Determination of Copper in Uniformly-Doped Silicon Thin Films by Isotope-Dilution Inductively Coupled Plasma Mass Spectrometry

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Uniformly-doped silicon thin films were fabricated by ion beam sputter deposition. The thin films had four levels of copper dopant concentration ranging between 1×10^{19} and 1×10^{21} atoms/cm^3. Concentrations of Copper dopants were determined by the isotope dilution inductively coupled plasma mass spectrometry (ICP-MS) to provide certified reference data for the quantitative surface analysis by secondary ion mass spectrometry (SIMS). The copper-doped thin films were dissolved in a mixture of 1 M HF and 3 M HNO_3 spiked with appropriate amounts of ^{65}Cu. For an accurate isotope ratio determination, both the detector dead time and the mass discrimination were appropriately corrected and isobaric interference from SiAr molecular ions was avoided by a careful sample pretreatment. An analyte recovery efficiency was obtained for the Cu spiked samples to evaluate accuracy of the method. Uncertainty of the determined copper concentrations, estimated following the EURACHEM Guide, was less than 4%, and detection limit of this method was 5.58×10^{16} atoms/cm^3.

Keywords : Copperdopant, Silicon thin films, ICP-MS, SIMS.

Introduction

Metal-contaminated silicon surfaces are known to generate harmful impact on the performance of semiconductor devices.[1,2] Therefore, it is important to characterize and control the metal contaminants on silicon surfaces. Secondary ion mass spectrometry (SIMS) is particularly useful for the measurement of trace levels of impurities in a thin film due to its high sensitivity. However, the quantitative analysis by SIMS suffers from severe matrix effects. Ionization yield of sputtered secondary particles can change by orders of magnitude from one matrix to another[3] and quantification of the surface impurities needs reference materials having the same matrix as the sample to be analyzed[4]. The reference materials for SIMS quantification are generally fabricated by ion implantation because it is easy to choose the doping elements and substrate materials. However, quantitative SIMS analysis using an ion implanted reference material requires a rather complex calibration procedure because the in-depth distribution of implanted element is not uniform. The whole range of the implanted zone must be profiled to sum up the number of the implanted atoms, and the sputtered depth must be precisely determined directly or indirectly by a profiler to estimate the analyzed volume.[5] Park *et al.*[6] have introduced a new type of reference material which has a uniform depth profile of boron dopant. They fabricated the reference material by the ion beam sputter deposition, and certified concentration of the boron dopant levels by the isotope dilution (ID) method. They also showed that the newly-developed reference material provided much simpler calibration for SIMS quantification. In this work, silicon thin films doped with natural-isotopic copper were fabricated by the ion beam sputter deposition. Four levels of silicon thin films were prepared to have different copper contents between 1×10^{19} and 1×10^{21} atoms/cm^3 for use in calibrating SIMS instruments. The copper concentrations in a unit volume of the silicon thin films were determined by isotope-dilution inductively coupled plasma mass spectrometry (ICP-MS) after dissolving the silicon thin films in a mixture of 1 M HF and 3 M HNO_3. Thickness of the silicon thin films was measured by transmission electron microscopy (TEM) to calculate copper atomic concentration per unit volume of the silicon thin film.

Experimental Section

Instrumentation. The ICP-MS instrument employed in this work was an ELEMENT (Finnigan MAT, Bremen, Germany). The instrument provides three fixed resolution settings ($m/\Delta m$=300, 3000 and 8000). All data were acquired in a low-resolution mode ($m/\Delta m$=300). For sample introduction, a Microconcentric nebulizer (MCN-100, CETAC, Omaha, NE, USA) and a Teflon PFA (perfluoroalkoxy) spray chamber were used with a peristaltic pump (Minipuls 3; Gilson, Villiers-le-Bel, France) to control the sample uptake rate. Details of the ICP-MS instrument components, operating conditions and data acquisition parameters are given in Table 1. The TEM instrument used to measure the thin film thickness was a CM20T/STEM (Philips, Eindhoven, Netherlands).

