# Solid-state Synthesis of $Cu_6Sn_5$ Intermetallic in Sn/Cu Thin Films

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**Abstract.** The study results of solid-state synthesis of the $Cu_6Sn_5$ intermetallic in the Sn/Cu thin-film systems during vacuum annealing from room temperature to $300\,^\circ C$ are presented. The initiation and finishing temperatures of the solid-state reaction between the Cu and Sn nanolayers and the phase composition of the reaction products were determined. The synthesized thin films were monophasic and consisted of the hexagonal $\eta$-$Cu_6Sn_5$ phase. It is assumed that the initiation temperature of the solid-state reaction in Sn/Cu thin films is associated with the start temperature of the reverse polymorphic transformation $\eta' \to \eta$ between the monoclinic and hexagonal $Cu_6Sn_5$ phases.

**Keywords:** thin films, solid-state synthesis, $Cu_6Sn_5$ intermetallic, $\eta \leftrightarrow \eta'$ reversible polymorphic transformations.

## Introduction

$Cu_6Sn_5$ is an important intermetallic for electric interconnects and anode materials of Li-ion batteries, with $\eta \leftrightarrow \eta'$ reversible polymorphic transformations between the hexagonal and monoclinic $Cu_6Sn_5$ phases. The polymorphic transformation of $Cu_6Sn_5$ has the potential to generate internal stresses in soldered joints during both the soldering process and the subsequent device operation involving thermal cycling [1]. It is known that a layer of $Cu_6Sn_5$ forms instantaneously between the Sn rich solder and the Cu substrate during the early stages of soldering [2–4]. However, fundamental understanding of intermetallic compound formation and the associated interface motion between the Cu and Sn nanolayers during the reaction is still very limited. An understanding of these fundamental properties is essential for better control and improvement of the process of nano-soldering and $Cu_6Sn_5$ intermetallic synthesis. The Sn/Cu thin films were chosen as a model system for $Cu_6Sn_5$ intermetallic synthesis.

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Numerous studies of solid-state synthesis in nanofilms show that as the annealing temperature at the interface of the film reagents is increased, a certain temperature $T_{in}$ (initiation temperature) is reached where only one phase, called the first phase, is formed. As the annealing temperature is further increased other phases can also occur, forming a phase sequence [5–7]. The formation of only one first phase among many equilibrium phases, the low initiation temperatures and the migration of only one element during the reaction [8, 9] are unique and inexplicable phenomena of solid-state synthesis in thin films.

Our previous works on solid-state reactions in thin films showed that the first phase is the phase that, according to the phase diagram, has the lowest temperature of structural phase transformation ($T_K$) and the initiation temperature ($T_{in}$) of the solid-state reaction coincides with the temperature of the solid-state structural transformation of the first phase ($T_{in} = T_K$) [10, and references therein]. The equality $T_{in} = T_K$ indicates the general nature of chemical interactions that control both solid-state transformations and solid-state reactions in bilayers. Consequently, low-temperature reactions in A/B bilayers occur only in binary systems A-B, which have corresponding low-temperature solid-state transformations. Therefore, if the A-B phase equilibrium diagram is well established then the equality $T_{in} = T_K$ makes it possible to predict the first phase and its initiation temperature. Conversely, the study of reactions in A/B bilayers with different layer ratios is the study and refinement of the low-temperature part of the A-B phase diagram [10].

This work presents the results of studying the synthesis of $Cu_6Sn_5$ thin films obtained by initiating a solid-state reaction in bilayer Sn/Cu film systems. The synthesis was carried out by vacuum annealing from room temperature to 300 °C. The initiation and finishing temperatures of the solid-state reaction between the Cu and Sn nanolayers and the phase composition of the reaction products were determined. Based on the analysis of the thin-film solid-state reactions, the general chemical mechanisms controlling both the synthesis of $Cu_6Sn_5$ in the Sn/Cu bilayer and the reversible polymorphic transformations $\eta \leftrightarrow \eta'$ between hexagonal and monoclinic phases $Cu_6Sn_5$ are affirmed.

