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ORIGINAL REPORT



# Spontaneous formation of sub-4 nm nanocrystalline alloy via polymorphic phase transformation

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## ABSTRACT

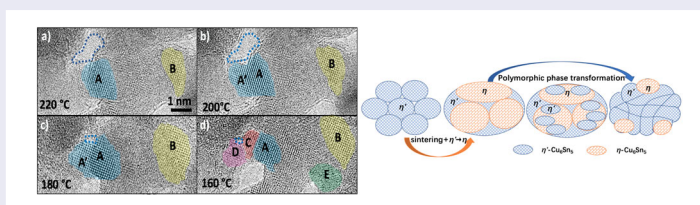
A new phase-transformation-induced path to spontaneous formation of extreme nanograin structure is reported. *In-situ-heating-mode*-microscopy exhibited a substantial grain-growth of Cu<sub>6</sub>Sn<sub>5</sub>. During cooling, the grain-growth continued, but it spontaneously switched to grain-refinement mode on phase transformation through  $\sim 180^\circ\text{C}$  from  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> to  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub>, ending up with an extremely small nanograin size of  $\sim 2.5$  nm. The cooling cycling always restores the nanograin size regardless of thermal exposure history, making this to be the first demonstration to *stabilize* the nanograin with its own spontaneous behavior. The Young's Modulus was significantly reduced by  $\sim \times 3$ , and the elongation was remarkably increased by  $\sim \times 8$  to  $\sim 9\%$ .

## ARTICLE HISTORY

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## KEYWORDS

Nanocrystalline; phase transformation; *in-situ* TEM; Cu<sub>6</sub>Sn<sub>5</sub>



## IMPACT STATEMENT

Monitoring cooling and phase transformation at atomic level revealed a new path to manufacture and stabilize extremely refined sub-4 nm grains by taking advantage of the spontaneous phase transformation behavior.

## Introduction

Nanograined or nanocrystalline alloys exhibit fascinating mechanical [1], chemical [2], optical [3], electrical [4] and magnetic [5] properties compared to conventional polycrystalline alloys. Binary alloy nanocrystals in particular have attracted worldwide attention because of the synergistic effects between two metal species and their unique roles in applications like catalyst [6], drug delivery [7], bio-imaging [8], smart electrical devices [8], and so forth. When the grain size reaches a sub-4 nm range, the grain boundary occupies almost 50% of the volume fraction of the material [9]. With such a large amount of grain boundary volume, the physical and chemical properties of sub-4 nm nanocrystalline alloys are destined to

be quite different from those of larger grained polycrystalline alloys [10], even from those exhibiting super high nanocrystal stability via low-angle grain boundaries [11].

After decades of metallurgical development of nanocrystalline alloys, there is still no significant breakthrough in the synthesis of pure, pore-free, sub-4 nm level grain sized nanocrystalline binary bulk alloys [9], without resorting to ball-milling [12], physical or chemical deposition [11], or plastic deformation and recrystallization [13]. These processing methods have problems of poor stability [14], high porosity [15], not sufficiently small grain size, difficulty in scale-up production, as well as unavoidable contamination and oxidation during handling [16]. For device applications, applying a plastic

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deformation for grain refinement is totally unacceptable. Therefore, it is highly desirable if a thermal-cycling-alone method can be utilized for nano grain refinement.

$\text{Cu}_6\text{Sn}_5$  is a useful engineering material with a bulk melting temperature of 415 °C, and with several key applications for electronic devices [17], chemical catalyst [18], and lithium batteries [19]. In our previous publications [20,21], pore-free  $\text{Cu}_6\text{Sn}_5$  nanocrystalline joints were prepared and utilized as a circuit interconnection material with creep-resistant characteristics, operable at temperatures (e.g. 300 ~ 350 °C) even higher than the soldering temperatures (e.g. 160 °C). The nanograined  $\text{Cu}_6\text{Sn}_5$  possesses a much lower Young's Modulus than the bulk  $\text{Cu}_6\text{Sn}_5$ . However, based on *in-situ* TEM heating part observations, the grains were seen to coarsen to tens of nanometers [20], which should not lead to such a large reduction in Young's Modulus [21]. Therefore, a further in-depth microstructural evolution of  $\text{Cu}_6\text{Sn}_5$  NPs was analyzed even during the cooling period to find out what is happening upon cooling at the atomic level to understand the mechanism better. Such a nanograin-inducing mechanism should lead us to a new way of synthesizing pore-free nanocrystalline structures with enhanced ductility.

