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A Highly Sensitive Determination of Bulk Cu and Ni in Heavily Boron-doped Silicon Wafers

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The new metrology, Advanced Poly-silicon Ultra-Trace Profiling (APUTP), was developed for measuring bulk Cu and Ni in heavily boron-doped silicon wafers. A Ni recovery yield of 98.8% and a Cu recovery yield of 96.0% were achieved by optimizing the vapor phase etching and the wafer surface scanning conditions, following capture of Cu and Ni by the poly-silicon layer. A lower limit of detection (LOD) than previous techniques could be achieved using the mixture vapor etching method. This method can be used to indicate the amount of Cu and Ni resulting from bulk contamination in heavily boron-doped silicon wafers during wafer manufacturing. It was found that a higher degree of bulk Ni contamination arose during alkaline etching of heavily boron-doped silicon wafers compared with lightly boron-doped silicon wafers. In addition, it was proven that bulk Cu contamination was easily introduced in the heavily boron-doped silicon wafer by polishing the wafer with a slurry containing Cu in the presence of amine additives.

Key Words : Copper, Nickel, Silicon, Wafer, Metrology, Contamination

Introduction

Bulk copper (Cu) and Nickel (Ni) contamination in heavily boron-doped (< 0.01 Ω-cm) silicon wafers has recently become an area of great concern in the semiconductor industry. Numerous studies on the effects of Cu and Ni in silicon have been carried out over the last few decades. Nano-scale device processes having a low thermal budget are more sensitive to metal contamination than previous processes[1-4] and are particularly susceptible to Cu and Ni, which are considered to be detrimental to the performance of these devices.[5-14] However, progress on the metrology for analysis of bulk Cu and Ni has been relatively slow. Due to lack of commercially available bulk metal standards and poor recovery yield in heavily boron-doped silicon wafers, analytical accuracy and precision cannot, so far, be guaranteed.[15]

In recent years, several methods for the assay of bulk Cu and Ni, including wafer digestion (WD) and low-temperature out-diffusion (LTOD) using heating plates or IR lamps, have been developed. Nonetheless, these methods are complex with rather low throughputs. WD is applicable in the detection of bulk Cu and Ni impurities at levels of 1×10^{11} atoms/cm^3 or above. Although LTOD is currently the most commonly used method for monitoring bulk Cu and Ni contamination for high volume manufacturing,[16,17] this method is limited by the fact that the recovery yield is influenced by the boron doping concentration as well as the bulk Cu concentration.[15]

In light of the limitations of the conventional analyses, we report herein the design of a new metrology for bulk Cu and Ni in heavily boron-doped silicon wafers, having a good recovery yield and low limit of detection (LOD) and improved analysis throughputs. The new method combines the poly-silicon gettering technique with vapor phase etching (VPE). Moreover, the source or mechanism for bulk metal contamination of heavily boron-doped silicon wafers during the wafer manufacturing process is hardly studied or reported. The proposed method enables us to explore the source of Cu and Ni contamination in the manufacturing processes.

Experimental

A Highly Sensitive Method for Measuring Bulk Cu and Ni in Heavily Boron-doped Silicon Wafers.

Reagents: Ultrapure water (specific resistance above 18.0 MΩ-cm) prepared using an EASYpure UV/UF purification system (Barnstead/Thermolyne, Fair Lawa, NJ, USA) was used throughout the experiment. HNO_3 (69%), HF (49%) and H_2O_2 (31%) were used in sample pretreatment and in preparation of the blank and standard solutions for ICP-MS analysis. HNO_3 and HF were used for cleaning labware. The level of contamination in the chemical reagents was less than 5 pg mL^{-1}. In order to measure the extremely low concentration of metals in the bulk silicon, very high purity chemical solutions are required for sample preparation. A multi-element stock solution (1 μgmL^{-1} of each element) was prepared from High-Purity Standards (Charleston, SC, USA). Working standard solutions were prepared prior to use by diluting the abovementioned multi-element stock solution.