## Experimental procedures

To prepare the bilayer Sn(110 nm)/Cu(60 nm) films, the thicknesses of the Cu and Sn layers were chosen from the composition ratio of the $Cu_6Sn_5$ intermetallic compound ($\cong$ 54.5 at.% Cu, $\cong$ 45.5 at.% Sn). The fabrication of the initial bilayer Sn/Cu films was carried out by thermal deposition of the Sn and Cu, with thicknesses of 110 nm and 60 nm, respectively, on a glass substrate in a vacuum at a residual pressure of $1.3 \times 10^{-4}$ Pa. To prevent an uncontrolled reaction between the Sn and Cu layers, the deposition was carried out at room temperature. Materials of a high level of purity were used for the evaporation: Cu (99.99 %), and Sn (99.995 %). The Sn and Cu layer thicknesses were determined by X-ray fluorescence analysis. The total thicknesses of the bilayer films under study were $\sim$ 170 nm.

The initial samples were annealed under a vacuum of $1.3 \times 10^{-4}$ Pa Pa at temperatures from room temperature to 300 °C in intervals of 50 °C, holding for 30 minutes at each temperature. The phase formations and structural changes occurring at the interface between the Sn and Cu layers as the annealing temperature increased were identified with a DRON-4-07 diffractometer ($CuK_\alpha$ radiation). The electron microscopy studies were performed on a Hitachi HT7700 transmission electron microscope equipped with a scanning transmission electron microscopy system and with an energy dispersion X-ray spectrometer.

## Results and discussion

The initial Sn/Cu samples were bilayer thin films consisting of Sn and Cu nanolayers. The diffraction pattern (Fig. 1a), obtained from the initial Sn/Cu film showed diffraction reflections

characteristic of the phases: $\beta$-Sn (the space group $I4_1/amd$, lattice constants: $a = 5.831\,\text{Å}$, $b = 5.831\,\text{Å}$, $c = 3.182\,\text{Å}$ PDF Card # 00-004-0673) and Cu (the space group Fm-3m, lattice constant $a = 3.615\,\text{Å}$ PDF Card # 00-004-0836)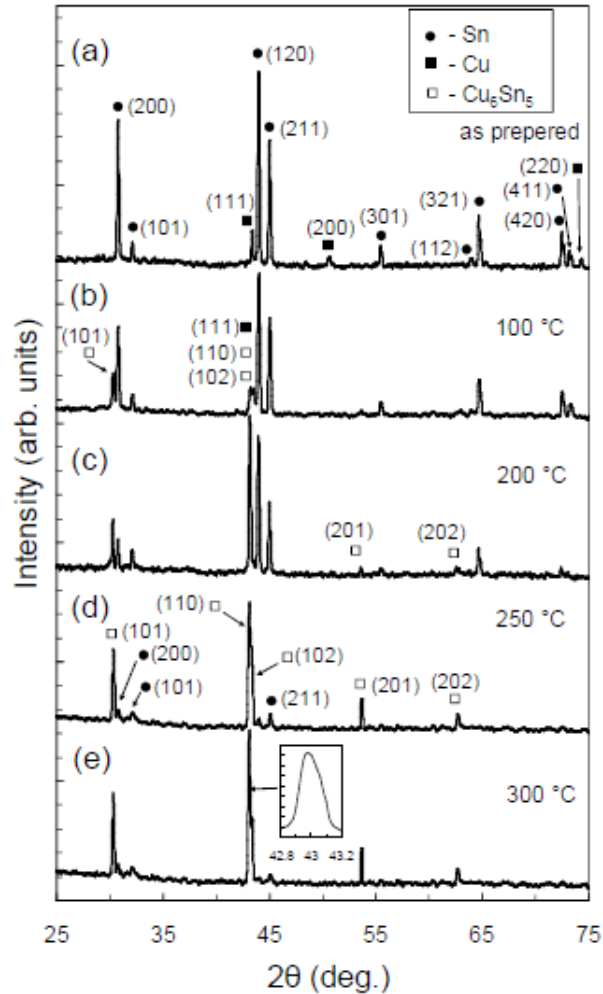. On Fig. 1c,d,e the diffraction patterns obtained at $200\,^{\circ}$C, $250\,^{\circ}$C and $300\,^{\circ}$C are shown.



