Analysis of Submicron Al and Al_2O_3 Particles by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

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INTRODUCTION

Particle composition analysis is done to support process/tool development, pilot line integrated circuit (IC) yield improvement, and yield improvement during volume IC manufacture. Composition analysis is a key enabler when determining the source of contamination. One of the few in line/off line methods of composition analysis is scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) and precision whole wafer sample stages. These systems are referred to as defect review tools (DRT). Optical microscopy is also used for in-line particle identification. Experienced microscopists use morphology and shape to categorize the particle. Focused ion beam (FIB) systems that employ SEM/EDS and precision, whole wafer sample stages for materials are used for characterizing of defect and particles buried by subsequent processing. High voltage (>5keV) SEM/EDS-based technology will not meet the analysis needs predicted for future IC generations.

Present x-ray detector technology limits analysis conditions. EDS detectors have modest energy resolution ($\Delta E \approx 50$ eV at 100-200 eV to 2-3 keV; $\Delta E = 130$ eV at 6 keV) and poor sensitivity to low energy x-rays (100-200 eV to 2-3 keV). Typical particle and defect analysis is done using high accelerating voltage electron beams (>10 keV, and often >20 keV) resulting in a large sampling volume for EDS based x-ray analysis. This is due to the inelastic scatter of electrons in the particle and sample. Characterization of small particles (sub 100nm diameter) and defects on patterned wafers will be difficult at these electron beam energies.

During 1994, the National Technology Roadmap for Semiconductors was developed [1]. The requirements for particle detection equipment are listed in the Materials and Bulk Processes (MBP) part of the Roadmap. The Metrology Roadmap lists potential off line, in line, and in situ characterization solutions for the metrology needs specified in the Roadmap [2]. Near- and long-term potential methods of particle composition analysis can be found in the MBP part of the Metrology Roadmap [2]. The particle size requirements for several generations of IC technology are shown in Table 1. Auger, time of flight-scanning ion mass spectroscopy (ToF-SIMS), and

Table 1 **Particle Size Roadmap for Particle Composition Analysis**

Year of First Shipment	1995	1998	2001	2004	2007	2010
IC Design Rule	0.35µm	0.25µm	0.18µm	0.13µm	0.10µm	0.07µm
Particle Size	0.12µm	0.08µm	0.06µm	0.04µm	0.03µm	0.02µm

scanning near field optical microscopy (NFOM) are considered to be ready for development into whole wafer particle and defect composition analysis tolls (i.e., DRTs). Longer term solutions include new x-ray detector technology to replace EDS and synchrotron x-ray source based micro-XANES (x-ray adsorption near edge structure).

Evaluation of analysis capability required a set of reference samples. Using a custom deposition system, particles with similar effective size/charge characteristics are deposited at high densities on silicon wafers. The objective is to have samples that allow rapid location of particles at a magnification of 1000x. To evaluate light element characterization by ToF-SIMS, sets of 0.5, 0.3, and 0.1 µm diameter aluminum and aluminum oxide particles were analysed. This paper reports the method of particle deposition and the results of particle composition analysis.

PARTICLE DEPOSITION PROCEDURE

Particle deposition was done at the National Institute of Standards and Technology (NIST) on 2.54 cm (1 in) diameter silicon wafers. Particle suspensions were made of three different powders: $5m^2/g$ aluminum and 5 and $14m^2/g$ alumina. The numerical designation refers to the surface area per unit mass. To prevent oxidation, the aluminum powder was mixed with isopropanol. Stock solutions of the metal powders were made using 2 g of aluminum per 50 ml of isopropanol or 2 g of alumina per 100 ml of water. The 14 m^2/g alumina was used when targeting 0.1 and 0.3 µm but the $5m^2/g$ aluminum was used for the 0.5 µm size. The particle deposition system consisted of an aerosol generation system, a differential mobility classifier (DMA) for selecting a monodisperse size fraction, a condensation nucleus counter for monitoring the aerosol concentration, and a cascade impactor for depositing the aerosol.

After the deposition was complete, the collection disk was taken to an optical microscope where the center of the deposit pattern was determined using 200X magnification. The magnification was increased to 1000X and the particles in one-quarter of the photograph area were counted in dark field to estimate if the intended density of particles was accomplished.

The CNC count average about $6/cm^3$ for the 15 minute deposition of 0.5 µm particles, so the total number of particles that entered the cascade impactor at 8.3 cm^3/s (0.5 1/min) was about 45,000. About 150 particles were observed in dark field in a 0.01 mm^2 moderately dense area of the collection disk for a density of $15000/mm^2$. Electron microscopy revealed a density of about $3000/mm^2$ for the same sample, but not necessarily at the same location.