$\text{Cu}_6\text{Sn}_5$  possesses a high temperature hexagonal  $\eta$ -phase ( $\text{P6}_3/\text{mmc}$ ) and a low temperature  $\eta'$ -phase ( $\text{C2}/\text{c}(15)$ ) with a transformation temperature of 186 °C [22]. During the *in-situ* HRTEM analysis in the present study, a special attention was paid on the cooling portion and associated phase transformation. Based on the discovery in this report, a new strategy was devised to create ultra-fine nanocrystalline intermetallic alloys by taking advantage of the reversible phase transformation behavior during thermal cycling treatment.

## Results and discussion

With a convenient co-precipitation method, size controllable synthesis of pure sub-10 nm  $\text{Cu}_6\text{Sn}_5$  nanoparticles (NPs) (mean diameter around 7 nm) was realized as reported earlier [21]. *In-situ* TEM heating was firstly conducted on  $\text{Cu}_6\text{Sn}_5$  NPs to monitor their grain coalescence behavior with a detailed process and coalescence mechanism(s) elaborated in Figure S1 and Figure S2. Sub-10 nm  $\text{Cu}_6\text{Sn}_5$  NPs exhibited the following characteristics: (i) They started to sinter at temperatures as low as 140 °C due to the nano dimension during the heating up stage (Figure S1), with the particle size increasing and the number of particles decreasing by merging of adjacent particles and Ostwald ripening (Figure S2); (ii) Generation, movement and disappearance of dislocations were observed in NPs if orientation attachment happens; (iii) The particles coarsened to reach a particle size of 10 ~ 30 nanometers in diameter after heating to 220 °C.

After the initial heating, the temperature change was reversed in the present study for cooling in the TEM. During the cooling process from above 240 °C, the remnant thermal energy was sufficient for  $\text{Cu}_6\text{Sn}_5$  grains to continue growing/coarsening before the temperature was dropped to around 180 °C (Figure 1(a) ~ (d)). There were two phenomena happening at the same time during cooling. One is the growth of the crystals: the overall area of the yellow color marked grain gradually expanded from 32.2 nm<sup>2</sup> at 240 °C (Figure 1(a)) to 71.2 nm<sup>2</sup> by the time the temperature cooled down to 180 °C (Figure 1(d)), by the assimilation of surrounding, somewhat disordered atoms by the large central crystal.

The other phenomenon observed was the densification of coalesced  $\text{Cu}_6\text{Sn}_5$  NPs as the blank area marked