Fig. 1. X-ray diffraction patterns of $Sn(110\,\text{nm})/Cu(60\,\text{nm})$ thin-film systems under vacuum annealing from room temperature to $300\,^{\circ}$C

The initial samples were annealed under a vacuum of $1.3 \times 10^{-4}\,$Pa at temperatures from room temperature to $300\,^{\circ}$C. The diffraction pattern did not change until the temperature reached $100\,^{\circ}$C, when, in addition to the reflections corresponding to the Cu and $\beta$-Sn phases, the diffraction reflections from the $\eta$-$Cu_6Sn_5$ phase appeared (the space group $P6_3/mmc$, lattice constants $a = 4.206\,\text{Å}$, $c = 5.097\,\text{Å}$, PDF Card # 00-047-1575), indicating the beginning of the reaction between the Cu and Sn nanolayers (Fig. 1b). On Fig. 1c the electron diffraction patterns obtained at $200\,^{\circ}$C are shown. Reflections corresponding to the $\eta$-$Cu_6Sn_5$ phase are observed, and the intensities of the reflections corresponding to the Cu and Sn phases decrease, which indicates the continuation of the reaction between Cu and Sn. During the annealing process at $250\,^{\circ}$C and $300\,^{\circ}$C and after cooling the sample to $25\,^{\circ}$C (Fig. 1d, e), the diffraction pattern contained

only the reflections from the $\eta$-$Cu_6Sn_5$ phase, confirming that the Cu and Sn have reacted completely. A small number of low-intensity reflections from the unreacted tin were also present in the diffractogram. When the film was cooled under a vacuum from $300\,°C$ to $25\,°C$, no phase transformation $\eta \to \eta'$ was observed.

From the foregoing, it follows that the reaction between the copper and tin nanolayers in the film begins at an initiation temperature of $100\,°C$ and proceeds up to a temperature of $250\,°C$ over a length equal to the total film thickness d $= 170$ nm. The synthesized thin films were monophasic and consisted of the hexagonal $\eta$-$Cu_6Sn_5$ phase with a small amount of unreacted tin. The $\eta$-$Cu_6Sn_5$ grain size was estimated from the width of the $Cu_6Sn_5$ (110) reflection (Fig. 1d, inset) by the Scherrer formula d $= k\lambda/\beta\cos\theta$, where d is the mean crystal grain size, $\beta$ is the diffraction maximum width measured at half the maximum, $\lambda$ is the X-ray radiation wavelength (0.15418 nm), $\theta$ is the diffraction angle corresponding to the maximum of the peak, and $k = 0.9$. The calculated size of the $\eta$-$Cu_6Sn_5$ crystal grains was $55 \pm 5$ nm, which agrees well with the data obtained by the electron microscope (Fig. 2).
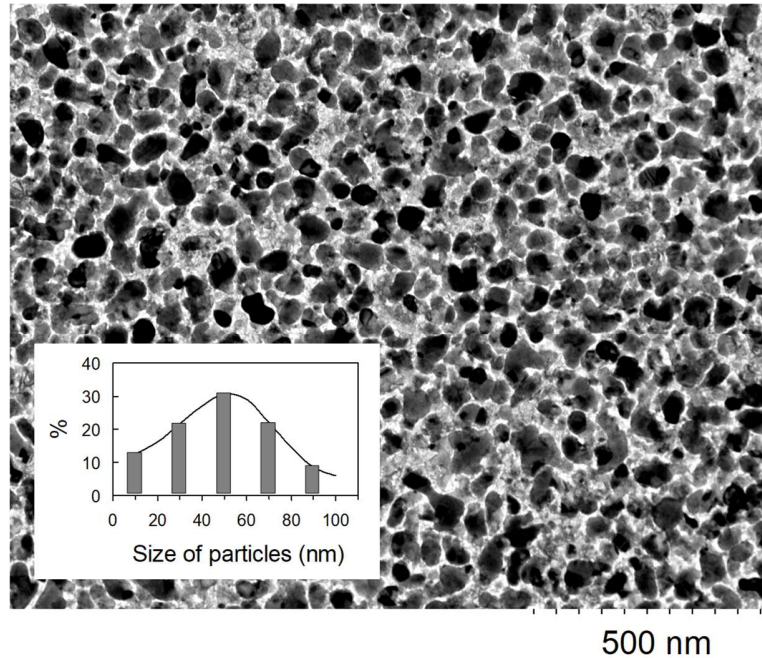


