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In-situ TEM investigation of amorphous Cu-Mn/C films for interconnect application

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Cu-Mn films are perspective contact and interconnect material [1]. However, their application on low-κ dielectrics (carbon doped oxides) is difficult since Mn can react with carbon extracting it from the dielectric and complicates interface chemistry. In this study we report in-situ TEM results obtained on thermal stability of metastable amorphous Cu-Mn films and solid phase reaction between the films and carbon substrates. The amorphous Cu-Mn films (with 50 and 70 at% Mn content) were deposited by DC magnetron sputtering at room temperature. Evaporated carbon foils were used as substrates to model low-κ carbon doped oxides in their reaction with Cu-Mn films. In-situ TEM investigations revealed that the amorphous state is stable below 300℃, where the films crystallize into Cu(Mn) and α-Mn-based solid solutions. While Cu-based solid solution remains stable up to 600oC, Mn-based phases alter. Mn carbide phases appear at 400℃ accompanied with the disappearance of α-Mn phase and the decrease of Mn content of Cu(Mn) phase. In the temperature range of 400-500℃ Mn23C6 and Mn5C2 carbide phases are present. As temperature increases, more carbon diffuses into the film and hence the compound of lower C:Mn ratio (Mn23C6) disappears and a new phase of higher C:Mn ratio, the Mn7C3 appears. Mn5C2 carbides have lamellar structure and show Arrhenius-type grain growth in the temperature range of 400-600oC. The activation energy of Mn5C2 growth is 101±20 and 88±22 kJ/mol respectively in the film containing 50 and 70 at% Mn, indicating that carbide growth is facilitated with increasing Mn content. In addition to carbide formation, surface oxidation occurs as well in the system. Thermodynamic considerations indicate that Mn carbide formation can only occur in the Cu-Mn-C-O system when the Mn is not fully oxidized and there are free metallic Mn atoms left.
1 J. Bogan, A. P. McCoy, R. O'Connor, P. Casey, C. Byrne, and G. Hughes, Microelectron. Eng. 130, 46 (2014).

Author: Mrs HAJAGOS-NAGY, Klára (Center for Energy Research, Hungarian Academy of Sciences)

Co-authors: Prof. RADNÓCZI, György (Center for Energy Research, Hungarian Academy of Scieces); Dr MISJÁK, Fanni (Center for Energy Research, Hungarian Academy of Sciences)

Presenter: Mrs HAJAGOS-NAGY, Klára (Center for Energy Research, Hungarian Academy of Sciences)

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