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Spontaneous barrier layer formation in SiO_2/Cu-Mn alloy film interface

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The Cu-Mn system is a prospective contact or interconnect material for memory or IC applications. In the current technology for advanced semiconductor devices, copper is the main material of transistor interconnects. The high diffusion rates for elemental copper in silicon and silicon oxides have required the development of diffusion barriers. As the semiconductor industry moves to smaller sizes, for future technologies 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 reaching this dimension can be the utilization of self-organised processes simultaneously meeting preconditions like conformal coating, small thickness of the barrier layer and small lateral sizes. The idea of using self-forming barrier layers involves the deposition of a copper alloy directly onto the dielectric layers. Subsequent annealing (400 ^{o}C for 60 min as published in [1]) can lead to the segregation of the alloying metal to the copper/dielectric interface, where it chemically reacts with the dielectric forming a thin barrier layer. The most promising results in the literature relate to copper-manganese (Cu-Mn) as contact and self-forming barrier material. In this aspect, a detailed investigation of the Cu-Mn system is aimed at the background knowledge for technological developments. The basic intention of this work is the detailed understanding of the structure of 40-70 at% Mn composition region in the Cu-Mn thin film system and the possible reaction between the film and silicon oxide substrate layer.

Cu-Mn alloy films were co-deposited by DC magnetron sputtering from Cu and Mn targets onto SiO_x and SiO_2 substrate at room temperature. The background pressure of $5x10^{-8}$ mbar and sputtering gas (Ar) pressure of $2x10^{-3}$ mbar were used. The thickness of the films was around 500 nm, and a deposition rate of 0.4 nm/s was applied. Cross-sectional samples for HRTEM were prepared by Ar ion milling using low angle sputtering. HREM investigation was carried out in Philips CM20 and in C_s corrected JEOL electron microscopes equipped with EELS possibilities.

A typical structure characteristic of the investigated composition region (40-70 at% Mn) is shown in Figure 1. The HREM image shows disordered structure, neither the lattice of Cu nor that of αMn could be detected. Apparently the film possesses an amorphous nature. For establishing short range atomic arrangements radial distribution function of the sample has been calculated [2]. It shows good agreement with αMn atomic arrangements (Figure 2.) where all peaks and relative intensities are similar in the two structures. The phenomenon, that the atomic density of the amorphous alloy is somewhat lower than that of αMn may be due to the fact that Cu atoms are larger than Mn atoms manifested also in larger coordination distances for the alloy structure.

Investigating the interface of the layers and the silicon oxide substrate we could find that at the interface a ~4 nm thick layer formed (Figure 3.). Its appearance is very similar to the one observed after annealing at elevated temperature in [1]. EELS measurements (Figure 4.) of elemental distributions across the barrier layer show that this layer is composed of a mixed oxide of Si and Mn. The distribution of Cu suggests that the thin mixed oxide layer stops migration of Cu atoms in the direction of the dielectric substrate, thereby acts as a barrier layer. The temperature history of the film shown in Figure 3 is its unavoidable treatment at 150^{o}C for 60 min during the sample preparation process. This (treatment) is much lower than the annealing described in the literature and applied for forming of the barrier layer [1].

As a conclusion we can state that the structure of the high Mn content alloy films (40-70 at% Mn) is amorphous and has a short range order similar to □Mn. The very low temperature or spontaneous formation of the barrier layer in the SiO_2/Cu-Mn alloy interface suggests a possible way of the utilization of this phenomenon in IC applications. Self-forming and spontaneous barrier layers may be prepared by depositing first a few nm thick amorphous layer of high Mn content which ensures barrier formation, then continuing deposition with a low Mn content crystalline film [3] serving as interconnect material.

