RIE PASSIVATION LAYER REMOVAL BY REMOTE H-PLASMA AND H_2/SiH_4 PLASMA PROCESSING

Hong Ying, J.P. Barnak*, Y.L. Chen*, and R.J. Nemanich**
Department of Electrical and Computer Engineering,
*Department of Materials Science and Engineering,
**Department of Physics, North Carolina State University, Raleigh, NC 27695-8202

ABSTRACT

Remote H-plasma and H_2/SiH_4 plasma processes were studied as potential dry cleaning processes following reactive ion etching (RIE). The processes were compared to a process of UV/ozone followed by an HF dip. The native oxide from Si(100) substrates was removed with an RIE etch of CHF_3/Ar. The RIE process produced ~150Å of a continuous fluorocarbon (CF_x) passivation layer on the Si surface. For the post-RIE-cleaning three approaches were studied and compared including (1) uv-ozone exposure followed by an HF dip, (2) remote H-plasma exposure, and (3) remote H_2/SiH_4 plasma exposure. Auger electron spectroscopy (AES) was used to investigate the surface chemical composition, and AFM was used to measure changes in surface roughness. All three processes showed substantial removal of the passivation layer. The CF_x polymer was completely removed in less than 1 min for samples exposed to a 100W remote H-plasma at 15mTorr and 450°C. With the addition of ~0.1% of SiH_4, the remote H_2/SiH_4 plasma also showed increased removal of residual oxygen contamination. The surface roughness of the plasma processed surfaces increased slightly.

INTRODUCTION

RIE processes are becoming more important in VLSI fabrication as device features become smaller. The advantages of RIE include high anisotropy and compatibility with in-situ, single-wafer processing.

Anisotropic SiO_2/Si selective etching has been studied[1-10] since it is an important step prior to producing contact holes[1] or to Si epitaxial growth[2]. Anisotropy is largely characteristic of the RIE technique, but selectivity is dependent upon the etch gases. The use of CF_4, $CF_4/x\%\ H_2$, and CHF_3 results in different SiO_2:Si selectivity[2-6]. It has been suggested that the deposition of a fluorocarbon (CF_x) film is crucial to achieve the SiO_2/Si etch selectivity[5,6]. The CF_x film is formed on the Si surface which prevents fluorine from attacking the Si, but not on the SiO_2. Therefore the Si etch rate decreases, while the SiO_2 etch rate remains relatively constant. The CF_x film must be removed prior to the next processing step. Processes that have demonstrated success as the post RIE treatment include thermally grown sacrificial oxide film followed by the oxide film removal[2], O_2 plasma/buffered HF dip[3,6,7], UV/O_2 exposures followed by diluted HF dip[8]. In each case, however, a wet etch step is involved.

It would be advantageous to use a dry cleaning process after RIE for the following reasons: (1) to be compatible with in-situ, single-wafer processing, (2) to reduce chemical waste, (3) to obtain a more effective clean than wet chemical cleaning as device features approach 0.1μm. A cleaning procedure based on hydrogen plasma has been reported by J.P. Simko *et al*[9]. Their results indicate that a 50Å fluorocarbon film is reduced to a 10Å

Mat. Res. Soc. Symp. Proc. Vol. 386 © 1995 Materials Research Society

carbon film which contains little fluorine. Post RIE treatment in an NF_3/Ar plasma has been studied by H. Cerva *et al*[10]. The CF_x polymer film is completely removed as well as the defect zone, but the surface roughness increases (up to 5nm).

In previous studies from this laboratory, it has been shown that the surface morphologies are dependent on substrate temperature and pressure during H-plasma cleaning[11,12]. The 450°C, 15mTorr, 20W H-plasma exposure of Si(100) substrates leads to a H-passivated surface, and the surface is smooth with no observable subsurface defects. AFM measurements indicated no discernible increase in the RMS roughness for these processes. Furthermore, the 450°C H-plasma process did not induce the near surface platelet defects often observed for H-plasma exposure with wafer temperatures less than 300°C[12]. In this study, the same H-plasma process was utilized as a post RIE cleaning process. The surface chemical composition and surface roughness were studied.

EXPERIMENTAL

Reactive Ion Etching Process

The substrates used in this study were Si(100), 25mm diameter, boron doped (p-type), with a resistivity of 0.8-1.2Ω-cm. An CHF_3/Ar RIE was used to selectively etch the Si native oxide from the Si substrates. RF power was 85W (power density was 0.15W/cm^2), and the gas flow rates were 40sccm of CHF_3 and 10sccm of Ar. The chamber pressure was set to 60mTorr for 1 min at which the SiO_2 etch rate was 75Å/min, and then to 90mTorr for 0.5 min at which a continuous CF_x polymer film was deposited on the Si surface.

