# Final report on the OTKA 81808 project
# 2010-2015

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### *Background*

In the current processing technology for advanced semiconductor devices, copper is the material of choice for transistor interconnects. The high diffusion rates for elemental copper in silicon and silicon oxides have required the development of new interconnect materials and diffusion barriers to prevent interdiffusion across the interface. As the semiconductor industry moves from the 45 nm technology node to 24 nm and beyond, the currently used barrier layers will not be a viable option, because of their thickness. The International Technology Roadmap for Semiconductors has targeted a 5.4 nm barrier for the 32 nm technology node and for future technologies; there will be a need to reduce the barrier width below 4 nm while retaining its diffusion integrity and adhesion, conductivity and mechanical properties. This emerging technology involves the deposition of copper alloys directly onto $SiO_2$ dielectric layers. Subsequent annealing leads to the segregation of the alloying metal to the copper/$SiO_2$ interface where it chemically reacts with the $SiO_2$ forming a thin barrier layer. The most promising results in the literature related to copper-manganese (Cu-Mn) system.

### *Why self-forming barrier layer?*

For the self-segregating Cu(Mn) interconnects the segregating element (Mn) accumulates at the interface between the metal interconnect and the dielectric material. The subsequent segregation of Mn results in that a $MnSi_xO_y$ interfacial mixed oxide layer forms which is inherently conformal. Up to 70% reduction in via resistance has been reported for the Cu-Mn self-segregating barrier formation.

### *Novel aspects*

The novel aspects of this project relate to the complex view of the formation of metal alloy film on dielectric substrate and simultaneously a barrier layer on the dielectric. In this view the morphology and structure of the Cu-Mn alloy films is investigated in the whole composition region. The kinetics and the atomic processes of structure formation are deduced from detailed structural, morphological and compositional characterisation of the films on the nm scale and below.

The scope of the project is to substantially contribute to the basic knowledge of atomic mechanisms and kinetics of self-organized interfacial layer formation in order to facilitate their use in technological processes. As a model system the Cu-Mn-$SiO_2$ system has been selected due to its promising future application on CMOS technology.

### *Basic Methodology*

The Cu-Mn alloy films were produced by DC magnetron sputtering in a UHV vacuum system, at a background pressure of ~$8x10^{-6}$ Pa. The purity of the Cu and Mn targets was 99.99% and 99.95%, accordingly. The purity of the Argon sputtering gas was 99.999 % and the sputtering pressure about $2x10^{-1}$ Pa. The films were grown on oxidised Si(001) wafers (200 nm thermal $SiO_2$), as well as thermally deposited 25 nm thick $SiO_x$ or amorphous carbon substrates. The whole composition range was covered.

The main analytical techniques used for achieving the above goals include transmission electron microscopy down to sub-nm resolution, electron diffraction, energy dispersive X-ray- and electron energy loss spectroscopies. Other techniques like X-ray diffraction, SIMS, AES were also used. Measurements as those of physical properties (electrical resistivity, mechanical properties) were contributing to understanding of the phenomena, taking place in the investigated structure.

The preparation of samples for TEM investigation was carried out by low angle Ar ion milling or FIB, or by using adhesive type tearing to avoid ion milling damage [1].

### *Results*

The experiments were started on a broad front as no experience with the Cu-Mn system was accumulated and the peculiarities of the experimental difficulties had to be surveyed. The primary goal was to map the non-equilibrium (corresponding to the actual growth parameters) phase diagram of the system including the forming phases and morphologies.

### *Structures and phases in the system*

For effective mapping of the reasonable experimental conditions, the composition dependence of the forming phases, structures and morphologies, combinatorial samples were prepared and investigated by TEM. Analysis of combinatorial samples revealed three different phase regions in the whole composition range: an fcc phase below about 35 at% of Mn, a disordered phase in the 40-65 at% Mn region and an αMn based structure above 70 at% Mn concentration.

