

Invited**Mechanisms Responsible for the Chemical Removal
of Fe and Cu from Si Surfaces**

M.L. Kniffin and C.R. Helms

Department of Electrical Engineering
Stanford University, Stanford CA 94305

Using Auger electron spectroscopy, we have examined the ability of a variety of standard aqueous chemical cleaning procedures to remove trace quantities of thermally deposited copper and iron atoms from the surfaces of silicon substrates. It was determined that the technique for preparing the metal contaminated test standard prior to metal deposition had a significant impact on the experimental results. This suggests that the silicon surface chemistry and the chemical environment of the metal impurities plays an important role in determining the cleaning efficiency of a given wet chemical processing sequence.

1. INTRODUCTION

It is well known that the presence of trace quantities of alkali and heavy metals on the surface of a silicon substrate can have catastrophic effects on both device performance and process yields. The development of efficient methods for the removal and control of these impurities is of critical importance to the advancement of integrated circuit technology.

The desire to optimize currently existing wet chemical processing techniques and the recent development of alternative wafer cleaning technologies^{1,2} have brought about a renewed interest in understanding the basic physics and chemistry behind the removal and control of metallic impurities. As part of a broader program to understand and improve the cleaning efficiency of newly developed wafer processing techniques, we have conducted a study of the ability of standard aqueous chemical cleans to remove trace metal impurities from silicon surfaces.

A systematic examination of the relative efficiency of various wafer cleaning techniques requires the development of an appropriate set of test standards with known concentrations of metallic surface contamination. Metal impurities can exist in numerous forms on a wafer surface and the most efficient technique for removing a given contaminant may depend strongly upon the chemical environment of the impurity atom as well as the chemistry of the silicon surface. Previous studies have focused primarily on the removal of metallic residues that were plated or deposited onto the silicon surface from intentionally contaminated aqueous chemical solutions^{3,4}. As a point of comparison, we have examined the removal of thermally deposited copper and iron atoms from the surfaces of both bare and oxidized silicon substrates.

2. EXPERIMENT

In order to fabricate the contaminated silicon wafers, an electron-beam evaporator was modified to facilitate the deposition of sub-monolayer concentrations of metal atoms. Depositions were performed by setting a very low evaporation rate ($< 10^{13}$ atoms-cm⁻²-sec⁻¹) with the shutter closed, then opening the shutter to expose the wafer surface for a fixed period of time. Using this technique it was possible to reproducibly and uniformly deposit trace quantities (10^{12} to 10^{15} atoms-cm⁻²) of metal impurity atoms over large portions of the surfaces of 4- and 6-inch diameter silicon wafers. With a more accurate mechanically activated shuttering mechanism, the controllable deposition of much lower ($\sim 10^{11}$ atoms-cm⁻²) concentrations of metallic impurities should be possible.

Using this deposition system, silicon wafers could easily be contaminated with many of the transition and noble metal impurities that are commonly encountered in integrated circuit fabrication. However, for the purposes of this investigation we focused primarily on the removal of iron and copper impurities from the silicon surface. These metals were chosen because they are commonly found in semiconductor process equipment and are frequently deposited onto the surfaces of silicon wafers during processing^{2,5,6}. The two metals also exhibit distinctly different aqueous chemistries⁷ and thus provide a measure of the importance of metal chemistry in determining the efficiency of a particular wafer cleaning technique.

Metal contaminated wafers were prepared using two different pre-deposition aqueous chemical cleaning procedures for the silicon substrate. These pre-deposition cleans were chosen to provide silicon substrates with distinctly different surface chemistries. This was done in order to ascertain whether or not the

chemical environment of the metal atoms and the chemistry of the silicon surface play a significant role in determining the ability of subsequent chemical cleans to remove trace metal contaminants from the wafer surface. The first method used to prepare the silicon substrates was as follows:

- I. $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:2:5) 70°C, 10 min.
DI water rinse, 5 min.
Nitrogen blow dry.

