Bimodal size distributed silver nanoparticles on copper substrate: in situ heat-treating under air and protective atmospheres

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ABSTRACT

Silver bimodal nano-suspension was prepared by a wet synthetic route. Organic cover protected the particles. Interaction with copper substrate was monitored. The phenomena starting with temperature activation of the free surface of metallic nanoparticles and finishing with the formation of a bulk layer of Ag in between two Cu substrate were monitored by different in situ methods of thermal analyse, microscopy and conductivity measurement. This monitoring was carried out under different outer gas conditions. An important outcome is the estimation of heat effect, which is produced during low-temperature sintering and aggregation of the Ag nanoparticles.

Keywords: aggregation; low temperature sintering; nano heat effect; DSC; FTIR.

1 INTRODUCTION

Wasted electronic devices represent remarkable sources of lead pollution and serious environmental problem. It exists an ongoing strong drive to find the better lead-free solder alternatives. Some alternatives to classical soldering process can be found for example in the field of nanoscience. Properties of metal and alloy nanopowders are significantly different from the behaviour of the bulk materials. Moreover, phase diagrams of nanopowders differ substantially from those of the bulk materials [1]. The dependence of liquidus temperature on the particle size is an important feature of nanoparticles.

The phenomenon of melting point depression of the metallic nanosized particles is under long time view [2], [3]. Melting point of metallic nanosized particles reveals the temperature depression potential up to 0.6 Tm of the bulk metal in some cases (Au, 2nm) [4], [2], [5].

Silver represents a simple model material, which can be used for theoretical study of metal nanosintering. The sintering temperature is usually reported ranging 220-380°°C that is about 0.42 Tm of bulk silver. Joining Cu substrates using the suspension Ag-nano particles seem to be a good alternative [6] to standard soldering but the mechanical properties of joints prepared on air below 350°°C are still doubtful.

The goal of this contribution is basic research of low-temperature sintering of silver nanoparticles revealing bimodal size distribution. The aim of consequent studies will be use of the knowledge that touch the mechanism of interactions of nanoparticles, nanoparticle protective shell, distribution of nanoparticles and nano-metal interaction with substrate.

2 EXPERIMENT

Silver nano-suspensions were prepared by a wet synthetic route [7]. Liquid phase consisted of an organic solvent and the particles had a bimodal distribution with a very narrow size distribution (compare Fig. 1.). The surface of the nanoparticles was protected from oxidation by an organic surfactant. Bimodal nanoparticle distribution (TEM diameters: (25±5) nm and (110±15) nm) was investigated because of it is more advantageous for some applications than unimodal. Wet synthesis has provided long-term stable suspension with an high fraction of nanoparticles. Share of Ag nanoparticles was higher then 55 wt%.

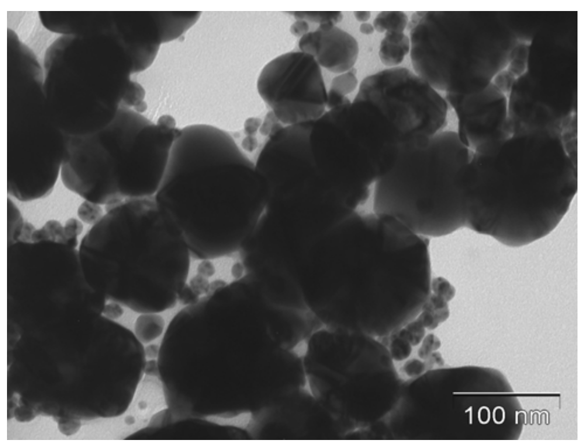

Fig. 1. Bimodal size distribution Ag nanoparticles (TEM).

Thermal activation of the free surfaces of metallic nanoparticles, nanoparticle aggregation, low-temperature sintering, and the formation of a bulk interlayer of Ag in between two Cu substrate were monitored via in situ methods (DSC / TG, FTIR, conductivity measurement and visualization in electron microscope). This in-situ monitoring was carried out under different conditions (inert, air, vacuum). An important outcome is the evaluation of heat effect, which is produced during low-temperature sintering and aggregation of the Ag nanoparticles.

The Ag-nanoparticle suspension and copper substrate plates were used for preparation of sandwich like samples: Cu / Ag-nano / Cu.