For clarification of the concentration boundaries between different phase states in the Cu-Mn thin film system individual samples of composition, selected on the basis of combinatorial investigations were deposited. The detailed TEM and HREM analysis provided further information on the structure and phase state of the films. This new structural information aided us in completing our view on the phase diagram of the Cu-Mn thin film system. Beside the fcc Cu and αMn phases observed for pure Cu and Mn films, the following one phase concentration zones were confirmed [2,4].

The low Mn content films (up to ~35 at% Mn) have Cu based fcc solid solution structure and columnar morphology. The composition dependence of the lattice parameter of the Cu-Mn solid solution [2] shows steeper linear dependence on the Mn content than expected from the Vegard's law (Fig. 1), in accordance with literature data for bulk alloys. From TEM and AFM measurements the grain size and from the broadening of electron diffraction lines the size of coherently scattering domains (CSD) in the films was measured. Their dependences on the composition show parabola like behaviour. The CSD size is in the 2-12 nm range for all compositions, and the minimum is 2-3 nm at about 45 at% Mn (Fig. 2) [2]. The size of the grains determined from the AFM images correlates well with the grain size measured from TEM (Fig. 3). With increasing Mn content the defect density increases, leading to subdivision of grains into CSD, measured from electron diffraction [7]. In addition we clarified (by HREM and EELS in Nagoya) that excess Mn is located in the grain boundaries of the fcc Cu-Mn solid solution grains in the 30 at% Mn sample [10]. From the difference between the grain size and CSD size and Mn segregation to grain boundaries in the fcc solid solution the operation of a phase separation mechanism (kinetic segregation) in these alloys could be predicted [5, 12,]. The parabolic dependence of the CSD size on composition correlates well with the surface roughness (Fig. 2), though the latter is about an order of magnitude smaller (below 1 nm) [7, 14].

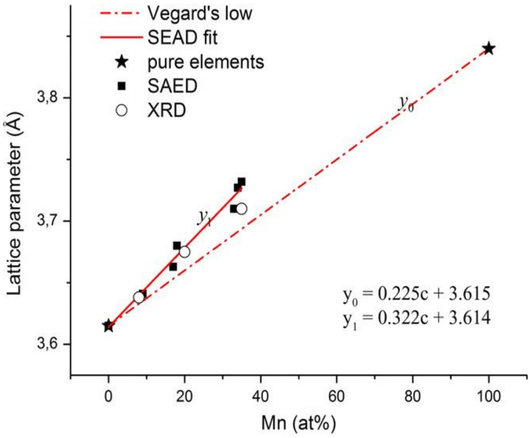

*Figure 1. The variation of the lattice parameter in fcc Cu-Mn solid solution films.*

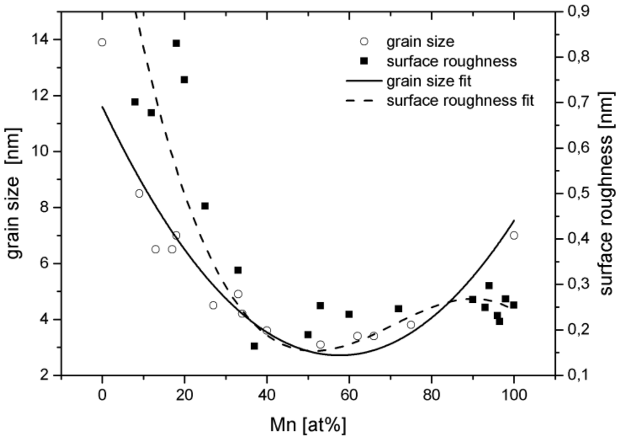

*Fig. 2. Composition dependence of CSD size and surface roughness of 50 nm thick Cu-Mn alloy films.*

Between 40 and 65 at% Mn content a disordered phase region was found. We used $C_s$ corrected high resolution TEM facilities in Ernst-Ruska Microscopy Centre (Jülich) and at Nagoya University (Japan) for characterising this structure [8]. We could clarify that the 40 and 65 at% Mn samples are of truly amorphous nature (Fig. 4) with some inhomogeneity in the Mn distribution [10]. Particularly for films containing 65 at% Mn we have shown by calculating and simulating the radial distribution functions that their short range order is close to that of crystalline αMn (fig. 5) [10]. We investigated also how the amorphous structure behaves when exposed to higher temperatures. In situ heat treatment of the amorphous films in the TEM showed that the crystallization temperature depends on composition and falls between 200 and 300 °C. The process of crystallization is fast and the forming crystalline phase has very small grain size. The quantity of the forming fcc γMn or αMn phases differs for different film compositions [15].

