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Hydrogen Plasma Removal of Post-RIE Residue for Backend Processing

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Reactive ion etching of a patterned silicon dioxide layer leaves behind a uniform fluorocarbon layer which must subsequently be removed. Both surface and via polymeric residues form during the reactive ion etch step and their removal using H_2 -based plasma clean processes is reported here. X-ray photoelectron spectroscopy was used to determine the composition of the residue. Scanning electron microscope images were taken before and after the dry clean treatment to determine the effectiveness of the residue removal process. A radio-frequency-generated hydrogen plasma was used in the dry clean experiments. Power, temperature, and pressure were varied while gas flow was kept constant at 75 sccm and the process time was 5-10 min. The surface residue (on the oxide) was most efficiently removed at 400 W, 450°C, and 15 mTorr when exposed to the plasma for 10 min. The in-via residue was best removed following a 5 min plasma exposure at 100 W, 450°C and 15 mTorr. © 1999 The Electrochemical Society. S0013-4651(98)08-076-8. All rights reserved.

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The current integrated circuit (IC) device fabrication process has over 400 individual process steps. At least 20% of these steps are surface cleaning and preparation steps which are used to decontaminate the wafer surface. Surface preparation processes should not only reduce the levels of unwanted particles and residues and terminate the surface from further chemical activity but also leave the bulk properties of the substrate unaffected. This study is concerned with the removal of the post-RIE (reactive ion etch) polymeric residue which occurs during a via or contact etch. As device dimensions become smaller it is increasingly important to explore in situ processes which can be applicable to small via dimensions (<1 μ m). The focus of this study is to assess the effectiveness of a hydrogen plasma process for the removal of the residue that remains in and around the interconnect via structures after an RIE process.

RIE.-Dry etching processes are commonly used for etching critical structures such as contact or interconnect vias.¹ The isotropic characteristic of wet etching limits the control over the process, particularly for structures with small dimensions.¹ RIE is typically used to achieve anisotropic etching¹⁻⁶ mainly to form contact and via holes. The etching mechanism involves both chemical and physical components.⁷ In a dry plasma etch process, the directional etching is achieved by physical sputtering.¹ However, one characteristic of the anisotropic hole etch is the polymeric residue left behind after the etch.¹⁻¹⁰ Previous studies have demonstrated that the residue is composed of fluorocarbon compounds.^{1,3,5-12} Several surface analysis tools [for example, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectroscopy (SIMS)] have previously been used to characterize the post-RIE residue.^{1,4,6-9,11} Oehrlein's¹ experiments confirm that the residue layer consists primarily of fluorine and carbon uniformly covering the substrate. Previous studies have also shown that the postetch residue forms a 30-40 Å layer on the surface of the substrate.^{1,7,10,13} The interaction of the photoresist, etch by-products, and etchants themselves form this polymeric material, which lines the walls and bottoms of vias.² If not controlled and removed, the residue contamination can inhibit device performance.

Selectivity of exposed materials during the RIE process is dependent upon the gas chemistry that is used in the process.³ Previous work has shown that the deposited residue is crucial to the achievement of good SiO₂/Si etch selectivity during a contact etch.^{1,4,9,10} The polymeric residue formation also prevents sidewall etching, leading to better anisotropy.²

This study is focused on the removal of the residual polymer both in and around the etched vias. Other work has focused on the removal of post-via-etch residue.⁵ An earlier study by Creva et al. used an NF₃/Ar plasma treatment to effectively remove the post-RIE residue.⁴ However, it was discovered that this treatment resulted in a roughened surface. O₂ ashing followed by an HF dip, as well as an O₂ ash with a chromic acid etch and HF dip, have been effective in removing the polymer.⁵ However, oxygen-based-plasma exposure to silicon requires an HF dip following the residue removal in order to strip the thin layer of SiO₂ that is formed.⁵

For the via structures in interconnects, there is no exposed Si and the formation of SiO₂ from an O₂ plasma process may not be as critical. However, the use of an O₂ plasma can result in the formation of an oxide on the metal or barrier layer, and the formation of any oxide may lead to a degradation of the interconnect resistance. In this study we explore the use of a hydrogen plasma process to remove the post-etch residue. Previous studies have established that the H plasma can result in an oxide-free surface when appropriately applied to Si surfaces.¹⁴⁻¹⁸

Hydrogen plasma.-Several wet and dry methods of removing processing residues have previously been explored.^{5,9,10,19} Wet cleaning methods include RCA cleans, HF dips, and H2SO4/H2O2. UVozone treatments have also been investigated but were found to be time consuming processes.⁵ The aqueous chemical cleaning approach is incompatible with low-budget in situ cleaning needs. A plasma technique is an attractive cleaning method for several reasons. Lower impurity concentrations are present in gases compared with liquid reagents. This reduces the problem of process-induced contamination when a plasma is used. Plasma cleaning can be clustered with the RIE etch or with metal deposition to provide an in situ process which can be used in current as well as future processing applications. Another advantage of a plasma clean is the reduction in the amount of discarded chemicals compared with wet cleans, which makes it favorable for environmental concerns. Typically, plasma chemistries that have been used for dry clean applications include $O_2,\,NF_3\!/Ar,\,and\,H_2^{.9,10,14,19}$ Oxygen plasmas oxidize the silicon surface rather quickly, causing high contact resistance. The NF₃/Ar plasma is effective for residue removal but roughens the surface. The H-plasma cleaning process can be applied at intermediate stages of the device fabrication process as a suitable surface contaminant removal process.^{16,21,22}