Fig. 2. The electron microscope image of $Sn(110\,nm)/Cu(60\,nm)$ thin-film after vacuum annealing at $300\,°C$

Our approach predicts that the solid-state reaction at the Sn/Cu interface should start with the formation of the first $Cu_6Sn_5$ phase at an initiation temperature $T_{in}$, regardless of the ratio of layer thicknesses, coinciding with the temperature of structural transformations in the $Cu_6Sn_5$ phase. According to the Cu-Sn phase equilibrium diagram the structural phase transition between the high-temperature hexagonal $\eta$-$Cu_6Sn_5$ and low-temperature monoclinic $\eta'$-$Cu_6Sn_5$ phases, which has a minimum temperature of $186\,°C$, is well established [11]. However, as is known, reversible phase transformations have a temperature hysteresis. For example, martensitic transformations are characterized by the temperature of the start $(M_s)$ and the finish $(M_f)$ of the direct transformation upon cooling and the temperature of the start $(A_s)$ and the finish $(A_f)$ of the reverse transformation upon heating. Therefore, it is reasonable to assume that the initiation temperature $T_{in}$ coincides with the reverse transformation start temperature $A_s$ $(T_{in} = A_s)$. The equality $T_{in} = A_s$ is satisfied by reactions in bilayers of Al/Ni [12], Ti/Ni [13], Mn/Fe [14] and

Cd/Au [15, 16], in which austenitic and martensitic phases are formed in the reaction products. Similarly, the $\eta \leftrightarrow \eta'$ reversible transformation can be characterized by the start $(T_s(\eta \to \eta'))$ and finish $(T_f(\eta \to \eta')$ temperatures of the direct transformation during cooling and the start $(T_s(\eta' \to \eta))$ and finish $(T_f(\eta' \to \eta))$ temperatures of the reverse transformation during heating. As the temperature rises, the transition temperature $T_s(\eta' \to \eta)$ can be defined as the starting temperature of the heating flow change using differential scanning calorimetry curves, which for Cu$_6$Sn$_5$ bulk samples is approximately equal to $\sim 150\,^\circ$C [17]. Studies of nanoscale systems have revealed that their phase transition temperatures are normally lower than those of bulk materials, which is due to the large surface area-to-volume ratio and the large number of defects [18, 19]. These factors and the extremely slow kinetics of the $\eta' \leftrightarrow \eta$ phase transformations may lead to the decreased start and finish temperatures of the direct and reverse transformations in the Cu$_6$Sn$_5$ thin films.

This study gives reason to assume that the temperature $T_s(\eta' \to \eta)$ coincides with the initiation temperature $T_{in}$ ($T_s(\eta' \to \eta) = T_{in} = 100\,^\circ$C). However, the real temperature $T_s(\eta' \to \eta)$ can be even lower. So K.N. Tu reports the growth of the $\eta'$-Cu$_6$Sn$_5$ phase at temperatures below room temperature [20]. This suggests a general scenario for solid-state synthesis in Sn/Cu bilayer films and reversible $\eta \leftrightarrow \eta'$ phase transformations: as the temperature increases to $T_{in} = T_s(\eta' \to \eta)$ the Sn/Cu interface remains sharp and at temperatures above $T_{in} = T_s(\eta' \to \eta)$ chemical interactions arise between the Sn and Cu atoms that destroy the chemical bonds in the Cu layer (Cu is the dominant diffusing species [20]) and transfer Cu atoms to the Sn layer to form the first $\eta$-Cu$_6$Sn$_5$ phase.