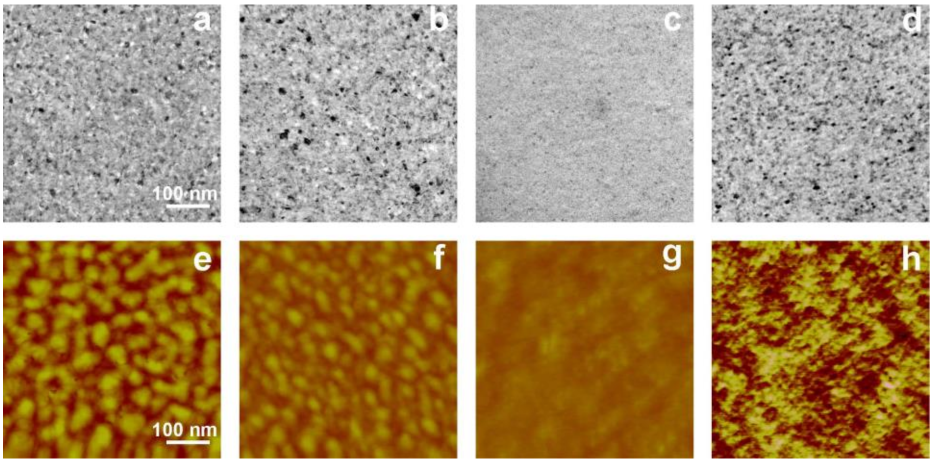

*Figure. 3. Lateral TEM (a)-(d) and AFM (e)-(h) images of Cu-Mn films with 8 at%, 25 at%, 66 at% and 92 at% Mn content, respectively*

Above ~80 at% Mn an αMn type solid solution forms with a fine grain columnar morphology.

Between these one phase regions narrow two-phase regions exist where the minority component is located mainly in the grain boundaries of columnar grains of the majority phase [2,4].

As the presence of MnO was observed in some diffraction patterns, the question of the location of MnO in the films has been arisen. For determination of the distribution of oxygen or MnO in the films ToFSIMS measurements were performed. The measurements have shown that MnO is present in the form of a surface layer, so the internal structure of the films is not affected by oxygen incorporation.

The structural and morphological mapping of the Cu-Mn films paved the route to tailor the barrier formation processes.

Amorphous barrier layers of 2-4 nm thickness in the polycrystalline Cu(Mn) alloy/$SiO_2$ interface after annealing the samples at 150-450 °C for 30 min were described in the literature and observed by us for films of different Mn content. However, spontaneous barrier layer formation was observed, first to our knowledge by us, in the amorphous Cu(Mn) alloy/$SiO_x$ interface (Fig. 6) using HRTEM, EELS and AES [10]. EELS measurements revealed that the layer is a mixed Si-Mn-oxide (Fig. 7) and in its structure and composition corresponds to the expected barrier layer. Cu component could be detected neither in the barrier layer nor in the neighbouring $SiO_x$ (Fig. 7). (The presentation of this result won the “best poster” award at the Electron Microscopy Conference in Regensburg, 2013). The possibility of spontaneous formation of the barrier layer opens new ways for using composition gradient layers in the interconnect- and self-forming barrier layer technology.

*High temperature structures in the system*

We investigated the structures grown at higher temperatures. In films at elevated temperatures (450°C) two phases were identified in the whole composition range: the fcc Cu based solid solution and αMn based solid solution [2,9]. This corresponds to the expectations from the equilibrium phase diagram.

