



# Formation of $\text{Cu}_6\text{Sn}_5$ phase by cold homogenization in nanocrystalline Cu–Sn bilayers at room temperature



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## ARTICLE INFO

### Article history:

Received 9 July 2015

Received in revised form 15 October 2015

Accepted 15 October 2015

Available online 23 October 2015

### Keywords:

Cu/Sn nanostructured thin film

Solid state reactions

Soldering

SNMS depth profiling

## ABSTRACT

Solid state reaction between nanocrystalline Cu and Sn films was investigated at room temperature by depth profiling with secondary neutral mass spectrometry and by X-ray diffraction. A rapid diffusion intermixing was observed leading to the formation of homogeneous  $\text{Cu}_6\text{Sn}_5$  layer. There is no indication of the appearance of the  $\text{Cu}_3\text{Sn}$  phase. This offers a way for solid phase soldering at low temperatures, i.e. to produce homogeneous  $\text{Cu}_6\text{Sn}_5$  intermediate layer of several tens of nanometers during reasonable time (in the order of hours or less). From the detailed analysis of the growth of the planar reaction layer, formed at the initial interface in Sn(100 nm)/Cu(50 nm) system, the value of the parabolic growth rate coefficient at room temperature is  $2.3 \times 10^{-15} \text{ cm}^2/\text{s}$ . In addition, the overall increase of the composition near to the substrate inside the Cu film was interpreted by grain boundary diffusion induced solid state reaction: the new phase formed along the grain boundaries and grew perpendicular to the boundary planes. From the initial slope of the composition versus time function, the interface velocity during this reaction was estimated to be about 0.5 nm/h.

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## 1. Introduction

Copper–tin (Cu–Sn) layers are of great technological and scientific interest, and are frequently used to avoid health and environmental problems caused by the use of lead-based alloys [1]. Sn thin films deposited on Cu-based substrate are often used for soldering of microelectronics devices [2]. According to the Cu–Sn phase diagram, there are two intermetallic phases which exist below 100 °C,  $\text{Cu}_3\text{Sn}$  ( $\epsilon$ -phase) and  $\text{Cu}_6\text{Sn}_5$  ( $\eta$ -phase). The latter is richer in Sn content as compared to the former and is the only phase formed in bimetallic Cu–Sn films aged at room temperature [3–7].

The formation and growth of intermetallic compounds of Cu–Sn have been extensively studied [4–13]. In the pioneering works of Tu and his coworkers [3,14,15] the most important conclusions, obtained in thin film systems with Sn and Cu thicknesses in the range of 180–2500 nm, were as follows: i) The reaction between the Cu and Sn started spontaneously during the deposition at room temperature and led to the formation of  $\text{Cu}_6\text{Sn}_5$  phase. Prolonged aging resulted in increase of amount of the (ordered)  $\text{Cu}_6\text{Sn}_5$  phase. No  $\text{Cu}_3\text{Sn}$  was detected even after very long annealing times. ii) Parallel with the formation of the  $\text{Cu}_6\text{Sn}_5$  phase it compressed the Sn and led to the formation of whiskers on the free surface of Sn. iii) The  $\text{Cu}_6\text{Sn}_5$  phase grew linearly with time,

but it was mentioned [15] that “The linear growth ... may suggest that the compound is not of layer type when the grains are very thin or small. The morphology of the  $\text{Cu}_6\text{Sn}_5$  phase in the early stage of formation deserves more detailed studies.” iv) From Rutherford backscattering investigations, using W markers, it was concluded that the dominant diffusing species is Cu. The phase grew into the Sn side and in their model of phase growth (see Fig. 6a in [15]) they neglected the diffusion of Sn into Cu arguing that in the growth of the phase both the interstitial diffusion of Cu in Sn and contribution from the transport along grain boundaries are important (the growth rate was slower in the thicker film [14]). The order of magnitude estimation of effective interdiffusion coefficient, related to the phase growth, gave  $10^{-17}$ – $10^{-16} \text{ cm}^2/\text{s}$  values [14,15].

In addition to the above results it was concluded, from the analysis of the data obtained between 160 and 200 °C using also inert markers [10,16,17], that a) the intermetallic growth was related to Sn diffusion into the nanocrystalline Cu, which is in contrast to the point iv) above and b) the growth rates were about 10 times larger for nano-grained thin films than in coarse-grained massive samples.