EXPERIMENTAL

The experiments were performed on the PHI-EVANS TRIFT Time-of-Flight Secondary Ion Mass Spectrometer. A pulsed, rastered ^{69}Ga Liquid Metal Ion Gun (LMIG) was used as primary ion source. This ion gun produces short ion bursts to stimulate secondary ion production and is currently capable of achieving pulsed spot sizes down to about 1000Å at 60pA continuous current. Further improvements in pulsed beam diameter are expected. The pulsed primary ion beam stimulates the emission of sample specific secondary ions which are electrostatically extracted, focused through the energy compensating spectrometer and strike the detector. Ions created at the sample surface are accelerated to the same nominal kinetic energy. The spectrometer system is roughly equivalent to a drift region. Since all ions enter the

spectrometer with the same kinetic energy, they will have different velocities according to the mass. Lighter ions will traverse the mass spectrometer faster than the heavier ones. The flight times to the detector are $t \sim (m)^{1/2}$, where m is the ion's mass. Ions of different mass will thus strike the detector sequentially but will still follow a similar path. Since the mass separation is only achieved by differences in flight times, TOF-SIMS offers in principle unlimited mass range. More importantly, TOF-SIMS provides high sensitivity surface analysis due to its inherent parallel detection capability, *i.e*. the analytical conditions can be chosen in such a way that practically all secondary ions of given polarity are also detected. This makes it possible to analyze surfaces with minimal primary ion beam damage. Typical ion doses required to perform a TOF-SIMS analysis are on the order of 10^{12} primary ions/cm^2 (static SIMS limit), making it possible to characterize both organic molecular and elemental contaminants.

RESULTS AND DISCUSSION

Location of the particles and initial data acquisition were accomplished with the instrument operated in a static SIMS mode, conditions that would be required to obtain organic molecular information. These conditions would be needed for the analysis of a particle of unknown origin. To distinguish Al from $C_2H_3^+$, the mass spectra were recorded in a higher mass resolution mode (shorter ion beam pulses of approximately 11 nanoseconds), resulting in a somewhat larger ion beam than longer pulse widths permit. In Figures 1 and 2, TOF mass spectra illustrating the separation of Al and $C_2H_3^+$ are shown for a large raster area containing 0.5, 0.3 and 0.1 μm Al (Figure 1) and Al_2O_3 (Figure 2) particles. In Figures 3 and 4, the difference in Al signal on and off a 0.5 (Figure 3) and 0.1 (Figure 4) μm Al_2O_3 particle is shown.

Because the particles were composed of compounds having high secondary ion yields (Al_2O_3 and the surface oxide on Al), maps of the Al^+ distribution were most useful to locate the particles. The Si ion and total ion maps generally resulted in less useful images for particle location. In Figures 5 and 6, Al maps of 0.3 μm Al and Al_2O_3 particles are shown. On one sample, containing 0.1 μm Al_2O_3, particles that were not alumina were observed in the pulsed ion images. Examination of the spectra and subsequent ion image acquisition indicated that Na^+ and K^+, but not Al^+ distributions were higher on these particles.

Both ion-induced secondary electron and total positive ion maps were able to locate the particles, but they were obtained using a continuous ion beam that would destroy organic molecular information on the surface. Since attempts were made to analyze the particles under static SIMS conditions (necessary for the analysis of unknown particles that might be organic/molecular), these images were not acquired until after the particles were located. Figure 7 shows a total positive ion image from the 0.1 μm Al particle sample.

In addition to locating particles on each of the samples, a second goal of this work was to differentiate the Al and alumina particles. However, under static SIMS conditions, the TOF-SIMS sampling depth of 1-3 monolayers (approximately 10 Å) would not penetrate beyond the native oxide layer of aluminum, meaning that surface spectra from the two types of particles are quite similar.

Al and Al_2O_3 could be differentiated by performing an analysis at depth in the samples. This was accomplished by obtaining a depth profile with the LMIG focussed on a single particle. For the alumina samples, the substrate oxide produced a relatively flat Al^+ profile (Figure 8).

However, in the case of the Al samples, oxide enhancement of the Al^+ signal was lost below the native oxide, and the Al^+ signal intensity decreased significantly at that point (see Figure 9).

CONCLUSIONS

The selection of appropriate analysis methods depends on the application. Typically, analysis tools are expected to serve more than one function. Although defect review tools are presently applied to particle/defect characterization, future tools are expected to have expanded roles during contamination analysis. TOF-SIMS is capable of characterization of non-particulate trace contamination. In addition, it is the only method capable of providing detailed analysis of organic contamination.

REFERENCES

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