Development of phases and morphology in DC sputtered Cu-Mn alloy thin films at temperatures below 600ºC

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Advanced large-scale integrated circuits use Cu interconnect lines. A diffusion barrier layer is necessary to prevent interdiffusion between Cu lines and dielectric insulating materials. As the semiconductor industry moves from the 45 nm technology node to 32 nm and beyond, there will be a need to reduce the barrier width below 4 nm while retaining its diffusion integrity and adhesion properties. One possible way for meeting these requirements can be the utilization of self-organised processes to form conformal barrier layer in dual-damascene interconnect structures, i.e. by annealing of Mn doped Cu thin films [1].

According to the equilibrium phase diagram there are no intermetallic phases in the Cu-Mn system. The observed solid solutions and phases are described in [2, 3] and recent development in the area is summarised in [4]. Those results are based on X-ray diffraction (XRD) analysis of alloys prepared from high purity Mn and Cu by melting or by sintering of powders at high temperature (~850ºC) followed by annealing and quenching [2]. Based on these reports the most prominent phase of Mn is the cubic α-Mn phase which shows negligible solubility of Cu [2]. The most described CuMn alloy phase is the face centred cubic (fcc) phase – referred to as γ-phase - forms a continuous solid solution in the whole composition range [2]. The fcc phase may transform into a face centered tetragonal (fct) phase at high Mn content. (Despite the transition the fcc-fct phase is communicated as a "uniform" γ-phase).

So far no phase investigation was reported for Cu-Mn alloy thin films. The aim of the present study is to achieve a detailed investigation of the Cu-Mn system deposited by DC sputtering as background knowledge for technological developments. Our basic intention is the detailed understanding of the Cu-Mn thin film phase diagram and how the microstructure and morphology of the alloys depend on the composition and temperature. The kinetics of the alloy segregation process for the Cu-Mn alloy and its role in the development of film morphology is also a key issue.

The Cu-Mn alloy films were deposited in a UHV system (base pressure of $4x10^{-6}$ Pa) by DC magnetron sputtering of Cu and Mn targets (purity of 99.99% and 99.95%, respectively) in $2x10^{-1}$ Pa Ar (99.999 % purity) with growth rates of 0.1-0.5 nm/s. The composition of the sputtered films covered the whole composition range from 0 to 100% Mn content. The two magnetron sources were tilted with 30 degrees from target surface normal, directed towards the substrate table, positioned at 12 cm distance from the sources. 50 nm thick Cu-Mn layers were deposited on C coated TEM grids for direct plan-view TEM investigation without further sample preparation. Thicker films were deposited on Si wafers for cross sectional studies. The films were examined by transmission electron microscopy (TEM) in a Philips CM20 electron microscope. Selected area electron diffraction (SAED) was used to identify the alloy phases. Film composition was determined using a NORAN Energy Dispersive Spectrometer (EDS) system with Ge detector.

The observed phases are summarised in Fig. 1. At room temperature Cu rich fcc and Mn rich α-Mn phases were formed. Mn solved in Cu up to ~33at% preserving the fcc structure. The dependence of the lattice parameter of the fcc phase is linear as a function of Mn content, though with higher slope than expected from Vegard's rule. A two phase region is found between 20 and 40 at% of Mn with decreasing width at higher temperatures. Above 40 at% of Mn a single phase solid solution is observed. This inherently nanocrystalline phase has an average grain size of ~2nm around the composition of 66 at% Mn. According to SAED, no phase transition can be observed at slightly higher temperature (up to ~200ºC), but larger grain size (10-30 nm) was obtained. The nanocrystalline phase could be identified as α-Mn, which was confirmed by SAED calculations. At high temperature (~300-600ºC) the Cu-Mn alloys separate to fcc-Cu and Mn. The Mn phase obtained at high temperature could be identified as a triclinic phase. At high Mn content the boundary of the low temperature α-Mn and high temperature triclinic phases decreases with Mn content from ~300ºC (100at%Mn) to ~220ºC (33at%Mn). The Cu solves Mn in the fcc phase at elevated temperature as well, but in decreasing fraction with increasing temperature [5].

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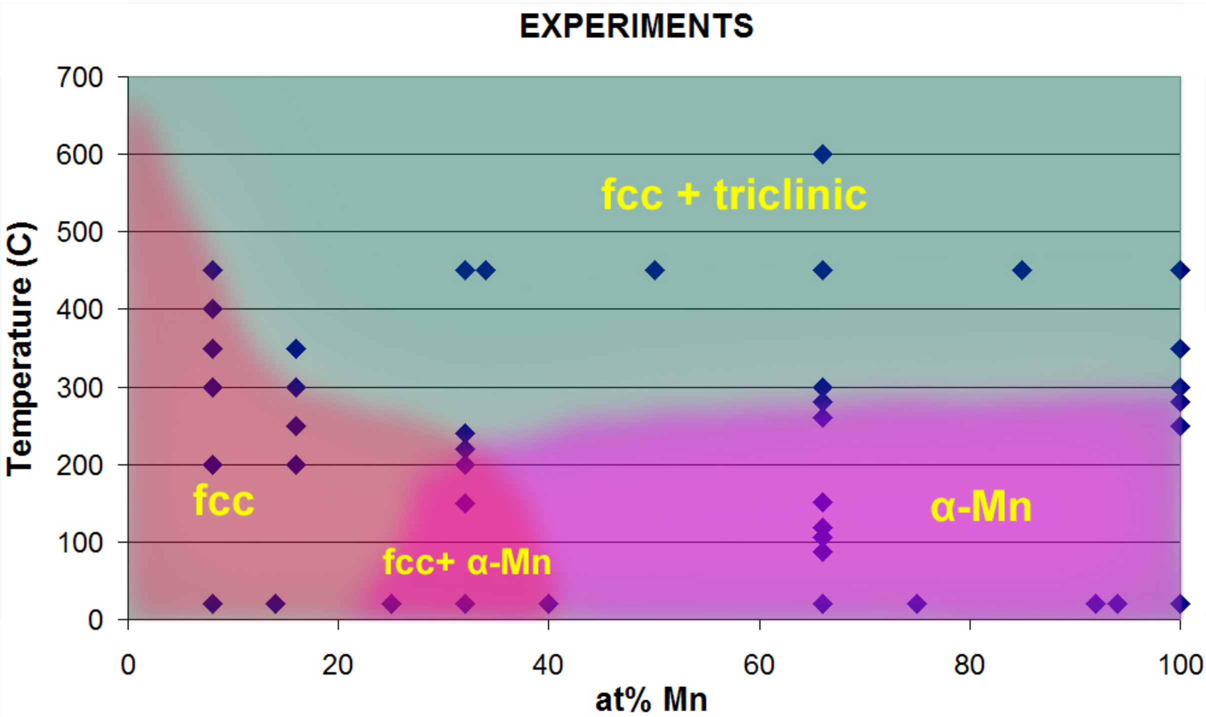

Figure 1. *Phase diagram of Cu-Mn alloy thin film deposited by DC magnetron sputtering*