Two more recent investigations also deserve attention. In [18] it was found that, in electroplated Cu/Sn bilayers the growth of the  $\text{Cu}_6\text{Sn}_5$  phase was parabolic, mentioning that the linear growth undergoes to parabolic one with increasing the thickness of the growing layer. Furthermore, the  $\text{Cu}_6\text{Sn}_5$  layer was continuous, but not uniform: at some locations it was very thin while at other positions relatively

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thick protrusions were observed. From the temperature dependence of the parabolic growth constant of the  $\text{Cu}_6\text{Sn}_5$  phase  $K = 2 \times 10^{-15} \text{ cm}^2/\text{s}$  can be estimated at room temperature.

In [19] a very careful and detailed investigation of solid state reaction between several microns thick Sn and polycrystalline, but bulk, Cu substrate was carried out at room temperature. The following observations were made: I) The  $\text{Cu}_6\text{Sn}_5$  phase was formed, predominantly at the intersections of the Sn grain boundaries with the Sn/Cu interface, on the Sn side and grew only into Sn. During continuous aging the  $\text{Cu}_6\text{Sn}_5$  proceeded significantly into the Sn grain boundaries, accompanied with a growth perpendicular to the grain boundaries (GBs). Upon prolonged aging the fine-grained  $\text{Cu}_6\text{Sn}_5$  phase appeared on the face of the Sn grains adjacent to the Sn/Cu interface. Heterogeneous nucleation of these  $\text{Cu}_6\text{Sn}_5$  islands and their subsequent coalescences led to the formation of a closed planar layer. II) In the interpretation of the above observations the authors of [19] expressed their opinion that the formation of the  $\text{Cu}_6\text{Sn}_5$  phase at the Sn/Cu interface is the result of volume diffusion. After the formation of the compact  $\text{Cu}_6\text{Sn}_5$  layer, the further planar growth of it was slower. At the same time the diffusion of Sn into the large grained Cu was neglected.

This study provides information concerning the effect of aging time on the growth kinetics and phase formation mechanism of  $\text{Cu}_6\text{Sn}_5$  in the Cu–Sn nanocrystalline films. In contrast to previous studies, in our films both sides were really nanostructured and the application of the SNMS depth profiling is a novelty.

## 2. Experimental

Two sets of nanocrystalline Cu–Sn thin film samples of different layer thicknesses were prepared by DC magnetron sputtering in a vacuum of  $10^{-7}$  mbar at room temperature. The films were obtained by consecutive sputtering of Cu followed by Sn onto (111) oriented SiN wafer that works as a barrier to prevent the Si diffusion in the system. Disk-shaped Cu and Sn targets with diameter of 2 in. were used as sputtering sources. The thicknesses of the layers were as follows: Sn(100 nm)/Cu(50 nm) and Sn(50 nm)/Cu(25 nm). The samples have the thickness ratio required for the formation of the intermetallic phase of  $\text{Cu}_6\text{Sn}_5$  [3].

In the sputtering process a plasma discharge was maintained above the targets, sputtered onto the SiN substrate by  $\text{Ar}^+$  ion bombardment ( $P = 5 \times 10^{-3}$  mbar). The deposition chamber was connected to ultra-high vacuum system (with  $10^{-7}$  mbar). The sputtering chamber has three magnetrons with shutters. The nominal thicknesses of layers were estimated from the sputtering time and the predetermined deposition rate of each target. The sputtering rates were calculated from the layer thickness measured by the AMBIOUS XP-1 profilometer.

The Cu–Sn thin films were aged for various times. The concentration–depth profiles were measured by Secondary Neutral Mass Spectrometry, SNMS (INA-X, SPECS, GmbH, Berlin) [20,21], which works with noble gas plasma and the bombarding ion current has an extremely high lateral homogeneity. The low bombarding energies (in the order of 100 eV) and the homogeneous plasma result in an outstanding depth resolution ( $<2$  nm) [22,23]. The SNMS data (intensity (cps)–time (s) spectra) were transformed into concentration–depth profiles, using the sensitivity factors of the elements and by using the proportionality between the intensity and the number of sputtered particles [24].

The structure of thin film couples and its changes due to diffusion and solid state reaction were studied by X-ray diffraction, XRD, using Siemens X-ray diffractometer, Cu-K $\alpha$  X-rays of wavelength  $\lambda = 0.154$  nm and the data were taken for the  $2\theta$  range between  $20^\circ$  and  $60^\circ$ .

