Electroless Nickel Ternary Alloy Films for Copper Interconnection Technology

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Recently, damascene copper electroplating for ultra large scale integration (ULSI) interconnects has been attracting attention as the new and attractive process. In connection with such wet process for ULSI, more epochal study, the process to fabricate barrier layer that prevents the diffusion of copper by using electroless deposition, was being advanced[1,2].

In this presentation, electroless NiWP and NiReP films were investigated for the aim of application to barrier and capping layer in the interconnects technology. These alloys containing a refractory metal and having the high melting point were expected to have ability to avoid electromigration effect. Electroless Ni alloy deposition on SiO_2 layer *without* sputtered seeding layer was also examined by utilizing self-assembled monolayer[3] as an adhesion and a catalyzed layer.

For the investigation of electroless NiWP and NiReP films' composition, polyimide films were used as substrates. On the other hand, the substrates which have a pile of layers of Cu (100 nm)/Ta (30 nm)/SiO_2 (500 nm) on Si wafer were used for the investigation of thermal stability, which is one of the most important factor for barrier layer. In order to adjust the contents of W or Re in the films, the concentration of sodium citrate contained in the electroless deposition baths for NiWP and NiReP films was varied.

The composition of NiWP and NiReP films were firstly investigated in order to know the relation between the composition and its thermal stability. Although the contents of W in the NiWP films were expected to change with variation of the concentration of sodium citrate added into the bath, the prepared NiWP films contained a little tungsten (W), and were scarcely changed. Other factors which seemed to affect the film composition were also varied, but there was no change in W content.

From the results of NiWP preparation, it isn't anticipated that the NiWP films have excellent thermal stability against interdiffusion with Cu layer, because the W contents in the films seemed to be insufficient. Hence, NiReP film, which is another candidate for electroless deposited barrier layer, was also investigated.

In contrast with NiWP, the composition of NiReP films was much affected by the concentration of sodium citrate. As expected, rhenium (Re) contents in the films increased with increasing the concentration of sodium citrate, which suggested that the film composition of NiReP could be adjusted as we hoped.

Based on the results discussed above, the thermal stability of several types of films was investigated by measuring their sheet resistances. A NiP film prepared from commercial electroless plating bath was also used to be compared with the other films, NiWP and three types of NiReP with different concentration of Re.

In Fig. 1, sheet resistance of each film varied with an increase in annealing temperature is shown. In the case of both NiP and NiWP films, interdiffsion had already suggested after annealing to 300 °C by increasing sheet resistance. On the other hand, all of the NiReP films were stable up to 400 °C, which was independent of Re contents in the films. From these results, it is apparent that the electroless NiReP films have satisfactory thermal stability against interdiffusion in the Cu/barrier interfacial region.

From the results in above, it is suggested that co-deposition of refractory heavy metal is effective to improve the thermal stability of electroless deposited Ni alloy films, but a little amount of heavy metal hardly affects the properties as barrier.

It was suggested that the NiReP films have good thermal stability and was feasible to diffusion barriers. However, diffusion barrier layer has to be formed on interlevel dielectrics, in this case, SiO_2. Although the NiReP films could be applied to capping layer, which is formed "on" Cu, it is preferable to utilize wet process for the formation of barriers. Thus, the fabrication process of electroless films on SiO_2 without sputtered seed was investigated. A Self-assembled monolayer of N-(2-aminoethyl)-3-aminopropyltrimethoxy silane were utilized as an adhesion/catalyzed layer.

A CVD-SiO_2 layer on Si wafer was used for substrate. After cleaning the substrate, organosilane self-assembled monolayer (SAM) was formed on it followed by the catalyzation process.

As the results, uniform NiP film was attained on SiO_2 layer covered with SAM. In the present state of experiment, however, it is a little difficult to form NiReP on SiO_2 substrate with SAM. The reason why NiReP was difficult to deposit was seemed to be caused by the difference of bath's property, such as its alkalinity and reactivity. To realize the fabrication process of barriers without dry processes, we utilized a two-step process; the NiReP barrier was formed on electrolessly formed NiP nuclei. By utilizing this process, the fabrication of electroless NiReP film on SiO_2 layer without sputtered seed was succeeded.

Although this process is still under construction, it has a great potential for realization of all-wet process integration for microelectronics.

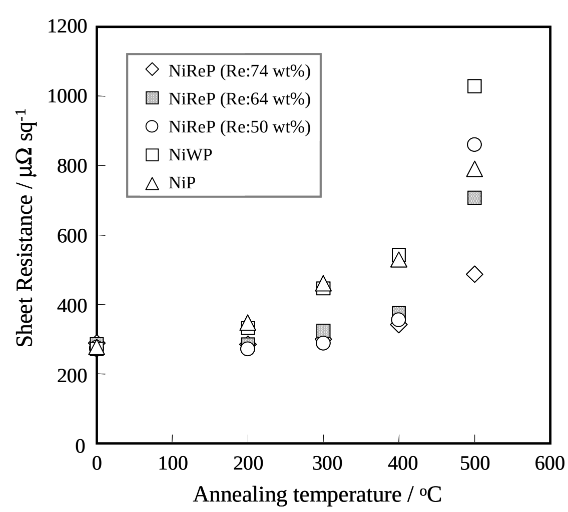

Fig. 1 Sheet resistance of each film under several annealing condition.

References

1. Y. Shacham-Diamand et al., *Electrochim. Acta,* **44**, 3639 (1999)
2. E. J. O'Sullivan et al., *IBM J. Res. Develop.*, **42**, 607 (1998)
3. S. L. Brandow et al., *J. Electrochem. Soc.*, **144**, 3425 (1997)