Hydrogen plasmas used to clean semiconductor wafers can be generated using rf, microwave, and ECR (electron cyclotron resonance) plasma sources.¹⁸ RF plasma treatment of the silicon surface has been investigated as a cleaning and conditioning step prior to silicon epitaxy.^{16,21,22} A radio frequency (rf) signal is applied to the reactant gas (in this case, hydrogen) creating excited and neutral species (a plasma). These species react with the substrate which can be either immersed in the discharge region or isolated from the region as in the case of a remote plasma.²³ Previous studies have shown that the hydrogen plasma clean effectively removes carbon

and fluorine. $^{14\text{--}16}$ In the case of SiO₂, longer hydrogen plasma exposure times can lead to some reduction, but in general, complete oxide removal is not obtained. 15

The development of surface roughness and subsurface defects during a hydrogen plasma exposure is an important issue. Prior studies in our laboratory concluded that lower substrate temperature (<200°C) resulted in an increase in silicon surface roughness, while higher process temperature (>450°C) showed little or no increase in surface roughness and no observable change in surface morphology.²⁰ The current study indicates that the hydrogen plasma effectively reacts with the fluorocarbon film left in the vias and on the oxide surface after an RIE plasma oxide etch process step.

Experimental

Wafers were prepared at Texas Instruments through via etch and photoresist (PR) strip and sent to North Carolina State University (NCSU) for dry clean processing. The wafers were 150 mm diam p-type Si(100) substrates which were prepared with an RCA clean followed by an HF dip. 1000 Å aluminum was sputtered onto the silicon and a 300 Å layer of TiN was deposited on top of the aluminum. A 9000 Å TEOS (tetraethoxysilane) layer was deposited on top of the TiN layer. The vias were patterned and formed by RIE down to the TiN layer using an Applied Materials high-density plasma (HDP) reactor with a C_2F_6 plasma process followed by an in situ O₂ resist strip. The etching processes were modified in order to produce a substantial quantity of the residue for the purpose of evaluating the dry cleaning processes. Two sets of residue conditions (surface and via) were generated, by varying the RIE process parameters, and used for dry clean process evaluations. Figure 1 schematically illustrates the structure of the residue on wafers and shows both types of residue, although the experiments were performed on wafers having primarily one type of residue. Scanning electron microscope (SEM) micrographs were obtained from die near the center and the edge of each wafer.

The hydrogen plasma system is one component of a multiple component cluster environment and is schematically illustrated in Fig. 2. The plasma was generated using an rf source. The rf is coupled into the system through a copper coil that is wrapped around a quartz tube. The hydrogen is fed into the chamber through the top of the quartz tube and the plasma is largely confined to the tube. The wafers were automatically positioned on three pins and located about 4 in. from the end of the plasma tube.

Previous work in our laboratory determined that CF_x polymeric residue formed during the contact etch could be effectively removed using a hydrogen plasma.¹⁵ Experiments were defined using a 2³ fullfactorial design and applied to both surface residue removal and via residue removal. This design allowed two levels for each of the variables and enabled us to deduce the main effects as well as two-factor and three-factor interactions. With this design, eight runs with two replicates at the center point were prepared for each residue type. The



Figure 1. Schematic diagram for patterned structure used on wafers in this experiment.



Figure 2. Schematic of the hydrogen plasma system used for this study.

design of experiment variable parameters were rf power, wafer temperature, and H_2 pressure. The power was varied from 100 to 400 W; the temperature was varied from 25 to 450°C, and the pressure was varied from 15 to 150 mTorr. The wafers were loaded simultaneously into the cluster (vacuum) environment and were processed individually in the plasma system. There was a delay of about 10-15 min between each run to allow the heater to cool down sufficiently prior to wafer transfer. Each sample was exposed to a hydrogen plasma for 5 or 10 min. The gas flow rate was held constant at 75 sccm. The wafers were removed from the vacuum environment at NCSU and transported back to Texas Instruments for analysis using an inline SEM.

Results and Discussion

Top-view SEM images were used to determine if the hydrogen plasma process removed the CF_x residue. The micrographs were visually analyzed, the data was quantified, and the most effective dry clean process parameters were determined from a statistical analysis of the SEM data. The SEM images were obtained from die near the center and the edge of each wafer following the H-plasma clean for both types of residue. Figure 3 displays the center and edge micrographs of the wafer before and after H-plasma processing of the surface residue. There is a higher density of the CF_x polymeric residue in the center of the wafer than at the wafer edge. Exposing the wafer to a hydrogen plasma at 400 W, 450°C, and 15 mTorr for 10 min, we observe that essentially all of the surface residue was removed.

