Extended Abstracts of the 1996 International Conference on Solid State Devices and Materials, Yokohama, 1996, pp. 864-865

New Cleaning Solution; Mixture of HF/HCl and Pure Water Containing a Little Dissolved Oxygen

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Copper (Cu) is the most annoying contaminants in cleaning processing. Many people have reported that formation of oxide Cu compound is necessary to remove the contaminant Cu from Si wafer surfaces. However formation of oxide compound of the other metals except Cu decreases the removal ratio of such metals. In addition, the treatment forming the Cu oxide must glow chemical oxide layer on the Si surface though hydrogen-terminated (H-terminated) surface is desired in ULSI fabrication processes. Therefore no cleaning solution, which is possible to remove metallic contaminants including Cu and native oxide without oxidizing and roughing Si surface and form H-terminated Si surface, have been found. However we found that the mixture of HF, HCl and ultra pure water containing little dissolved oxygen (LDO) solved this problem.[1] Cleaning ability of this new solution depend on mixing ratio of HF to HCl and treatment temperature. Cu was not removed effectively in the mixture ratio in which ratio of HF to HCl was 1 but was dramatically eliminated in a HF/HCl/LDO mixture (HF:HCl:LDO=1:5:500). Moreover the amount of all residual metals decreased with treatment temperature rise. (Fig. 1) This phenomena couldn't be explained by the model using the Standard electrode potential and pH value in equilibrium. Thus, we try to reveal the mechanism of Cu removal from Si surface in this new solution.

4inch P and N-type CZ Si(100) wafers with a resistivity of 10 Ω-cm was used for this study. All the HF/HCl/LDO mixture treatments performed in a closed glove box in which oxygen concentration in ambience was so as to satisfy Henry's low between the ambience and the LDO at room temperature. After RCA cleaning, we removed native oxide from sample wafers by 5%HF solution and contaminated the sample wafers intentionally by immersing in the SC-1 solution including metallic contaminants (Al, Cr, Cu, Fe, Mn, Ni).

We performed experiments as follows. 1. We compared cleaning ability of the HF/HCl/LDO mixture with that of the mixture of HF, HCl and conventional ultra pure water containing dissolved oxygen of about 8ppm (HDO). 2. We removed the native oxide of the contaminated wafers in an HF/LDO mixture, subsequently added HCl to the HF/LDO mixture to prepare the HF/HCL/LDO solution before pulling out the sample wafers. 3. We immersed clean H-terminated wafers into an intentionally contaminated HF/HCl/LDO mixture. Cleaning ability was evaluated by measuring the amounts of residual contaminant metals. The amounts of residual metals on the Si-surface were measured by Atomic Absorption Spectrometry (AAS) and Inductively coupled plasma mass spectrometry (ICP-MS). Figure 2 shows the amounts of residual metals after HF/HCl/HDO treatment. The contaminant metals including Cu were also eliminated in the HF/HCl/HDO mixture close to the level got in the HF/HCl/LDO mixture. Thus, dissolved oxygen concentration in ultra pure water doesn't play significant role in this cleaning. Moreover Cu was not eliminated from the Si surface at all in the experiment where HCl subsequently added to the HF/LDO mixture. (Fig. 3 ; addition HCl to HF/LDO solution after sample wafers were immersed in HF/LDO solution is Treatment B) This result shows that HCl must exist in the solution at the moment when the native oxide has been just removed. We have confirmed that a lot of HCl molecules adsorb on Si surface after the HF/HCl/LDO mixture cleaning when the absorption peak of monohydride change as shown in Fig. 4. (Fig. 4 ; (111) Si prisms were used in this FT-IR-ATR observation to detect surface morphology change clearly.) Moreover as shown in above, cleaning ability was low in the mixture with HF/HCl ratio of 1, on the other hands metal contaminants were removed effectively in the mixture with HF/HCl ratio of 0.2. These results suggest that covering ratio of HCl on the Si surface is significant meaning in the removal phenomena of contaminant metals.

Therefore we propose a model that HCl molecules immediately passivated Si surface at least just after Cu atoms detached from Si surface to prevent re-adsorption of Cu atoms.

