Sub-nanoscale structural analysis of corrosion protection film for copper fine wires on semiconducting devices by in-liquid AFM

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The miniaturization of copper (Cu) interconnections is one of the most important factors in recent progress in the semiconductor integration technology. These interconnections are formed using the damascene method, which involves three steps: (1) patterning on SiO_2, (2) Cu embedding, and (3) removing the excess Cu with chemical-mechanical planarization (CMP). CMP significantly impacts on the quality of Cu interconnections. The Cu-CMP slurry solution contains solvents, abrasives, oxidants, and anticorrosive agent, such as benzotriazole (BTA). Therefore, polishing occurs through a competitive reaction between these components. Despite the use of BTA to form anticorrosive films on Cu surfaces, localized corrosion still occurs in semiconductor manufacturing processes. Understanding the origin of this corrosion requires visualizing the structure and formation process of BTA anticorrosion coatings and identifying defects at the molecular level. In this study, we used frequency-modulation atomic force microscopy (FM-AFM) and three-dimensional scanning force microscopy (3D-SFM) in liquid to perform sub-nanoscale-resolution imaging of the formation process and three-dimensional structure of the anticorrosion coatings.

First, we performed FM-AFM imaging of the Cl-terminated Cu(111) substrate while flowing the BTA solution. The reaction progress was controlled by gently flowing a dilute BTA solution, and the formation process of the BTA film was observed (Fig. 1). At 0 min, a Cu(111)-Cl reconstructed surface was visualized. After 14 min , the structure gradually changed into a non-periodic, irregular structure, which is likely a BTA molecular film. By 15 min, the surface was completely covered by this structure. 3D-SFM measurements taken at this stage revealed the tilted stripe structures near the surface (Fig. 2). They are probably either the BTA molecules themselves or the hydration structures formed on them. To clarify this point, we plan to compare this AFM data with simulation results.

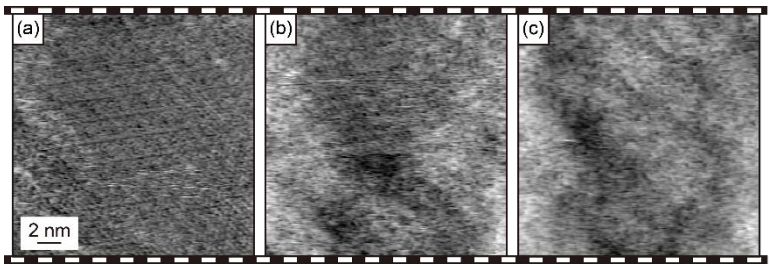

Fig. 1: FM-AFM images showing BTA film formation on Cu(111) surface. (a) 0 min. (b) 14 min. (c) 15 min.

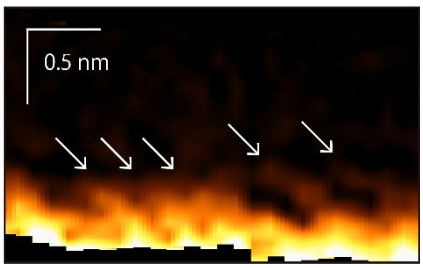

Fig. 2: XZ slice taken from the 3D Δf image of BTA/Cu(111).