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**RESONANCE IONIZATION OF SPUTTERED ATOMS:  
QUANTITATIVE ANALYSIS IN THE  
NEAR-SURFACE REGION OF SILICON WAFERS\***

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# RESONANCE IONIZATION OF SPUTTERED ATOMS: QUANTITATIVE ANALYSIS IN THE NEAR-SURFACE REGION OF SILICON WAFERS

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The unambiguous identification and quantification of low levels of metallic impurities on Si wafers are difficult problems due to the rapidly changing chemical activity near the surface. Air-exposed Si surfaces typically possess a native oxide layer several atoms thick plus a top monolayer of various silicon-containing molecules. Resonance ionization spectroscopy (RIS) used for postionization in secondary neutral mass spectrometry (SNMS) is uniquely suited to this task. The high sensitivity of this technique allows detection of metals at parts per billion levels with monolayer sensitivity. The high selectivity of RIS allows unambiguous identification of elements, while the reduced matrix effects of SNMS allow quantification of the photoionized element. Characterization of Si surfaces using RIS/SNMS has been explored by measuring the concentration profiles of Ca in the near-surface region of Si wafers of varying degrees of cleanliness. Calcium detection can be problematic due to the isobaric interference with SiC, particularly in the near-surface region during fabrication of devices due to the use of organic photoresist. Three different resonance ionization schemes for Ca have been examined and compared for effectiveness by calculating detection limits for Ca in Si in the chemically active near-surface region.

## INTRODUCTION

Surface analysis and materials characterization have played key roles in many of the remarkable advances made by the electronics industry, and it is anticipated that this trend will continue in the future. Secondary neutral mass spectrometry (SNMS) combined with postionization techniques that employ resonance ionization spectroscopy (RIS) is an emerging method that could help meet this future need of the semiconductor industry.(1) RIS/SNMS instruments are very sensitive tools for the unambiguous identification of elemental impurities in bulk materials and on surfaces. Because of the high selectivity and sensitivity of the technique, concentrations of various contaminants at part per billion (ppb) levels and below can be obtained on or near the surface.(2-4) In addition, the technique has the potential for quantitative determinations(2-4) and imaging(5,6) at these low concentrations.

One key advantage of RIS is the unambiguous identification of a specific element in the sputter flux. Because atomic transitions are discrete and narrow, a laser tuned to an atomic absorption can ionize that element without ionizing the remainder of the sputtered flux. In traditional mass spectrometry, identification of elements can be compromised by isobaric interferences. A prime example is  $^{28}\text{Si}^{12}\text{C}$  with  $^{40}\text{Ca}$ . This is a difficult problem for semiconductor manufacturing where photoresist may be used for patterning. Typically, such interferences are circumvented by monitoring a minor isotope of an element that is free from isobaric interferences or by using a high resolution instrument.(7) In either case, suppression of the interference results in reduced sensitivity. RIS, on the other hand, can selectively photoionize an element from a large

background of potentially interfering neutral molecules and atoms, eliminating mass analyses that reduce sensitivity.

The ability to distinguish elemental impurities in the presence of mass-interfering molecules makes RIS/SNMS instruments particularly well-suited for trace analysis in samples of rapidly changing chemical composition such as a Si wafer. Metallic Si reacts with air at room temperature to form a thin self-limiting oxide. On top of the silicon oxide is a mixed layer of air contaminants sometimes called an aerosol layer. Determining trace metallic impurities in these thin layers is very difficult, because the amount of material available for analysis is small and backgrounds are generally large due to isobaric interferences. In addition to the benefit from selectivity, SNMS has a specific advantage because secondary neutral yields of ground state atoms remains relatively constant even during compositional changes of the matrix improving quantitative measurements. Thus, due to the high selectivity and small matrix effects, elemental impurity concentrations in the aerosol, oxide, and metallic layers can be measured, permitting determinations of depth versus concentration profiles for these thin layers.

This paper describes experiments that examined the detection of Ca in Si by RIS/SNMS. The aim was to evaluate ionization schemes that could be used to detect Ca on the surface of Si wafers, where SiC concentrations are anticipated to be large enough as to present a severe isobaric interference problem. To that end, a series of Si wafers in various states of cleanliness has been analyzed by three different RIS schemes, the sensitivity and selectivity of each scheme have been evaluated, and detection limits determined.

