## Nanostructure of sputtered Cu-Mn alloy films

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The structure and morphology of Cu-Mn alloy films is of scientific interest because of their possible application as contact or interconnect materials in memory devices or integrated circuits [1]. To produce the same properties, structures and morphologies in a technological process reproducibly the knowledge of mechanisms playing role in the film formation processes is essential. As the direct observation of atom by atom growth during thin film deposition is not possible, indirect methods have to be used to reveal the growth mechanisms. One plausible way of doing this is the detailed (close to atomic resolution) investigation of the structure. Then from the morphological and diffraction investigations one can be able to deduce the possible growth mechanisms, which can be confirmed by experiments or simulations.

The Cu-Mn films were prepared by co-deposition in a DC magnetron sputtering system onto  $SiO_x$  substrate at room temperature. The base pressure was  $8x10^{-8}$  mbar; while the sputtering gas was Ar at  $2x10^3$  mbar pressure. Deposition rate corresponded to 0.3 nm/s. Composition of the films was controlled by calibrating deposition rates as the function of sputtering power. The thickness of the films was about 500 nm. Cross-sectional specimens were prepared using low-energy Ar ion milling preceded by mechanical grinding. Structural and chemical characterisation of the layers was carried on using various conventional and aberration-corrected transmission electron microscopy (TEM) techniques.

Cu-Mn alloy films form a nanograin or apparently amorphous structure in the composition range of 50-70 at % of Mn. The formation mechanism of this structure is not conforming at a first glance with any known growth mechanism [2,3]. Fig. 1 shows the cross section image of a Cu<sub>35</sub>Mn<sub>65</sub> film and the corresponding diffraction pattern. The bright field image shows homogeneous contrast, where no diffraction contrast is visible. The dark field image reveals a nanograin structure, however, it remains still an open question if the film contains an amorphous component. On the contrary, the diffraction pattern displays crystalline nature, in which the crystallites are textured. (The sharp reflections in the diffraction pattern belong to the Si substrate). Based on the diffraction pattern, we can conclude, that basically one crystalline alloy phase is present which corresponds to the cubic (58 atom) unit cell  $\alpha$ -Mn phase, though according to the equilibrium phase diagram [4] at this composition the film should contain nearly equal amount of  $\alpha$  and  $\gamma$  phases, the later being an fcc phase of Cu and Mn solid solution. Dark field images show some correlation between crystalline particles along the growth direction. High-resolution TEM images reveal crystallites of a few nm size belonging mostly to the  $\alpha$  phase as well as MnO (thought to be due to the thinning procedure or to the atmosphere exposure of the crystallites). The crystallites, however, do not form a polycrystalline network, amorphous regions can be surmised between them (Fig. 2). In certain parts of the film amorphous areas can also be detected (Fig. 3) with fragments of undulated fringes. In the Fourier transform anisotropic ordering, corresponding to the period of  $\langle 330 \rangle$  reflection of  $\alpha$ -Mn structure is visible (Fig. 3). The ordering of the layers is parallel to the growth direction and in its appearance is similar to the ordering of graphene like planes in amorphous carbon nitride films [5].

The above structural information can be utilized for establishing some steps of the formation mechanism in these films. We can propose that the nanostructure of the  $Cu_{35}Mn_{65}$  films forms most probably in two steps. First an amorphous anisotropic structure forms, composed of layers parallel to the growth direction and having the period close to 0.21 nm (330 of  $\alpha$ -Mn). This structure undergoes transformation through formation of nanocrystals of the size 2-5 nm. The orientation of the crystallites is mainly determined by the anisotropy of the amorphous structure, leading to the texture, observed in these films [6].

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Figure 1. Bright field (a) and dark field (b) image and diffraction pattern (c) of a cross section of Cu<sub>35</sub>Mn<sub>65</sub> film.



Figure 2. HREM image(a) and Fourier transform (b) of a nanocrystalline region in the Cu<sub>35</sub>Mn<sub>65</sub> film.



Figure 3. HREM image(a) and Fourier transform (b) of an amorphous region in the Cu<sub>35</sub>Mn<sub>65</sub> film.