Instrumentation and Operating Conditions: The ICP-MS system used for determination of the Cu and Ni concentration was the Varian model 820MS (Australia), equipped with a micro-concentric PFA nebulizer, PFA spray chamber,

Table 1. Operating conditions for the ICP-MS

	Condition
Model	Varian 820MS
Rf-power	1200 W
Nebulizer type	Micro-concentric PFA 100 uL/min
Nebulizer flow	1.0 L/min
Plasma gas flow rate	21 L/min
Auxiliary gas flow rate	1.45 L/min
Sampler and Skimmer cone	Pt
Collision Cell Gas	H_2 Gas
Quadrupole scan mode	Peak hoppinig
Detector	ETP

plasma torch with a platinum injector and Cetac AS-100 auto-sampler. The mass spectrometer was used in peak hopping mode. ICP was operated under hot plasma conditions for all elements. The operating conditions for the ICP-MS were optimized with an optimization solution and are listed in Table 1.

Advanced Poly-silicon Ultra-Trace Profiling (APUTP) Method: Figure 1 shows the procedure applied in the newly designed metrology. APUTP is a bulk metal test method that utilizes the poly-silicon gettering technique combined with vapor phase etching of the silicon wafer using acid solution. Gettering refers to the phenomenon whereby metal impurities are trapped in specific sites of the wafer, such as oxygen precipitates, poly-silicon layer or backside damage. First of all, a thin layer (50 nm) of poly-silicon is deposited onto both the front and back surfaces of a test wafer using low pressure chemical vapor deposition (LPCVD) of SiH_4 at 570 for about 17 minutes. During the CVD process, more than 90% of bulk Cu and Ni can be gettered by the thin poly-silicon layer.[15] The poly-silicon gettering layer is then etched with a an acid vapor mixture containing HF, HNO_3 and H_2O and rolled over the entire wafer surface with a specific collection solution containing HF and H_2O_2, in order to collect the metal residue on the silicon wafer surface, in a manner similar to the vapor phase decomposition (VPD) method used to analyze the surface metal impurities in silicon wafers.[16] The collection solution is then transferred to a perfluoroalkoxy polymer (PFA) beaker and dried on a hot plate at a temperature of 240 °C for 180 min, to leave a residue. The residue is subsequently re-dissolved by adding a reconstitution solution, containing a mixture of 10.2 µL of ultra-pure hydrofluoric acid (49%), 173.9 µL of ultra-pure nitric acid (69%) and 815.9 µL of ultra-pure water. Finally, the Cu and Ni concentration in the reconstitution solution is analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Cu is determined at the m/q of 63 or 65 and Ni at the m/q of 58 or 60, both with medium resolution, after micro-nebulizer sampling. When using a quadrupole ICP-MS system.

Optimization of APUTP Conditions: As shown in Figure 1, the residual metal should be collected using a specific solution containing a mixture of HF and H_2O_2, in order to determine the metal concentration after vapor phase

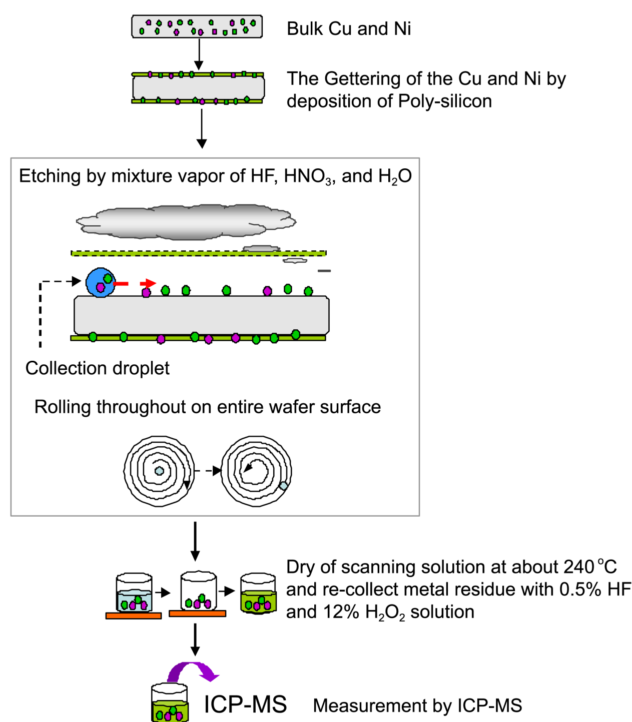


Figure 1. The schematic drawing of the newly designed metrology.