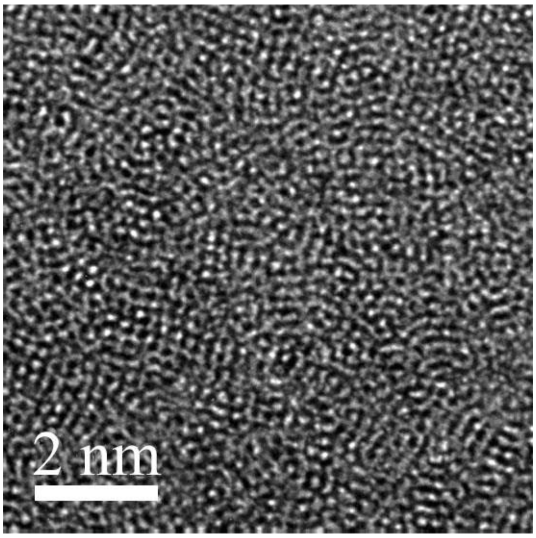

*Figure 4. HREM image of the amorphous structure of the amorphous Cu-Mn film (65 at% Mn).*

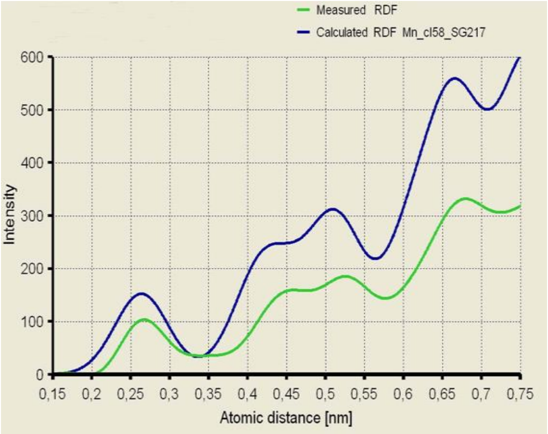

*Figure 5. Radial distribution function of the amorphous Cu-Mn film and that, calculated for amorphous a-Mn structure.*

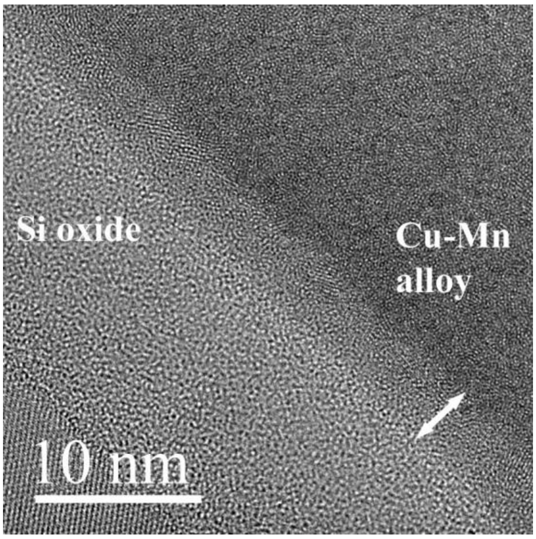

*Figure 6. HREM image of spontaneous barrier layer between Si-oxide and Cu-Mn alloy film.*

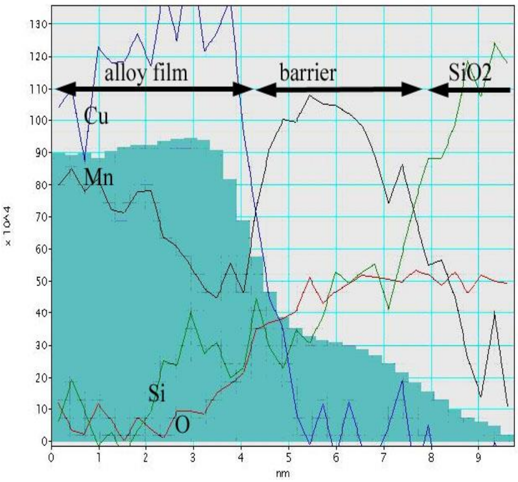

*Figure 7. The variation of the components across the barrier layer. The Cu content vanishes on the Cu-Mn alloy/barrier interface.*