Post RIE Cleaning

Three approaches were studied and compared.

(1) UV-ozone & HF dip

The cleaning consists of a 10 min uv-ozone exposure followed by a 1 min dilute HF(10:1) dip. The procedure was repeated twice.

(2) Remote H-plasma Cleaning

The H-plasma was generated inductively by an rf field through a copper coil encircling a quartz tube[11,12]. The samples were positioned 40cm downstream relative to the center of the plasma tube, and were exposed to a H-plasma at 15mTorr and 450°C. The rf power was 20W or 100W.

(3) Remote H_2/SiH_4 plasma Cleaning

A dilute mixture of SiH_4 in H_2 was flowed into the plasma chamber. The gas flow rates were 86sccm of H_2, 10sccm of H_2/1% SiH_4, and the chamber pressure was 25mTorr. The samples were exposed to a 100W H_2/SiH_4 plasma at a substrate temperature of 450°C.

The plasma chamber was connected to a UHV surface analysis system which included AES and LEED[11]. Following the cleaning processes, the samples were transferred to the analysis system. The AES was used to investigate the surface chemical composition. The sample surfaces were characterized with atomic force microscopy(AFM) and cross-sectional transmission electron microscopy(TEM). The AFM used in this study was a Park Scientific SFM-BD2. The piezoscanner had a 10μm scanning range in both X and Y directions.

RESULTS AND DISCUSSION

Figure 1 represents a cross-sectional TEM micrograph of the reactive ion etched Si. Approximately 150Å of Ti was deposited in order to distinguish between the CF_x film and the epoxy glue used in the TEM specimen preparation. It is observed that the RIE resulted in the formation of ~150Å of a continuous CF_x passivation layer on the surface. In addition, a layer with a high density of defects is observed within several hundred Å of the surface.

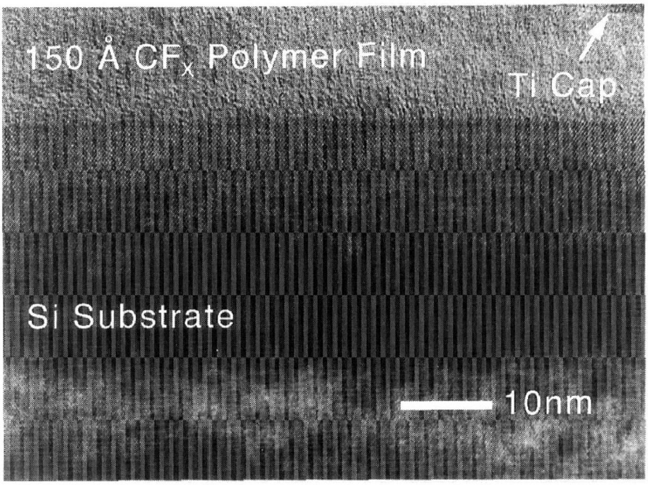


Fig. 1 Cross-sectional TEM micrograph of a Si wafer after the reactive ion etching process.

The AES spectra of the CF_x film removal by remote H-plasma is shown in Fig. 2. By exposing to 100W H-plasma at 15mTorr and 450°C, the CF_x polymer film was completely removed in less than 1 min. Longer exposure leads to a further decrease but not complete removal of the oxygen contamination. The oxide was apparently formed during the RIE process and might be buried in the defect sites at the near surface region. For comparison, the AES C/Si and O/Si peak-to-peak ratio are plotted versus the post-RIE-cleaning time in Figure 3 for the different cleaning approaches. In each case the F is below the AES detection limit. This agrees with the experimental observation that F is more effectively removed from the contamination layer than C[9]. The solid lines connecting the points are to correlate similar processes, and should not be viewed as representing the actual time dependence of the contaminant removal process. The data does establish the trends of lower surface contaminant with longer processing times. All three processes exhibit a significant reduction in surface contaminant with essentially submonolayer carbon and oxygen residuals. Both in situ techniques show no detectable C after a 10 min exposure, while the ex situ approach of uv-ozone & HF dip shows some C that could be attributed to the wafer transfer into the AES system. Both plasma processes show slight increases of oxygen after the removal of the RIE CFx passivation layer. It is probable that this oxygen formed during the RIE process as the passivation layer was formed. With the addition of a small amount of SiH_4, the remote H_2/SiH_4 plasma is more effective for oxygen removal[13]. In another study in this same volume it was shown that the very dilute H_2/SiH_4 plasma results in SiO_2 etching with no Si deposition on any oxide surfaces[13].

