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Characterization of a Cleaning Technology for Silicon Surface by Hot Pure Water Containing a Little Dissolved Oxygen

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A new cleaning technology using a pure water containing a little dissolved oxygen (LDO water) was introduced. Hot water treatment at boiling point using the LDO water removed metallic contaminants from silicon wafer surfaces and etched native oxide. This cleaning effect depends on dissolved oxygen concentration, treatment temperature, and treatment time. A hot water treatment at boiling point using 1ppb LDO water removed metallic contaminants by 30 minutes, thus this cleaning technique has enough throughput for manufacturing the semiconductor devices.

Introduction

Surface cleaning technology has influenced production yield and performance reliability of ULSI devices strongly. Thus a lot of alterations of cleaning sequence of the RCA clean and development of new cleaning solutions have been tried and demonstrated[1)-5)]. Every cleaning technology newly developed aims control of surface condition including native oxide removal adding to the conventional cleaning purpose: removal of particles and contaminants. However, these cleaning technologies base on treatments in several alkaline or acid solutions, thus waste treatment of these solutions is necessary to use them industrially. This paper introduces a new cleaning technology using hot pure water containing a little dissolved oxygen (hot LDO water)[6)-8)], which has potentiality to solve such ecological and sociological problems.

Experimental

All hot LDO water treatments performed in a closed glove box in which oxygen concentration in ambience was controlled so as to satisfy Henry's low between the ambience and the LDO water at room temperature. A scheme of the glove box is shown in Fig. 1. N-type 4-inch CZ Si(100) wafers with resistivity of 10 Ω -cm were used for this study. After conventional RCA clean, we removed native oxide from the silicon wafer surface by 5% HF solution and contaminated them intensionally in $NH_4OH/H_2O_2/H_2O$ mixture (APM) including metallic contaminants. The contaminated APM solution was prepared by addition of the standard solutions for atomic absorption spectroscopy to the APM solution following the standard RCA recipe. State of metallic contaminants on the wafer surface was analyzed by X-ray photoelectron spectroscopy (XPS) and total reflection X-ray fluorescence (TRXRF). After rinsing the contaminated samples in the hot LDO water, we etched sample surface by HF/HNO_3 mixture and measured the metallic contaminants, which dissolved into the HF/HNO_3 mixture, by atomic absorption spectrometry (AAS) and

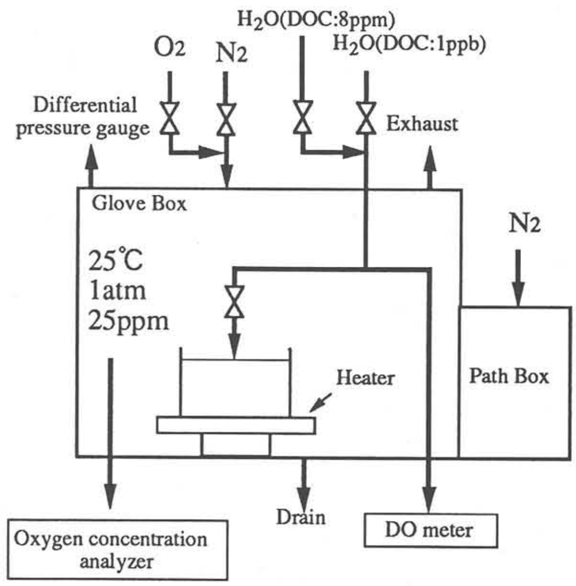

Fig. 1 Experimental environment

inductively coupled plasma mass spectroscopy (ICP-MS). In addition, we analyzed the wafer surface by Fourier transformed infrared reflection absorption spectroscopy (FT-IR-RAS) and contact angle method to reveal the interaction of the hot LDO water with the surface. In the FT-IR-RAS analysis, absorption peaks due to the longitudinal and the transverse optical (LO and TO) phonon of the stretch vibration mode of Si-O bond were observed.

