Effect of Plasma Sulfur Activation of SiLK on the Adhesion of Copper

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Over the last several device nodes [1], there has been a drive to reduce the RC delays in IC interconnects. To reduce the capacitance between metal lines various new materials with low dielectric constant (low-k) are currently under development including organic polymers and xerogel materials [2]. SiLK [from Dow Chemical Company] is one low-k (2.65) material, and is an isotropic aromatic hydrocarbon polymer that contains no silicon or fluorine. Copper has replaced aluminum alloys as a material for interconnects due to its lower electrical resistivity (1.67 μΩ-cm vs. 2.8 μΩ-cm based on pure Al) and higher electromigration resistance.

Since dielectric materials usually have poor adhesion with copper and are not effective barriers for Cu diffusion, a base layer that serves as an adhesion promoter and diffusion barrier is required. β-Ta and TaN liners have resistivities (150-200 μΩ-cm) that are much higher than that of bulk copper. To keep total resistance down, it is important to reduce the liner thickness; a long-term goal would be to eliminate the liner; i.e., to deposit copper directly on the dielectrics. In this case, adhesion at the interface of copper and SiLK is one of the critical problems to be solved. Copper is known to be a nearly noble metal that has poor adhesion to dielectric materials [3]. Previous work shows that adhesion is improved by thiolating polymers or modifying polymer surfaces with oxygen containing chemical moieties [4]. In this work, activation of SiLK surface with sulfur was undertaken via a plasma enhanced chemical vapor deposition (PECVD) method.

Sulfur activation was undertaken on a SiLK coated silicon wafer (760 μm) using the following sequence. A sulfur was deposited using an RF PECVD system with hydrogen sulfide (H_2S, 99.9995% Air Products Inc.) and helium (He) chemistry. The RF power was 150 W over a 8 inch diameter electrode, the total pressure was 120 mTorr, the substrate was not heated, and depositions lasted 2 min. After deposition, any excess sulfur was removed using carbon disulfide (CS_2) at room temperature. It can be clearly seen in the XPS spectra (Fig. 1) that sulfur exists at the SiLK surface after removing excess sulfur with CS_2. After activation of the SiLK, a 350 nm-thick copper film was deposited in a CVC AST-601 sputter system. Adhesion energies of the copper/SiLK interfaces were estimated by a four-point bending method [5] using "beam type" specimens. These samples were created by bonding the copper coated substrates with silicon substrates (650 μm). Epoxy resin (T-88 from System Three Resins, Inc.) was used to bond two substrates. Bonded samples were left for at least 24 hours to get the full adhesion strength. The bonded wafers were then cut into 6 mm x 40 mm size beams using a diamond dicing saw and precrack was fabricated on the center of the SiLK coated silicon substrate as shown in the schematic vertical structure (Fig. 2). The beam was then placed in a four point bending geometry which causes crack initiation from the tip of the precrack throughout the SiLK layer followed by crack propagation along the copper/SiLK interface. Four point bending experiments result in force vs. traveling distance diagrams. In the case of non-activated SiLK, plateau load was about 5 N and load increased again up to 15 N and then finally the sample broke. The calculated strain energy release rate G_c of non-activated calculated SiLK was ~1 J/m^2. According to the results by Litteken et. al. [6], the interfacial adhesion energies of SiLK/TaN and SiLK/Ta were 4.6 and 10.1 J/m^2 respectively that are higher than that of non-activated SiLK/Cu interface. In the case of sulfur activated SiLK, however, plateau load was not obtained and the sample broke at a total applied force of about 18 N without revealing adhesion failure at the interface of copper and SiLK. From this result it could be reasoned that the adhesion can be improved by modifying the SiLK surface with PE-CVD sulfur.

This paper presents the details of XPS results of non-activated and sulfur activated SiLK surfaces, as well as the dependence of adhesion on activation and thermal annealing conditions.

References:
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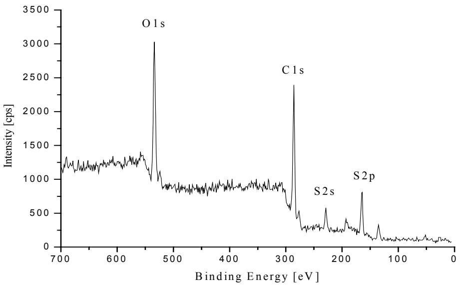

Figure 1. The full XPS spectra of SiLK after removing excess sulfur with CS_2.

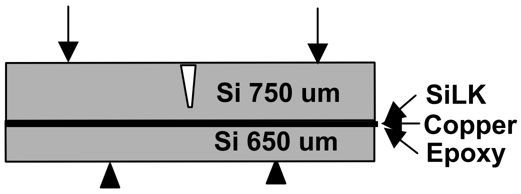

Figure 2. Schematic structure of the beam specimen.

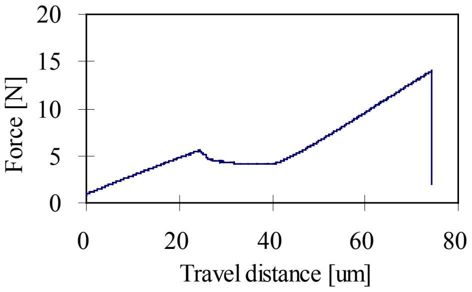

Figure 3. Force-traveling distance diagrams of four point bending for copper/non-activated SiLK specimen.