Mechanical properties and microstructure of model lead-free joints for electronics made with use of nanopowders

Jiří Buršík[1], Vilma Buršíková[2,3], Zbyněk Pešina[4] and Jiří Sopoušek[5]

[1]Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, Brno, Czech Republic
[2]Masaryk University, Faculty of Science, Regional R&D center for low-cost plasma and nanotechnology surface modifications, Kotlářská 2, Brno, Czech Republic
[3]Masaryk University, CEITEC, Kotlářská 2, Brno, Czech Republic
[4]Brno University of Technology, Faculty of Mechanical Engineering, Technická 2, Brno, Czech Republic
[5]Masaryk University, Faculty of Science, Department of Chemistry, Kotlářská 2, Brno, Czech Republic

Introduction

•Classical solders based on lead and tin represent a serious health risk and environmental problem. A requirement for lead-free solders was implemented into the EU legislation.

•The introduction of lead-free solders is associated with practical difficulties - lead-free solders presently used have worse mechanical properties and higher melting temperature T_m.

•A promising approach in lowering melting point is the use of lead-free solder pastes [1,2].

In this work, we studied the effect of lowering melting point of silver powder, prepared in our laboratory by wet chemical analysis. The melting point of bulk silver (962°C) is substantially lowered, making silver and its powdered alloys applicable as solders.

Theory

The dependence of melting point depression of a small particle T_m on its diameter r in comparison to the melting point T_m^{bulk} of a bulk material [3-5]. H_m^{bulk} is the enthalpy of fusion of the bulk material, σ is the surface free energy and ρ is the density of solid (S) and/or liquid (L) phase, respectively.

$$\Delta T = T_m^{bulk} - T_m(r) = \frac{2T_m^{bulk}}{H_m^{bulk}\rho_s r}\left[\sigma_s - \sigma_L\left(\frac{\rho_s}{\rho_L}\right)^{\frac{2}{3}}\right]$$

Experimental

Wet chemical synthesis of Ag nanoparticles proceeded in two steps:

$$AgNO_3 + 2NH_2C_{12}H_{25} \xrightarrow{CH_3CN} \left[Ag\left(NH_2C_{12}H_{25}\right)_2\right]NO_3$$

$$\left[Ag\left(NH_2C_{12}H_{25}\right)_2\right]NO_3 + NH_2C_{12}H_{25} \xrightarrow{\Delta t} \text{nano Ag}$$

Sandwiches **copper - silver nanopowder – copper** were prepared and annealed at various temperatures from 200°C to 350°C for 25 to 30 min. Cross sections were studied using electron microscopy and depth sensing indentation. Shear tests were performed on sandwiches to evaluate the quality of joints.

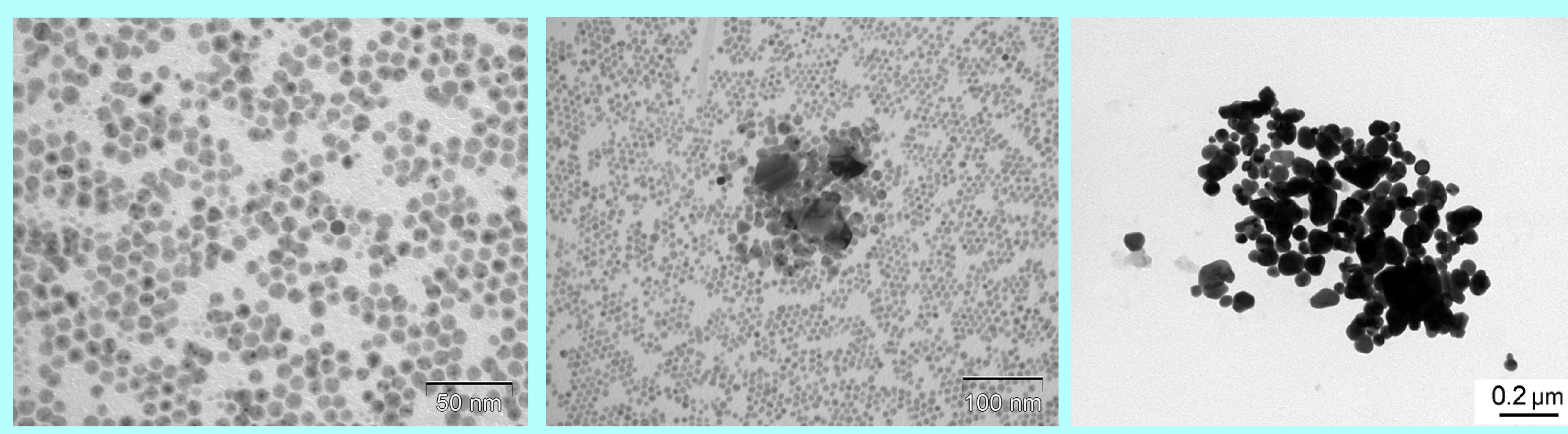
References

1. F.P. McCluskey, M. Dash, Z. Wang, D. Hurd, Microel. Reliability **46** (2006) p1910.
2. J.I. Youn, W. Ha, Y.J. Kim, Adv. Mater. Res. **15- 17** (2007) p995.
3. Pawlow, P.: Z.Phys.Chem. 65 (1909), 545.
4. Buffat, P., Borel, J.-P.: Phys.Rev.A 13 (1976), 2287.
5. Borel, J.-P.: Surf.Sci 106 (1981), 1.

