Improvement of SC-1 Bath Stability by Complexing Agents

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One of the major drawbacks of the SC-1 type (NH_3-H_2O_2-H_2O) solution is the continuous need of refreshment of the solution. The evaporation of NH_3 and H_2O can be suppressed to a large extent by using proper covers, whereas the decomposition of H_2O_2 is mainly caused by metal contamination, especially by Fe^{3+} and Cu^{2+}.[1] The metal contamination originates mainly from the chemicals, and therefore the continuous refreshment of the bath even accelerates the decomposition of hydrogen peroxide. As H_2O_2 constitutes the largest expense of the bath its stability has large economic value.

In the present report, the suppression of metal effect and thereby the increase of the bath lifetime was studied by adding different complexing agents to the SC-1 cleaning solution (NH_3:H_2O_2:H_2O = 1:1:5). The complexing agents were:

- triethanolamine (TEA)
- ethylenediaminetetraacetic acid (EDTA)
- 1,2-cyclohexanediaminotetraacetic acid (CDTA)
- diethylenetriaminopentaacetic acid (DTPA)
- diethylenetriaminepenta (methylenephosphonic acid) (DTPMP)
- hydroxyethyldiphosphonic acid (HEDP)

The baths were intentionally contaminated with multimetal standard solution. In addition, the effect of some metals, Fe, Cu, Mn and Al were studied separately. Hydrogen peroxide lifetime was monitored *in situ* by optical NIR analyzer.

Silicon wafers were added to baths in order to study the adsorption of metals. Metal concentrations were measured by TXRF and GFAAS combined with VPD sample preparation. Ligand residues on the wafers were also analyzed. In addition, the effect of complexing agents on metal adsorption was studied at room temperature by spin-coating wafers with SC-1 solution which contained metals and complexing agents.

Fe and Cu were found to increase the decomposition of H_2O_2. Iron is more efficient than copper in accordance with previous reports.[1,2]

In the bath stability tests, which were performed at the common process temperature 65 °C, CDTA, DTPMP and HEDP were found to prevent the decomposition of hydrogen peroxide in the bath for several hours (Fig. 1). EDTA and DTPA stabilized H_2O_2 for about 20 minutes before they most probably were decomposed.

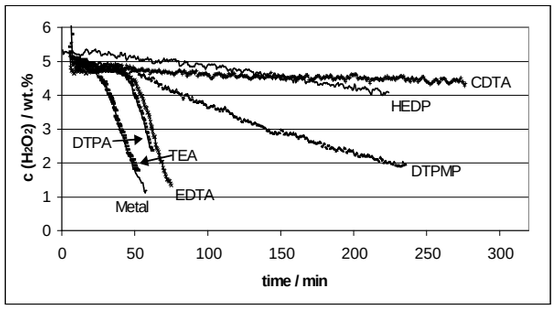

Figure 1. The effect of different complexing agents on concentration of H_2O_2 in SC1 bath at 65 °C. The measurements were started when the solutions were cold. “Metal” denotes SC-1 solution where only multimetal standard was added.

All complexing agents suppressed the adhesion of the studied metals to wafers, except that of aluminum, at room temperature but DTPMP had effect also on Al.

It is concluded that it is possible to diminish chemical expenses and simultaneously decrease adsorption of metals to wafers by adding appropriate complexing agent to SC-1 baths.

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2. Coupeau, S., Trinhm., Voillot, C., and D’Aveni, A., *Revue A.T.I.P.*, **49**, 223, (1995).