<u>*Relation between structure and properties*</u>

The resistivity measurements and the structural information obtained by TEM were used for modelling the conduction mechanisms in the films. By combining the Matthiesen's rule and the Mayadas-Shatzkes model the scattering contribution of solute atoms and grain boundaries was calculated. As a result, we could conclude, that in the fcc solid solution region and in the amorphous structures the resistivity is composed from thermal and solution (Nordheim) scattering (Fig. 8). In the two phase regions and in the Mn based solid solution region in addition to the above scattering mechanisms grain boundary scattering is giving a significant contribution. In the concentration regions, where the contribution of solute scattering is important Moiij correlation (high resistivity and small negative TCR) was also observed. The resistivity values and their close to zero temperature coefficients (Table I) are promising for their use as contact or interconnect layers. The results could also be utilized for refining the concentration boundaries of different phase regions [4, 11, 13]

TABLE I. Summary of the specific resistivity, TCR and hardness of Cu-Mn films.

| Mn (at. %) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\rho_{273K}$($\mu\Omega$cm) | 1.7 | 29 | 59 | 97 | 108 | 137 | 165 | 190 | 205 | 200 | 174 |
| $TCR_{273K}$ $10^{-5}$(1/K) | 399 | 2.72 | -8.39 | -6.9 | -23.3 | -37.7 | -41.5 | -45.3 | -30.8 | -6.32 | 3.8 |
| grain size (nm) TEM | 1000 | 30 | 15 | 15 | - | - | - | 10 | 10 | 10 | 15 |
| Hardness (GPa) | 4 | 9 | 9 | 9 | 5.5 | 7.5 | 9 | 9 | 10 | -- | 14 |

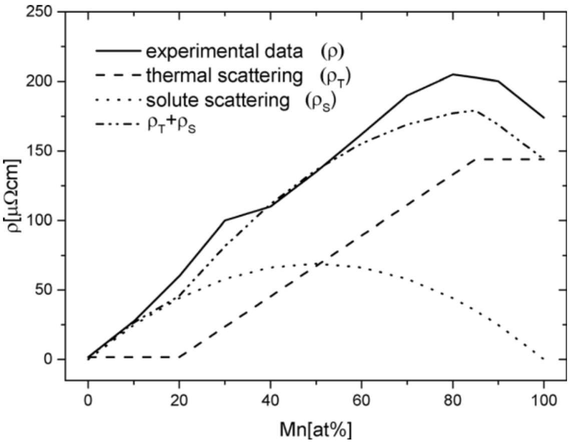

*Figure 8. The calculated contribution of thermal- and solute-scattering to the resistivity and their sum compared with the experimental data as a function of Mn content.*

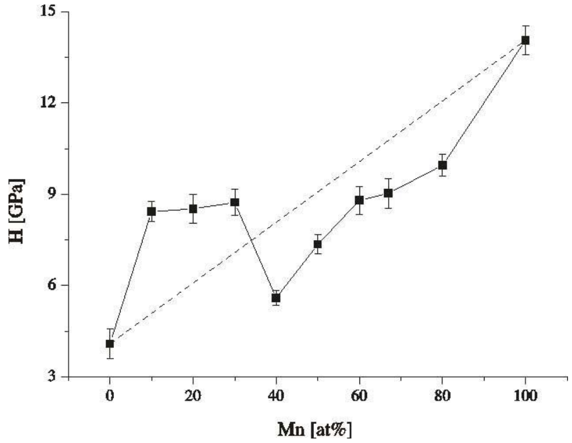

*Figure 9. Composition dependence of nano-hardness of 1 μm thick Cu-Mn alloy films.*