## Conclusion

The solid-state synthesis of the Cu$_6$Sn$_5$ intermetallic compound was carried out by vacuum annealing of Sn(110 nm)/Cu(60 nm) thin films from room temperature to $300\,^\circ$C. The thicknesses of the Cu and Sn layers were chosen to correspond to the composition ratio of Cu$_6$Sn$_5$ ($\cong 54.5$ at.% Cu, $\cong 45.5$ at.% Sn). The synthesis of the $\eta$-Cu$_6$Sn$_5$ phase begins at the initiation temperature $T_{in} \sim 100\,^\circ$C and proceeds up to a temperature of $\sim 250\,^\circ$C over the entire film thickness d = 170 nm. No phase transformation $\eta \to \eta'$ was observed when the film was cooled in the vacuum from $300\,^\circ$C to $25\,^\circ$C. The synthesized thin films were monophase and consisted of the hexagonal $\eta$-Cu$_6$Sn$_5$ phase with a small amount of unreacted tin. It is assumed that the initiation temperature of the solid-state reaction in Sn/Cu thin films is associated with the start temperature of the reverse polymorphic transformation $\eta' \to \eta$ between the monoclinic and hexagonal Cu$_6$Sn$_5$ phases. The analysis of the results obtained in this and many other works shed new light on the nature of atomic migration and first phase formation in the process of solid-state reactions in nanomaterials at low temperatures.

## References

[1] F.Somidina, H.Maenob, M.A.A.Mohd Sallehc, X.Q.Trana, S.D.McDonald, S.Matsumurab, K.Nogita, Characterising the polymorphic phase transformation at a localised point on a Cu$_6$Sn$_5$ grain, *Materials Characterization*, **138**(2018), 113–119.
DOI: 10.1016/j.matchar.2018.02.006

[2] Q.Yin, F.Gao, Z.Gu, J.Wang, E.A.Stach, G.Zhou, Interface dynamics in one-dimensional nanoscale Cu/Sn couples, *Acta Mater.*, **125**(2017), 136–144. DOI: 10.1016/j.actamat.2016.11.051

[3] M.A.A.Mohd Salleh, S.D.McDonald, H.Yasuda, A.Sugiyama, K.Nogita, Rapid Cu$_6$Sn$_5$ growth at liquid Sn/solid Cu interfaces, *Scr. Mater.*, **100**(2015), 17–20. DOI: 10.1007/s00339-016-0543-4

[4] M.A.A.M.Salleh, C.M.Gourlay, J.W.Xian, S.A.Belyakov, H.Yasuda, S.D.McDonald, K.Nogita, In situ imaging of microstructure formation in electronic interconnections, *Sci. Rep.*, **7**(2017), 40010, 1-11.   DOI: 10.1038/srep40010

[5] Thin Films-Interdiffusion and Reaction, edited by J.M.Poate, K.N.Tu and J.W.Mayer, Willey-Interscience, New York, 1978.

[6] R.Pretorius, C.C.Theron, A.Vantomme, J.W.Mayer, Compound Phase Formation in Thin Film Structures, *Crit. Rev. Solid State Mater., Sci.* **24**(1999), 1-62.

[7] J. J. Hoyt, L.N. Brush, On the nucleation of an intermediate phase at an interface in the presence of a concentration gradient, *J. Appl. Phys.*, **78**(1995), 1589–1594.

[8] C.M.Comrie, D.Smeets, K.J.Pondo, C. van der Walt, J.Demeulemeester, W.Knaepen, C.Detavernier, A.Habanyama, A.Vantomme, Determination of the dominant diffusing species during nickel and palladium germanide formation, *Thin Solid Films*, **526**(2012), 261–268.   DOI: 10.1016/J.TSF.2012.10.113

[9] K.S.Chi, L.J.Chen, Dominant diffusing species in the growth of amorphous interlayer between Yb metal thin films and crystalline Si, *J. Appl. Phys.*, **92**(2002), 927–931. DOI: 10.1063/1.1486050

[10] V.G Myagkov, L.E.Bykova, V.S.Zhigalov, A.A.Matsynin, D.A.Velikanov, G.N.Bondarenko, Solid-state synthesis, rotatable magnetic anisotropy and characterization of Co$_{1-x}$Pt$_x$ phases in 50Pt/50fccCo(001) and 32Pt/68fccCo(001) thin films, *J. Alloys Compd.*, **861**(2021), 157938(1-9).   DOI: 10.1016/j.jallcom.2020.157938

[11] N.Saunders, A.P.Miodownik, The Cu-Sn (Copper-Tin) system, Bull. Alloy Phase Diagr. **11**(1990) 278–287.

