Vapor phase hydrocarbon removal for Si processing

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Ultraviolet/Oxygen (UV/O_2) based vapor phase cleaning of Si(100) surfaces dosed with specific organic molecules has been studied by surface and gas phase analytical techniques. The treatment results in chain scission and carbon volatilization as CO and CO_2. At room temperature partial trapping of carbon-containing species in the oxide is observed, while at elevated temperatures complete hydrocarbon removal occurs. UV/O_2-cleaned samples closely resemble those produced by the standard RCA clean in terms of hydrocarbon removal and oxide formation and this process appears suitable as vapor phase final Si wafer clean.

As device dimensions continue to shrink, increasingly precise control over contaminants and particles is required. New approaches to semiconductor processing emphasize multichamber processing, which permits in situ integration of a sequence of processes. In situ surface cleaning techniques play a key role in this trend, particularly vapor phase processes, which can be either new (e.g., UV/O_2)^1 or extensions of wet chemistries (e.g., HF). The increasing demands of process control magnify the need for mechanistic understanding of such surface cleaning processes.

Fundamentally important mechanistic issues related to semiconductor surface cleaning have been actively pursued recently, as in the studies involving contaminant identification and removal. Removal of a particular contaminant can result in new surface residues, necessitating additional cleaning procedures. For example, Si surfaces prepared by the RCA procedure to remove hydrocarbons and metals also produce a chemical oxide. This oxide must then be fully removed (e.g., using HF) in some cases, such as when the subsequent process step is low-temperature deposition of epitaxial silicon.5

The present work addresses the physical and chemical mechanisms of hydrocarbon removal by vapor phase UV/O_2 cleaning as an alternative to the conventional liquid phase RCA cleaning^ procedure. It demonstrates a methodology for such investigations using real-time gas phase product analysis and post-cleaning surface analysis. We determined the UV/O_2 procedure involves hydrocarbon chain scission and thermally activated product volatilization, both of which depend on the molecular character of the hydrocarbon and occur simultaneously with Si surface oxidation.

Wafers (3.25 in. diameter, p-Si(100), 0.005 and 2 Ω cm) were precleaned by RCA clean and then introduced through a load dock into a N_2-purged glove box for final cleaning treatments. The glove box and the cleaning reactor are part of a large ultraclean, integrated processing facility with in situ analysis capabilities. In the glove box the chemical oxide was stripped in 10% HF solution, and a drop of a specific hydrocarbon (chosen from alcohols, acids, cycloalkanes, and others) was deposited on the hydrophobic (HF-treated) surface. The surface was then spin dried in a nitrogen gas stream. The fully dried wafer was transferred without air exposure into an attached reactor in which ozone and atomic oxygen were generated by passing O_3 over a 30 W ultraviolet (UV) lamp. The wafer was positioned at a distance of 5 mm from the lamp with the hydrocarbon-exposed side facing the lamp. Hydrocarbon removal was then carried out at atmospheric pressure under 1000 sccm O_2 flow conditions, at room temperature and in some cases at 100°C. Under such conditions the ozone concentration in the O_2 ambient is ~0.1% (since the relative concentration of O and O_3 is a complex function of reactor geometry, gas pressure, and wafer-to-lamp distance, identification of the true active species is not straightforward and so the methodology is only referred to as the UV/O_2 process). Real-time differentially pumped mass spectrometry was used to monitor the composition of the cleaning environment and the evolution of volatile reaction products by direct sampling of the effluent gas flow.

The as-cleaned wafers were moved without air exposure through a vacuum load lock (~10^-8 Torr base pressure) into an ultrahigh vacuum (UHV) wafer transport system on a five-wafer cassette (TiN coated). The wafers were then transported and analyzed in situ by surface analytical techniques, such as x-ray photoemission (XPS), high-resolution electron energy loss spectroscopy (HREELS), and thermal desorption spectroscopy (TDS).

Contamination of surfaces by hydrocarbons is inherently difficult to characterize because of an immensely large number of possible species and the low-surface coverage of each. We therefore chose to deliberately dose well-characterized surfaces with known hydrocarbons. Hydrocarbons used in these studies were chosen to exemplify straight-chain and aromatic types, different chain lengths, and different functional groups. By adsorbing molecules with known structure and reactivity in a controlled way, it has been possible to unambiguously determine changes in their surface chemical configuration during UV/O_2 treatment and elucidate mechanisms for the cleaning process.

Surface vibrational spectroscopy reveals key aspects of the adsorption behavior of hydrocarbons on the HF-cleaned surface and also of the changes these hydrocarbons undergo upon UV/O_2 treatment. Figure 1 shows a sequence of HREELS spectra of an HF-cleaned sample exposed to cyclohexane [Fig. 1(a)], and after subsequent...
UV/O₂ treatment for 45 s [Fig. 1(b)] and 5 min [Fig. 1(c)]. After HF dip clean, the Si(100) surface is hydrogen passivated, i.e., it is covered with SiH and SiH₂ groups. The SiH surface species can be seen as a rather weak feature in the spectra at ~2200 cm⁻¹. Superimposed are the quite strong features of the adsorbed hydrocarbon, clearly distinguishable as a peak labeled ν(CH) (around 2900 cm⁻¹) and the broad feature at low loss energies (∼1000 cm⁻¹). The surface does not exhibit OH species (no peak at 3600 cm⁻¹), reflecting the hydrophobicity of the starting HF-treated surface. HREELS is very sensitive in detecting hydrogen-containing species, the detection limit being in the 10¹² cm⁻² range for hydrocarbons or OH species. Details of the XPS and TDS spectra reveal that the hydrocarbons investigated here do not break or replace the surface SiH/SiH₂ bonds, indicating that they bond only weakly to the hydrogen-saturated surface.