Reagents. A stock standard solution (1 mg/g) of copper was prepared by dissolving a high-purity copper (99.99%) with 3 M HNO_3. The copper isotopic standard was purchased from NIST (Gaithersberg, MD, USA) and the enriched isotope ^{65}Cu was purchased from NIST (Gaithersberg, MD, USA). A 1 μg/g working standard solution was

Table 1. Operating conditions and data acquisition parameters of ICP-MS

ICP-	
Rf power	1300 W
Sample uptake rate	0.3 mL/min
Argon gas flow rates	
Coolant	13.3 L/min
Auxiliary	1.0 L/min
Carrier	0.7 L/min
Torch	Finnigan torch
Nebulizer	MCN-100 (T2E)
Spray chamber	HF-resistant PFA spray chamber
Sampler cone	Aluminum, 1.0 mm orifice diameter
Skimmer cone	Aluminum, 0.7 mm orifice diameter
Data acquisition	
No. of passes	1000
Mass window	5%
Search window	100%
Integration window	100%
Samples per peak	200
Sample time	0.002 s
Dead time	25 ns

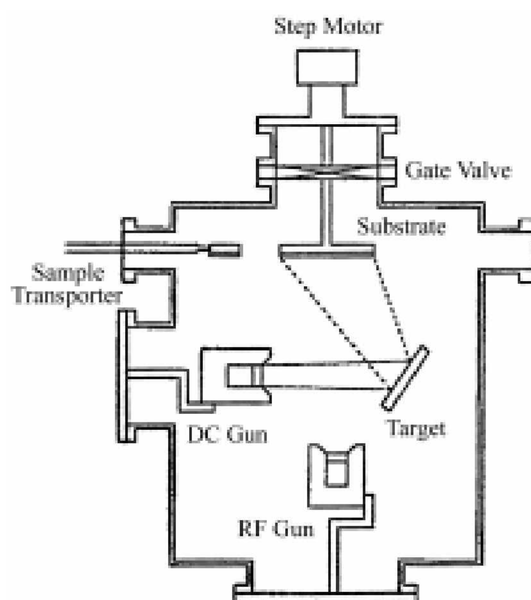

Figure 1. Schematic diagram of ion beam sputter deposition system.

prepared by serial dilution of the stock standard solution. HF and HNO_3 were of electronic grade purchased from Korea Yamanaka Materials (Gongju, Korea) and Dongwoo Pure Chemicals (Iksan, Korea), respectively. Deionized water was obtained from a Milli-Q Plus water purifier (Millipore, Bedford, MA, USA).

Fabrication of copper-doped silicon thin films. The copper-doped silicon thin films were grown in an ion beam sputter deposition chamber to which a surface analysis system was connected. Schematic diagram of the ion beam sputter deposition system is shown in Figure 1. The chemical state and composition of thin films grown at the deposition chamber can be analyzed by X-ray photoelectron spectroscopy (XPS). A small piece of copper nitride target on a Si wafer was sputter deposited on a substrate by 1 keV Ar^+ ion beam. Concentration of the copper dopant was controlled by varying the target position on the wafer. Sample C1 was grown when the target was placed at the center of the wafer. Samples C2, C3 and C4 were grown when the target was placed at 1, 2 and 3 cm outside from the center of the wafer, respectively. Thickness of the thin film layer was controlled by the growth time. The growth rate was calibrated by TEM measurement of a preliminary thin film grown in a given time. The thin film was deposited on a circular substrate of six inches in diameter, one half of which is a silicon wafer and another half of which is a polyester film. The substrate was rotated at a speed of 30 rotations per minute (rpm) during the thin film growth to improve its homogeneity. The thin films grown on polyester films were used for determination of the copper dopant concentration by ICP-MS and for measurement of the film thickness by cross-sectional TEM. The thin films grown on the Si wafer was cut into 10 mm×10 mm specimens to be used as reference materials for the quantitative analysis by SIMS.

Sample preparation. The sample disks of uniform size were transferred into a PFA beaker and 0.5-2.2 g of 0.508 μg/g ^{65}Cu spike solution was added to it for the isotope dilution analysis. Since thickness of the thin film samples is assumed uniform, area of dissolved sample should be accurately measured to get the copper concentration per unit sample volume. The silicon thin film samples were cut into disks of 0.998 ± 0.005 cm in diameter using a stainless steel punch made in this laboratory. The punch was carefully cleaned with ethanol and deionized water before use. Diameter of the sample disk was measured by a profile projector (Model PJ311, Miltutoyo, Tokyo, Japan). The copper-doped thin films were dissolved in 3 mL of a mixture of 1 M HF and 3 M HNO_3 and were evaporated to near dryness on a quartz hot plate. The residues were re-dissolved in 10-90 mL of 0.2 M HNO_3 for the ID analysis.

