Cu Electroplating on High Resistivity TiN Barrier by Aid of Pd Activation

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As a feature size decreases to about 0.1 ㎛, it is difficult to deposit a desirable Cu seed layer at high aspect ratio damascene feature. Therefore, plating of Cu directly onto a diffusion barrier will be the most preferred process choice. However, seedless electroplating of low resistivity Cu film applicable to deep sub-micrometer damascene feature has been known to be difficult. In this study Pd activation[1] was introduced to direct Cu electroplating on high resistivity TiN barrier to get high quality Cu film.

The substrates used were CVD TiN (100 Å) / PVD Ti(150 Å) / Si(p-type). Pd activation on the TiN layer was performed in an activating solution composed of $PdCl_2$, 35% HCl, and 50% HF. Cu electroplating onto TiN layers both without and with Pd activation (denoted as substrate T and P, respectively) was performed in the electrolyte composed of 1 M H_2SO_4, 0.05 M $CuSO_4 \cdot 5H_2O$, and DI water. PEG (Mw 3400) was used as an adhesion promoter of the plated Cu film. Annealing at 400 ^oC for 30 min in a N_2 atmosphere[2] was processed.

Fig. 1 exhibits the electrochemical impedance analysis (EIS) of Cu electroplating on both substrates. The surface charge transfer resistance for substrate P is much smaller than that of substrate T that means Pd on the substrate P serves as a bridge of electron transfer between TiN surface and electrolyte. For Cu plating on substrate T, clusters are observed after several seconds of incubation time (less than 5 sec.). Further plating is taken place at the existing clusters by sticking to them, resulting in anisotropic growth (Fig. 2 (a)). On the contrary, the electroplating on the substrate P showed a continuous film with shiny surface (Fig. 2 (b)). Accordingly, sheet resistance (R_s) changes during the plating process showed different aspects as exhibited in Fig. 3. R_{si} and R_{sf} are the sheet resistances of the samples before and after Cu electroplating. R_s of substrate T is not changed with plating time due to the isolated clusters shown in Fig. 4 (a). However, R_s of substrate P showed a sudden decrease with the plating time on account of the continuity of plated Cu film (Fig. 4 (b)), which also contributed to the low resistivity (3.1 μΩ·cm after annealing). The poor adhesion between the substrate P and plated Cu was greatly promoted with the addition of PEG. Further improvement of adhesion strength was observed after 400 ℃ annealing at N_2 atmosphere. Attempt to fill the 0.13 μm damascene structure through Pd activation was made and the result is shown in Fig. 4 (c). Direct plating on patterned substrate P showed discontinuous filling with voids at the middle of via. However, considering that this is the first attempt to fill deep sub-micrometer damascene structure through the direct plating on high resistivity barrier, and that this plating is performed without additives indispensable for void-free filling, this results suggest a possibility of application of Pd activation to seedless filling of sub-0.2 μm damascene structure.

References:
1. J. J. Kim, and S. H. Cha, *Jpn. J. Appl. Phys.*, **40**, 7151 (2001)
2. J. J. Kim, S. –K. Kim, and J. –U. Bae, Thin Solid Films **415**, 101 (2002)

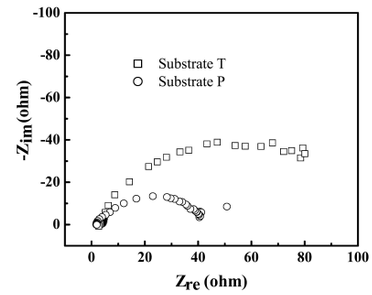

Fig. 1. EIS of Cu electroplating on each substrate at –500 mV vs. SCE with superimposed 5 mV AC signal.

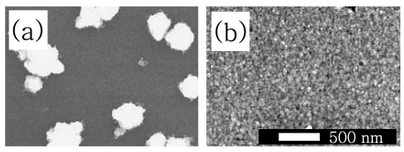

Fig. 2. FESEM images of electroplated Cu for 10 seconds on (a) substrate T and on (b) substrate P.

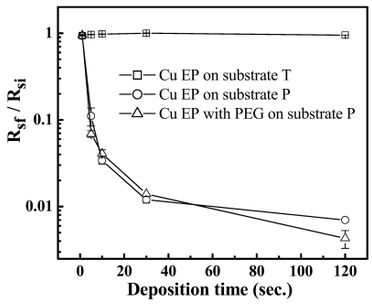

Fig. 3. Sheet resistance changes of electroplated Cu on both substrate T and P according to plating times.

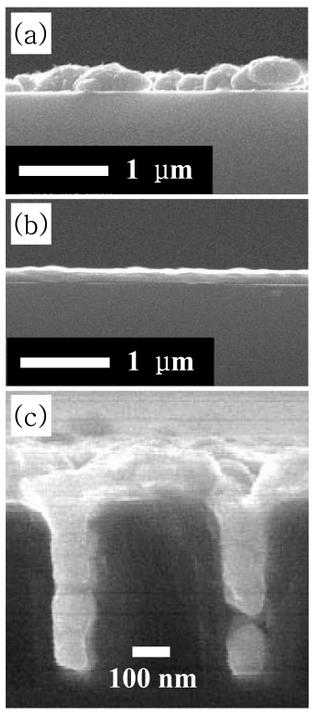

Fig. 4. FESEM images of electroplated Cu for 2 minutes on (a) substrate T, (b) substrate P, and (c) substrate P with 0.13 μm patterns (Aspect ratio of 3.5).