Chemical contamination of thin oxides and native silicon for use in modern device processing

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The characterization of native oxide residuals and contaminants during the clean-up of silicon substrates prior to oxide growth is crucial for the development of accurate growth algorithms. Studies of contaminant concentrations based on Auger analysis are reported, showing carbon to be the critical contaminant. A critical etching time is established, for which carbon content and residual native oxide thickness are minimal. Variations in refractive index with etching period and native oxide thickness are also reported, showing an increase in refractive index with increase in native oxide thickness. These results should prove useful in improving the accuracy of ellipsometric techniques, and will aid in growth algorithm development.

1. Introduction

Numerous studies have been done on the contamination of silicon substrates during initial clean-up (Raider et al. 1975, Kalnitsky et al. 1990, Kobeda and Irene 1988). These studies have identified the contaminants during hydrofluoric acid (HF) etching (Yang et al. 1975, Gould and Irene 1988) and have detected the presence of a residual layer after clean-up (Gould and Irene 1988). With the trend towards thinner oxides in modern MOS and MEMS technology, the development of high quality, well-characterized oxide growth technique has become crucial. Thus, in recent years, attempts have been made to characterize growth and contamination in thin oxide films (Kalnitsky et al. 1990).

This paper details Auger analysis and ellipsometric studies made during the HF clean-up of silicon wafers. The data and analysis presented will enable the development of more accurate film growth algorithms, and will reduce the uncertainty in characterizing thin oxide film growth. The characterization of thin native oxide layers is vital, as these layers affect subsequent film growth. Contaminant percentages are identified, and refractive index changes and film thicknesses are analysed. The data will also prove useful in improving ellipsometric measurement techniques.

2. Experimental details

Ultraclean fluoroware containers were used for the cleaning of silicon samples. The containers were thoroughly washed with class 100 clean room standard 18 MΩ deionized (DI) water, followed by an acetone rinse. Next, the containers were treated with 1% HF solution, followed by a final rinse in DI water. Crysteco-made prime grade p-type silicon wafers of <100> orientation and 0.5 Ω cm resistivity were used.

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for experiments. The wafers were kept in acetone for 24 h, and then rinsed in DI water for 10 min. This was followed by ultrasonic cleaning in a trichloroethylene (TCE) bath. Finally, the samples were rinsed in acetone, and then again in DI water. Two different methods were used for the final etch:

Method A

Samples were boiled in a solution of H₂O: 30% H₂O: 37% HCl (86:11:3) for 10 min, rinsed in DI water, dipped in H₂O: 30% H₂O₂: 28% NH₄OH (4:1:1) for 2 min, rinsed in DI water, dipped in BHF, which is 40% NH₄F: 50% HF: H₂O: 28% NH₄OH (14:2:11:3), rinsed in DI water, and dried in nitrogen.

Method B

Samples were treated with 30% H₂O₂, dipped in dilute HF (10% or 25% HF), rinsed in DI water, and dried in nitrogen.

BHF (method A) and dilute HF (method B) treatment times were varied and the native oxide thickness was observed using Auger analysis using a 30 µA primary electron beam current, 3 keV primary beam energy, 6 eV modulation energy, and a sensitivity of × 40. Oxides were grown on the cleaned samples using dry thermal oxidation at 950°C in an O₂ ambient.

3. Results and discussion

Auger analysis of the cleaned samples did not detect metallic impurities such as Fe, Zn, etc. This suggests that contamination by these elements was insignificant. The prominent contamination was by oxygen and carbon. In some samples, a very small percentage of nitrogen was also detected, possibly because of the N₂ ambient drying. Carbon contamination is a major concern, and has already been reported by some authors (Yang et al. 1975, Gould and Irene 1988, Raider et al. 1975). Plots of C contamination against etching time for the two etching methods are presented in Figs 1 and 2. For this calculation, the silicon lower energy peak (LMM) was used, and two plots were obtained based on the selectivity of Si in oxide form (0.158) and in pure elemental form (0.023). These two plots were calculated because studies have shown thin oxides to have a different structure from pure SiO₂. The thin oxide is expected to be relatively Si-rich, and thus the plot assuming elemental Si selectivity is shown. Note the minima in contamination at a clearly defined time. This is referred to as critical time t₀₁.

Studies have already shown thin grown oxide to have a higher refractive index than the expected 1.46 for thick oxides (Kalnitsky et al. 1990). This is verified in Fig. 3. The native oxide, however, is found to exhibit increasing refractive index with increasing thickness, as shown in Fig. 4. This result will prove extremely useful in improving ellipsometric analysis of native oxide thickness (Archer 1962, Lucovsky et al. 1987, Vedam et al. 1969). This refractive index is dependent on the cleaning procedure. This is easily explained by the dependence of refractive index on carbon contamination levels.

The transition of etched Si substrates from a hydrophilic to a hydrophobic nature has already been identified (Ljunberg et al. 1993, Seo et al. 1993). This occurs at the critical time t₀₁. This phenomenon explains the minima in Figs 1 and 2, and also explains the minima in Figs 5 and 6, which plot native oxide thickness against etching time. Combining Fig. 4, which plots refractive index versus native
Figure 1. Characteristic curve of percentage carbon contamination against etching time for samples cleaned using method A. +, Si sensitivity = 0.023, ◊, Si sensitivity = 0.158.

Figure 2. Characteristic curve of percentage carbon contamination against etching time for samples cleaned using method B. +, Si sensitivity = 0.023, ◊, Si sensitivity = 0.158.
Figure 3. Refractive index versus oxide thickness for grown oxides.

Figure 4. Refractive index versus oxide thickness for native oxides.
Figure 5. Native oxide thickness versus etching time for samples cleaned using method A.

Figure 6. Native oxide thickness versus etching time for samples cleaned using method B.
Figure 7. Refractive index versus etching time for samples cleaned using method A.

Figure 8. Grown oxide thickness versus native oxide thickness.
oxide thickness, and Fig. 5, we would expect a plot of refractive index against time
to resemble Fig. 5 in basic outline. This is found to be true in Fig. 7, which shows
refractive index against etching time for samples cleaned using method A. Note the
consistency in $t_{01}$ in all these plots. The transition point from hydrophilic to
hydrophobic is dependent on numerous factors (Backlund et al. 1992). For example,
a higher HF concentration increases the initial etching rate, and decreases $t_{01}$.

To show the dependence of oxide growth on native oxide thickness, the etching
time was varied on samples using the same clean-up method. Oxides were then grown
and thicknesses calculated. The plot of grown oxide against native oxide is shown in
Fig. 8. The structure of the thin oxide films is not precisely known. Thus, the plot has
rather a high degree of uncertainty. However, the plot clearly establishes the depen-
dence of growth rate on initial clean-up, making this critical for thin oxide films. The
date presented on native oxides can be used to reduce the uncertainty using iterative
techniques (Kalnitsky et al. 1990) and to improve models for this film oxide growth.

4. Conclusion

The contamination of Si substrates during clean-up has been studied. RefRACTive
index variation in native oxides has been characterized, along with native oxide
thickness variation. The dependence of the oxide growth rate on these parameters
has been established. The data obtained will prove useful in improving ellipsometric
accuracy, and in developing suitable oxide growth algorithms to improve growth
characterization of thin oxide films.

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