Results and Discussion

From the results of TRXRF and XPS analysis, it was confirmed that the absorbed metallic contaminants existed almost uniformly and atomically in the chemical oxide formed by the APM. In the hot LDO water rinsing at boiling point during 30 minutes, the amount of metallic contaminants remaining on the surface except for Cu decreased with decreasing in dissolved oxygen concentration (Fig. 2-a). Decrease in residual metals was not detected obviously in the 500 ppb hot

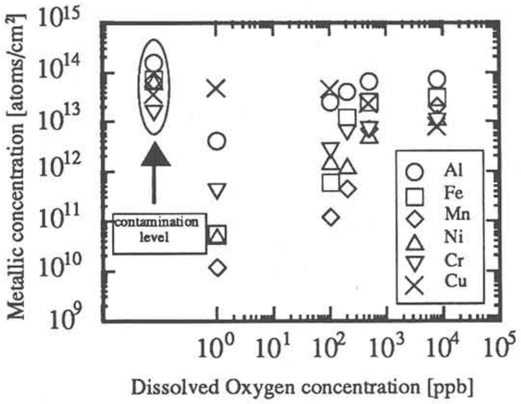

Fig. 2 (a) The dependence of metallic contamination removal on dissolved oxygen in pure water

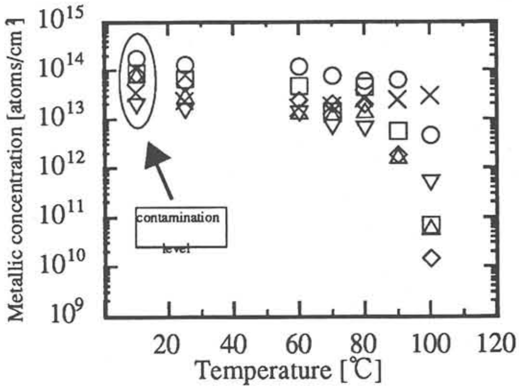

Fig. 3 (a) The dependence of metallic contamination removal on rinsing temperature