The hardness of the interconnect- and contact layers strongly influences their reliability. Nano-hardness of the Cu-Mn layers has been measured in the whole composition range (Fig. 9). The nano-hardness of the pure Cu film (grain size about 1 μm) is 4 GPa. The hardness of the crystalline alloy layers (10-30 at% Mn) is about 9 GPa. At 40 at% Mn content the hardness goes to minimum, then "linearly" increases to 14 GPa for the pure Mn layer, showing not strong influence of the nanostructure of the actual composition. The minimum at 40 at% Mn is connected to the amorphous structure [11] of the film, which may change or even crystallize under the indentation effect as suggested by TEM measurement. The low Mn content crystalline films show a hardness increase due to the drastic decrease of their grain size compared to pure Cu film (Table I), however, the increase of hardness on the other side of the composition interval (above 40 at% Mn content) cannot be connected to any microstructural deformation mechanism. It is rather understood if the increase of bonding strength with increasing Mn content is taken into consideration.

Summarizing the results it can be concluded that Cu-Mn alloys in the 10-30 at % Mn region on the basis of their resistivity, hardness and surface properties are a good candidate for the use in IC interconnect applications. Detailed structural analysis of the Cu-Mn alloy films and their interfacial reactions with $SiO_2$ substrates revealed the possibility of spontaneous formation of barrier layers in the 40-70 at% Mn concentration region. The possibility of spontaneous formation of the barrier layer opens new ways for using gradient layers in the interconnect- and self-forming barrier layer technology.

*Related work*

Parallel to the work on the Cu-Mn system jointly we performed investigation on the Cu-Ag, Ni/MgAl-oxide [3] and TiAlN films [6] studying the phenomena of phase formation and phase separation in these systems. These investigations broadened our view and helped in understanding, modelling and interpretation of the similar phenomena occurring in the basic to the project Cu-Mn system.Concerning the work on the Cu-Ag system a manuscript is 80% ready for publication.

A further manuscript on thermal stability of Cu-Mn amorphous films is under preparation and is about 50 % ready.

*Education and training*

Receiving of undergraduate students for research training and education including diploma workers in the frame of the project was also planned and realised.

We had three outstanding results (2 first and 1 second place) in TDK (national student competition), three summer training students, six finished BSc theses and three MSc theses. Besides of these, two of the project participants were receiving the János Bolyai scholarship (Fanni Misják, Zsolt Czigány) for facilitating their professional development.

*Summary*

It can be concluded that Cu-Mn alloys in the 10-30 at % Mn region on the basis of their structural- and surface properties, resistivity and hardness are a good candidate for the use in IC interconnect applications. Detailed structural analysis of the Cu-Mn alloy films and their interfacial reactions with $SiO_2$ substrates revealed the possibility of spontaneous formation of barrier layers in the 40-70 at% Mn concentration region. The possibility of spontaneous formation of the barrier layer opens new ways for using gradient layers in the interconnect- and self-forming barrier layer technology.

The project was very successful in involving students in research activity. We achieved three outstanding results (2 first and 1 second place) in TDK (national student competition), three summer training students, six finished BSc theses and three MSc theses. Besides of these, two of the project participants were receiving the János Bolyai scholarship.

