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Inhibition of copper corrosion by removal of H_2O_2 from CO_2-dissolved water using palladium catalysts

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In a Si wafer washing process with CO_2-dissolved water (CO_2 DIW) corrosive dissolution of copper wires becomes a serious problem. CO_2 DIW is one kind of rinse water whose specific electrical resistance is lowered to 0.05 ~ 0.2 MΩ·cm by adding carbon dioxide to DIW, and it is widely used for preventing electrostatic destruction of devices and adhesion of fine particles on a wafer surface. Tokuri et al. have shown that copper corrosion is dependent on the concentration of dissolved oxygen in CO_2 DIW, and a slightly acidic condition of CO_2 DIW (pH 4.0 ~ 5.5) increases the corrosion rate.[1]

This study has been conducted in order to validate the effects on copper corrosion by H_2O_2-containing CO_2 DIW. Ultraviolet rays with wavelength less than 200 nm are usually irradiated in DIW used in a semiconductor manufacturing process for reducing total organic carbon (TOC). Hydroxyl radicals remove organic contaminants, but some hydroxyl radicals recombine, resulting in H_2O_2.[2] In our survey, it is revealed that the concentration of H_2O_2 in DIW reaches to 10 ~ 40 µg/L and the CO_2 DIW also contains H_2O_2 at the same level. However, no studies have been made on the effects of H_2O_2 in CO_2 DIW on copper corrosion.

As a test piece, a Cu film (200 nm) was deposited on a Ti/Si wafer by the sputtering method. Rinse of the Cu film was performed by use of a wafer spin cleaner. Changes of sheet resistance (ΔR_s) caused by the thickness decrease of the Cu film were measured using the 4-point probe method. For removal of H_2O_2, we used a palladium catalyst loaded on to a monolithic anion exchanger.[3] This catalyst can remove H_2O_2 from DIW at the high flow rates (space velocity SV = 5000 h^{-1} or more) with the high efficiency (< 1 µg/L).

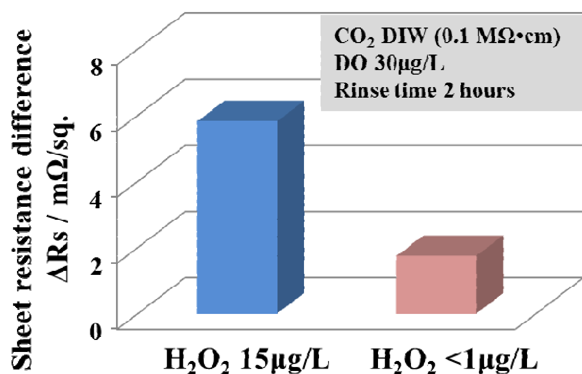

Fig. 1. Sheet resistance difference of the Cu films treated with: Left) CO_2 DIW containing 15µg/L H_2O_2 , and Right) H_2O_2-free CO_2 DIW.

It is obvious from Fig. 1 that copper corrosion was inhibited to approximately one-third by eliminating H_2O_2 from CO_2 DIW. Furthermore, over a wide concentration range of dissolved oxygen (DO) up to 800 µg/L, H_2O_2-free CO_2 DIW was able to reduce corrosion of the copper film compared to CO_2 DIW prepared from normal DIW containing H_2O_2 (Fig. 2). Figure 3 shows the scanning probe microscope (SPM; SII SPA-400) images of Cu films treated with 130 µg/L of DO for 16 hours in order to clarify morphological changes. Although holes were generated due to corrosion in the surface of both the films, holes created by H_2O_2-free CO_2 DIW were obviously much shallower.

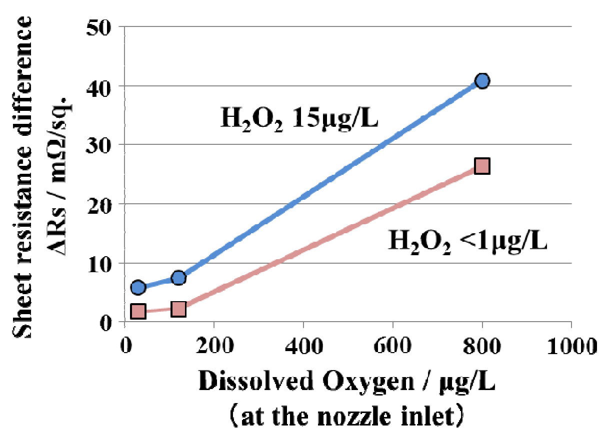

Fig. 2. Relationship between the sheet resistance change and the concentration of dissolved oxygen in CO_2 DIW.

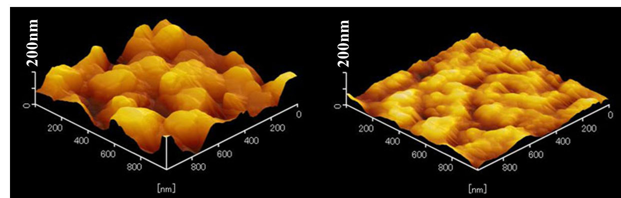

Fig. 3. SPM images of the Cu film surfaces treated with: Left) CO_2 DIW containing 15µg/L H_2O_2, and Right) H_2O_2-free CO_2 DIW.

For obtaining information concerning the reaction mechanism, X-ray photoelectron spectra (XPS) for the copper films treated with various types of rinse water were measured by use of a VG Scientific ESCALAB 220i spectrometer with a monochromatic AlKα 1486.6eV radiation source. We found that the XPS spectra didn't depend on the presence of H_2O_2 and also CO_2 in DIW (Fig. 4). This result indicates that although H_2O_2 increases the copper corrosion rate, resulted copper surface chemical states don't depend on the presence of H_2O_2 and CO_2 in DIW.

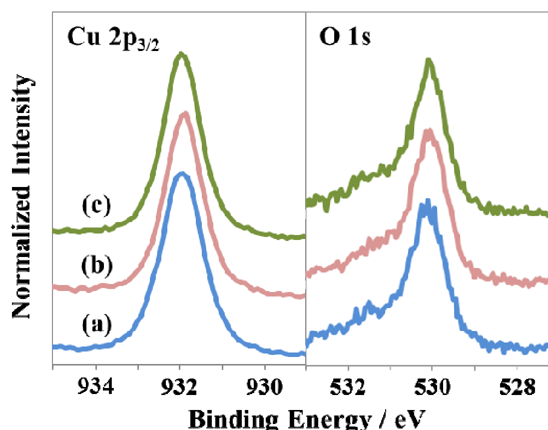

Fig. 4. XPS spectra in the Cu $2p_{3/2}$ and O1s regions for the surfaces of the copper films treated with various types of rinse water: (a) CO_2 DIW containing 15µg/L H_2O_2, (b) H_2O_2 free CO_2 DIW, (c) H_2O_2 free DIW.

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