## 3. Results

### 3.1. Phase formation in Sn(100 nm)/Cu(50 nm) films

Fig. 1a shows the intensity versus sputtering time of the as-deposited Sn(100 nm)/Cu (50 nm)/SiN sample. The intensity was converted to

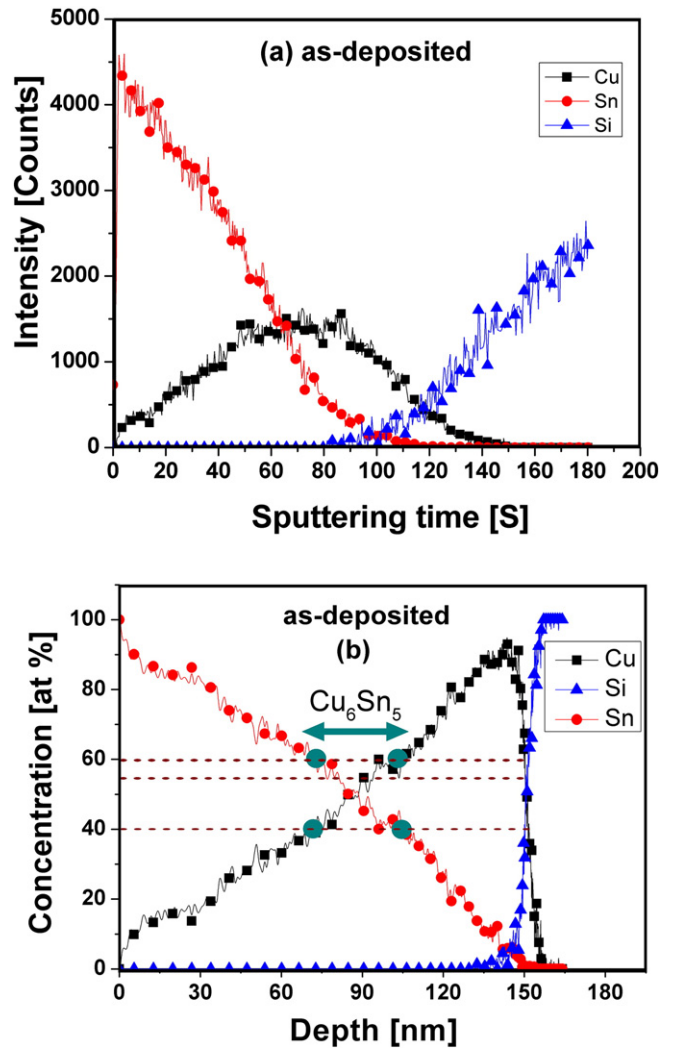


Fig. 1. SNMS profile of the as-deposited Sn(100 nm)/Cu(50 nm)/SiN sample; (a) Intensity versus sputtering time. (b) Concentration versus depth. The presence of intermetallic phase is indicated by a nearly flat region around the initial interface on the Cu and Sn curves (see also the text).

concentration using the sensitivity factors of the elements and the sputtering time was also converted to depth as shown in Fig. 1b. In the initial state, Cu is observed throughout the entire layer of Sn. Sn atoms

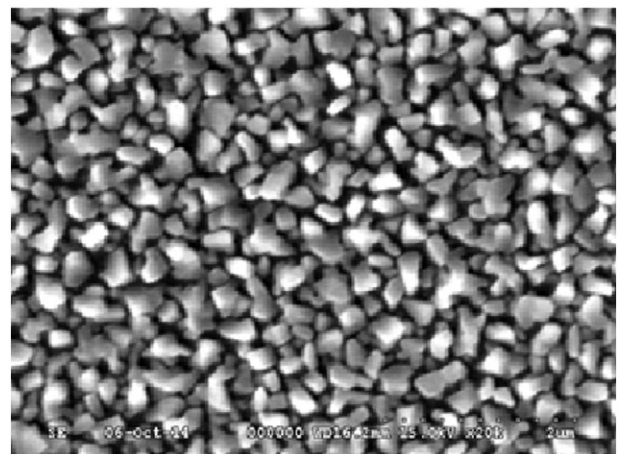


Fig. 2. SEM shows the top view of the as-deposited Sn(100 nm)/Cu(50 nm)/SiN sample. The average size of the granules is about 200 nm.

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