This treatment tends to yield a silicon surface which is relatively free of carbon contamination, but is passivated by a thin native oxide layer⁸). Metal atoms deposited onto these surfaces are expected to exhibit oxide- or silicate-like bonding. The second method used to prepare the silicon substrates was as follows:

- II. $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:2:5) 70°C, 10 min.
DI water rinse, 5 min.
 $\text{HF}:\text{H}_2\text{O}$ (1:50), 1 min.
Nitrogen blow dry.

This cleaning procedure tends to leave the silicon surface relatively free of carbon and oxygen contamination⁸). Substrates prepared in this manner were immediately inserted into the evaporation chamber following the final etch step, in order to minimize the accumulation of carbon and oxygen that inevitably occurs during exposure of a bare silicon surface to the laboratory ambient⁸). Metals deposited on these surfaces might be expected to exhibit more silicide-like bonding than those deposited onto a surface passivated with a native oxide. They are also more apt to be incorporated into a re-grown native oxide layer or covered in a carbonaceous film.

The metal contaminated wafers were cleaved into quarters and subjected to a variety of different chemical cleaning sequences aimed at reducing the surface impurity concentration. These cleaning sequences were based on combinations of the various process steps found in several different standard procedures for silicon substrate preparation^{3,4,9-11}).

To assess the relative efficiency of the various chemical cleans, both the as-deposited and post-cleaning surface metal concentrations were monitored using Auger electron spectroscopy (AES). In order to enhance the detectability limit for metallic impurities, the operating conditions for the analysis system and the Auger scan parameters were chosen to give the maximum achievable signal to noise ratio. Under the appropriate operating conditions, we found that this technique could detect metal impurities at relatively low concentrations ($\sim 5 \times 10^{12}$ atoms/cm²).

A comparison of the Fe_{LMM} (703 eV) or Cu_{LMM} (920 eV) Auger signal strength to the substrate Si_{KLL} (1619 eV) Auger signal intensity was used to obtain a quantitative estimate of the residual metal contamination. The relative Auger signal strengths were converted to absolute metal concentrations using experimentally determined elemental sensitivity factors. The sensitivity factors were calculated from total reflection X-ray fluorescence (TRXF) measurements taken on a representative subset of the as-deposited metal contaminated standards. The correlations between the

relative metal and silicon Auger peak-to-peak heights and the surface impurity concentrations are plotted in figure 1. The iron and copper signal intensities vary in direct proportion to the metal concentration over several orders of magnitude, thus providing an accurate measure of the surface impurity concentration.

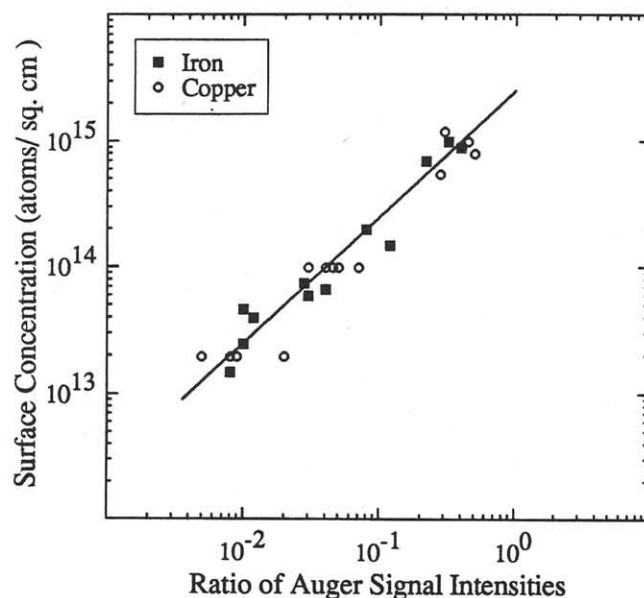


Figure 1. Plot of the $\text{Cu}_{\text{LMM}}:\text{Si}_{\text{KLL}}$ and $\text{Fe}_{\text{LMM}}:\text{Si}_{\text{KLL}}$ Auger signal intensity ratios as a function of surface copper or iron concentration as measured by total reflected x-ray fluorescence. The intensity ratios exhibit a linear dependence on concentration over several orders of magnitude.