[12] V.G.Myagkov, L.E.Bykova, S.M.Zharkov, G.N.Bondarenko, Formation of NiAl Shape Memory Alloy Thin Films by a Solid-State Reaction, *Solid State Phenomena*, **138**(2008), 377–384.   DOI: 10.4028/www.scientific.net/SSP.138.377

[13] V.G.Myagkov, L.E.Bykova, L.A.Li, I.A.Turpanov, G.N.Bondarenko, Solid-phase reactions, self-propagating high-temperature synthesis, and martensitic transformations in thin films, *Dokl. Phys.*, **47**(2002), 95–98.   DOI: 10.1134/1.1462075

[14] V.S.Zhigalov, V.G.Myagkov, O.A.Bayukov, L.E.Bykova, G.N.Bondarenko, A.A.Matsynin, Phase transformations in Mn/Fe(001) films: Structural and magnetic investigations, *JETP Lett.*, **89**(2009), 621–625.   DOI: 10.1134/S0021364009120066

[15] V.G.Myagkov, L.E.Bykova, G.N.Bondarenko, Solid-state synthesis and martensitic transformations in thin films, *Dokl. Phys.*, **48**(2003), no.1, 30–33.   DOI: 10.1134/1.1545371

[16] V.G.Myagkov, Yu.L.Mikhlin, L.E.Bykova, G.V.Bondarenko, G.N.Bondarenko, Long-range nature of chemical interaction in solid-phase reactions: Formation of martensite phases of an Au-Cd Alloy in Cd/Fe/Au film systems, *Dokl. Phys. Chem.*, **431**(2010), 52–56. DOI: 10.1134/S0012501610030036

[17] H.Zhang, C.W.Wei, J.J.Han, H.J.Cao, H.T.Chen, M.Y.Li, Growth evolution and formation mechanism of $\eta'$-$Cu_6Sn_5$ whiskers on $\eta$-$Cu_6Sn_5$ intermetallics during room-temperature ageing, *Acta Mater.*, **183**(2020), 340–349.    DOI: 10.1016/j.actamat.2019.11.032

[18] A.Baldi, T.C.Narayan, A.L.Koh, J.A.Dionne, In situ detection of hydrogen-induced phase transitions in individual palladium nanocrystals, *Nat. Mater.*, **13**(2014), 1143–1148. DOI: 10.1038/nmat4086

[19] F.Gao, Z.Gu, Melting Temperature of Metallic Nanoparticles, In: Aliofkhazraei M. (eds), Handbook of Nanoparticles. Springer, Cham., (2016) 661–690. DOI: 10.1007/978-3-319-15338-4_6

[20] K.N.Tu, Interdiffusion and reaction in bimetallic Cu-Sn thin films, *Acta metall.*, **21**(1973), 347–354.

# Твердофазный синтез интерметаллида $Cu_6Sn_5$ в тонких пленках Sn/Cu

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**Аннотация.** Приведены результаты исследований твердофазного синтеза интерметаллида $Cu_6Sn_5$ в тонкопленочной системе Sn/Cu при отжиге в вакууме от комнатной температуры до 300 °C. Определены температуры начала и окончания твердофазной реакции между нанослоями Cu и Sn, а также фазовый состав продуктов реакции. Синтезированные тонкие пленки были однофазными и состояли из гексагональной фазы $\eta$-$Cu_6Sn_5$. Сделано предположение, что температура начала твердофазной реакции в тонких пленках Sn/Cu связана с температурой начала обратного полиморфного превращения $\eta' \to \eta$ между моноклинной и гексагональной фазами $Cu_6Sn_5$.

**Ключевые слова:** тонкие плёнки, твердофазный синтез, интерметаллид $Cu_6Sn_5$, обратимый фазовый переход $\eta \leftrightarrow \eta'$.