Each sample sandwich was inserted between two electrodes (one of them equipped with thermocouple). This arrangement was given into preheated furnace (on constant temperature in range from 200 to 350°C) with air and both electrical resistance and parallel temperature measurements in situ were performed. The joined Cu/Ag/Cu sandwich samples were obtained. These sandwich samples, prepared at the isothermal external conditions (IEC), were used for further investigation.

Apparatus for DSC thermal analysis (STA409) was also used for in-situ preparing sandwiches of Cu/Ag/Cu. Each sample sandwich was closed in small alumina crucibles, the device was closed and the sample heated constantly up. Thermal effects were measured under different atmospheres. The prepared Cu/Ag/Cu (DSC) sandwiches were subjected to the same analysis as the Cu/Ag/Cu (IEC) samples.

DSC measurement was complemented by Fourier transform infrared spectroscopy (FTIR). DSC furnace with heated sample was connected with FTIR spectroscope via capillary heated on 300˚C. All gas species produced during DSC experiment were led into FTIR spectroscope and analysed.

3 RESULTS

Suspension of the synthesized Ag nano-particles was characterised by means of transmission (TEM) and high-resolution electron microscopy (HTEM). The HTEM showed that the particles have a very regular lattice of the fcc silver phase (see Fig. 2., view in the direction 111). The surface oxidation of the silver nanoparticles has not been observed.

In-situ results of paralel both temperature monitoring and electrical resistance were recorded during the Cu/Ag/Cu (IEC) sample preparation in preheated furnace. The obtained records enable to distinquish several stages during sandwich preparation. First stage is caused by solvent phase evaporation. Consequent stages reflect nanoparticle protective shell destruction, sintering, and copper substrate oxidation.

The prepared Cu/Ag/Cu (IEC) sandwich samples were observed by means of both optical and electron microscopy. The presence of the compact sintered Ag layer between the copper substrates was revealed (see Fig. 3.). The Cu_2O interlayer between Ag bulk and Cu substrate was occurred at higher temperatures but it exists a lower temperature range for which this oxide does not form at given operating conditions.

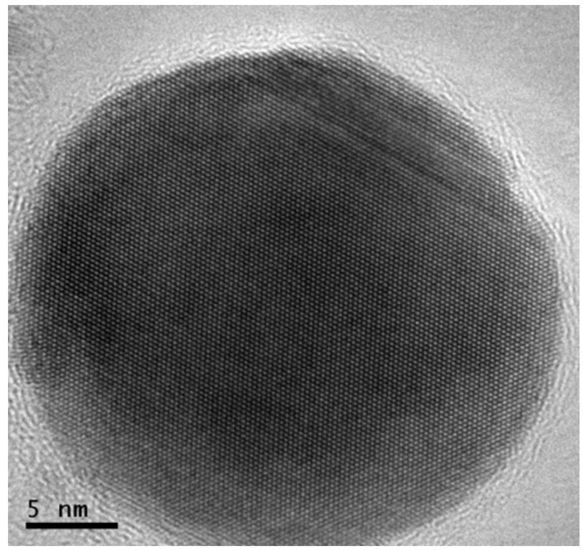

Fig. 2. Detail of one silver nanoparticle (HTEM).

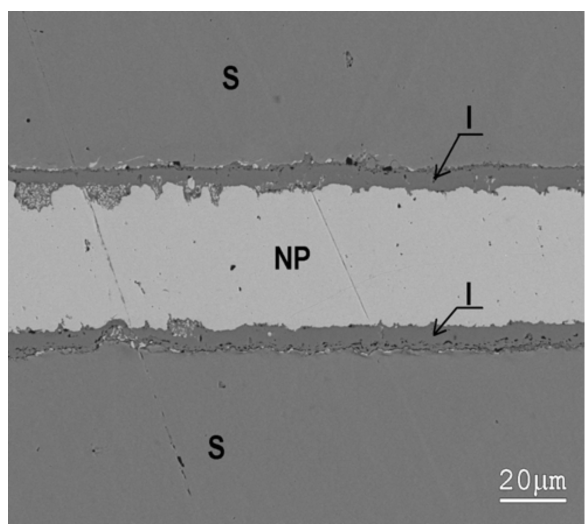

Fig. 3. Micrograph of the Cu/Ag/Cu (IEC) sandwich sample prepared at 350°C/4hrs (TEM). S (Cu substrate), NP (sintered Ag nano powder), I (Cu_2O interlayer).