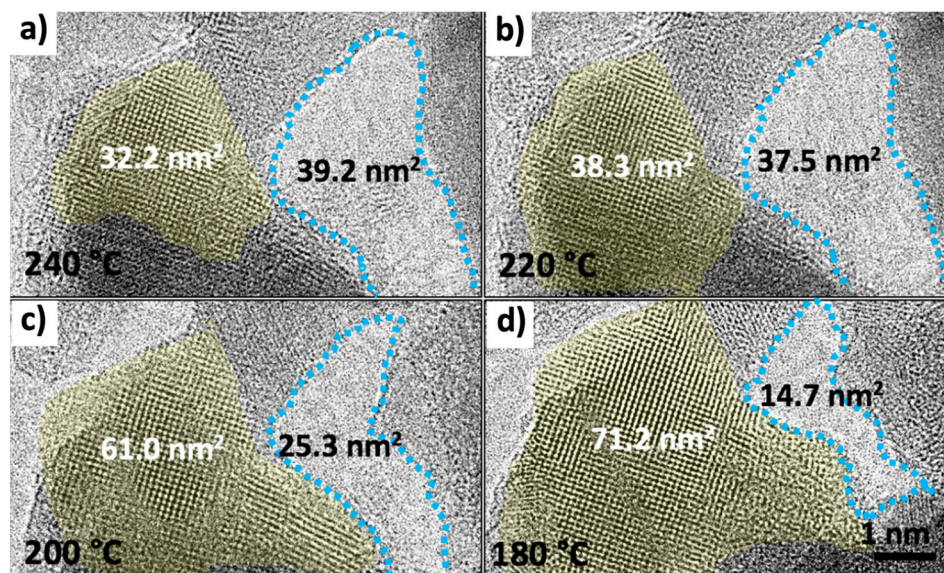


**Figure 1.** Bright field TEM images of crystal evolution of  $\text{Cu}_6\text{Sn}_5$  NPs during cooling. a) 240 °C. b, i) 220 °C. c) 200 °C. d) 180 °C.

by the blue dashed lines reduced from  $39.2 \text{ nm}^2$  in Figure 1(a) to  $14.7 \text{ nm}^2$  in Figure 1(d). This behavior is beneficial for reducing the porosity and gaining a desirably densely sintered structure. Thus, normally, the diameter of the grains after cooling should be tens of nanometers, if this kind of evolution keeps going in other materials.

Conversely, Figure 2 shows the HRTEM of samples cooled down from  $300^\circ\text{C}$  to  $20^\circ\text{C}$  with a cooling rate of  $20^\circ\text{C}/\text{min}$ . The diameter of these grains ranged from only 1.6 nm to 4.0 nm, much smaller than the coarsened structure in Figure 1. The yellow dashed lines represent the length and observed crystal orientation of the nano-sized grains. In Figure 2(a) and 2(b), the orientations for each grain varied, but most of them shared similar orientation with the large ‘round-shape particle base’, indicating that they were differentiated and refined from

an original larger grain in the size of  $\sim 20 \text{ nm}$ . The specimens in Figure 2(c) to 2(f) possessed mean grain diameter of  $\sim 2.15 \text{ nm}$  and  $\sim 1.86 \text{ nm}$ , respectively, with no grains larger than  $3.5 \text{ nm}$ . The orientation varied significantly as well. The FFT pattern in the inset of Figure 2(e) confirmed the stability (restorability of nanograin geometry) and purity of  $\text{Cu}_6\text{Sn}_5$ , indicating  $\text{Cu}_6\text{Sn}_5$  grains can retain their crystal structure and nanograin dimension after experiencing heating up to e.g.  $\sim 300^\circ\text{C}$  and then cooling down to  $20^\circ\text{C}$ . Twinning crystal structures were also discovered in the  $\text{Cu}_6\text{Sn}_5$  NPs after cooling, Figure 2(g), 2(h). Twinning nanograins have been proven to exhibit better ductility and other interesting mechanical properties [23]. Such a pore-free structure with grains in the sub-4 nm size regime is very difficult to achieve in other metallic materials. Such a nanograin structure is also responsible for the significantly enhanced (eight-fold increased) ductility in such ultra-nanograin materials.

After comparing the HRTEM structure before and after cooling, it is not difficult to come up with a hypothesis that during cooling the microstructure experienced an abrupt switching from a grain growth mode to a grain refinement mode. This process should also be spontaneous. As  $\text{Cu}_6\text{Sn}_5$  possesses a phase transformation temperature (PTT) at  $\sim 186^\circ\text{C}$ , the atomic level microstructural evolution around this temperature was closely monitored during *in-situ* cooling HRTEM. We observed a surprising and fascinating phenomenon of dramatic grain refinement. In Figure 3(a) ~ (c), before reaching  $180^\circ\text{C}$  on cooling, similarly as in Figure 1, the blue-color-marked A grain expanded to A + A' by assimilating the atoms adjacent to it. The enhancement of FFT patterns from Figure 3(e) to Figure 3(f) proved the growth of grain A. However, when the temperature was further reduced in Figure 3(d), a reverse phenomenon, i.e. a spontaneous grain refinement occurred, instead of continuous grain growth. Specifically, after the specimen went through the temperature lower than  $180^\circ\text{C}$ , the A + A' grain was differentiated into A + C + D grains, respectively marked with blue, red and pink colors in Figure 3(d). The FFT pattern in Figure 3(g) confirmed the difference in *d*-spacing between grain A and grain D. The yellow colored B area also went through grain growth from Figure 3(a) to Figure 3(c) in the early cooling stage, but then suddenly got refined and differentiated into smaller B grain and a new E grain in Figure 3(d). Thus, while the temperature is lowered through  $180^\circ\text{C}$ , coalesced  $\text{Cu}_6\text{Sn}_5$  grains went through a dramatic transition of paradigm, from *grain growth* to *grain refinement*.