3. RESULTS AND DISCUSSION

Our results for RCA-based^{3,4}) and MPR-based¹¹) cleans are summarized in Table I. One can see that in many instances the technique used to prepare the metal contaminated test standard had a major impact on the ability of a given wet chemical processing sequence to successfully reduce the surface impurity concentration.

The removal of Fe and Cu from the surfaces of silicon wafers which had been precleaned in an ammonium hydroxide-hydrogen peroxide solution proved to be relatively simple. Any cleaning sequence involving an aqueous chemical solution in which the particular metal is expected to be soluble readily reduced the metal impurity concentration to below the detectability limit of our analysis technique. This observation is consistent with the results of previous studies which have examined the removal of chemically deposited copper and iron impurities^{3,4}) from the silicon surface.

Cleaning sequences which stripped the native oxide from the silicon surface were also able to substantially reduce the concentration of iron and copper atoms present on the surfaces of these wafers, regardless of the expected solubility of these metals in the etch bath. As a consequence, any processing sequence involving immersion in a chemical solution containing hydrofluoric acid also tended to lead to a substantial reduction in the surface impurity concentration.

	Fe Preclean		Cu Preclean	
	HF:H ₂ O	NH ₄ OH:H ₂ O ₂	HF:H ₂ O	NH ₄ OH:H ₂ O ₂
As deposited	1 x 10 ¹⁴ atoms-cm ⁻²	6 x 10 ¹⁴ atoms-cm ⁻²	1 x 10 ¹⁵ atoms-cm ⁻²	2 x 10 ¹⁴ atoms-cm ⁻²
<u>RCA</u>	6 x 10 ¹³	below detectability limit	3 x 10 ¹⁴	below detectability limit
<u>RCA + HF</u>	below detectability limit	below detectability limit	below detectability limit	below detectability limit
<u>MPR</u>	2 x 10 ¹³	below detectability limit	1 x 10 ¹⁴	below detectability limit
<u>MPR + HF</u>	below detectability limit	below detectability limit	below detectability limit	below detectability limit

Table I. Efficiency of copper and iron removal for RCA-based and MPR-based cleans, as determined by Auger electron spectroscopy. The standard RCA clean consists of a 10 minute immersion in a NH₄OH:H₂O₂:H₂O (1:2:5) solution at 80°C, followed by a 10 minute immersion in a HCl:H₂O₂:H₂O (1:2:7) solution at 80°C. The standard MPR clean consists of a 10 minute immersion in a H₂SO₄:H₂O₂:H₂O (1:1:5) solution at 95 °C followed by a 10 minute immersion in a HNO₃:HCl (1:3) solution at 70°C. The RCA + HF and MPR + HF cleans include a 30 second HF:H₂O (1:50) etch between sequential process steps.

Metals deposited onto silicon surfaces which had been cleaned in a dilute hydrofluoric acid solution were significantly more tenacious. Substantial reductions in the concentration of copper and iron impurities present on the surfaces of these wafers could only be realized by subjecting the sample to a cleaning procedure which removed the top surface of the substrate *via* the growth and subsequent dissolution of a thin native oxide layer. This could be achieved by introducing an intermediate hydrofluoric acid etch step to the standard RCA and MPR cleans. Immersing the substrate in a solution containing hydrofluoric acid and a mild oxidant such as dilute nitric acid or dilute hydrogen peroxide was also effective. A similar observation has been made by Hosoya *et al.*, who has examined the removal of metallic impurities introduced during reactive ion etching of the silicon surface¹².

These results demonstrate that chemistries for metal removal are strongly dependent upon the silicon surface chemistry and the chemical environment of the metal impurities. This is an important consideration when interpreting the literature and when evaluating the applicability of a cleaning technique to a given process.

4. ACKNOWLEDGEMENTS

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