## List of publications

1. Zs. Czigány: Plan-View Preparation of TEM Specimens from Thin Films Using Adhesive Tape, Microscopy and Microanalysis 17, p. 886-888, (2011).
2. Zs. Czigány, F. Misják, O. Geszti, Gy. Radnóczi, Structure and phase formation in Cu–Mn alloy thin films deposited at room temperature, ACTA MATERIALIA 60:(20) pp. 7226-7231. (2012).
3. Gábor P Szijjártó, Zoltán Pászti, István Sajó, András Erdőhelyi, György Radnóczi, András Tompos, Nature of the active sites in $Ni/MgAl_2O_4$-based catalysts designed for steam reforming of ethanol, JOURNAL OF CATALYSIS 305: pp. 290-306. (2013).
4. F Misják, K H Nagy, P Lobotka, G Radnóczi, Electron scattering mechanisms in Cu-Mn films for interconnect applications, JOURNAL OF APPLIED PHYSICS 116:(8) Paper 083507. 8 p. (2014)
5. Radnóczi G, Misják F, Biro D, Barna PB, Revealing Phase Separation Mechanisms in Alloy Thin Films, the Impact of Electron Microscopy, Imaging &Microscopy 4 (2014) p. 46-49, Wiley-VHC Verlag GmBH & Co. KGaA (2014)
6. L Székely, G Sáfrán, V Kis, Z E Horváth, P H Mayrhofer, M Moser, G Radnóczi, F Misják, P B Barna, Crossover of texture and morphology in $(Ti_{1-x}Al_x)_{1-y}Y_yN$ alloy films and the pathway of structure evolution, SURFACE & COATINGS TECHNOLOGY 257: pp. 3-14. (2014).
7. F. Misják, K.H. Nagy, P.J. Szabó, G. Radnóczi, Effect of Mn Alloying on the Internal and Surface Structure of Cu Thin Films Designed for Interconnect Applications, in Proceedings of Surface Modification Technologies XXVIII, Tampere, Finland, Edited by T. S. Sudarshan, Petri Vuoristo and Heli Koivuluoto pp. 627-634, Valardocs, (2015), ISBN Number: 978-81-926196-1-3.

8. Fanni Misják, Zsolt Czigány, András Kovács, György Radnóczi, Nanostructure of sputtered Cu-Mn alloy films, In: Proceedings of the 15th European Microscopy Congress. Manchester, England , 2012.09.16 -2012.09.21, Paper 0178.
9. Zsolt Czigány, Fanni Misják, György Radnóczi, Development of phases and morphology in DC sputtered Cu-Mn alloy thin films at temperatures below 600ºC. In: Proceedings of the 15th European Microscopy Congress, Manchester, England, 2012.09.16 -2012.09.21: Paper 0044.

10. F Misják, J Yamasaki, Y Yamamoto, J L Lábár, N Tanaka, G Radnóczi, Spontaneous barrier layer formation in $SiO_2$/Cu-Mn alloy film interface, In: Reinhard Rachel (ed.), Proc. Microscopy Congress 2013. Universitätsverlag Regensburg, pp. 579-580. ( I.) Materials Science.
11. K Nagy, F Misják, P Szommer, P Lobotka, G Radnóczi, Composition dependence of morphology, electrical and mechanical properties of sputtered Cu-Mn alloy films In: Reinhard Rachel (ed.), Proc. Microscopy Congress 2013. Universitätsverlag Regensburg, pp. 567-568. ( I. ) Material Science
12. G Radnóczi, F Misják, D Biro, P B Barna, The impact of electron microscopy on revealing phase separation mechanisms in alloy thin films, In: Reinhard Rachel (ed.) Proc. Microscopy Congress 2013. Universitätsverlag Regensburg, pp. 363-364. ( I. ) Material Science, Regensburg, 2013.08.25 -0213.08.30.
13. Misják F, Nagy K H, Lobotka P, Radnóczi G, Structural features contributing to electrical resistivity in Cu-Mn alloy films, In: Pavel Hozak (ed.), Proceedings of 18th International Microscopy Congress. Prague, Czech Rep., 2014.09.07-2014.09.12. Praha: Czechoslovak Microscopy Society, 2014. Paper MS-3-P-2205. 2 p.
14. Nagy K H, Misják F, Czigány Z, Radnóczi G, Relation between Surface and Internal Structure of Cu-Mn Thin Films, In: Pavel Hozak (ed.), Proceedings of 18th International Microscopy Congress. Prague, Czech Rep., 2014.09.07-2014.09.12. Praha: Czechoslovak Microscopy Society, 2014. Paper MS-3-P-2213. 2 p.
15. Radnóczi G, Nagy K H, Tóth-Kiss R, Misják F, In situ crystallization of Cu-Mn amorphous alloy films, In: Proceedings of 18th International Microscopy Congress. Prague, Czech Rep., Czechoslovak Microscopy Society, Pavel Hozak (ed.), 2014. Paper MS-3-P-2303. 2 p.