Notes

Standard Sample Preparation for the Analysis of Several Metals on Silicon Wafer

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Since high cleanness of silicon wafer surfaces (below 10^{10} atoms cm^{-2}) is required in current semiconductor manufacturing, many kinds of sensitive analytical methods are used to evaluate contamination. During the last several years, total-reflection X-ray fluorescence spectrometry (TXRF)¹ has come into wide use because it is a non-destructive and highly sensitive method (detection limit: $10^9 - 10^{10}$ atoms cm^{-2}), and requires no special skills for measurements. In this method, calibration standard samples are required in order to convert the signal intensity into concentration. Because of some special characteristics of TXRF, there are some indispensable conditions for its standard samples: depth-profile reproducibility, uniformity in the surface, and homogeneity in a batch. We have proposed a new preparation method of TXRF standard samples², called IAP, which is short for Immersion in Alkaline Hydrogen Peroxide Solution. In the IAP procedure, one or more silicon wafers are immersed in an intentionally contaminated ammoniac hydrogen peroxide solution. The added metal ions are adsorbed on the surface oxide layer with a thickness of *ca.* 1 nm. Since this adsorption reaction is governed by chemical equilibria³, the obtained wafer shows a suitable property as a TXRF standard sample—reproducible depth profile, good uniformity on the whole surface and good homogeneity in a treatment batch.² In our last paper, we were interested in Fe, Ni and Zn because they are typical contaminants in semiconductor manufacturing. In the present paper, we consider IAP applications to several other metals, such as Ca, Co, Cr and Mn. The stability of IAP wafers prepared for Ca, Mn, Fe, Co, Ni and Zn has also been examined.

Experimental

Sample preparation

The wafers examined in this work were silicon single crystals with a polished (100) face; the conductivity at

Fig. 1 Sample preparation with the IAP method.

room temperature was $8 - 12 \Omega \text{ cm}$ for both the n- and p-type. The wafer diameter was 125 mm and the thickness was $500 - 600 \mu\text{m}$.

The IAP method is schematically shown in Fig. 1. The wafers were dipped in an HF-H₂O₂-H₂O cleaning solution⁴ for 10 min at 35°C in order to remove any initial metal contamination. They were then rinsed in deionized water and dried with a spindrier. They were subsequently immersed in a testing SC-1 solution⁵ (29% NH₄OH:31% H₂O₂:H₂O=1:1:5 volume ratio) for 10 min at 80°C, rinsed in deionized water and dried with a spindrier. A certain amount of metal standard solution for atomic absorption spectrophotometry (AAS) was added to make the concentration level of the testing SC-1 solution $10^{-9} - 10^{-5} \text{ mol dm}^{-3}$ (*ca.* 0.1 – 1000 ppb).

The chemicals used in this work were of EL grade,

which contain transition-metal impurities below 0.5 ppb, except for AAS standard solutions. The contents of the AAS standard solutions are as follows: Ca, CaCO_3 in 0.1 mol dm^{-3} HCl; Cr, $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.01 mol dm^{-3} HNO_3 ; Mn, Mn in 0.1 mol dm^{-3} HNO_3 ; Fe, Fe in 0.2 mol dm^{-3} HNO_3 ; Co, Co in 0.1 mol dm^{-3} HNO_3 ; Ni, Ni in 0.1 mol dm^{-3} HNO_3 ; Zn, Zn in 0.1 mol dm^{-3} HNO_3 . The deionized water contained transition metal impurities below 10 ppt.

The IAP wafers were stored in an air-purged wafer cassette made of polypropylene, and the cassette was kept in a clean bench.

All of the above-mentioned processes were carried out in a class-100 clean room, and wet chemicals were treated inside a clean draft in the room.

AAS and TXRF measurement

The surface-metal concentration was assigned with a graphite-furnace (GF) AAS using a Perkin-Elmer Z-5100. In the GF-AAS measurement, surface metal contamination on a wafer was collected with 5 ml of mixed acid of HF and HNO_3 , injected into the furnace and measured. The surface-metal concentration was measured with a TXRF (Rigaku SYSTEM3726) using monochromatic W-L_{β} X-ray (9.67 keV) excitation. The applied voltage and current were set at 30 kV and 400 mA, respectively, so as to obtain high sensitivity. In a normal measurement, the glancing angle was 0.10 degree and the integration time was 100–5000 s. However, for an angle scan measurement, the applied current was turned down below 100 mA so as to avoid saturation of the SSD caused by intense scattered X-rays at high glancing angles. The measured point was the center of the wafer.