Results and Discussion

Isotope dilution method. All the analytical data reported here were quantified by the ID method, which is an especially useful method when a sample has to undergo some chemical pretreatment before analysis because any loss of anlyte during the pretreatment does not affect the final results.[7] The ID method is based on addition of a known amount of an enriched isotope to a sample. After equilibration of the spike isotope with the analyte in the sample, the altered isotope ratio of the mixture solution is measured to calculate the analyte concentration by the ID Eq. (1) given below. Details of the ID equation can be found in the literature.[8,9] Copper has only two stable isotopes, ^{63}Cu and ^{65}Cu. In the ID equation, this isotopic composition in the sample and primary standard solution can be assumed to be eaqul.

$$C_s = C_p \cdot \frac{m_{sp}}{m_s} \cdot \frac{m_p}{m^r_{sp}} \cdot \frac{\Sigma R_{is}}{\Sigma R_{ip}} \cdot \frac{R_{sp}-R}{R_{sp}-R^r} \cdot \frac{R^r-R_p}{R-R_s} \quad (1)$$

where C_s = analyte concentration in the sample (mol/g); C_p = concentration of the primary standard solution (mol/g); m_p = mass of the primary standard solution (g) used for the spike-primary standard mixture; m_s = mass of sample (g) used for the sample-spike mixture; m_{sp} = mass of the spike (g) used for the sample-spike mixture; m^r_{sp} = mass of the spike (g) used for the spike-primary standard mixture; ΣR_{is} = sum of isotope ratios in the sample; ΣR_{ip} = sum of isotope ratios in the primary standard solution; R=isotope ratio ($^{63}Cu/^{65}Cu$) measured from the sample-spike mixture; R^r=isotope ratio ($^{63}Cu/^{65}Cu$) measured from the spike-primary standard mixture; R_s=isotope ratio ($^{63}Cu/^{65}Cu$) in the sample; R_p=isotope ratio ($^{63}Cu/^{65}Cu$) in the primary standard solution; and R_{sp}=isotope ratio ($^{63}Cu/^{65}Cu$) in the spike.

Dead time correction. At high count rates (>10^6 counts/s), various effects can cause pulse counting systems to register less events than occurring. After an ion generates a pulse in the multiplier, there is a finite time during which the system is incapable of recording another ion, which is termed dead time (τ). This becomes important when dealing with isotopes in strongly differing abundances and also affects the accuracy and precision of isotope ratio measurements.[10] Therefore, prior to isotope ratio measurements of the analytes, the detector dead time has to be appropriately estimated. To do so, Cu isotopic standard solutions of different concentration levels that the count rates of maximum concentration are about 10^6 counts/s were prepared, and their isotope ratios were measured with the dead time correction option of the ICP-MS software deactivated. The measured intensities were corrected using Eq. (2).

$$I_{true} = I_{meas}/(1 - \tau \cdot I_{meas}) \quad (2)$$

where τ is the dead time, I_{true} is true count rates, and I_{meas} is measured count rates.[11] The detector dead time was determined by plotting normalized isotope ratios (measured isotope ratios/reference value) versus the dead time used for correction. Then the dead time of the interaction point of the curves from different concentration is the determined dead time. Figure 2 shows the Cu isotope ratio curves obtained with five Cu standards ranging from 5 to 40 ng/g. The estimated dead time was 20 ns which was very close to the instrument software value of 25 ns but somewhat lower than that reported previously for the Element.[11,12] The dead time can be different for each ICP-MS instrument due to the different characteristics of the pulse counting circuit.

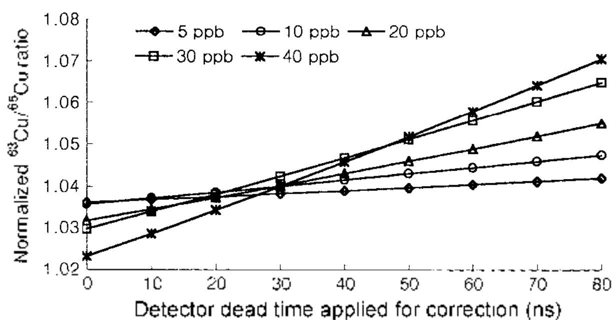

Figure 2. Determination of detector dead time using Cu isotopic standard solutions.