Figure 4 shows SEM images of the via residue from wafer edge and wafer center die before and after a hydrogen plasma treatment. For the via residue, there appears to be more residue near the edge than near the wafer center. As noted previously, the RIE process was altered to produce a large amount of via residue to more clearly observe the effect of the H-plasma process. After a 5 min, 100 W plasma process, the residue in the via was significantly reduced. This was also accomplished at 450°C and 15 mTorr. It is evident that there is a small amount of residue remaining on the sidewalls of the via. We have not yet determined the effect of this small amount, but we believe that further process optimization will result in the removal of this residue. Previous experiments in our laboratory have shown that removal of the residue does not substantially affect the silicon oxide.15 The hydrogen plasma appears to have very good selectivity to SiO₂.¹⁵ The SEM images then indicate that the hydrogen plasma significantly removes RIE-generated residue from both the surface and within the via structure.

XPS data was obtained from the post-RIE wafers to identify the chemical composition of the etch residue. The XPS survey spectra of



Figure 3. SEM images of surface residue before and after H-plasma clean: (a) preplasma, wafer edge region; (b) post-plasma, wafer edge region; (c) pre-plasma, wafer center region; (d) post-plasma, wafer center region.

the residue wafers, for both a surface residue condition as well as a via residue condition, are shown in Fig. 5. The XPS survey spectra was obtained from 1100 to 0 eV. The spectra identified a fluorocarbon compound on the wafer surface. The F (1s) and C (1s) spectral lines were easily detected. Individual spectra for these elements demonstrate various types of bonding. Previous experiments in our laboratory have associated the peaks for C (1s) between 288 and 294 eV to be attributed to CF, CF₂, and CF₃ type bonding.²⁴ Peaks between 284 and 288 eV can be associated with C–C, CH₂, C–O, and C–H bonding.²⁴ The F (1s) peak is usually centered on 685.6 eV for a CF_x residue.²⁴ Unfortunately, long air exposure of the wafers precluded using the same XPS technique for chemical analysis for post-hydrogen-plasma-treated wafers. Therefore, we relied on the SEM measurements as the analytical means to determine whether or not the residue was removed.

Experiments conducted by Simko and Oehrlein help in understanding the probable mechanism for hydrogen reaction with CF_x polymers. They show that a hydrogen plasma can reduce a 50 Å fluorocarbon film to a 10 Å carbon film, which contains little or no fluorine.¹⁴ This proves that the plasma is more effective in reducing the amount of fluorine than the amount of carbon. Thermodynamic and kinetic properties indicate that the H–F bond (569 kJ/mol) is stronger than the C–F bond (552 kJ/mol) as well as the C–H bond (444 kJ/mol for CHF₃) for any species that hydrogen can make with carbon.¹⁴ The strength of the H–F bond makes it favorable for fluorine to be removed from the fluorocarbon residue, leaving the carbon behind. The etch by-products after a hydrogen plasma treatment include HF and fluorohydrocarbons. A 400 W H plasma contains more atomic hydrogen species than a 100 W H plasma. The surface residue removal required a 400 W plasma, whereas the via residue was removed with a 100 W plasma. We believe that this is attributed to both the density of the residues as well as the difference in how both of the residues were produced. The surface residue was a dense network of the polymer film and required a higher power plasma to remove. The via residue wafers contained only a small amount of residue inside the via, which was efficiently removed using a lower power plasma.

Conclusion

We have demonstrated an effective process for the removal of RIE-generated CF_x polymeric residue using a hydrogen plasma. The experiments were accomplished on 150 mm via patterned wafers. The results have shown that optimal removal of surface and via residues required different plasma-processing conditions. The most effective process for the removal of surface residue was 400 W, 450°C, and 15 mTorr for a 10 min exposure time. The optimal process for via residue removal was a 5 min plasma exposure at 100 W, 450°C, and 15 mTorr. XPS data obtained from the residue indicates that it is a fluorocarbon polymer. Pre and post H-plasma exposure SEM images show that a significant amount of the residue was removed from the wafer surface and from inside of vias. The optimal plasma processing conditions differ for the via and surface residues due to the chemical difference in the residues which were generated using different RIE conditions. Removal of postetch residue is a critically important process, as poor device quality would otherwise be expected. The hydrogen plasma dry clean process shows excellent results for residue removal post-contact and post-via hole etches. High selectivity to SiO₂ makes the process potentially very useful in state-of-the-art semiconductor processing.



(a)



(c)

Acknowledgments

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Figure 5. XPS survey spectra of surface-generated and via-generated residue. Both surface and via residue wafers display the C (1s) and F (1s) spectral lines associated with the fluorocarbon film.

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Figure 4. SEM images of via residue before and after H-plasma clean: (a) pre-

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