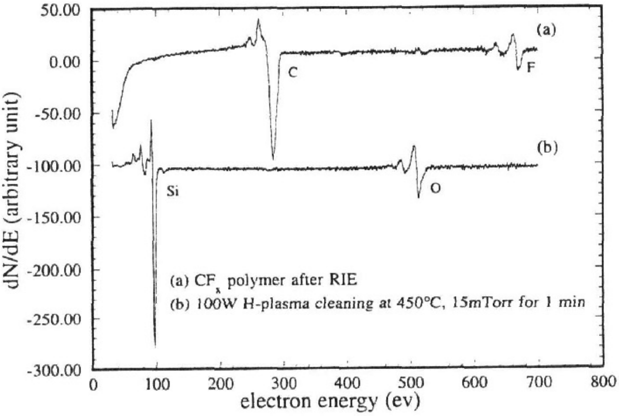


Fig.2 RIE passivation layer removal by remote H-plasma cleaning.

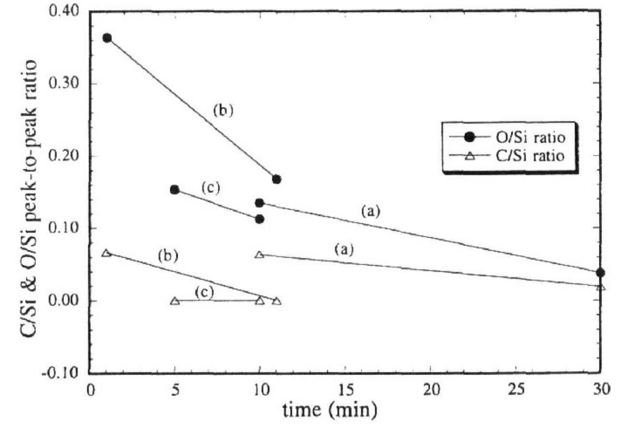


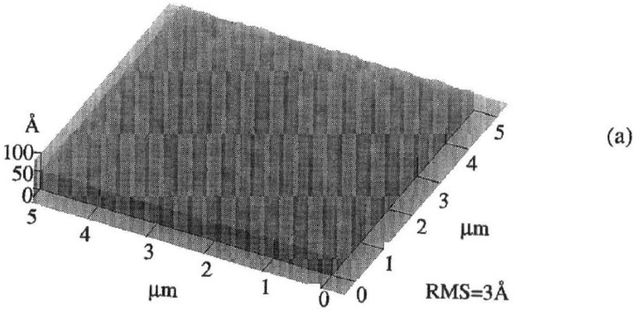
Fig. 3 AES C/Si and O/Si peak-to-peak ratio vs post-RIE-cleaning time.

(a) uv-ozone exposure followed by dilute HF dip

(b) H-plasma cleaning at 450°C, 15mTorr. The power was 20W for the first 1min and 100W after

(c) 100W H_2/SiH_4 plasma cleaning at 450°C, 25mTorr

Figure 4 shows representative AFM images of the surfaces. The RMS surface roughness increased from 3Å to 8Å after the H-plasma exposure for the conditions studied.



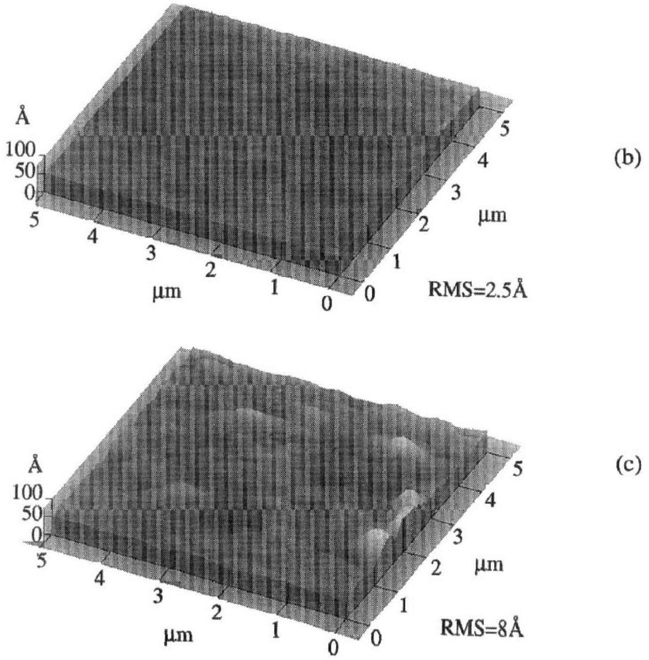


Fig. 4 AFM images of the samples (a) after RIE with ~150Å CF_x passivation layer
(b) after RIE and uv-ozone, HF dip
(c) after RIE and 100W H_2/SiH_4 plasma cleaning at 450°C, 15mTorr for 10 min

Although there is a small increase in roughness, low energy electron diffraction (LEED) measurements display the expected 2x1 reconstruction indicating that the surface is crystalline and not amorphized by either the RIE or the H-plasma clean. Future studies will explore whether the epi quality will be effected by the small increase in roughness.

