratio is at 2.0 and 2.5 and the reflectance from the sample is close to 0 % in the wave-

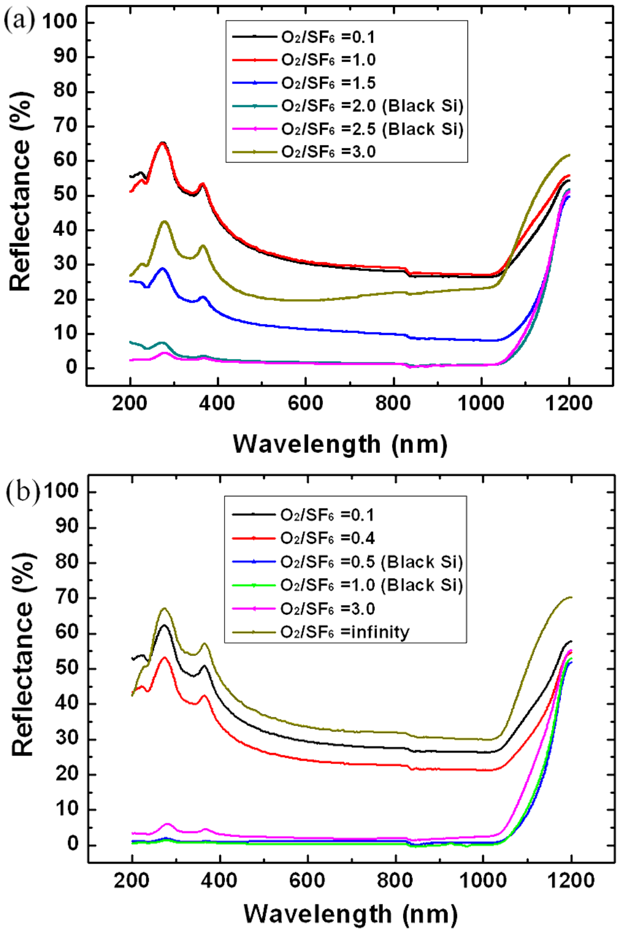

Fig. 4. Reflectance as a function of wavelength for various O_2/SF_6 ratios when a bare Si substrate was etched by using plasma at (a) room temperature and (b) cryogenic temperature (–50 °C).

length range of 200 – 1000 nm. The results of Figure 4(b) were obtained for a Si substrate at –50 °C: black Si is observed when the O_2/SF_6 ratio is at 0.5 and 1.0 and the reflectance is close to 0 %, similar to Figure 4(a). Note that the reflectances detected from all the samples with various O_2/SF_6 ratios sharply increase when wavelength is $>\sim$1000 nm, as shown in Figure 4(a) and (b). It can be understood using the formula $\lambda = hc/E$. Minimum light energy to be absorbed on Si corresponds to its bandgap is 1.1 eV. That is to say that, most of light with wavelengths $>\sim$1130 nm corresponding to 1.1 eV is reflected without being absorbed.

2. Cryogenic Etching Processes

As discussed above, an optimized processing condition to minimize the undercut and local bowing is obtained at –50 °C (Si substrate temperature) and 0.5 (O_2/SF_6 ratio). This condition is applied to obtain the results of

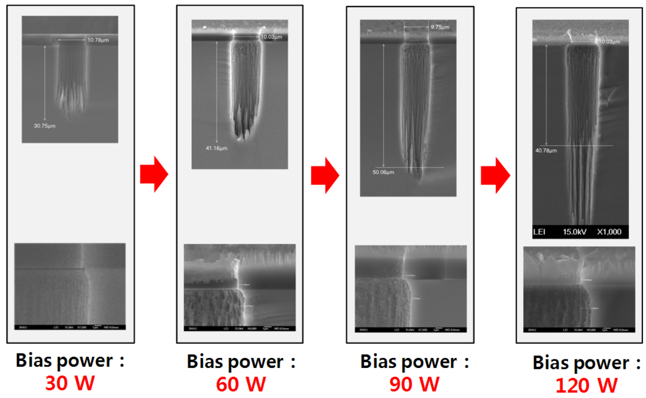

Fig. 5. Si via profiles as a function of bias power for a Si substrate at cryogenic temperature.