## EXPERIMENTAL

All analyses were performed with a SNMS instrument especially designed and built for high detection sensitivity when employing laser postionization. The instrument, commonly called surface analysis by resonance ionization of sputtered atoms (SARISA), is composed of a pulsed ion source, a time-of-flight mass spectrometer, and tunable dye lasers. Data collection and control of the instrument are accomplished via a personal computer. Details of the instrument have been previously reported.(8)

For these experiments, the primary ion beam was composed of 4 keV Ar<sup>+</sup> ions having a peak current of 3  $\mu$ A in a 250  $\mu$ m diameter spot. During analyses the ion beam was typically pulsed on target for 600 ns prior to the triggering of the laser. The same ion beam was also used to clean and ion mill (sputter erode) samples for measuring depth profiles. Here the ion beam impinged on the sample continuously while being swept in a 2  $\times$  2 mm square raster pattern, allowing rapid removal of material (~1 monolayer/s) and preventing crater wall effects from biasing results during depth profile measurements.

Postionization was accomplished by employing resonance ionization to detect sputtered neutral ground-state calcium atoms. Three different ionization schemes were tested to determine ionization efficiency and the photoionization background that they generate. These are shown in Fig. 1. Two excimer-pumped dye lasers were used to produce the desired frequencies of laser light. A single XeCl excimer laser (308 nm) operating at >100 mJ/pulse and 77 Hz was used as the pump laser. Each dye laser produced between 1 and 5 mJ/pulse of tunable light depending upon the efficiency of the dye. The 240-nm light was generated by frequency doubling 480-nm light and had an intensity of about 0.1 mJ/pulse. The cross sections of the laser beams were reduced to a 1-mm spot in front of the sample using a long focal length lens. Saturation of the photoionization was confirmed by plotting signal versus laser intensity for each wavelength. Only the ionization step for the 1-color (240 nm + 240 nm) scheme did not reach saturation. During

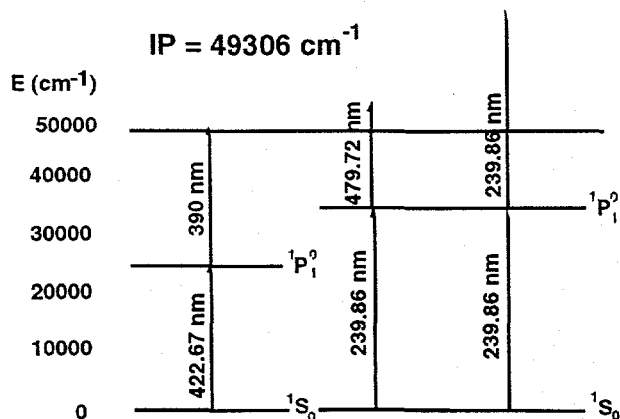


FIGURE 1. Schematic energy level diagram showing the resonance ionization schemes used to detect Ca.

experiments, the intensity of each laser beam was attenuated as much as possible while still maintaining saturation of each transition in order to minimize nonresonant ionization.

Samples were prepared at Bell Laboratories. One sample consisted of an uncleaned Si substrate topped by 100 nm of SiO<sub>2</sub>. The other samples had only the typical native oxide layer. Photoresist was laid down on all wafers and ashed by plasma. The samples without the oxide cap were then cleaned by various procedures, before being shipped to Argonne for analysis. The Si wafers were cleaved into squares, 0.5 mm on a side, and attached to sample stubs with conductive epoxy in a class 10 desktop Cleansphere (Safetech, Ltd.) before being loaded into the SARISA instrument.

Alignment and calibration of the instrument were accomplished using a pure Ca metal target as described previously.(9) Measurements on the Ca target were performed before and after each day's analyses to determine whether the instrument calibration had drifted over the day. Significant memory effects were found to occur due to the sputtering of the pure Ca target. However, it was determined that sputtering a Si or Mo target for an hour between the Ca metal measurement and a sample measurement eliminated any discernible memory effect.

Data were collected as a function of depth by measuring and integrating the <sup>40</sup>Ca mass spectral peak as the Si surface was eroded by the ion beam. To probe changes in composition in the near-surface region, a number of spectra were collected sequentially with only the pulsed ion beam, as it probed the sample, used to erode the surface. Once a dose equivalent to approximately one monolayer removed was accumulated in this mode, additional data were collected by ion milling the surface between periods of data collection. Depth was calculated from the total ion fluence assuming a sputtering yield of 1.5.