Important experiment is measurement of thermal effects in situ during the preparation of Cu/Ag/Cu (DSC) sandwich samples. The DSC/TG results at 10K/min heating rate are shown in Fig. 4.

Thermogravimetry curve reveals massive solvent evaporation at temperature range (60-90) ˚C. Further mass loss between (110-320) ˚C represents an destruction of the nanoparticle protective shell and oxidation of the organic residuals.

Endothermic peak (under air) can be observed with the onset given by evaporation of suspension liquid phase. Also the other stages corresponding to stages occurred during in-situ electrical conductivity measurement were found. Micrograph of the Cu/Ag/Cu (DSC) sandwich sample is given on Fig. 5.

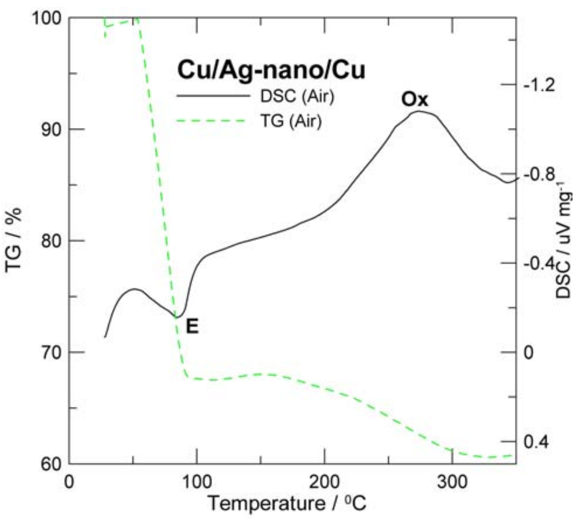

Fig. 4. The TG/DSC signals of the Cu/Ag-nano suspension /Cu samples under synthetic air (first heating sequence). DSC curve reveals liquid phase evaporation (E) and oxidation of organic species (OX).

The FTIR detection was used to determine species occurring during heating. Measured IR spectra revealed presence of the evaporated liquid phase, residuals of protective organic shell, products of combustion, and of course water and carbon oxides.

The atmosphere change of the synthetic air for extra pure argon showed completely different thermal effects. Oxidising peak of organic residuals was no occurred. Two exothermic peaks were occurred. We suppose that the peaks represent aggregation of both small and big Ag nanoparticles. Thanks to high sensitivity of the DSC apparatus the calorimetric method enabled us to estimate the total heat of aggregation and sintering. The value is ranging (40-75) J / (1 mg Ag nanoparticles) and depends on mass fractions of the small and big nanoparticles.

All endothermic and exothermic signals were occurred only during first heating sequence of the DSC/TG measurement. Consequential second and third heating sequences do not reveal any heat signals or effects. Consequential TG curves do not show weight changes of the Cu/Ag-nano/Cu sandwich sample.

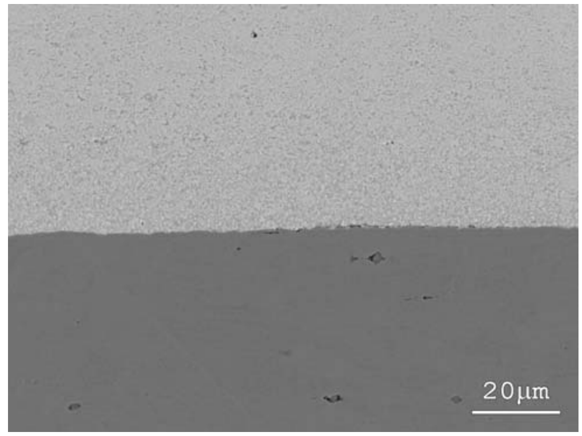

Fig. 5. Micrograph of the Cu/Ag/Cu (DSC) sandwich sample (SEM). Cu/Ag interface cross-section (Ag sintered above, Cu substrate below).

4 DISCUSSION

The application of the wet synthesis enables to prepare the bimodal suspension of the Ag nanoparticles, which involves high fraction of the silver metal. This bimodal suspension is more suitable for joining two solid copper substrates at low temperatures. The suspension of the Ag-nanoparticles in liquid organic phase is more effective than use of solid nanopowder.

