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Cleaning of Si Surfaces by Lamp Illumination

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Abstract: Cleaning of silicon surfaces using lamp illumination in ambient air at atmospheric pressure (ROST process) was investigated. It is demonstrated that an increase of wafer temperature up to 300°C by white light illumination for 30 seconds is sufficient to remove most volatile contaminants from the Si surface. Organic contaminants originating from wafer storage and handling ambient as well as from IPA drying are easily removed by ROST. This process is very effective in suppressing uncontrolled variation of the apparent thickness of ultra-thin oxide resulting from organic contamination. Furthermore, the process is effective in removing pseudo-volatile contamination such as sulfuric acid but not non-volatile contaminants such as salts and metallic ions. In general, the efficiency of lamp cleaning decreases for contamination deposited during long wafer storage times.

Introduction

The concept of Si surface cleaning using lamp illumination in ambient air at atmospheric pressure was explored and preliminary results were presented in our earlier reports [1,2]. The technique is implemented using Rapid Optical Surface Treatment (ROST) apparatus [3]. The ROST uses brief illumination with halogen lamps in an ambient air to restore the chemical state of the Si surface. The main goal of lamp cleaning is to remove volatile contaminants accumulated on the Si surface during wafer processing, handling in the clean room as well as during wafer shipping and storage in plastic containers. Moreover, the ROST process is further explored in this study as a method for removing organic compounds remaining on the Si surface after IPA (isopropyl alcohol) drying. In this work we also investigated the effectiveness of ROST in reducing the surface concentration of elemental contaminants of Si surfaces found in process environment such as metallic ions, sulfur and chlorine. The introduction of the ROST technology is a result of the effort to develop inexpensive and efficient gas-phase methods of controlling surface organics and other volatile contaminants. In this experiment several new aspects of ROST cleaning are considered.

Experimental

A commercial ROST apparatus developed by QC Solutions, Inc. was used in this investigation [4]. In this system Si wafers are exposed to radiation from halogen lamps in ambient air at atmospheric pressure. Typical closed-loop controlled process temperature was 300°C and time of exposure was 30 seconds.

The performance of the lamp cleaning process was monitored here using a variety of methods including Thermal Desorption Gas Chromatography Mass Spectroscopy (TDGC-MS), Multiple Internal Reflection - Fourier Transform Infra-Red (MIR-FTIR), Total Reflection X-Ray Fluorescence (TXRF), and ellipsometry as well as contact angle measurements.

Airborne organic contamination removal

Figure 1, which shows GC-MS spectra taken from the Si surface exposed to clean room air for 24 hours before and after ROST, demonstrates the effectiveness of this process in controlling surface organic contamination. Through removal of organic contaminants by ROST the effect of

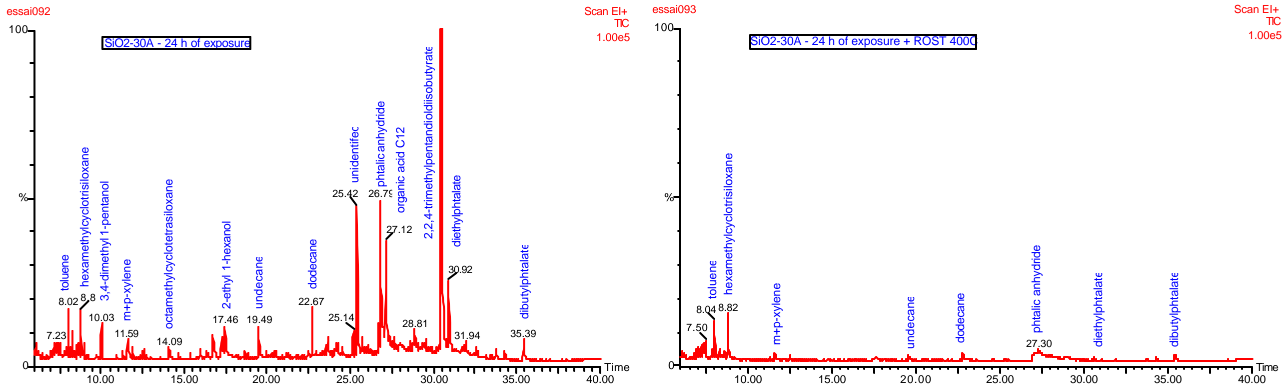

Fig. 1: GC-MS spectra from Si surface before (left) and after (right) ROST (400°C, 30 s).

surface aging on the ellipsometric measurements can be reversed. As shown in Figure 2 the change of the chemical composition of the Si surface reflected in the change of thickness of the oxide becomes detectable by ellipsometry in less than 15 minutes after air exposure. ROST restores the original conditions of the surface and allows accurate determination of the thickness of ultra-thin oxide. As Figure 2 also demonstrates, the apparent oxide thickness following ROST was identical to the initial thickness which means that no additional oxide is grown as a result of a typical ROST exposure of oxides thicker than 2 nm.