etching. The recovery yield of this analytical method is strongly dependent on the composition of the collection solution used to collect the residual metal on the surface of the wafer following vapor phase etching. It is, however, difficult to determine the optimal conditions for the collection of residual metal by rolling throughout the entire wafer surface, because there is a significant amount of $(NH_4)_2SiF_6$ on the silicon wafer following vapor etching of the poly-silicon layer with acid vapor, and the properties of the collection solution may be easily degraded by $(NH_4)_2SiF_6$.[17,18] Therefore, the 'mixture experiment design' was applied in order to optimize the recovery yield. Mixture experiments are a special class of response surface experiments in which the product under investigation is made up of several components or elements. Figure 2 shows the experiment point of

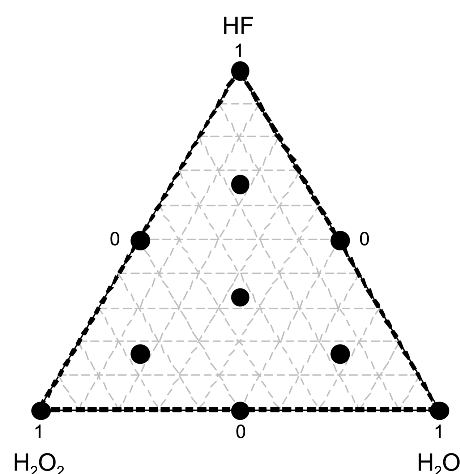


Figure 2. Design of scanning solution for optimization.

the mixture experiment design. In this study, several sets of heavily boron-doped ($9 \times 10^{18} \sim 2 \times 10^{19}$ atoms/cm^3) 300 mm silicon wafers were prepared from the same <100> Czochralski (CZ) ingots with an initial oxygen content of $5.5 \times 10^{17} \sim 6.5 \times 10^{17}$ atoms/cm^3 (New ASTM) and using the same wafering process. The amount of bulk Cu and Ni was measured with the designed APUTP method at the whole mixture experiment point as shown in Figure 2.

Investigation of Bulk Ni and Cu Contamination During Wafer Manufacturing. Bulk Cu and Ni contamination in heavily boron-doped silicon wafers during the wafer manufacturing process, that consists of slicing, lapping, etching, grinding and polishing, has been rarely studied or reported. In this study, two sample groups were prepared from <100> Czochralski ingots with an initial oxygen content of $5.5 \times 10^{17} \sim 6.5 \times 10^{17}$ atoms/cm^3 (New ASTM). The first set consists of heavily boron-doped ($9 \times 10^{18} \sim 2 \times 10^{19}$ atoms/cm^3) 300 mm size silicon wafers and the other of lightly boron-doped ($8.9 \times 10^{14} \sim 1.5 \times 10^{15}$ atoms/cm^3) silicon wafers. The two sample groups were subjected to KOH or NaOH etching and polishing with a slurry including either an amine-containing or amine-free additive after slicing and lapping. The samples were then evaluated using the newly developed APUTP method.

Result and Discussion

A Highly Sensitive Method for Measuring Bulk Cu and Ni in Heavily Boron-doped Silicon Wafers.

Optimization of Recovery Yield: The vapor phase etching and collection technique was optimized for application to the newly designed APUTP method as follows. Initially, the etching uniformity and etching time were considered because good uniformity may guarantee smooth scanning in the subsequent steps, and a shorter etching time is desirable provided that etching satisfies the target uniformity requirement and the target removal amount. The optimal analytical conditions are presented in Table 2. Poor uniformity of the etched surface, which limits the capacity for rolling the entire wafer surface, was achieved using 49% HF and 69% HNO_3 without H_2O. Therefore, a new etching formula (Table 2) was developed. Good uniformity was achieved using vapor phase H_2O with 49% HF and 69% HNO_3. The conditions for the wafer scanning step, used to collect remaining metal residue on the wafer surface following etching of the poly-silicon layer with the acid vapor phase, were optimized using the 'mixture experiment design' (Figure 2). The recovery