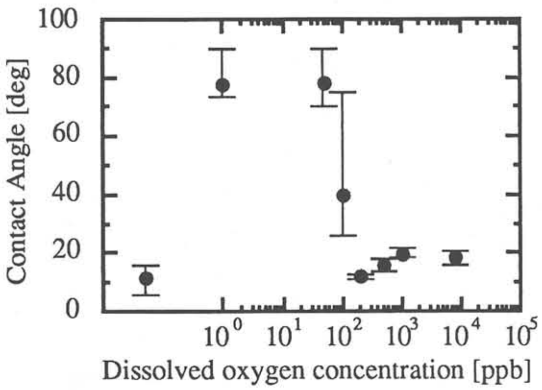

Fig. 2 (b) The dependence of contact-angle on dissolved oxygen in pure water

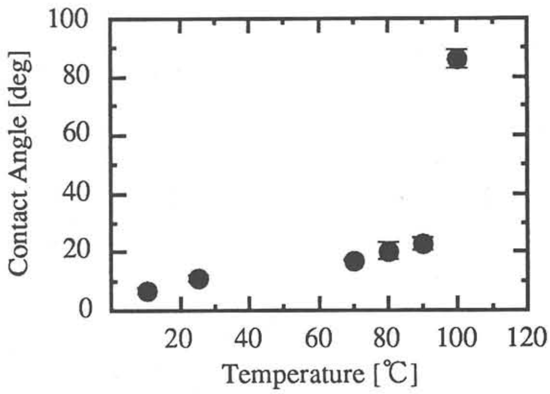

Fig. 3 (b) The dependence of contact-angle on rinsing temperature

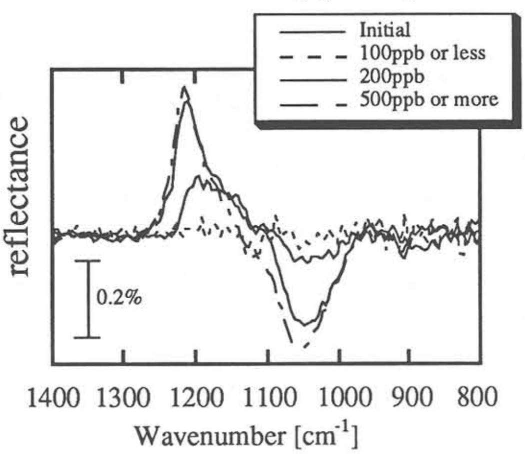

Fig. 2 (c) IR absorption spectra - DOC dependence -

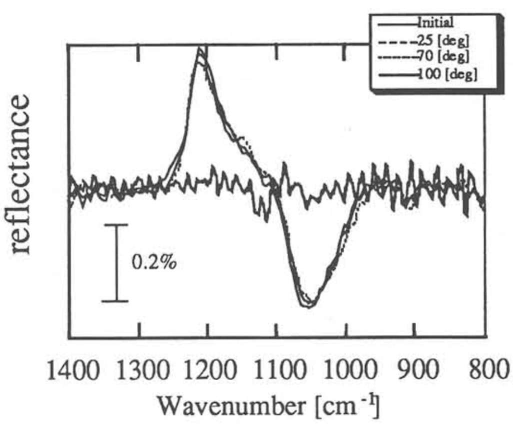

Fig. 3 (c) IR absorption spectra - Temperature dependence -

water treatment but was observed a little in the 200 ppb hot water treatment and became obvious in the 1 ppb hot water treatment. The change in the contact angle and the FT-IR-RAS spectra in this experiment were shown in Fig. 2-b and -c. Contact angle was constant to 200 ppb but increased abruptly at 100 ppb and reached about 90 degrees in the LDO less than 50 ppb. This change in the contact angle was consistent with the change in the IR-RAS spectra and indicated that native oxide was removed by the hot water treatment of less dissolved oxygen than 100 ppb.

This relation among the amount of residual metals, contact angles, and FT-IR-RAS spectra was observed also in the experiment to examine the dependence of the cleaning effects on treatment temperature and treatment time (Fig. 3). In the 1 ppb LDO water cleaning of 30 min, the metal contaminants started to be removed with native oxide etching at