It is seen that after short exposure to the UV/O₂ ambient, an oxide is formed on the surface (especially visible at the clearly resolved peak around 400 cm⁻¹, the SiO bending vibration, c.f., Fig. 1). XPS also indicates very rapid oxidation of the Si surface within the first 45–60 s at room temperature. Since the hydrocarbons are still present on the surface at that time, the oxidation of the Si substrate appears to occur underneath the contaminant layer. The surface hydrogen that saturated the surface after the HF dip clean is transformed into OH groups during the UV/O₂ cleaning procedure. OH groups can be seen in Fig. 1 at high loss energies [ν(OH)]. Thermal desorption spectra indicate strong reduction of the amount of hydrogen in the near-surface region and increased bond strength, typical for hydrogen present in OH groups or buried underneath a thin oxide. Examination by HREELS reveals the presence of a thin, low-density oxide film that is consistent with a structure with significant OH incorporation. The UV/O₂ treatment results, therefore, in rapid initial oxide formation and transforms the previously hydrophobic surface into a hydrophilic surface in the process.

Hydrocarbon removal is a relatively slow process at room temperature. Significant hydrocarbon removal only occurs after ~5 min of UV/O₂ treatment (Fig. 1). Further details of the mechanism by which hydrocarbons are removed from the surface are illustrated in Fig. 2, which shows the C₈ region of XPS spectra of an HF-cleaned surface exposed to heptanol. Rapid oxidation of the hydrocarbon is seen to take place, transforming former CH bonds into CO-type bonds. Nevertheless, carbon atoms remain bonded to neighboring C atoms as well as to hydrogen (CH species seen in HREELS) and thus remain adsorbed at the surface. Volatilization of the hydrocarbons appears to proceed via slow oxidation of the long carbon chain at every carbon atom; in the final stage of this process the carbon desorbs as CO₂. However, at room temperature some C-containing species remain at the surface even after extended treatment times.

To identify the desorbing gas phase products of the UV/O₂ reaction we have carried out real-time monitoring of the gas phase composition using differentially pumped mass spectrometry. It is found that mostly CO and H₂O evolve. H₂O evolves in part from the conversion of SiH species into SiO species. Gas phase product evolution related to hydrocarbon removal (especially CO₂) is relatively slow, consistent with the slow removal rates observed by HREELS and XPS. For short-chain hydrocarbons (< three carbon atoms per molecule) a different reaction channel becomes apparent: rapid evolution of CO followed by the slower CO₂ evolution. Apparently short chain hydrocarbons fragment more readily and can desorb before complete oxidation of all fragments has occurred. Hydrocarbon chain scission is thus the rate-limiting step in the removal of longer chain hydrocarbons; oxidation to CO₂ at every link of the chain proceeds more rapidly than product desorption.

Room-temperature UV/O₂ treatment yields only incomplete removal of hydrocarbons. XPS and HREELS results suggest that species such as H-C=O or O-C=O might be retained either within the growing oxide or at its surface, probably linked to other molecular fragments. Furthermore, HREELS results clearly indicate that OH
groups, resulting either from SiH group conversion or hydrocarbon chain oxidation, remain adsorbed in substantial number at the surface at room temperature. It appears that the vapor pressure of these species is insufficient at room temperature to permit complete product desorption. Figure 2 also includes an XPS spectrum of a heptanol-contaminated wafer which has been UV/O₂ cleaned at 100 °C; integrated area analysis shows that the original surface carbon concentration of ~0.65 monolayers (MLs) is reduced to <0.15 ML after UV/O₂ cleaning. HREELS spectra indicate that UV/O₂ treatment at elevated temperatures (>60 °C) also removes the OH surface groups. Providing some thermal energy in addition to the photoexcitation of reactant species is therefore sufficient to completely remove all reaction products.

Aside from removing hydrocarbons, the UV/O₂ cleaning procedure creates a surface oxide. These surface modifications are also characteristic of the standard wet RCA cleaning procedure. We have compared RCA-cleaned wafers with UV/O₂-cleaned wafers by XPS, HREELS, TDS, and electrical measurements. Figure 3 shows a comparison of HREELS spectra of such wafers, where the UV/O₂ clean was performed at room temperature. Oxide peak positions indicate very similar oxide densities and stoichiometries. Both oxides reveal considerable amounts of incorporated OH groups. The limiting oxide thickness is also very similar, as further supported by ellipsometric measurements. Comparison of the two spectra underscores the similarity of the two different oxides: RCA and UV/O₂ processes not only remove hydrocarbons but also create very similar oxides.

RCA-cleaned wafers and UV/O₂-cleaned wafers have been used to grow thermal oxides in an integrated gate oxide process.¹⁴ These precleans yield very similar breakdown statistics, interface state densities, and oxide growth kinetics. The UV/O₂ oxide appears electrically very similar to the standard RCA clean.

These results demonstrate how the UV/O₂ gas phase cleaning process removes hydrocarbon surface contamination from Si(100) wafers. By exploiting the methodology of deliberate dosing combined with in situ processing and analysis, reaction pathways for contamination removal have been elucidated. Identification of the rate-limiting steps in the cleaning process should help in addressing issues crucial to applications in manufacturing (e.g., process optimization and control, tool design, etc.).

The RCA clean and modifications thereof are in widespread use throughout the semiconductor industry, typically at several stages through the course of a manufacturing process. Because of the trend towards integrated (multichamber) vacuum processing as a means to reduce molecular contamination as well as particle defect densities, effective vapor cleaning processes compatible with hot processing in such systems are crucial. This work suggests that final UV/O₂ vapor cleaning has strong potential in integrated processing.

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