Table 2. Experimental condition for developing the new metrology

Step	Process	Condition
1	Poly-silicon deposition	50 nm thickness (570 °C, 17 min)
2	Vapor etching of poly-silicon layer	- 49% HF: 5 L/min - 69% HNO_3: 4 L/min - 0.5% H_2O_2: 1 L/min - Time: 20 min
3	Scanning	1 mL, twice scanning
4	Dry and collection	- 240 °C, 180 min with Hot plate and PTFE vessel - collection during 30 min with 0.5%HF12%H_2O_2
5	Measurement	ICP-MS (Varian 820)

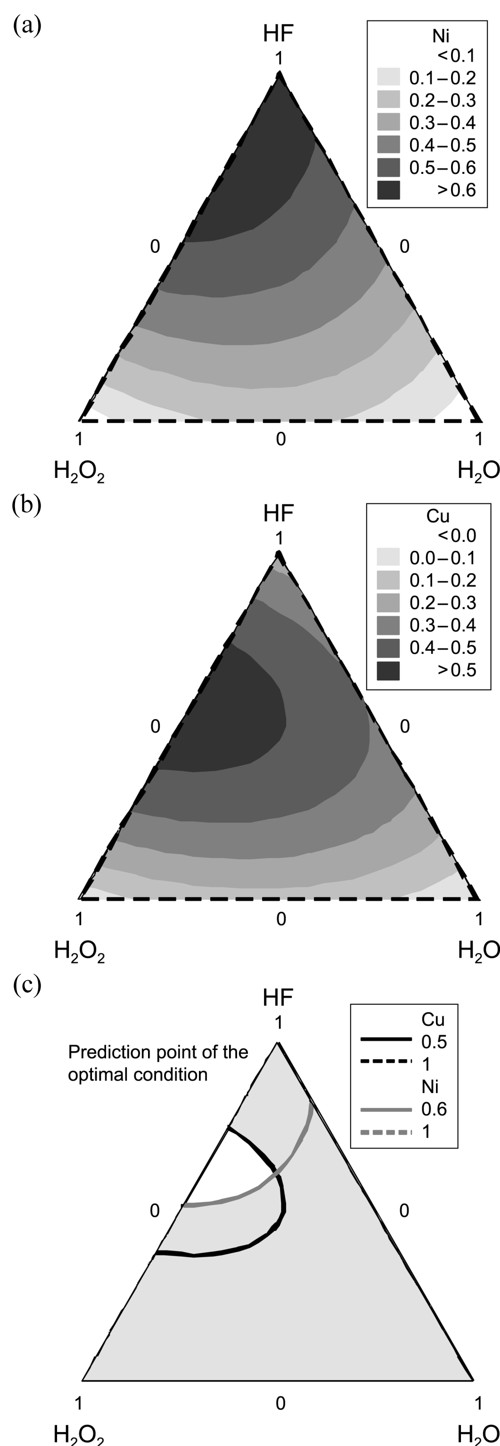


Figure 3. (a) The contour plot of Ni recovery yield predicted by statistical with experimental result. (b) The contour plot of Cu recovery yield predicted by statistical with experimental result. (c) The overlaid contour plot to optimize Cu and Ni recovery yield together.

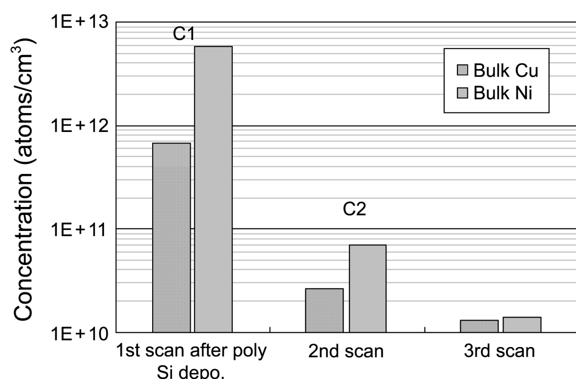


Figure 4. The Verification of the APUTP recovery through the repeated analysis with same wafer.

