Characterization of low-k materials in terms of Copper Contamination by Copper Electroplating Solution

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Copper (Cu) contamination by Cu electroplating solution in the Cu dual damascene process was thought to be one of the key challenges when they install low-k materials as interlayer dielectrics because of their porous nature. Thus far no papers have been published that describe the relationship between the kinds of low-k materials and the degree of Cu contamination by Cu electroplating solution. This is the first report that could reveal the relationship between them, and that CVD-type SiOC low-k, SOG-type porous organic polymer low-k and SOG-type porous MSQ low-k could be easy to be contaminated by Cu electroplating solution.

As the trend towards higher integration density and higher signal speed continues, some extensive literature has existed on the advantages of Cu and low-k dielectrics over aluminum and silicon oxide as dielectrics and on the optimization of the interconnect RC delay. During the implementation of Cu dual damascene process, Cu film has been fabricated by Cu sputtering, Cu electroplating techniques and Cu CMP process, and Cu contamination would occur in three different ways. Especially, when they install low-k materials, Cu contamination by Cu electroplating solution could be one of the severe problems, because the higher porosity of low-k films could cause the higher permeability of Cu electroplating solution into them and this Cu would be Cu contamination of the films.
In this report, we would like to show the characterization results about the relationship between properties of low-k dielectric films and Cu contamination by Cu electroplating solution.

Interlayer dielectric materials which were used in this investigation were, A) TEOS (k-value = 3.5 - 4.0), B) SOG-type organic polymer low-k (k-value = 2.6 - 2.8), C) SOG-type MSQ low-k (k-value = 2.6 - 2.8), D) CVD-type SiOC low-k (k-value = 2.6 - 2.8), E) SOG-type porous organic polymer low-k (k-value = 2.0 - 2.5), F) SOG-type porous MSQ low-k (k-value = 2.0 - 2.5).
Each dielectric film was immersed into Cu electroplating solution ($CuSO_4$ without additive) at room temperature for 5 min and we got Cu-contaminated film.
Each Cu concentration at the surface of the Cu contaminated film was measured with TXRF. The Cu contaminated film was etched with Ar gas at 2 kV, 20 mA and measured the Cu concentration with XRF, respectively.

Figure 1 shows Ar etch rate of these six dielectric films. From this figure, it was suggested that Ar etch rate of SOG-type organic polymer low-k, SOG-type porous organic polymer low-k and SOG-type porous MSQ low-k looked fairly high. But that of CVD-type SiOC low-k was very low, and that was lower than that of TEOS.

Cu concentration at the surface of six kinds of dielectric films was described in figure 2 and that after 5 nm Ar etching was showed in figure 3.

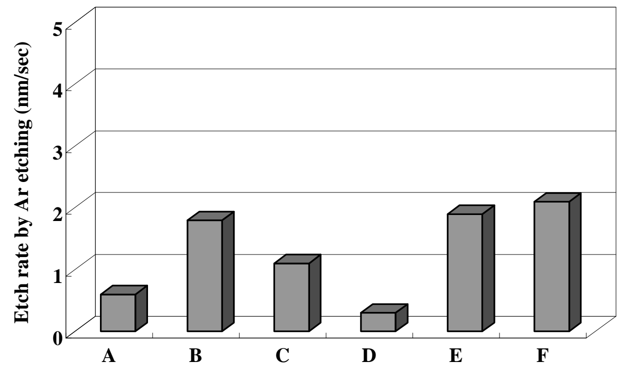

Figure 1: Ar etch rate of dielectric films

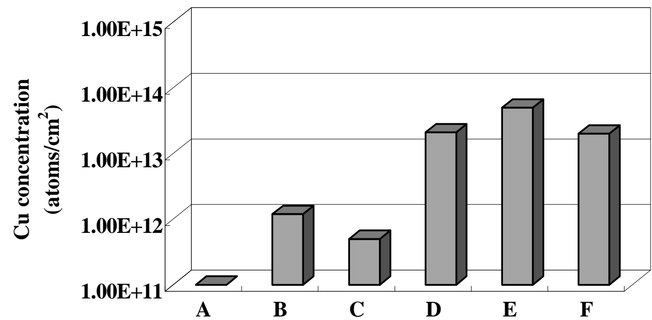

Figure 2: Cu concentration at the surface of dielectric films by Cu electroplating solution

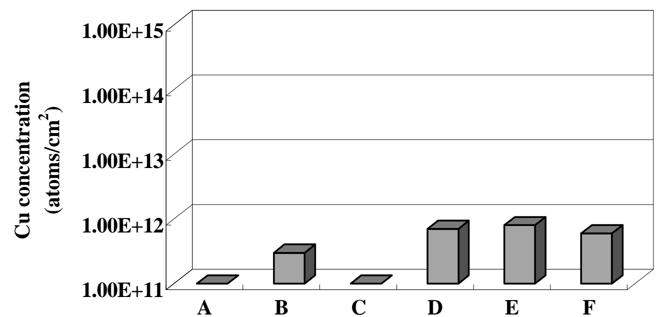

Figure 3: Cu concentration after 5 nm etching of dielectric films by Cu electroplating solution

These figures suggested that Cu contamination at the surface and inside the film of SOG-type organic polymer low-k, CVD-type SiOC low-k, SOG-type porous organic polymer low-k and SOG-type porous MSQ low-k was pretty high because of their high porous nature.

From these results, the following issues were concluded.
1) CVD-type SiOC low-k film has very good physical strength but could be easy to be Cu-contaminated by Cu electroplating solution.
2) SOG-type organic polymer low-k, SOG-type porous organic polymer low-k and SOG-type porous MSQ low-k film have low physical strength and have high Cu contamination by Cu electroplating solution.