All of the measurements were performed in a class-1000 clean room, and the AAS pretreatment was carried out inside a clean draft in this room.

Results and Discussion

Adsorption isotherms

When TXRF is used for semiconductor analysis, the contamination level is generally in the range between 10^{10} and 10^{13} atoms cm^{-2} for transition metals. To achieve a reliable determination at this level, calibration standard samples of this concentration range must be prepared.

In order to clarify the applicable concentration range of the IAP method for several metals, we examined the relationship between the added metal ion concentration and the surface-metal concentration. The results, called "adsorption isotherm", are shown in Fig. 2 for all metals. Chromium was not detected on the surface at all in this experiment. We then added Cr as CrCl_3 ; the result was the same: it was not detected. According to the pH-potential diagram of Cr^6 , the metal easily transforms stable Cr(VI) . Since the adsorption species of transition metals are the dissolved hydroxide complexes³, it is considered that the hexavalent chromium, which never

Fig. 2 Adsorption isotherms of calcium (▲), manganese (▽), iron (●), cobalt (△), nickel (○) and zinc (□) on silicon wafer in SC-1 solution.

forms hydroxides⁶, is hard to be adsorbed. Except for Cr, the surface-metal concentration increases monotonically along with the solution concentration in most regions. The linearity means that a chemical reaction governs the metal-ion adsorption, and that the reaction attains an adsorption equilibria. The applicable concentration range for Ca is at least between 2×10^{11} atoms cm^{-2} and 8×10^{12} atoms cm^{-2} ; it can be extended to a higher and lower region by controlling the metal concentration in the solution. As for Co, the range is at least between 3×10^{10} atoms cm^{-2} and 1×10^{13} atoms cm^{-2} . Since the surface Mn concentration shows a saturant tendency, its higher limit is 6×10^{12} atoms cm^{-2} . Although the lower limit of Mn seems to be 2×10^{12} atoms cm^{-2} from Fig. 1, it can be lowered because a monotonic decrease of surface Mn along with the added concentration is analogically expected. The lower limit may at least achieve 10^9 – 10^{10} atoms cm^{-2} , which is the detection limit of TXRF.

Although the accuracy of the adsorption isotherms was not examined minutely in this study, the deviation of the y-axis is expected not to exceed 20% from our previous study.⁷ On the whole, IAP can be applied to most transition metals.

Depth profile

The depth distribution of the objective element on a standard sample is an essential factor for the determination with TXRF.² We have examined the depth distributions of each of the metals on the IAP wafers by measuring the angle scan profiles.

Figure 3 shows the angle scan profiles of each of the metals examined in this present work. The measurements were carried out just after the production. The

Fig. 3 Angle scan profiles for some IAP wafers just after production ($\blacktriangle$, calcium 7.5×10^{12} atoms cm^{-2} ; ∇ , manganese 6.4×10^{12} atoms cm^{-2} ; $\bullet$, iron 4.0×10^{12} atoms cm^{-2} ; $\triangle$, cobalt 1.2×10^{13} atoms cm^{-2} ; $\circ$, nickel 6.2×10^{12} atoms cm^{-2} ; $\square$, zinc 2.4×10^{13} atoms cm^{-2}).

fluorescent X-ray intensity is normalized with the maximum value for a comparison of the profiles. They agreed well with each other. This indicates that the IAP method offers the same depth distribution, not only across the samples², but also across the elements.

The reproducibility of the depth distribution originates in the nature of the IAP method itself. It was reported that metal ions which form stable soluble hydroxides, $\text{M}(\text{OH})_x$, are adsorbed on the surface SiO_2 film of a silicon wafer in an alkaline hydrogen peroxide solution.³ Since the adsorption reaction is common to the metals examined here (Ca, Mn, Fe, Co, Ni and Zn), the obtained samples show the same quality in depth distribution.

Stability

In the present work, we examined the long-term stability of IAP wafers, because a standard sample is generally used for some months or longer.

We measured the shift in angle scan profiles of the samples prepared for Ca, Mn, Fe, Co, Ni and Zn. Figure 4 shows the profiles measured after more than five months from the production. The consistency of the profiles across the elements, which was observed just after the production (Fig. 3), did not change within this period. It is considered that the long time stability originates due to stable metal-O-Si bonds in the oxide layer formed during the treatment in SC-1 solution.

The IAP method offers standard samples of many metals. The applicable metals are Ca, Mn, Fe, Co, Ni

Fig. 4 Angle scan profiles for some IAP wafers after five months from the production (symbols are the same as Fig. 3).

and Zn. Their depth distributions are the same as each other, and are consistent for a long time.

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