Severe surface reconstruction and grain differentiations were observed in all the samples subjected to *in-situ* TEM heating and then cooling. Figure 4 is the comparison of the morphology of  $\text{Cu}_6\text{Sn}_5$  NPs before

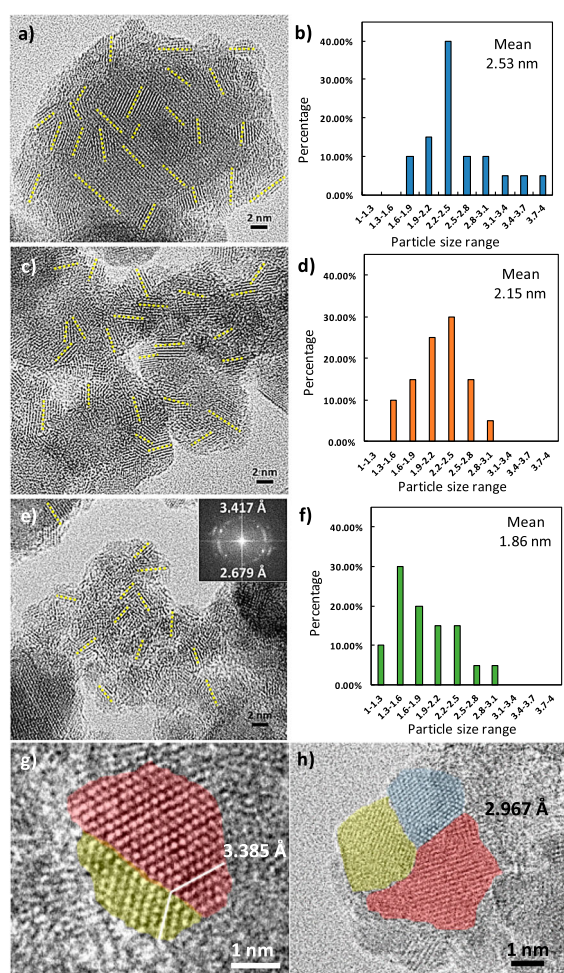


**Figure 2.** HRTEM results and grain size distribution of  $\text{Cu}_6\text{Sn}_5$  NPs after heating to  $300^\circ\text{C}$  and then cooling down with a rate of  $20^\circ\text{C}/\text{min}$ . a), c), e) HRTEM images of fully cooled samples. Yellow dotted lines represent the ‘diameter’ of each grain. b), d), f) Grain diameter distribution of a), c), e). g, h) Twinning of nanograin after cooling.

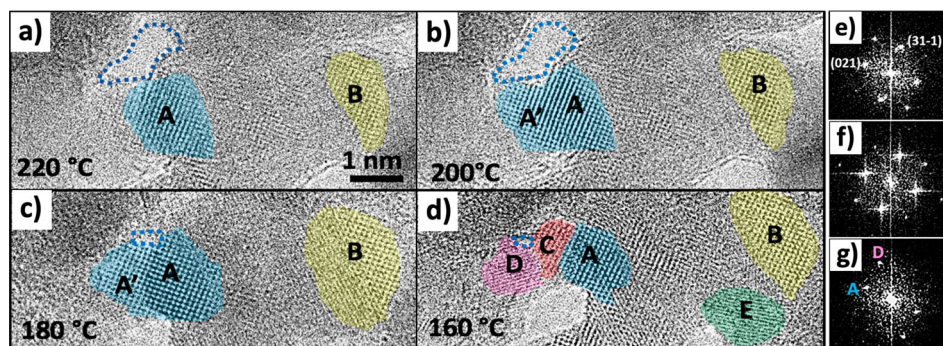


**Figure 3.** Crystal evolution of  $\text{Cu}_6\text{Sn}_5$  NPs during cooling. a) 220 °C. b) 200 °C. c) 180 °C. d) 160 °C. e), f) The FFT pattern of the blue-color marked area in a) and c). g) The FFT pattern of the A + C+D grains in d).