## RESULTS AND DISCUSSION

The potential of RIS for unambiguous elemental determinations is shown in Fig. 2, where two mass spectra from a Si sample in the mass region near Ca are presented. The data result from removing  $1.5 \times 10^{11}$  ions in a 250  $\mu$ m spot ( $7 \times 10^{14}$  ions/cm<sup>2</sup>) for each spectrum, corresponding to 12,000 averages for our particular instrument. Thus, the data were collected with removal of approximately one monolayer. The two mass spectra are identical except that the wavelength of the dye laser used to access the Ca resonance transition was tuned off the atomic absorption by 0.2 nm for the off-resonance spectrum. As can be seen in Fig. 2, when the laser is tuned on resonance, Ca atoms are ionized and detected by the mass spectrometer. When the resonance transition is not accessed, no Ca atoms are detected. It therefore is straightforward to identify the actual Ca signal, even in the presence of large backgrounds, by subtracting the two spectra. The results shown in Fig. 2 indicate that Ca is present in the aerosol layer of this particular sample at a concentration of 3 ppm.

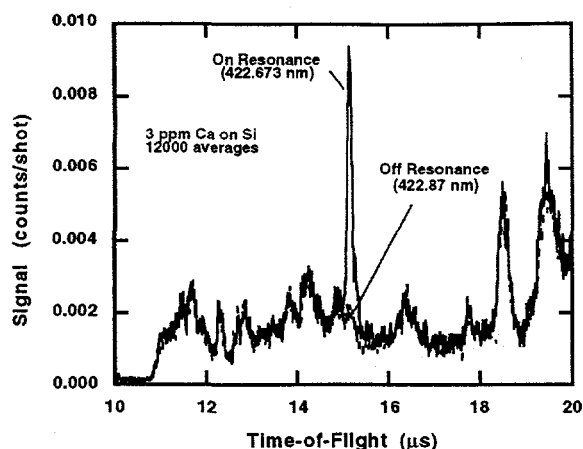


FIGURE 2. Mass spectra showing how the signal from Ca can be distinguished from a large background by tuning on (422.673 nm) and off (422.870 nm) a resonance frequency.

Besides the Ca signal, the mass spectra contain several peaks that correspond to major constituents sputtered from the surface as neutrals and then photoionized nonresonantly. Three of these peaks (i.e., Si, Si<sub>2</sub>, and SiO) can be used to monitor the transitions between the aerosol, oxide, and metal layers.<sup>(10)</sup> For the oxide-capped wafer, a signal change is observed very near to the known oxide thickness

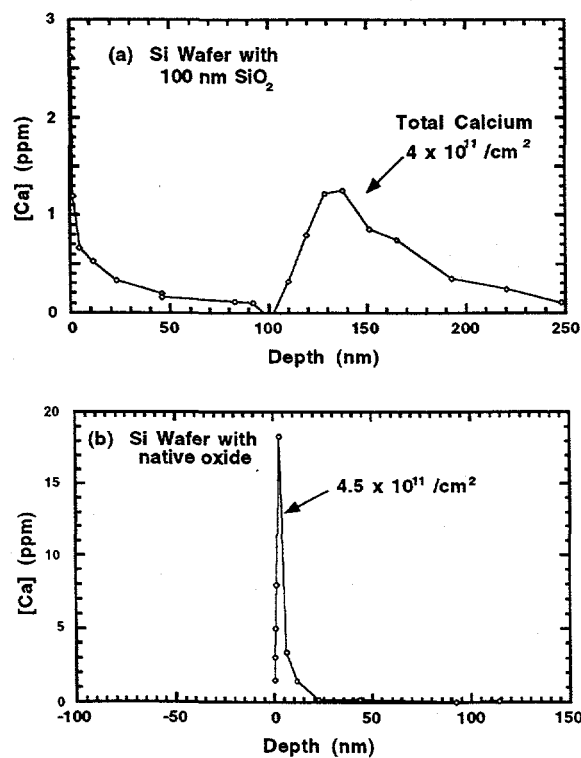


FIGURE 3. Depth profile of Ca concentration in an (a) oxide-capped and (b) cleaned Si wafer. Note that the depth axis in spectrum (b) has been shifted so that the oxide/metal interfaces for the two spectra are approximately aligned.

of 100 nm, indicating that our dose to depth conversion is approximately correct. For the "cleaned" wafers, the nonresonant signals indicate that the metal/oxide interface is in the region between 1 and 10 nm, a reasonable thickness for a native oxide layer on Si. Changes in signal levels for Si, Si<sub>2</sub>, and SiO much nearer the surface (<1 nm) are also observed in all depth profiles. These signal changes mark the location of the aerosol/oxide interface. However, because the sputtering yield from the aerosol layer is unknown, the calibration of the depth scale at these very small distances is highly uncertain.