The research has been supported by the Czech Science Foundation (Project 106/09/0700).

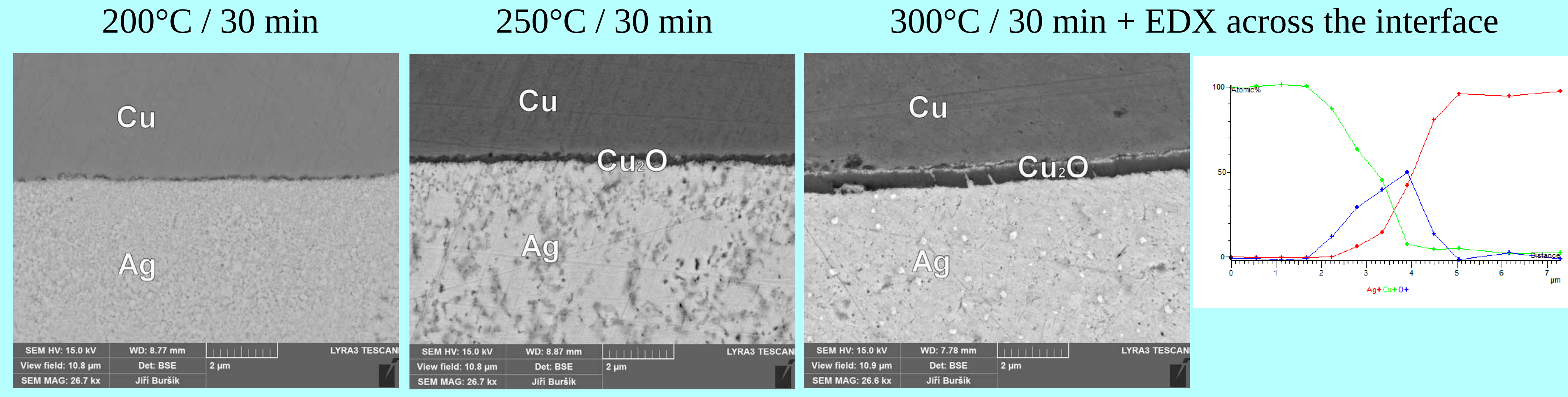
Results

TEM micrographs of Ag nanoparticles on a holey carbon film. The majority of particles have diameter around 10 nm, the size distribution is narrow. Sporadic clusters of larger particles were found. The commercial powder on the last image has substantially higher average particle size (note different scale bars).



Cross sections of **Cu/nanoAg/Cu** sandwiches were studied using a TESCAN LYRA 3XMU FEG/SEMxFIB and JEOL JSM 6460 SEM with Oxford Instruments INCA Energy analyser. Increasing thickness of interface oxide layer can be observed with increasing temperature of annealing.

200°C / 30 min | 250°C / 30 min | 300°C / 30 min + EDX across the interface



Depth sensing indentation tests (Fischerscope H100) were performed on cross sections in the central nanoAg region to characterize local mechanical properties of the sintered powder. Moreover, shear tests were carried out on sandwiches at two shear loads (Zwick Roell):

Results of depth sensing indentation tests:

sample	T[°C]	t[min]	HM[GPa]	H_{IT}[GPa]	Y[GPa]	CR[%]
1	250	25	0.90±0.10	1.15±0.07	20±2	3.3±0.9
2	300	25	1.08±0.25	1.82±0.15	37±3	1.3±0.4
3	200	30	0.72±0.12	1.10±0.25	17±4	4.2±1.5
4	250	30	0.87±0.14	1.20±0.18	18±4	3.5±1.2
5	300	30	1.00±0.46	1.43±0.44	32±4	3.0±1.1
6	350	25	0.85±0.06	1.07±0.09	35±2	3.0±1.0

Results of shear tests on the sample annealed at 350 °C:

aux. load [g]	E [GPa]	Rm [MPa]
500	20.0	23
100	12.0	16

Samples 3,4,5 were heated up inside the furnace from the room temperature, the other samples were placed in the furnace already at the declared temperature. Martens hardness HM, indentation hardness H_{IT}, elastic modulus $Y=E/(1-n^2)$ and creep CR values were obtained at testing load of 5mN. The creep values are expressed as the percentage of the maximum indentation depth.

Summary

Comparison between the in-house prepared Ag nanopowder and a commercial product shows smaller average particle size and more uniform particle size of the former.

For Ag nanopowder the annealing temperature as low as 200°C is sufficient to produce a continuous Ag layer and to form a firm junction between copper plates. A Cu_2O transition layer of increasing thickness is observed at the Cu-Ag interfaces annealed at 200 to 350°C.

Mechanical properties of the sintered Ag nanopowder layer reflect obviously the choice of annealing temperature. Moreover also other details play important role, namely the heating rate.