yield at all proportions of the three components was predicted statistically by the commercial Minitab statistical program, using the recovery yield acquired under ten experimental conditions. Figure 3 presents the predicted recovery yield of Ni (a), the predicted recovery yield of Cu (b) and the overlaid optimal area for acquiring a high recovery yield of Cu and Ni together (c). Based on the results of mixture regression, a high recovery yield was achieved when a volume ratio of 49% HF, 30% H_2O_2, and H_2O of 1.83, 1 and 0 was applied. The Estimated Regression Equations are presented below:

$$\text{Recovery yield of Ni} = 0.69\text{HF} + 0.96\text{HF} \times H_2O_2 \quad (1)$$

$$\text{Recovery yield of Cu} = 0.22\text{HF} + 1.95\text{HF} \times H_2O_2 + 1.38\text{HF} \times H_2O + 0.89H_2O_2 \times H_2O \quad (2)$$

The predicted maximum recovery yield was 66% for Ni and 55% for Cu. In order to achieve a higher recovery yield, another continuous scan of the same wafer with the same mixture solution (HF:H_2O_2 = 1.83:1) was adapted. The optimized vapor etching conditions, the composition of the scanning solution and the repeated scanning produce a good recovery yield of both bulk Cu and Ni as shown in Figure 4. The first Cu and Ni concentration measured by APUTP is in excess of 90% compared with the second and third concentrations. The equation for the recovery yield is

$$(1 - C_2/C_1) \times 100 \quad (3)$$

C_1 is the concentration from the first measurement using APUTP and C_2 is the concentration from the second measurement. The recovery yield of Cu and Ni were 96.0% and 98.8%, respectively, using Equation (3).

Correlation of APUTP and Reference Method: The APUTP method was validated by comparison with the WD technique. Although the APUTP and WD methods are not identical, good correlation was achieved for both Cu and Ni. Figure 5 demonstrates the correlation result for bulk Cu and Ni respectively, which indicates that the compatibility and accuracy of the newly designed APUTP method are acceptable.

LOD of APUTP: A lower LOD could be achieved by using a mechanical mixture vapor etching technique instead

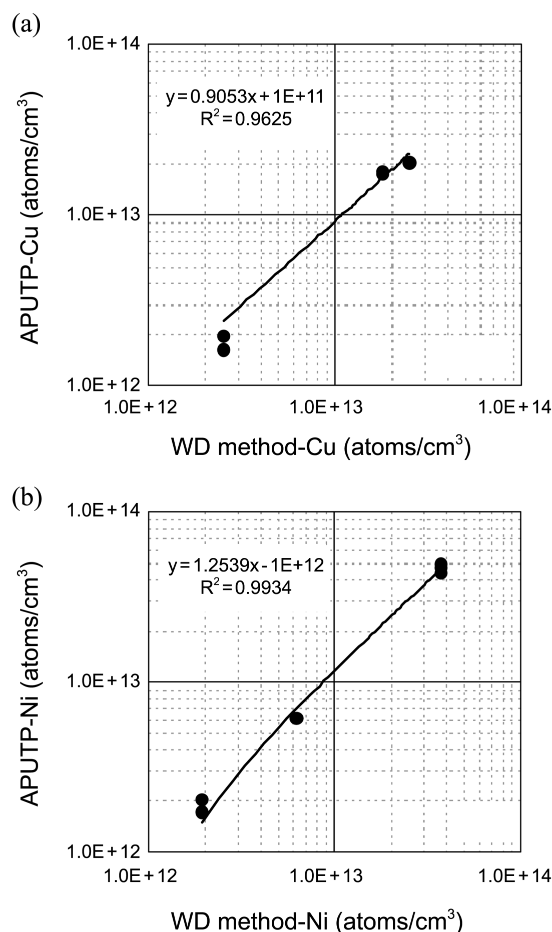


Figure 5. (a) Bulk Cu correlation between APUTP and WD method. (b) Bulk Ni correlation between APUTP and WD method.

of the conventional liquid phase etching. A set of 300 mm lightly boron-doped (~10^{15} atoms/cm^3) silicon wafers was taken from the same CZ ingot and mirror polished in the same batch to minimize the wafer-to-wafer variation. Each day, for 3 consecutive days, two wafers were pulled for APUTP testing. The LOD in this study was defined as three times the overall standard deviation of the 3 day repeated measurements. This estimate contains all of the possible variables, including potential contamination induced by APUTP sample preparation, contamination or variation caused by etching and blank solution preparation and ICP-MS measurement errors. Because the influence of the wafer-to-wafer variation in the test wafers cannot be excluded, the LOD determined in this study actually represents the worst case scenario. As shown in Table 3, the LOD of APUTP, which was calculated as 3 times the standard deviations of repeated tests over 3 days, was 2.34×10^{10} and 1.02×10^{10}