Spectral interference. For an accurate isotope dilution analysis, the two isotopes of the analyte should be free from isobaric interference. The interference could be caused by polyatomic species from gases in the plasma, water and the major components of matrix.[11] For accurate determination of Cu, almost complete elimination of the Si matrix from the sample solution was a necessity to avoid spectral interference from SiAr molecular ions. The final sample solutions were checked for presence of the SiAr molecular ions by measuring ion intensities at masses 66($^{28}Si^{38}Ar$ + $^{30}Si^{36}Ar$) and 68($^{30}Si^{38}Ar$ + $^{28}Si^{40}Ar$).

Recovery study. In order to evaluate accuracy of the present analytical method, recovery efficiency was tested. Before sample dissolution, 0.5 μg and 1.0 μg quantities of Cu were added, respectively, into the PFA beaker with the silicon thin film. Recovery efficiencies of the added amounts were determined using the analytical method. Table 4 shows that recovery efficiency is about 96.6% with 3.4% RSD for 0.5 μg spiking, and 100.4% with 3.7% RSD for 1.0 μg spiking. The accuracy of the method can be assessed from the slope of linear regression line plotted as added Cu standard solution versus calculated Cu concentration. Figure 3 shows an excellent linearity for copper standard addition curve.

Analysis of silicon thin films. The four silicon thin film samples were separately spiked with the ^{65}Cu and analyzed using the ID method. Thickness of the thin film sample was

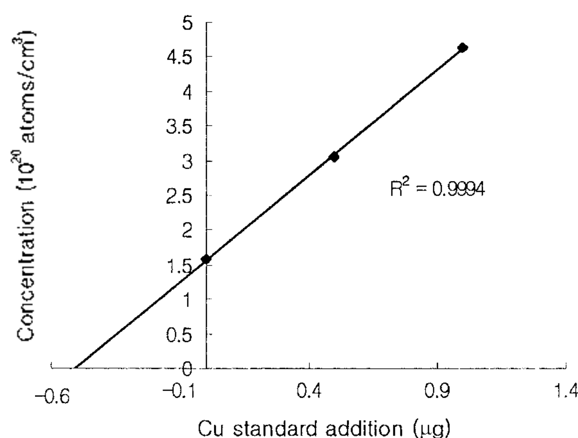

Figure 3. Copper standard addition curve for recovery efficiency.

Table 2. Thin film thickness and No. of sample disks used In ID analysis

Sample	Measured thickness (nm)	No. of sample disks used in ID analysis
C1	402 ± 4.5	1
C2	405 ± 4.5	1
C3	398 ± 4.5	1
C4	409 ± 4.5	5

Table 3. Copper dopant concentrations determined by the ID method

Sample	Spiking No.	Concentration (atoms/cm^3)
C1	1	1.900×10^{19}
	2	1.927×10^{19}
	3	1.931×10^{19}
	4	2.035×10^{19}
	Mean (RSD)	1.948×10^{19} (2.84%)
C2	1	1.496×10^{20}
	2	1.480×10^{20}
	3	1.499×10^{20}
	4	1.543×10^{20}
	Mean (RSD)	1.519×10^{20} (4.43%)
C3	1	4.700×10^{20}
	2	4.669×10^{20}
	3	4.517×10^{20}
	4	4.825×10^{20}
	Mean (RSD)	4.713×10^{20} (3.42%)
C4	1	8.572×10^{20}
	2	8.555×10^{20}
	3	9.102×10^{20}
	4	8.902×10^{20}
	Mean (RSD)	8.856×10^{20} (2.75%)

Table 4. Recovery efficiency for the Cu spiked sample

Run	Recovery efficiency (%)	
	0.5 μg addition	1.0 μg addition
1	94.3	97.8
2	99.0	103.1
Mean ± SD	96.6 ± 3.4	100.4 ± 3.7

measured with TEM to get the copper dopant concentration per unit volume. Table 2 shows the measured thickness of each sample and the number of sample disks used in each ID analysis. Analytical results for the four samples are presented in Table 3. Detection limit of the method, determined as the concentration corresponding to three times the standard deviation of the blank of the sample, was calculated to be 5.58×10^{16} atoms/cm^3.