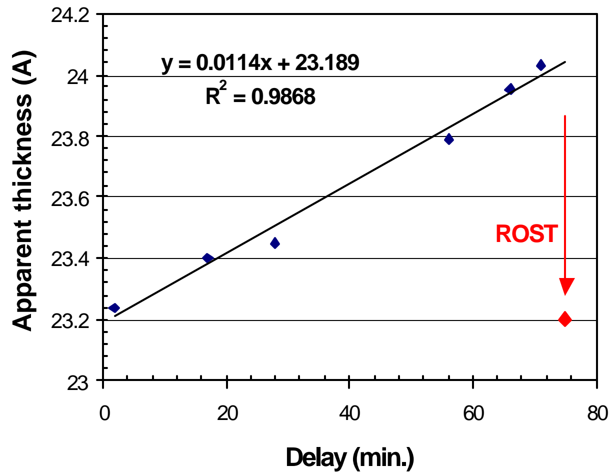

Fig. 2: Kinetics of organic contamination of a Si wafer exposed to clean room air, as seen by ellipsometry.

IPA removal after alcohol drying

An important part of this investigation was an evaluation of the performance of lamp cleaning in removing organic contaminants remaining on the Si surface following IPA drying process. While widely adopted in the semiconductor industry, the IPA drying process cannot be considered to be entirely benign. A fairly high level of organic surface contamination resulting from IPA drying may have an adverse effect on the subsequent process if not adequately controlled. Figure 3 shows the high efficiency of a brief illumination at 300°C in removing IPA residues left on the surface by a commercial alcohol dryer. The post-IPA contamination is strongly adsorbed on the polar oxide surface and cannot be removed by a 10 min. DI water rinse (Fig.3). As demonstrated by Fig. 4, the efficiency of ROST cleaning of IPA dried surfaces increases with wafer temperature.

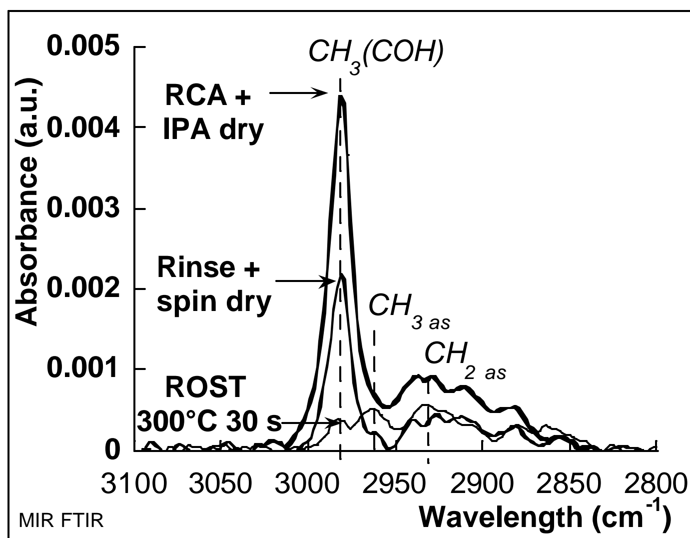

Fig. 3 MIR FTIR spectra of IPA contaminated wafers showing efficiency of ROST.

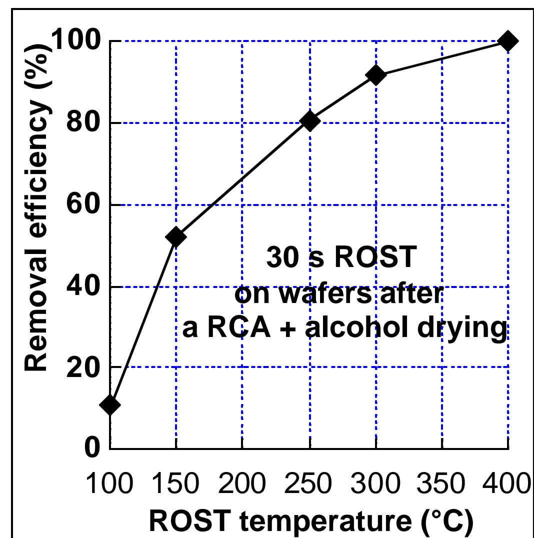

Fig. 4 IPA removal efficiency by ROST at different temperatures.

Pseudo-volatile contaminant removal

It is important to recognize the fact that there are a variety of inorganic contaminants present in the process ambient that can be transferred to the wafer surface in the gas-phase. Similarly to organic contamination, inorganic contaminants may have an adverse effect on the subsequent process if not properly controlled. In order to illustrate this type of contamination, sulfuric acid representing an intermediate boiling point (330°C) was investigated. Sulfur contamination coming for example from the ambient air (sulfates, H_2SO_4, etc.), partial rinse after SPM (H_2SO_4), and advanced dry etching (SO_2), is highly hydroscopic. After a certain time, this contamination is growing by absorbing humidity from the air which results in a severe haze on the surface that can sometimes be observed even with the naked eye. In this experiment sulfuric acid was deposited on the surface by a partial rinse after a conventional SPM treatment. As shown in Fig. 5, TXRF measurements before and after ROST demonstrate the higher efficiency of this process (>99%) as compared to an additional 10 minutes DI water rinse. Furthermore, an additional 30 s ROST process (2nd ROST in Fig. 5) decreases the concentration of sulfur on the surface even further.