Examination of Cu/Ag/Cu (IEC) sandwich samples reveals a consistency between the sandwich microstructure observed after sample preparation and the in-situ measuring during their preparation. The microstructures agree with phase diagram of Cu-Ag-O system [8].

The liquid phase evaporation, which enables to start a destruction of the surfactant protective shell, enables to decrease of electrical resistance in the second stage of the sandwich preparation because only then can Ag nanoparticles aggregate to form the sintered Ag layer. The increase in electrical resistance in the final stage can be easily explained by the fact that Cu substrate and oxygen form the layer of copper oxide Cu_2O, which is a semiconductor.

It is more evident how Cu/Ag/Cu (DSC) sandwich join in flow of high pure argon is created if we look on the results of the experiment, which was carried out in the STA calorimeter. Here the process of the low temperature sintering of the Ag nanoparticles can be monitored using DSC method in situ. The start of the first heating curve reveals a distinct endothermic peak, which is caused by the evaporation of the carrying liquid phase. We suppose, the organic protective shell of nanoparticles is destroyed subsequently and metallic surfaces of Ag nanoparticles come into contact. Further, the first heating curve reveals double of distinct exothermic peaks, which reflect the silver metal agglomeration. The over heating of the sample reach approximately 2-3stC with respect to reference crucible. This is a simple mechanism how Ag nano-particles can get rid of the surface energy.

This aggregation and sintering effects were measured. The heat released during exothermic storyline from 120 to 210°C is about +(40-85) J per 1g of Ag. (Note: the latent heat of melting of Sn38wt%Pb solder is –46J per 1g of alloy [9]).

The protection of nanosilver from oxidation at low temperatures (below the sintering end at 210°C) is important. The production of the oxygen gas above cca 240°C causes a violation of the connection. Generally it is believed that decomposition temperature of bulk silver oxide in air is easy but detailed analysis of the kinetics of deoxidation of Ag in air performed Raman spectroscopy shows that the situation may be more complicated [01Geo]. Decomposition temperature probably also depends on the particle size of the silver oxide.

An important influence on the mechanical strength of the Cu/Ag/Cu join has the heating rate. Generation of vapour phase from the liquid suspension of Ag nano-particles may give rise to plumes of Ag-nanoparticles and thereby impair the mechanical strength. Therefore, there is a speed limit of heating, which cannot be exceeded. Its value depends mostly on the content of Ag nano-particles in suspension and on the geometry of the joints.

5 CONCLUSION

The results obtained during in-situ preparation of Cu/Ag/Cu joints allow better understanding the processes to occur when using a suspension of bimodal Ag nanoparticles in order to create the conductive bonding with the Cu substrate at low temperatures. The important factor is to protect the surface of the Ag-nanoparticles against oxidation. It was confirmed that the preparation of low temperature joints is more effective when the Ag nanoparticles suspension in the liquid phase is applied. Oxygenated Ag-nanoparticles can form also bulk silver interlayer (also under air) but at temperature above 320ºC when silver oxide and all organic species are decomposed.

The starting temperature of the both fine and coarse Ag nanoparticle aggregation can be controlled by the choice of liquid phase and surfactant if the nanopowders are free of silver oxide. We observed the aggregation temperature between 120 210ºC. The aggregation and sintering was occurred as exothermic effect +(40-85) J per 1g of the Ag nanoparticles. The determination of the heat effects of low temperature sintering and aggregation is particularly important for determining the surface energy of Ag nanoparticles and thermodynamic driving forces for creating bulk Ag. It is also one of the necessary inputs for the model calculations of the nanoalloy phase diagrams on the basis of Ag.

The results of the work suggest that the aggregation and sintering properties of the Ag nanoparticles and of the other metal nanoparticles can be used as an alternative to lead-free soldering. Metal nanopowders are promising materials for the preparation of lead-free nanosolders. The prepared joints are applicable at temperatures higher than processing temperature.

These findings are important for other applications in order to use nanoscale properties for advanced nanotechnology. The knowledge gained will enable better and more effectively carry out optimization of conditions for the preparation of nano-engineering systems that match better needs of mechanical resistance, electrical/thermal conductivity, low degree of cracks and defects, quick preparation, etc.

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