Pretreatment for Copper Electroless Plating on Tantalum Substrate

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With decreasing feature size in integrated circuit, interconnection material having low resistivity is essential. The resistivity of Cu is low enough to replace Al as interconnects in microelectronics. However, Cu shows higher diffusivity into Si devices than Al, which implies that diffusion barrier with higher quality should be required for Cu interconnection. TiN barrier, which has been researched as diffusion barrier against Cu film [1] with a columnar type structure, provides a fast diffusion path. Meanwhile, since Ta is polycrystalline through which it takes long time to diffuse out [2], Ta has superior property as a diffusion barrier to TiN. But, for Cu electroless plating, the pretreatment procedure on Ta barrier has not been developed fully owing to the oxidation of Ta surface. In this research, the pretreatment procedure for Cu electroless plating on Ta substrate was studied.

Ta is naturally oxidized to Ta_2O_5 which keeps from surface activation using Pd (Fig. 1). In our experiment, HF and the mixture of HF and HNO_3 were selected as the etchant of Ta oxide. In HF solution, there were two parallel processing of Ta oxide formation and Ta oxide etching. However, in the case of the mixture of HF and HNO_3, the removal of Ta oxide was highly efficient due to improved etching capability of Ta oxide based on pH decrease.

Pd was to be deposited on Ta substrate to play a role of active sites where the oxidization of the reducing agent in electroless plating solution took place. In one step Pd activation normally used in TiN barrier, Pd ion is reduced by electrons generated by oxidizing substrate. But, in the case of Ta, Ta is oxidized not to Ta ion but to Ta oxide at all condition of pH and potential [3]. Hence, one step Pd activation was not applied to Ta layer because Ta oxide generated through Pd activation step kept Pd from being deposited, whereas Sn ion adsorbed on surface reduced Pd ion in two step Sn sensitization – Pd activation. Therefore, as shown in Fig. 2, Pd was deposited successfully by two step Sn sensitization – Pd activation.

Incubation time of Cu electroless plating was measured to decide the optimal Sn sensitization time and Pd activation time. As the density of Pd nuclei was high, incubation time was reduced. The increase of Sn sensitization time and Pd activation time resulted in high density of Pd nuclei. As a result, the optimum Sn sensitization time and Pd activation time were decided to be 3 min and 20 sec, respectively.

When Cu was electrolessly deposited at room temperature, the resistivity of Cu film was measured to be 6.3 μΩ·㎝ due to oxygen contamination. It is known that two step Cu electroless plating is efficient to lower the resistivity of Cu film [4]. As a result of two step Cu electroless plating for 15 min and subsequent annealing process at 400℃ for 30 min, Cu film with the resistivity of 2.7 μΩ·㎝ and the thickness of 190 ㎚ was achieved. AES depth profile analysis informed that oxygen content in Cu film was the main cause of high resistivity (Fig. 3). The rms roughness of deposited Cu film was about 10 ㎚ which was below 10% of thickness of Cu film.

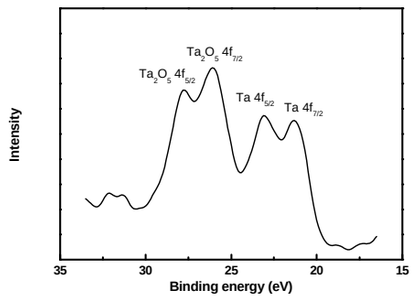

Fig. 1. XPS spectrum of Ta substrate.

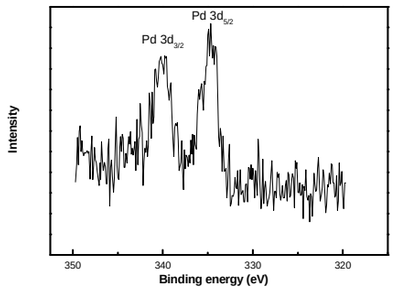

Fig. 2. XPS spectrum of Pd peak on Ta substrate deposited by two step Sn sensitization – Pd activation.

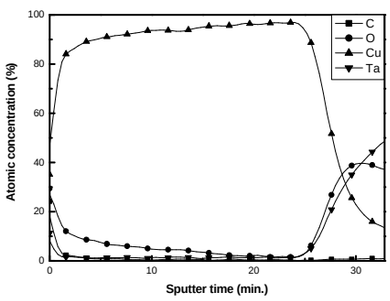

Fig. 3. AES spectrum of Cu film deposited by two step Cu electroless plating method.

References

1. J. J. Kim and S. H. Cha, *Japanese Journal of Applied Physics*, **40** (2001) 7151.
2. A. E. Kaloyeros and E. Eisenbraun, *Annual Review of Materials Science*, **30** (2000) 363.
3. D. A. Jones, *Principles and Prevention of Corrosion* (Prentice-Hall, the United States of America, 1996) 2nd ed., p. 50.
4. J. J. Kim, S. H. Cha and Y. –S. Lee, *Japanese Journal of Applied Physics*, **42** (2003) L953.