Uncertainty of the analytical results was estimated using the EURACHEM Guide.[13] The ID Eq. (1) was modified into Eq. (3) to take into account of the mass bias correction (K_r for R; K_{rr} for R^r; K_s for R_s and K_p for R_p) and blank subtraction.

$$C = C_p \cdot \frac{m_{sp}}{m_s} \cdot \frac{m_p}{m_{sp}^r} \cdot \frac{\Sigma R_{is}}{\Sigma R_{ip}} \cdot \frac{R_{sp} - K_r \cdot R}{R_{sp} - K_{rr} \cdot R^r} \cdot \frac{R^r - K_p \cdot R_p}{R - K_s \cdot R_s} - Blank \quad (3)$$

Table 5. Uncertainty Budget for the Determined Copper Concentrations according to EURACHEM Guide[13]

ID parameter	C1		C2		C3		C4	
	Typical Value	RSU^a	Typical Value	RSU	Typical Value	RSU	Typical Value	RSU
C_p (mmol/g)	17.2	0.00200	17.2	0.00200	17.2	0.00200	17.2	0.00200
M_s (cm^3)	9.30E-05	0.01000	3.10E-05	0.01000	3.10E-05	0.01000	3.10E-05	0.01000
M_{sp} (g)	0.248	0.00403	0.498	0.00200	1.398	0.00072	2.203	0.00045
M_p (g)	0.996	0.00100	0.992	0.00100	0.992	0.00100	0.992	0.00100
M^r_{sp} (g)	1.003	0.00099	0.994	0.00100	0.994	0.00100	0.994	0.00100
ΣR_{is}	3.4099	0.00034	3.4099	0.00035	3.4099	0.00035	3.4099	0.00035
ΣR_{ip}	3.4099	0.00034	3.4099	0.00035	3.4099	0.00035	3.4099	0.00035
R	0.8493	0.00282	1.0058	0.00288	1.0175	0.00275	1.1175	0.00242
R^r	1.0029	0.00289	0.9895	0.00313	0.9895	0.00313	0.9895	0.00313
R_s	2.4099	0.00310	2.4099	0.00278	2.4099	0.00278	2.4099	0.00278
R_{sp}	0.003	0.0100	0.0030	0.0100	0.0030	0.0100	0.0030	0.0100
R_p	2.4099	0.00311	2.4099	0.00278	2.4099	0.00278	2.4099	0.00278
K_r	1.07	0.00359	1.03	0.00359	1.03	0.00359	1.03	0.00359
K_{rr}	1.07	0.00359	1.03	0.00359	1.03	0.00359	1.03	0.00359
K_s	1.07	0.00359	1.03	0.00359	1.03	0.00359	1.03	0.00359
K_p	1.07	0.00359	1.03	0.00359	1.03	0.00359	1.03	0.00359
K_{sp}	1.07	0.00359	1.03	0.00359	1.03	0.00359	1.03	0.00359
Blank ± SD (atoms/cm^3)	8.42E+16 ± 1.86E+16		7.60E+17 ± 1.04E+17		7.60E+17 ± 1.04E+17		7.60E+17 ± 1.04E+17	
Combined RSU	0.01861		0.01892		0.01882		0.01917	
C_s (atoms/cm^3)	1.95E+19		1.53E+20		4.72E+20		8.86E+20	
Combined SU^b (atoms/cm^3)	3.63E+17		2.89E+18		8.89E+18		1.70E+19	
Combined SU^c (atoms/cm^3)	3.64E+17		2.89E+18		8.89E+18		1.70E+19	
Expanded SU^c (atoms/cm^3 (k=2))	7.28E+17		5.78E+18		1.78E+19		3.40E+19	

^{a}Relative standard uncertainty contribution to the final concentration. ^{b}Standard uncertainty before blank subtraction. ^{c}Standard uncertainty after blank subtraction

For each parameter of the Eq. (2), relative standard uncertainty contribution to the final concentration was estimated, and the combined standard uncertainty was calculated by taking the square root of the sum of squares. The evaluated uncertainty budget is listed in Table 4 for the four thin film samples.

Conclusion

An ion beam sputter deposition method was employed to fabricate silicon thin films with uniform copper dopant profiles. The silicon thin films were dissolved in the mixture of 1 M HF and 3 M HNO_3 and analyzed by the isotope dilution ICP-MS to determine the copper dopant concentrations in the thin films.

Uncertainty of the determined copper concentrations, estimated following the EURACHEM Guide, was less than 4%. The determined dead time of high resolution ICP-MS was about 20 ns which is similar to the value set in the instrument software. Analyte recovery efficiency was satisfactory 96.6 ± 3.5 % for 0.5 μg and 100.4 ± 3.7% for 1 μg spiking to the sample. The uniformly-doped silicon thin films certified by the proposed analytical method can be used as a new type of reference material for quantitative surface analysis of silicon thin films by SIMS.

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