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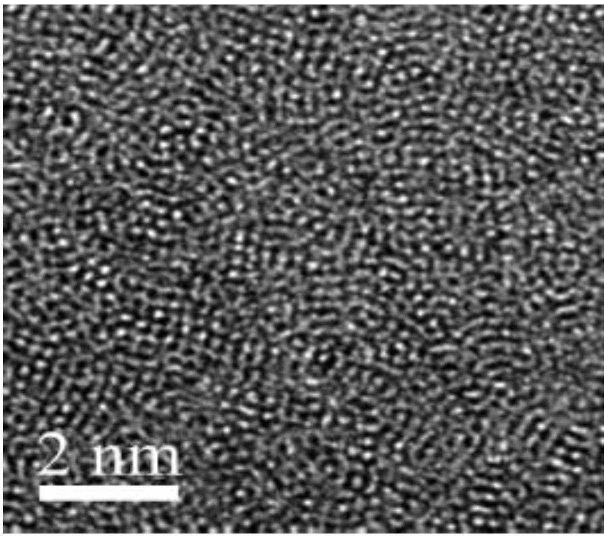

Figure 1. High resolution image of 65 at% Mn alloy film

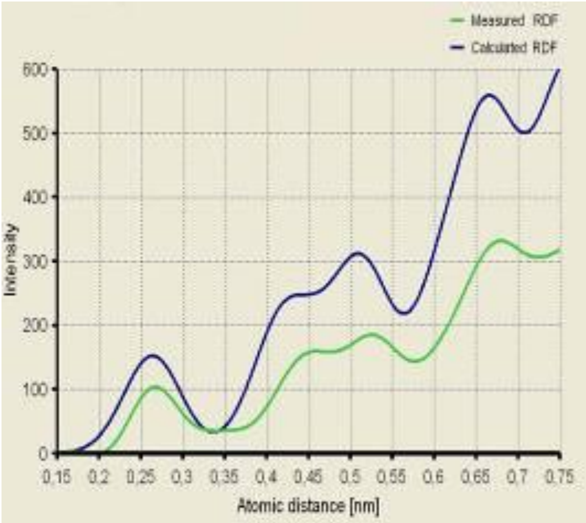

Figure 2. Radial distribution functions of □Mn (blue) and that of the 65 at% Mn content Cu-Mn alloy film (green).

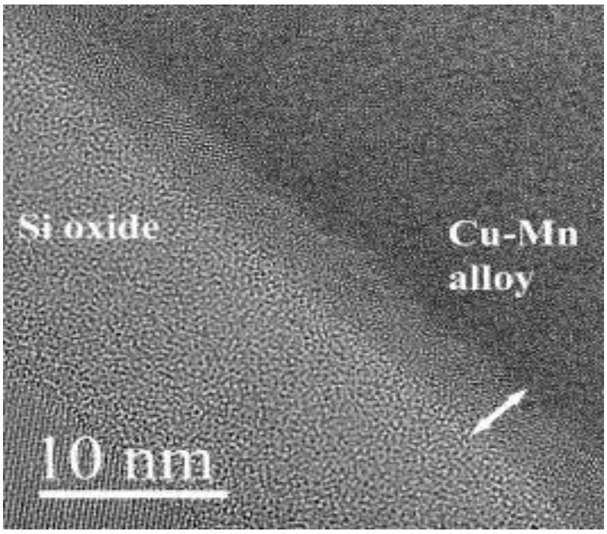

Figure 3. HREM image of a typical interaction layer (arrow) between the Cu-Mn alloy film and the Si oxide

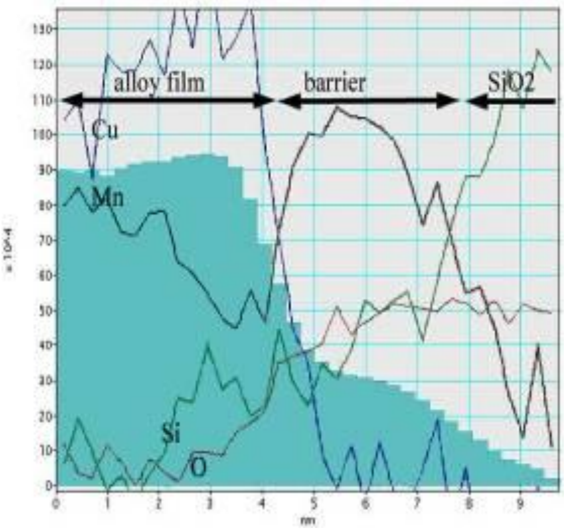

Figure 4. EELS elemental distribution profiles across the barrier layer (40 at% Mn sample)