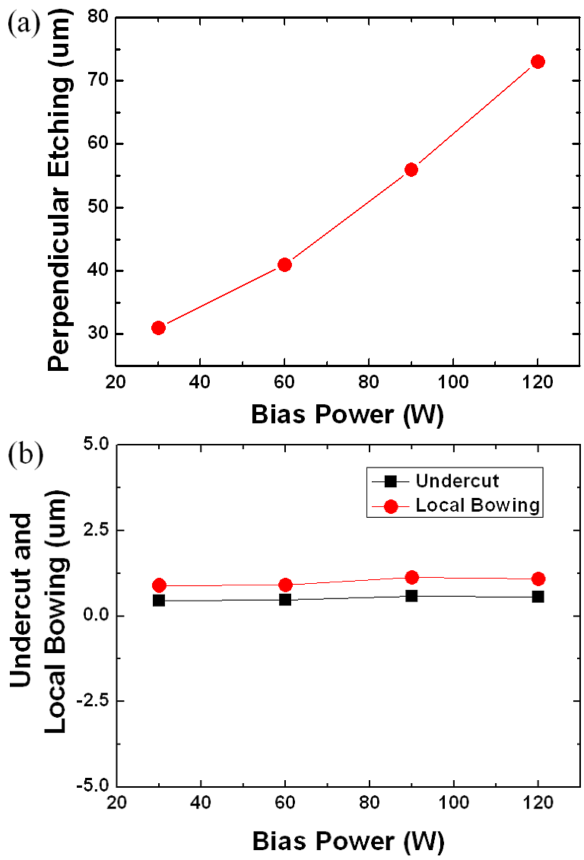

Fig. 6. (a) Perpendicular etching and (b) undercut and local bowing of Si via profiles as a function of bias power for a Si substrate at cryogenic temperature.

Figure 5 and Figure 6.

Figure 5 shows the via profile as a function of the bias power. Figure 6 shows that the etching depth increases with increasing bias power while the undercut and local bowing rarely change as the bias power is being increased. This fact can be explained with the help of Figure 2. In the reactor, ions such as SF_a^+, O^+, O^- and SF_b^- and radicals such as O^*, SF_c^* and F^* are generated in a SF_6/O_2 plasma discharge. Positive ions are perpendicularly pulled by the bias voltage applied to the Si substrate. These positive ions physically bombard the via's bottom and this enhances the perpendicular etching rate inside the vias. On the other hand, this mechanism adversely influences the anisotropic property because positive ions attack the via's sidewall and the phoresist mask, as well as the via's bottom. Physical ion bombardment to the via's sidewall and the photoresist causes undercut, local bowing and reduced etching selectivity of Si with respect to the photoresist. However, at low temperatures, the SiO_xF_y layer formed on the via's sidewall and the photoresist stands more stably against physical bombardment because lowering the temperature enhances the strength of the SiO_xF_y and of the photoresist. As a result, a high bias power can be applied to a cryogenic plasma etching process for the purpose of enhancing ion bombardment onto the via's bottom so as to increase the vertical etching rate.

IV. CONCLUSION

Black Si was more conspicuous with increasing O_2/SF_6 ratio, irrespective of the Si substrate temperature. However, when the O_2/SF_6 ratio was very high, black Si was no longer observed because the passivation layer grew faster due to the increasing density of oxygen radicals. Meanwhile, black Si was more conspicuous with decreasing Si substrate temperature. The SiO_xF_y passivation layers that are partially formed on the bare Si surface are thought to grow faster at lower Si substrate temperature, irrespective of the O_2/SF_6 ratio. From the relation between black Si phenomenon and Si via formation, minimum undercut and local bowing are known to be attained for certain O_2/SF_6 ratios and Si substrate temperatures that give rise to black Si. By applying the black Si phenomenon and using cryogenic temperature, one can realize a high etching rate and minimum undercut and local bowing during the etching of high-aspect-ratio deep vias.

ACKNOWLEDGMENTS

This work was supported by the Association of the Growth Engine for Next Generation Semiconductors of the Ministry of Knowledge Economy in South Korea.

REFERENCES

[1] T. Fukushima, H. Kikuchi, Y. Yamada, T. Konno, J. Liang, K. Sasaki, K. Inamura, T. Tanaka and M. Koyanagi, IEEE Intl Electron Devices Meeting, Tech. Dig. 985 (2007).

[2] M. Kawano, N. Takahashi, Y. Kurita, K. Soejima, M. Komuro and S. Matsui, IEEE Trans. Electron Devices **55**, 1614 (2008).

[3] F. Laemer and A. Schip, *WO94/14187* (DE93/01129, US patent US5501893).

[4] S. Tachi, K. Tsujimoto and S. Okudaira, Appl. Phys. Lett. **52**, 616 (1988).

[5] W. J. Park, Y. T. Kim, J. H. Kim, S. J. Suh and D. H. Yoon, Surface & Coating Tech. **193**, 314 (2005).

[6] M. Boufnichel, S. Aachboun, F. Grangeon, P. Lefaucheux and P. Ranson, J. Vac. Sci. Technol. B **20**, 1508 (2002).

[7] M. Boufnichel, P. Lefaucheux, S. Lefaucheux, R. Dussart and P. Ranson, Microeletronic Engineering **77**, 327 (2005).

[8] H. Jansen, M. de Boer and M. Elwenspoek, *IEEE, Micro Electro Mechanical Systems, MEMS '96, Proceedings* (San Diego, CA, 1996), p. 250.

[9] H. Jansen, M. de Boer, H. Wensink, B. Kloeck and M. Elewenspoek, Microelectronics J. **32**, 769 (2001).

[10] L. Sainiemi and S. Franssila, J. Vac. Sci Technol. B **25**, 1071 (2007).

[11] C. Yang, S. H. Ryu, Y. D. Lim and W. J. Yoo, NANO **3**, 169 (2008).

[12] D. R. Lide and H. P. R. Frederiks, CRC Handbook of Chemistry and Physics, 70th ed., B-127, D-83 (1997).