A STUDY OF THE EFFECTIVENESS OF THE REMOVAL OF HYDROCARBON CONTAMINATION BY OXIDATIVE CLEANING INSIDE THE SEM.

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A poster paper presented at Microscopy and Microanalysis 2002, Quebec City, Quebec, Canada

Abstract published in Microscopy and Microanalysis, Vol 8, Supplement 2, 2002, 720CD

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Critical Dimension measurements for process control in semiconductor lithography are routinely made using Scanning Electron Microscopy (CD SEM). In many situations, organic contamination of the CD SEM chamber cannot be prevented due to the outgassing of hydrocarbons present in the photoresist films used to define device structures. In other cases advantageous hydrocarbons are deposited from the room air before the wafer is brought into the machine, or there are residual deposits left over from manufacturing of the tool. The interaction of the primary beam with these hydrocarbons, resident in the SEM chamber, results in a deposition of a hydrocarbon film, whose thickness is dependant upon the total dose provided to the structure of interest. This deposited film not only reduces the available image contrast but also physically changes the size of the measured feature. In extreme cases, such changes have been reported to be as large as several nanometers during a typical measurement sequence. Such a value approaches the entire metrology error budget for the most advanced processes. The semiconductor industry has been moving steadily to small feature sizes on integrated circuits. With the advent of DUV technology line widths have moved from 250 nm to less than 130 nm and will soon be below 100 nm. At 250 nm it was common to on various models of CD SEMs to have line width measurement precisions (3 sigma) of 5 nm. Part of this precision error was cause by measurement "carry over" where hydrocarbon contamination is deposited by the electron beam and changes the measured feature size during repeated measurements. CD SEM metrology error budgets for the sub 100 nm technology node must be below 1nm at three sigma. It is critical that the measurement carry over due to hydrocarbon contamination be well below this value.

The resident hydrocarbons in the chamber may come various sources and can be hard to remove. The sources of hydrocarbons in electron microscopes are:

1) Vacuum pump oils.

2) Oils built into system during manufacturing, airborne dust and impurities, lubricants, and plasticizers.

3) Sample born: Dirty specimens and advantageous hydrocarbons from air.

4) Leaks
The cures for these problems are:

1) Prevention: Traps, Foreline bleed, Low vapor pressure pump oils, oil free pumps, and good vacuum practice (keep things clean!). The manufacturers of CD SEMs universally use oil free roughing pumps and turbopumps to prevent pump oil problems. The machining and assembly of large oil free vacuum chambers and stages in a major challenge for CD SEM manufacturers.

2) Cleaning: Baking, solvent cleaning, purging (SEM-CLEAN nitrogen purging system), and plasma cleaning (Dry ashing, glow discharge cleaning). Cleaning can attack hydrocarbons from all sources.

The EVACTRON® SEM-CLEAN anti-contamination system is plasma cleaning system that is designed to control contamination in SEMs. The EVACTRON device (US Patent 6,105,589) is designed to remove hydrocarbons from SEM specimens and SEM chambers to prevent contamination artifacts in-situ within the electron microscope. The device uses a low-powered RF plasma to make oxygen radicals from air that then oxidize and chemically etch away hydrocarbons from the interior of the SEM. The device is mounted on a specimen chamber port. The plasma itself is confined to the EVACTRON chamber, which prevents ion and electron bombardment damage to the instrument or specimen. The radicals are carried out of the plasma into the whole of the specimen chamber by convection. These radicals oxidize hydrocarbons to make CO, H2O, and CO2 gases to be removed by the vacuum pump. The use of air as an oxygen source is convenient to the SEM operator, but limits the cleaning effectiveness of the system in relatively short time to easily oxidized carbon species such as vacuum pump oil and skin oil hydrocarbons.

**Oxygen Radical Production from Air**

Plasma cleaning using air requires that the RF plasma be operated at low temperature to produce sufficient Oxygen radicals. At higher plasma temperatures Nitrogen ion production becomes significant and lead to the destruction of the O radicals to produce NO+ ions. The NO+ ion is a low energy species that is stable and has no cleaning ability. The Evactron® system's ability to create a low-temperature plasma is an important part of the method for generation the oxygen radicals from air. When oxygen is ionized a series of reactions lead to the formation of oxygen radicals:

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O_2 + O^+ > O_2^+ + O
\]

\[
O_2^+ + e^- > O + O
\]

Compared to the ions these radicals are long-lived species and may leave the plasma region. Oxygen radicals are lost in reactive collisions with surfaces and other gases. They are not lost in collisions with O2 and N2. The recombination of two radicals does not occur unless there is a third body to remove the excess energy.