Table 3. Comparison of LOD

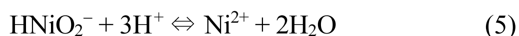
	Cu (atoms/cm^3)	Ni (atoms/cm^3)
APUTP (new method)	2.34×10^{10}	1.02×10^{10}
WD or PUTP (previous method)	8×10^{10}~5×10^{11}	3×10^{10}~5×10^{11}

atoms/cm^3 for Cu and Ni respectively.[19] This LOD level is better than that of any of the previously reported methods.[15]

Investigation of bulk Ni and Cu Contamination During the Wafer Manufacturing Process. The source or mechanism for bulk metal contamination of the silicon wafers during the wafer manufacturing process has been rarely studied or reported. Bulk metal contamination along the various stages of the manufacturing process was investigated in two sample groups that had been subjected to KOH etching or NaOH etching and polishing with a slurry that either included amine or excluded amine. The samples were then evaluated using the newly developed APUTP method.

Bulk Ni Contamination: Based on the experimental results shown Figure 6, more bulk Ni contamination was observed in the heavily boron-doped silicon wafers than in the lightly boron-doped silicon wafers, during alkaline etching. There are many potential sources of Ni impurity, among which, the Ni contained in the alkaline solution is a major source. ICP-OES measurement of the Ni concentration in KOH indicated a value below 5 ppb and that in NaOH was about 100 ppb. Ni leached from these sources may then react with the hydroxide ion in the etching solution to form the soluble $HNiO_2^-$ ion. Some $HNiO_2^-$ may precipitate onto the interior walls of the etching container, and some remains dissolved. As a result, an equilibrium concentration of dissolved nickel, represented by Equation (4),[20] is present in essentially all of the alkaline etching solutions in the containers:

$$Ni(s) + H_2O + OH^-(aq) \Leftrightarrow HNiO_2^-(aq) + H_2(g) \quad (4)$$



$$HNiO_2^- + 3H^+ \Leftrightarrow Ni^{2+} + 2H_2O \quad (5)$$

The equilibrium concentration of $HNiO_2^-$ is sufficient to pose a significant threat of contamination to any wafers processed in the contaminated solution. Therefore, when the silicon wafer is etched in alkali solution, the negatively charged wafer surface will be easily contaminated by the positive Ni ion and Ni contamination increases in proportion to the amount of Ni in the alkaline solution. Ni can contaminate the surface of the silicon wafer, but the bulk Ni concentration was very low in the case of the lightly boron-doped wafer. In contrast, the bulk Ni concentration in the heavily boron-doped silicon wafer was very high as shown in Figure 6. The energy band model of the heavily boron-doped wafer is different from that of the lightly boron-doped wafer, and the heavily boron-doped silicon wafer has metal-like characteristics. Electrons generated by silicon etching have a high probability of recombining with holes, thereby slowing or halting the etching reaction.[21] Therefore, the possibility that Ni impurities will be absorbed on the silicon wafer surface increases in case of the heavily boron-doped silicon wafer. Further, the Ni diffusivity in the heavily boron-doped silicon wafer will be much faster than the etching rate of silicon, based on our experiment. The Ni diffusivity is 1.6 μm/min at the temperature (85 °C) used to etch silicon with KOH, and the removal rate is 1 μm/min in the case of the heavily boron-doped wafer (boron concentration: 8.5×10^{18}

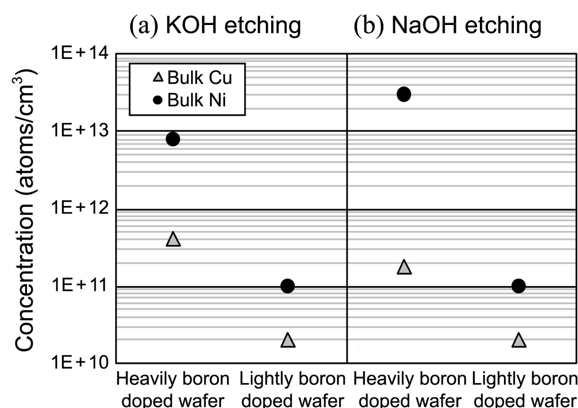


Figure 6. Investigation of bulk Ni contamination during alkaline etching.