It is also relevant to comment on the subsurface defect formation. The presence of subsurface defects were identified in the Si after the RIE. In addition it has been shown that H-plasma processing can result in the formation of platelet and other extended defects in the near surface region. In another study from this laboratory, it has been shown that H-plasma exposure results in substantial defect formation at wafer temperatures of 100 to 300°C, but for H-plasma exposure at 450°C no subsurface defects are observed in plan view or cross section TEM measurements[12]. We employed similar H-plasma processing conditions in the experiments described here, so it is anticipated that there should be no increase in subsurface defects due to the H-plasma. Future studies will explore issues related to whether the H-plasma produces defects in the RIE processed surfaces or whether the RIE damage can be affected by the process.

CONCLUSIONS

The results presented here display three processes that have potential to be employed as a post RIE clean after the formation of a CF_x passivation layer. The uv/ozone process followed by an HF dip showed the lowest oxygen residual, but a slightly increased C residual attributed to the exposures following the HF dip. The two plasma processes demonstrate effective and rapid removal of the passivation layer, and only slightly increased oxygen levels and rms surface roughness. The presence of a small amount of silane in the plasma results in a reduction in the oxygen concentration. The H-plasma exposure at a wafer temperature of 450°C has previously been shown to result in cleaning without defect formation, and we suggest this may be the case here also. Future studies will focus on issues related to epi growth and defect structures. The plasma processes described here could prove useful as cleans in single wafer clustered systems.

ACKNOWLEDGMENTS

This work is supported by the NSF Engineering Research Center for Advanced Electronic Materials Processing at North Carolina State University. The authors would specially like to thank K. Violette, M.C. Öztürk for the valuable discussions and R. Haymaker, J. Todd in the Microelectronics Lab of NCSU for their help in RIE processes.

REFERENCES

1. G.S. Oehrlein, Phys. Today. **39(10)**, 26 (1986)
2. J.C. Lou, W.G. Oldham, H. Kawayoshi, and P. Ling, J. Appl. Phys. **71**, 3225 (1992)
3. L.M. Ephrath and R.S. Bennett, J. Electrochem. Soc., **129**, 1822 (1982)
4. M.A. Jaso, and G.S. Oehrlein, J. Vac. Sci. Technol. **A6**, 1397 (1988)
5. G. E. Potter, G.H. Morrison, P.K. Charvat, and A.L. Ruoff, J. Vac. Sci. Technol. B10, 2398 (1992)
6. G.S. Oehrlein, G.J. Scilla, and S.J. Jeng, Appl. Phys. Lett. **52**, 907 (1988)
7. K. Reinhardt, B. Divincenzo, C.-L. Yang, P. Arleo, J. Marks, P. Mikulan, T. Gu, and S. Fonash, Mat. Res. Soc. Symp. Proc. vol 315, 267 (1993)
8. T. Gu, R.A. Ditizio, S.J. Fonash, O.O. Awadelkarim, J. Ruzyllo, R.W. Collins and H.J. Leary, J. Vac. Sci. Technol. **B12**, 567 (1994)
9. J.P. Simko and G.S. Oehrlein, J. Electrochem. Soc., **138**, 277 (1991)
10. H. Cerva, E.-G. Mohr, and H. Oppolzer, J. Vac. Sci. Technol. **B5**, 590 (1987)
11. T.P. Schneider, J. Cho, Y.L. Chen, D.M. Maher, and R.J. Nemanich, Mat. Res. Soc. Symp. Proc. vol 315, 197 (1993)
12. T.P. Schneider, J.S. Montgomery, H. Ying, J.P. Barnak, Y.L. Chen, D.M. Maher, and R.J. Nemanich, Electrochemical Soc. Proc. vol **PV94-7**, 329 (1994)
13. J. Barnak, H. Ying, Y.L. Chen, and R.J. Nemanich, Mat. Res. Soc. Symp. Proc. (this volume)