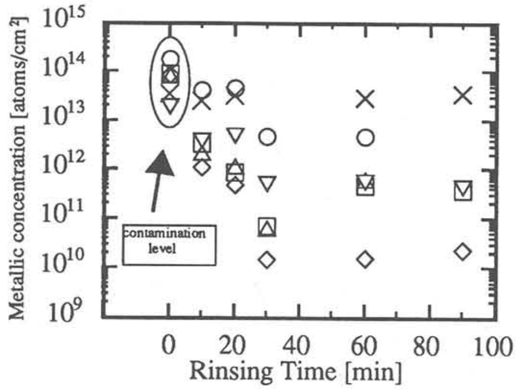

Fig. 4 (a) The dependence of metallic contamination removal on treatment time

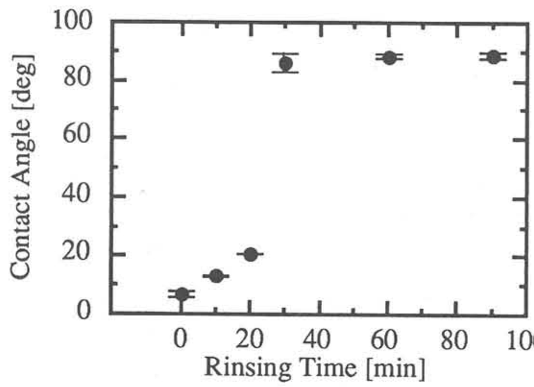

Fig. 4 (b) The dependence of contact-angle on treatment time

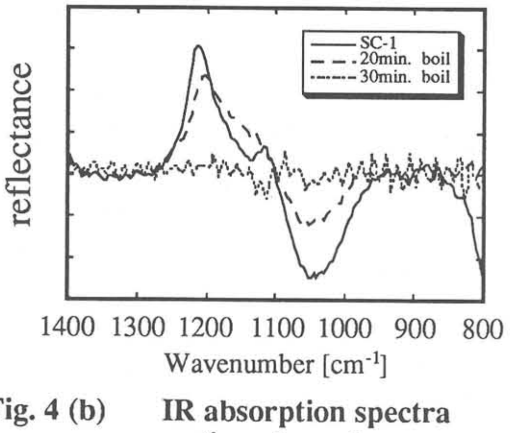

Fig. 4 (b) IR absorption spectra - time dependence -

80 ℃, and at boiling point treatment, contact angle jumped up to about 90° and the feature of SiO_2 disappeared from the IR-RAS chart simultaneously and then removal ratio of the metal contaminants reached maximum. Moreover, the experiment to prove time dependence of the cleaning effects of the 1pp LDO at boiling point, the amount of residual contaminants decreased to 30 min and became constant in longer time treatment (Fig. 4-a). The contact angle increased sharply 90ÅKto about at 30 min and then the LO and the TO phonon peaks disappeared from the IR-RAS chart (Fig. 4-b, -c).

In the 30 min cleaning of wafers less contaminated intensionally than above samples at boiling point, the amount of residual metals except for Al decreased to under the detection limit when the hot LDO water containing less dissolved oxygen than 100ppb. Thus the amount of residual metals after longer treatment than 30 min in Fig. 4 was not the limit of cleaning ability of the hot LDO water. In the experiment that clean hydrogen terminated silicon wafers immersed in the intensionally contaminated hot LDO water, only aluminum readsorbed on the wafer surface, thus reason of low removal effect to aluminum as shown in Fig. 4. is that aluminum concentration on the wafer was equilibrated with that in the LDO water.

Adding to above results, we have confirmed that the cleaning effect of the hot LDO water is not different between n-type and p-type silicon and thermally grown oxide is also etched by the hot LDO water.

Conclusion

Cleaning effects of pure water containing a little dissolved oxygen (LDO water) was confirmed. The hot LDO water removed metallic contaminants from silicon wafer surface with etching of native oxide. This cleaning effect depends on dissolved oxygen concentration, treatment temperature, and treatment time. In particular, the hot 1ppb LDO water treatment at boiling point has enough performance for the semiconductor device manufacture.

References

1) T. Ohmi, T. Isagawa, M. Koguro, and T. Imaoka, J. Electrochem. Soc., 140 (1993) 804.
2) T. Ohmi, T. Imaoka, T. Kezuka, J. Takano, and M. Kogure, J. Electrochem. Soc., 140 (1993) 811.
3) M. M. Heyns, M. Meuris, S. Verhaverbeke, P. W. Mertens, H. F. Schmidt, A. L. P. Rotondaro, T. Q. Hurd, Z. Hatcher, and D. Graf, Proc. Int. Conf. AMDP, March 3-5, Sendai, 1994 (Tohoku University, Sendai, 1994) p.59.
4) M. L. Kniffin, T. E. Beerling, and C. R. Helms, J. Electrochem. Soc., 139 (1992) 1195.
5) C. R. Inomata, H. Ogawa, K. Ishikawa, and S. Fujimura, J. Electrochem. Soc., submitted.
6) S. Watanabe and Y. Sugita, Surf. Sci., 327 (1995) 1.
7) S. Watanabe and Y. Sugita, Appl. Phys. Lett., 66 (1995) 1797.
8) H. Ogawa, K. Ishikawa, M. T. Suzuki, Y. Hayami, and S. Fujimura, Jpn. J. Appl. Phys., 34 (1995) 732 .