~ 2×10^{19} atoms/cm^3). However, in the lightly boron-doped silicon wafer, the Ni diffusivity is similar to the etching rate of silicon at 1.4 μm/min. That is to say, Ni contamination will be removed by the silicon etching reaction and the probability of diffusion into the bulk silicon will be low, even though the wafer surface has been contaminated with Ni.

Bulk Cu Contamination: Figure 7 shows the bulk Ni and Cu content of the wafers subsequent to polishing. It has been reported that bulk Cu and Ni contamination occurred during the polishing process.[15] However, no additional bulk Ni contamination was observed during the polishing process used in this study. The bulk Ni contamination decreased instead upon mechanical removal of silicon by polishing. In comparison, the bulk Cu contamination increased during the polishing process when an amine slurry was used. This can be explained in terms of the formation of a complex between the amine and Cu, which plays the role of a catalyst in the transfer of Cu into the silicon wafer. The silicon surface in contact with the polishing slurry is covered with substituent X, which can be OH, H, F, and OSi. The first step of the reaction is a nucleophilic attack of the OH^- ion at a silicon atom, which is positively polarized by the substituent X having a higher electro-negativity than the Si-Si bond. The weakened Si-Si bond takes a proton from the ambient water, producing a Si-H bond, leaving the catalytic OH^- ion, which again reacts with adjacent silicon atoms. The reaction products are Si-H species in a low oxidation state of silicon and

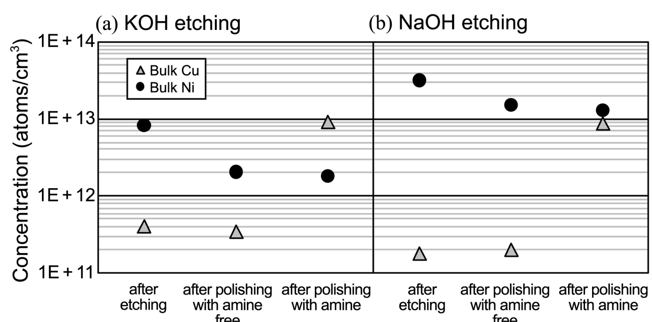


Figure 7. Investigation of Cu contamination during polishing with amine and amine-free slurry.

a silicon surface covered with Si-H groups. The Cu ion forms a square planar complex with the amine during polishing. The square planar complex has a steric configuration suitable for subsequent nucleophilic attack of the Si-H bond; and electrostatic interaction between the negatively polarized Si-H surface and the positively charged, square planar, Cu tetra-amine complex increases the probability of the substitution reaction. The nucleophilic attack of the negatively polarized Si-H bond at the Cu ion is followed by an electron transfer from hydrogen to copper gaining total reduction of Cu at the Si surface. The Cu ion thus produced diffuses into the bulk silicon, even at room temperature, due to its small ionic radius of 60 pm, and atomic radius of 129 pm. In other words, the amine additives facilitate copper ion diffusion into the bulk silicon following complexation with the coppers ions.[22,23] However, Cu contamination from the polishing process can be prevented by use of an amine free slurry.

Conclusion

A new method termed Advanced Poly-silicon Ultra-Trace Profiling (APUTP) was developed for measuring bulk Cu and Ni in heavily boron-doped silicon wafers. The method has a recovery yield of 98.8% for Ni and 96.0% for Cu, which was achieved by optimization of the vapor phase etching conditions and surface scanning conditions, after vapor phase etching. Two techniques were crucial to the success of the process. The first involved the use of H_2O with 49% HF and 69% H_2O_2 for vapor phase etching of the poly-silicon, which leads to improved etching uniformity and enables the collection of residual metal on the vapor-etched surface of 100 mm to 300 mm wafers, and for complete collection of the trace metal. The second is the performance of a repeat collection using the solution in which 49% HF and 31% H_2O_2 are mixed in a proportion of 1.83 to 1. A lower limit of detection (LOD) could be achieved through the use of mixture vapor phase etching instead of the conventional liquid phase etching.