The ionization potential of oxygen is 12.1 eV and nitrogen is 15.6 eV. Thus oxygen ionization takes place in a lower temperature or lower energy plasma than nitrogen. By lowering the average temperature of the electron-energy- distribution oxygen
ionization is favored. When nitrogen ions are produced in an air plasma they react with O radicals by the following fast reactions:

$$\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$$

$$\text{N} + \text{O} \rightarrow \text{NO}^+ + e^-$$

Thus two oxygen radicals are destroyed by every nitrogen ion produced. Because nitrogen is the major constituent of air, this destruction takes place quickly once nitrogen ionization begins. In addition NO$^+$ is a stable ion with a low ionization potential (9.5 eV). It is unable to react with the neutral diatomic gases in air and reacts with hydrocarbons to form nitrogen oxide polymers that are resistant to further oxidation and removal. The transition from an oxygen-dominated plasma to a nitrogen ion-dominated plasma is function of the plasma temperature. In the Evactron system an operating pressure and plasma temperature are adjusted such that the oxygen radical flux to the surfaces is maximized.

The EVACTRON SEM-CLEAN was developed for use on analytical SEMs. In these SEMs the chambers and specimen are typically cleaned with relatively short cleaning times of 2 to 5 minutes. CD SEMs have larger chambers to handle wafers up to 300mm in diameter. To give full access to the surface of the wafer, the chamber dimension are close to 1 meter square. This makes for very large SEM chambers volumes and surfaces to be cleaned. The question was whether the Evactron SEM-CLEAN system could clean a large chamber in a reasonable time to stop line width measurement drift.

The experiments were done using both a 200mm and a 300mm CD SEM system. An XEI Scientific "Evactron SEM-CLEAN™" system was mounted on one port. When the cleaning system was operated the specimen chamber vacuum was maintained at 100 Pa by a controlled leak of air into the device. At this pressure this leak created a viscous flow of gas to the roughing pump that quickly removed the oxidation product gases. Inside a low-powered, RF (13.56 MHz) glow discharge created oxygen radicals. The RF power level was about 10 Watts. The Evactron was run under these operating conditions for approximately 25 minutes. After operation the leak is turned off and the system allowed to pump to high vacuum. When operating vacuum was achieved replicate line width measurements were made.

Contamination rate measurements were conducted prior to and immediately following the operation of the Evactron unit for both the 200mm and 300mm system. Each of the measurements replicate a typical production CD measurement and are conducted over a series of 20 repeats. The results are shown in figures 1 & 2 below.
Data collected on the 300mm chamber over four months from the initial Evactron cleaning has demonstrated consistent contamination performance with no further degradation observed. Since this system is in a production environment, running primarily photoresist coated samples, the initial contamination observed is believed to have been due to organic residue which originated in the system manufacturing process. The present system performance is shown in Figure 3.
Cleaning Time

Tests on various large chamber systems by XEI Scientific have shown that several short cleaning are preferable to leaving the Evactron on for extended periods of time. Three short cleaning of 30 minutes each with 2 hour rest periods are just as effective for contaminant removal as leaving the Evactron system on for 7 ½ hours continuously. The reason for this is that after the initial removal of all accessible hydrocarbons by the oxygen radicals, the remaining hydrocarbon molecules must escape from various hiding places (virtual leaks) and redistribute themselves inside the chamber via molecular flow processes. During this period the oxygen radicals have no easy destruction mechanism (oxidation of hydrocarbons) and may attack other surfaces, detector windows and coatings within the system. Colloidal carbon paint used for electron conduction will be oxidized and removed. Metals surfaces with have oxide layers increased. By using rest periods of 2 or three hours or overnight the contamination molecules have time to redistribute and establish a new equilibrium with the surfaces of the whole chamber.

During manufacturing of large chamber SEMs, a good protocol is to clean the chamber three or four times for 30 minutes each over a two day period and then wait a week for a final cleaning. Once installed CD SEM contamination should monitored and EVACTRON cleaning preformed when the metrology error budget limit is approached.3

Line of Flow Cleaning

The Evactron device produces oxygen radicals that are carried into the chamber by convection flow and flow toward the roughing pump. The radicals will react with hydrocarbons found in the line of flow of the radicals either in the chamber atmosphere or surfaces. For best results the specimen examination area should be in between the Evactron port and the roughing pump. Also the Evactron should be mounted reasonably close to the specimen examination area, preferably it should be within 18 inches of the Evactron port.

The chamber pressure during Evactron cleaning is 600 milliTorr resulting in viscous flow rather than molecular flow. This pressure insures that the reaction products are swept out to the vacuum pump. This pressure is low enough that three body reactive collisions of the radicals have a very low occurrence rate, resulting in longer lifetimes for the radicals. This pressure also results in a mean free path too short for sputtering damage in the plasma source.

Greater oxygen radical production can be achieved by increasing the flow by increasing the rough pumping speed of the chamber and increasing air flow through the plasma. Large conductance roughing lines (1.5" to 2") between chamber and pump are needed to achieve higher flow rates while maintain a constant pressure.

Pump down times are reduced by Evactron operation. The Evactron device produces UV light that helps water vapor desorb from chamber walls and increases the desorption and reactivity of hydrocarbons. Since the desorption occurs during viscous flow pumping of the chamber water vapor is removed during Evactron operation.