Shown in Fig. 3 are the Ca signals as a function of depth for two Si wafers. The upper panel (Fig. 3a) shows results for the capped oxide wafer. The lower panel (Fig. 3b) shows data from a wafer where the photoresist has been removed by cleaning. There are two features that are striking about the results. First, in both measurements, the Ca is found to be located at the SiO<sub>2</sub>/Si interface. This was found to be true for all measurements. Second, the total amount of Ca detected in each measurement is the same within experimental uncertainty. Integrating the Ca versus depth curves in Fig. 3, the amount of Ca detected is found to be approximately  $4 \times 10^{11}/\text{cm}^2$  for both samples.

As can be seen in Fig. 3, the Ca is spread over a much wider depth range (50-100 nm) in the oxide-capped wafer. By examining the nonresonant Si, SiO and Si<sub>2</sub> signals, it was found that the Ca had diffused from the SiO<sub>2</sub>/Si interface into the Si metal phase. Presumably, the Ca was present on the wafer before the oxide cap was laid down and diffused into the Si upon heating during plasma etching.

It was anticipated that the cleaning procedures would remove most if not all of the Ca; and so, it was a surprising that Ca was detected on all samples at such high and similar concentrations. The most reasonable explanation for this result is that the wafers were contaminated by Ca after cleaning rather than during the photoresist steps. If this is the case, then the Ca must be diffusing across the native oxide layer to the SiO<sub>2</sub>/Si interface during the analysis and piling up there. Similar results have been reported for other elements in Si, particularly alkali metals.<sup>(11,12)</sup> To investigate this hypothesis, the nonresonant signal from potassium as a function of depth was examined. It was found that the potassium concentration tracked the Ca concentration and also piled up at the oxide/metal interface. It thus appears that the observation of Ca at the SiO<sub>2</sub>/Si interface is due to charge- or ion-induced diffusion and that the source of Ca is contamination following wafer preparations.

Calcium detection limit for the three resonance ionization schemes used in this study have been determined. They were calculated assuming that the uncertainties in the measurements are dominated by random error associated with pulse counting (Poisson statistics). For measurements where a background is subtracted from a signal and assuming a limiting signal-to-noise ratio of unity, the detection limit,  $D_L$ , is calculated from the background count

Table 1. Calcium detection limits (ppb) in the aerosol layer and bulk when analyzing a Si matrix. The two measurements correspond to removing  $6 \times 10^{11}$  and  $2 \times 10^{13}$  atoms, respectively.

RIS Scheme	Aerosol Layer	Bulk Si
240 + 240 nm	5000	110
240 + 480 nm	640	11
423 + 390 nm	80	5

rate,  $B$ , the number of averages,  $n$ , and the sensitivity of the instrument,  $S$ , from

$$D_L = S \cdot \frac{1 + \sqrt{1 + 8nB}}{2n} \quad (1)$$

Calculations of  $D_L$  have been made for two types of analyses and are presented in Table 1. Detection limits were calculated for measurements in the aerosol layer where the amount of material is limited. Here it is assumed that one monolayer ( $6 \times 10^{11}$  atoms =  $1.2 \times 10^4$  averages) would be removed. The second set of detection limits is for a bulk measurement and assumes that data collection time, which is controlled by the laser repetition rate, limits the analysis. For our present instrument, if the signal and background are both averaged for  $5 \times 10^5$  shots (about 1 hour at 77 Hz), approximately  $2 \times 10^{13}$  atoms of Si are consumed (25 monolayers) during the analysis.

As can be seen from Table 1, there are wide variations in detection limits for the different ionization schemes and also between the aerosol layer and bulk for each scheme. The bulk detection limits are expected to be lower than the aerosol limits by about a factor of 6.5 because of the larger number of averages assumed for these analyses. The bulk detection limits are lower than the aerosol detection limits by more than 6.5 for all three ionization schemes. This is because the backgrounds in the aerosol layer are larger than the corresponding backgrounds in the bulk Si. This is found to be true independent of laser intensity or frequency, suggesting that the increase in background is due to secondary ions. It appears that the much larger secondary ion yield in the aerosol, compared to the bulk Si, overwhelms SARISA's secondary ion suppression capabilities. Methods for improving suppression of secondary ions are currently being examined.