1) Y. Hayami et al.: Ext. Abst. of The 43rd Spring Meeting of The Japan Society of Applied Physics and Related Societies, 28p-K-4

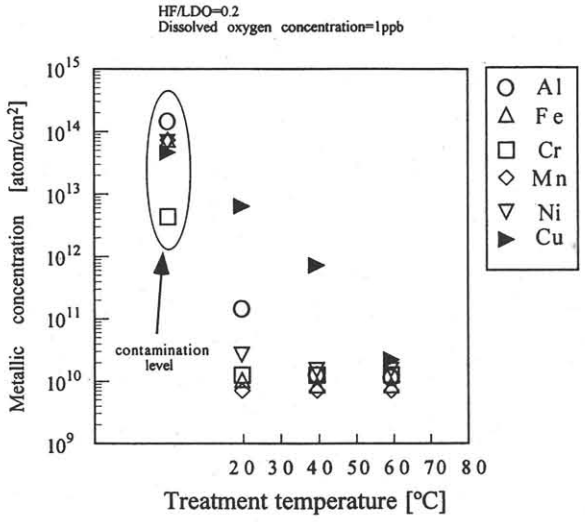

Fig. 1 The dependence of contaminants removal on treatment temperature in the HF/HCl/LDO treatment

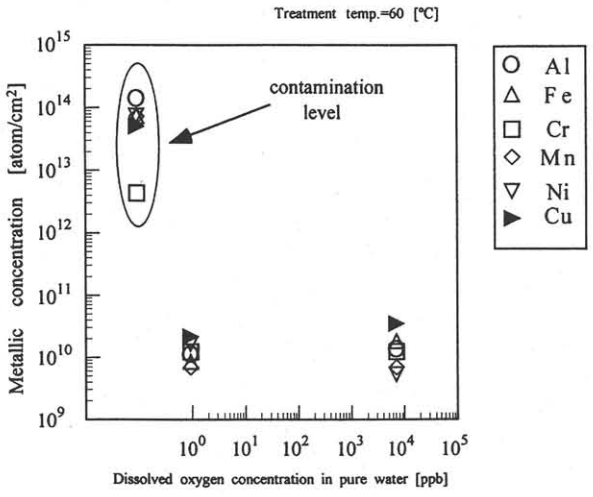

Fig. 2 The comparison of cleaning ability betweem the HF/HCl/LDO treatment and the HF/HCl/HDO treatment

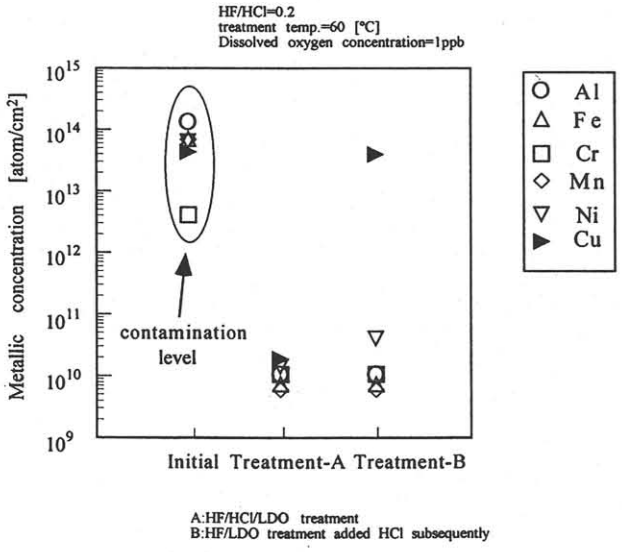

Fig. 3 The comparison of cleaning ability between Treatment A and Treatment B

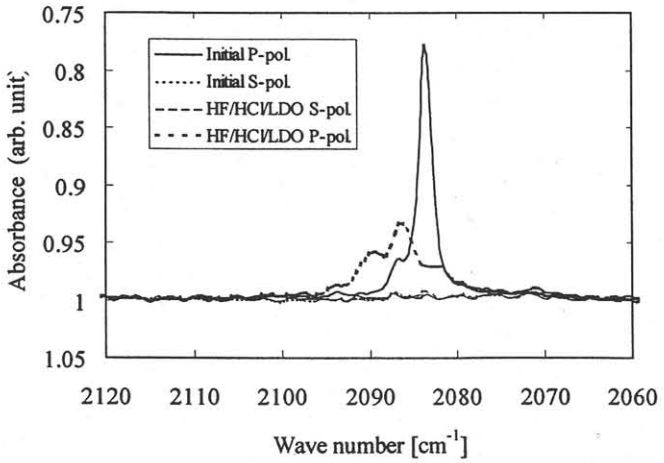

Fig. 4 IR absorption spectra arising from Si-H streching vibrations