From this advanced metrology, it was found that a higher bulk Ni contamination arose when heavily boron-doped silicon wafers were etched with alkaline solutions and that bulk Cu contamination was introduced by polishing the silicon wafer with a slurry containing Cu impurity and an amine additive.

References

1. Weber, E. R. *Physica B* **2003**, *1*, 340.
2. Shabani, M. B.; Shiina, Y.; Shimanuki, Y. *Solid State Phenom.* **2004**, *359*, 95.
3. Hoelzl, R.; Blietz, M.; Fabry, L.; Schmolke, R. In *Semiconductor Silicon*; 2002; 9th International Symposium, Huff, H. R., Fabry, L., Kishino, S., Eds.; PV 2002-2; The Electrochemical Society Proceedings Series, Pennington, NJ, 2002; 608.
4. Kumano, H.; Soyama, H. *Electrochem. Solid-State Lett.* **2004**, *7*, G51.
5. Alpern, P.; Bergholz, W.; Kakoshke, R. *J. Electrochem. Soc.* **1989**, *136*, 3841.
6. Holzl, R.; Huber, A.; Fabry, L.; Range, K. J.; Blietz, M. *Appl. Phys. A: Mater. Sci. Process* **2001**, *72*, 351.
7. Scott, W. D. S.; Stevenson, A. *J. Electrochem. Soc.* **2004**, *151*, G8.
8. Tokuda, N.; Nishiguchi, S.; Yamasaki, S.; Miki, K.; Yamabe, K. *J. Electrochem. Soc.* **2004**, *151*, F81.
9. Kohn, A.; Lipp, E.; Eizenberg, M.; Shacham-Diamand, Y. *Appl. Phys. Lett.* **2004**, *85*, 627.
10. Matsukawa, K.; Yamamoto, H.; Mashiko, Y. *Jpn. J. Appl. Phy. Part 1* **2002**, *41*, 5900.
11. Tokuda, N.; Kanda, T.; Yamasaki, S.; Miki, K.; Yamabe, K. *Jpn. J. Appl. Phys. Part 2* **2003**, *42*, L160.
12. Oborina, E.; Campbell, S.; Hoff, A. M.; Gibert, R.; Persson, E.; Simpson, D. *Malter. Res. Soc. Symp. Proc.* **2002**, *716*, 651.
13. Koveshnikov, S.; Beauchaine, D.; Radzimski, X.; Ling, L.; Ravi, K. V. *Solid State Phenom.* **2002**, *82-84*, 393.
14. Kim, Y. H.; Lee, K. S.; Chung, H. Y.; Hwang, D. H.; Kim, H. S. Cho, H. Y.; Lee, B. Y. *J. Korean Phys. Soc.* **2001**, *39*, 348.
15. Fabry, L.; Hoelzl, R.; Andrukhiv, A.; Matsumoto, K.; Qiu, J.; Koveshnikov, S.; Goldstein, M.; Grabau, A.; Horie, H.; Takeda, R. *J. Electrochem. Soc.* **2006**, *153*, G566-G571.
16. Shabani, M. B.; Shiina, Y.; Kirscht, F. G.; Shimanuki, Y. *Mat. Sci. Eng.* **2003**, *B102*, 238.
17. Kabacelik, I.; Ulug, B. *App. Sur. Sci.* **2008**, *254*, 1870.
18. Prewett, W.; Promphutha, M. *Anal. Chim. Acta* **1997**, *339*, 297.
19. Jong, J. D.; Schoemann, V.; Lannuzel, D.; Tison, J. L. *Anal. Chim. Acta* **2008**, *623*, 126.
20. Nakano, M.; Sato, M. U.S. patent 6503363, 2003.
21. Seidel, H.; Csepregi, L.; Heuberger, A.; Baumgartel, H. *J. Electrochem. Soc.* **1990**, *137*, 3626.
22. Falster, R. *et al*., U.S. patent 006100167, 2000.
23. Tetsuo, S. *et al*., U.S. patent 6884634, 2002.