The poorer detection limits for the 1-color scheme (240 nm + 240 nm) are mainly due to the fact that saturation of the ionization step was not achieved for this scheme. However, even if a more intense 240-nm laser beam was available, the benefit may not be as great as anticipated because the 240-nm light appears to photoionize the isobarically interfering SiC molecules more efficiently than the other wavelengths. In fact, the poorer detection limit for the 1-color scheme is at least partially attributable to nonresonant photoionization of SiC by 240-nm light.

The uncertainty in the detection limits listed in Table 1 is about a factor of two.(9) Thus, when analyzing Ca in

bulk Si, it is unclear whether there is any difference between the two 2-color ionization schemes that were tested. However, when searching for Ca in the aerosol layer, the benefit of using the 423-nm resonance is clear. This difference is mainly due to background differences since both ionization schemes were saturated and thus produced similar sensitivities. As mentioned above, 240-nm light appears to photoionize SiC; however, only low-intensity 240-nm light ( $\sim 10 \mu\text{J}/\text{pulse}$ ) was used in the 2-color scheme, since this resonance transition is strong and saturates at low laser intensities. While we were unable to find any spectroscopic information on SiC, it has been reported that SiC<sub>2</sub> absorbs near 480 nm.(13) It may be that the background at mass 40 is due to fragmenting SiC<sub>2</sub>.

## CONCLUSIONS

Resonance ionization schemes for the detection of Ca by postionized SNMS have been tested to determine sensitivity and detection limits in a Si matrix. The two-photon, two-color schemes that were tested both work well for clean bulk Si, producing detection limits in the low ppb range. For Ca detection at the surface, where SiC may be present, the ionization path using the resonance transition at 423 nm was clearly superior. The ubiquitous nature of Ca appears to have caused contamination of the wafers after preparation at a level of  $4 \times 10^{11}$  atoms/cm<sup>2</sup>.

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## REFERENCES

- Calaway, W. F., Coon, S. R., Pellin, M. J., Gruen, D. M., Gordon, M., Diebold, A. C., Maillot, P., Banks, J. C., and Knapp, J. A., *Surf. Interface Anal.* **21**, 131-137 (1994).
- Pellin, M. J., Young, C. E., Calaway, W. F., Whitten, J. E., Gruen, D. M., Blum, J. D., Hutcheon, I. D., and Wasserburg, G. J., *Phil. Trans. R. Soc. Lond. A* **333**, 133-146 (1990).
- Arlinghaus, H. F., Spaar, M. T., and Thonnard, N., *J. Vac. Sci. Technol. A* **8**, 2318-2322 (1990).
- Pappas, D. L., Hrubowchak, D. M., Erwin, M. H., and Winograd, N., *Science* **243**, 64-66 (1989).
- Ma, Z., Thompson, R. N., Lykke, K. R., Pellin, M. J., and Davis, A. M., *Rev. Sci. Instrum.* **66**, 3168-3176 (1995).
- Wood, M., Zhou, Y., Brummel, C. L., and Winograd, N., *Anal. Chem.* **66**, 2425-2432 (1994).
- Niehuis, N., "Time-of-Flight SIMS," in *Proceedings of the Eighth International Conference on Secondary Ion Mass Spectrometry (SIMS VIII)*, 1991, pp. 269-280.
- Pellin, M. J., Young, C. E., and Gruen, D. M., *Scanning Microsc.* **2**, 1353-1364 (1988).
- Calaway, W. F., Coon, S. R., Pellin, M. J., Young, C. E., Whitten, J. E., Wiens, R. C., Gruen, D. M., Stingeder, G., Penka, V., Grasserbauer, M., and Burnett, D. S., *Inst. Phys. Conf. Ser.* **128**, 271-274 (1992).
- Emerson, A. B., Ma, Y., Wise, M. L., Green, M. L., and Downey, S. W., *J. Vac. Sci. Technol. B* **14**, 301-304 (1996).
- Magee, C. W., and Harrington, W. L., *Appl. Phys. Lett.* **33**, 193-196 (1978).
- Morgan, A. E., and Maillot, P., *Appl. Phys. Lett.* **50**, 959-961 (1987).
- Verma, R. D., and Nagaraj, S., *Can. J. Phys.* **52**, 1938-1948 (1974).