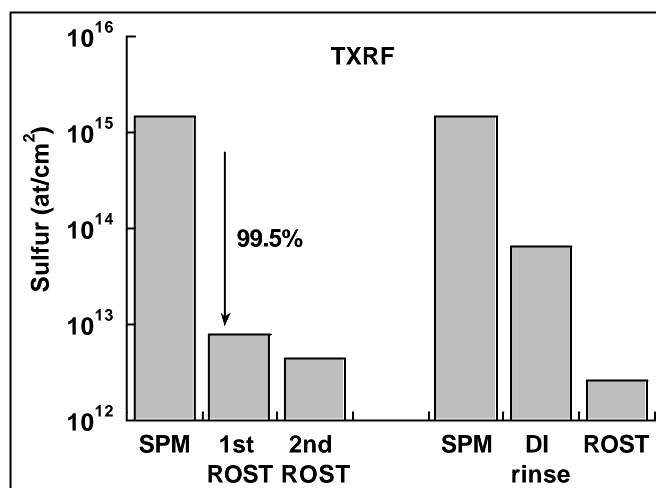

Fig. 5: Sulfur (H_2SO_4) removal by different processes as measured by TXRF.

Non-volatile contamination removal

In contrast to volatile contaminants, the efficiency of lamp cleaning in removing transition metals such as Fe, Ca, Cr, Ni deposited by spin coating in the 1E13 at/cm^2 range was investigated without success. The ROST even at 400°C is not able to remove these contaminants. KCL salt was also investigated but also in this case ROST was ineffective. As Fig. 6 illustrates the best way to control KCL is to dissolve it using DI water rinse.

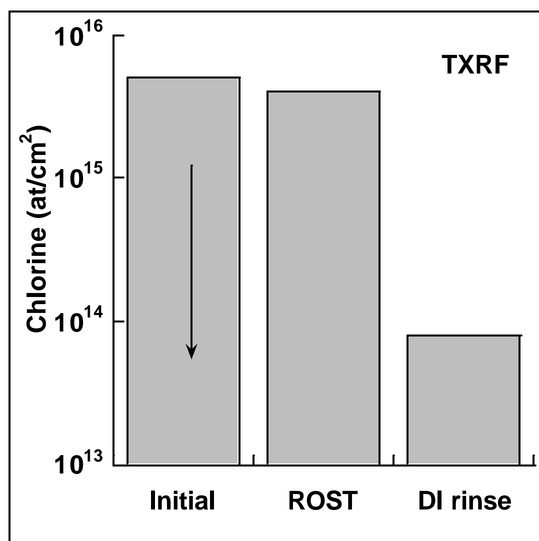

Fig. 6 KCl removal by ROST (30 s at 300 °C) and by a 10 min. DI water rinse.

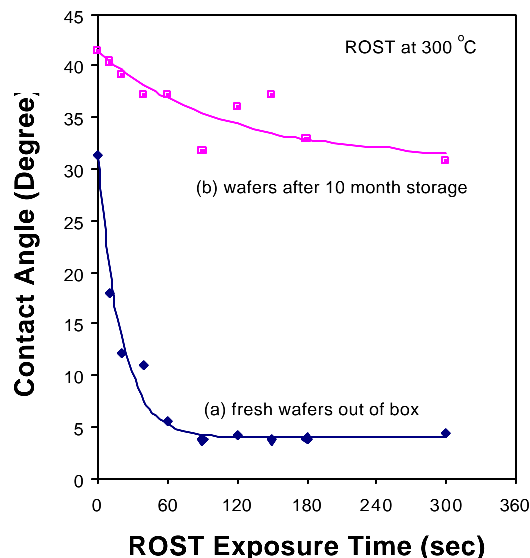

Fig. 7 The effect of wafer storage time on the efficiency of ROST.

Effect of storage time

The efficiency of ROST was found to decrease with the wafer storage time. Figure 7 shows contact angle evolution as a function of ROST for wafers from the box that was opened for the first time after delivery and wafers that were taken out of the same box ten months later. The difference observed is a result of the surface "aging" process resulting from the reaction between the moisture from the ambient air and surface organics. In the separate experiment in this study it was shown that the surface "aging" process can be effectively prevented by subjecting stored wafers to ROST every two days or so.

Summary

The results obtained in this investigation confirmed the effectiveness of lamp cleaning in controlling interactions of Si surfaces with volatile contaminants, both organic and inorganic, originating from the process and storage ambients. In particular, the efficiency of ROST in removing organic contaminants remaining on the surface after IPA drying was demonstrated. On the other hand, the surface concentration of transition metals was not affected by ROST. It was also shown that the efficiency of lamp cleaning decreases with an increase of wafer storage time.

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