ELECTROTHERMAL VAPORIZATION ICP-MS(ETV-ICP-MS) DETERMINATION OF IMPURITIES IN PHOTORESIST FOR VERY LARGE SCALE INTEGRATED CIRCUIT(VLSI)

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Abstract A method was developed for the determination of Na, Fe, Mn, Ni and Cu in photoresist for VLSI by ETV-ICP-MS. Photoresist samples were diluted 10 times with an ethoxy ethyl acetate (EEA). The standard addition method was used for the determination of impurities. Ashing temperature, vaporization temperature and carrier gas flow rate were optimized for impurities and some molecular ions in the photoresist. The analytical results obtained were in good agreement with those obtained by graphite furnace atomic absorption spectrometry (GFAAS). The detection limits of Na and Fe in photoresist were 0.06ppb and 0.2ppb respectively.

Key words electrothermal vaporization, ICP-MS, photoresist

A positive type photoresist is widely used as the material for pattern etching on the silicon wafer. Impurities in this photoresist, especially alkaline metals and some transition metals have serious influence on reliability of the VLSI because of the breakdown-field of gate SiO_2 film and lifetime degradation of the silicon device. Especially, Na and Fe are easily found in the atmosphere, reaction and carrying vessels. Care must be taken to control these contamination problems.

Some analytical methods have been used for impurity analysis in photoresist. 1) GFAAS or ICP-AES after pretreatment by ashing, 2) GFAAS or ICP-MS after 7 to 10 times dilution by an organic solvent. The GFAAS analysis consumes much time so also pretreatment by ashing. The ICP-AES analysis lacks detection ability of low concentrations. The ICP-MS analysis has some problems; molecular ion peaks and unstable ion intensity for the mass analyzer contamination by carbon atoms in photoresist. Features of ETV-ICP-MS are as follows; 1) very small amount of sample requirement, 2) less contamination in the mass analyzer, 3) decrease of molecular ion peaks caused by carbon or oxygen. These features are very useful for the analysis of photoresist samples.

EXPERIMENTAL

Apparatus A model EV300 electrothermal vaporizer with graphite tube was connected to a model SPQ8000 quadrupole mass analyzer. A model SAS7500 graphite furnace atomic absorption spectrometer was used to compare the analytical results.

Reagents and Solutions An ethoxy ethyl acetate (EEA) purified by sub-boiling distillation was used for sample dilution. A standard solution containing 5 elements was prepared by diluting Conostan metallo-organic standards. All solutions were prepared and saved in PTFE bottles.

Sample Preparation Two kinds of photoresist were diluted 10 times with EEA. A standard solution was added to one of the photoresists. Two standard solutions were prepared: the first containing 2ng g^{-1} ; the second containing 5ng g^{-1} . Calibration curves were used to determine the concentration of impurities in the photoresist.

Measurement $10\mu\text{l}$ of the sample solution was injected in the graphite tube with a micropipette and elements were vaporized after the drying and ashing stages. Through 1m of PTFE tube, vapor was led to the plasma with Ar carrier gas. Analytical signals were detected for Na, Fe, Mn, Ni and Cu simultaneously.

RESULTS

Ashing temperature, vaporization temperature and carrier gas flow rate were optimized for Na, Fe, Mn, Ni, Cu and some molecular ions in the photoresist. The ashing temperature was varied from 600°C to 1400°C. Fig.1 shows the effect of ashing temperature on ion intensity of Na, Fe and some molecular ions. As the ashing temperature was increased, the Na and Fe signals gradually decreased. Some molecular ions, such as the C_2^+ , CO_2^+ , decreased to very low levels at 700°C. At above 700°C almost all carbon caused by decomposition of the photoresist was removed. Therefore, 700°C was chosen as the optimum ashing temperature.

Fig.1. Effect of ashing temperature on ion intensity of Na, Fe and some molecular ions

The vaporization temperature was varied from 1600°C to 2400°C. As the vaporization temperature was increased, the C_2^+ and CO_2^+ signals gradually increased. The Na and Fe signals were not changed above 1800°C. Therefore, 1800°C was chosen as the vaporization temperature.

Fig.2. Effect of vaporization temperature on ion intensity of Na, Fe and some molecular ions

The Ar carrier gas flow rate was varied from 1.0 L min^{-1} to 1.9 L min^{-1} . The signals increased as the Ar carrier gas flow rate was increased to 1.8 L min^{-1} . Especially C_2^+ and CO_2^+ signals increased sharply at above 1.5 L min^{-1} , but again decreased at 1.9 L min^{-1} . The decrease in signals were probably due to a decrease in effective temperature in the plasma. Based on the optimization of ETV-ICP-MS, the optimum operating conditions were as follows: ashing temperature, 700°C; vaporization temperature, 1800°C; carrier gas flow rate, 1.5 L min^{-1} . Analytical data were obtained using these optimum conditions. Table.1 shows the analytical results of Na, Fe, Mn, Ni and Cu in some photoresists. The results of Na and Fe were compared with the results of GFAAS. The two sets of values were in good agreement.

Table.1. Analytical results of Na, Fe, Mn, Ni and Cu in photoresists

Sample	Na		Fe		Mn	Ni	Cu
	This work	GFAAS	This work	GFAAS			
1	10.3	10.4	37.4	40.0	0.5	3.2	7.5
2	20.3	20.7	42.5	46.1	0.4	3.7	5.0

All values are ng g^{-1}