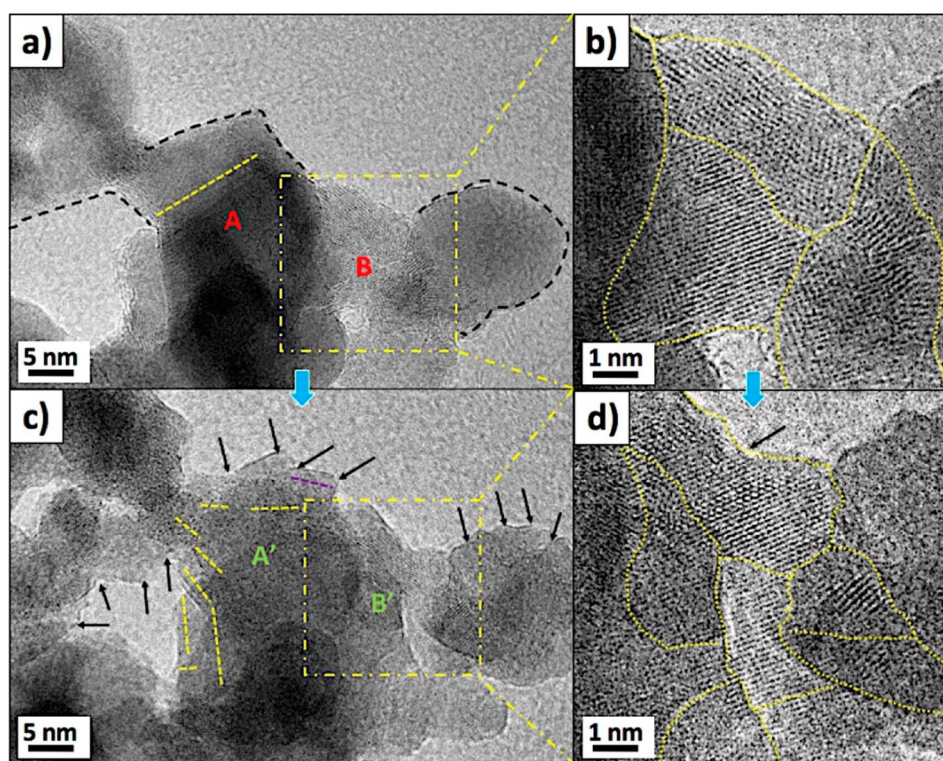


**Figure 4.** Grain differentiation, refinement, and surface reconstruction during *in-situ* TEM cooling of  $\text{Cu}_6\text{Sn}_5$  NPs. a), b) Before cooling. c), d) After cooling.

(Figure 4(a), (b)) and after (Figure 4(c), (d)) cooling through 180 °C. After further cooling, compared with A and B areas in Figure 4(a), (b) before phase transformation, A' and B' areas in Figure 4(c), (d) consisted of many more grains with different grain orientations (marked by dashed lines). The surface of grains became more rugged than that of the intact large grains having a smooth surface. As confirmed by previous research [24,25], 186 °C is the phase transformation temperature (PTT) for  $\text{Cu}_6\text{Sn}_5$  (the PTT of NPs is normally lower than in the case of a bulk material [26]), and it is not an order–disorder transition, but a polymorphic transformation with surface reconstruction and volume change (2.15%) [24,27].

Therefore, it is highly possible that the polymorphic phase transformation of  $\text{Cu}_6\text{Sn}_5$  is responsible for the spontaneous grain differentiation, refinement, and surface reconstruction.

To confirm the above hypothesis, the diffraction pattern evolution during heating and cooling was monitored and displayed in Figure 5. The as-synthesized  $\text{Cu}_6\text{Sn}_5$  contained low temperature  $\eta'$ -phase (C2/c(15)) only as shown in Figure 5(a). When the temperature was increased to 200 °C in Figure 5(b), #1 diffraction ring which belonged to  $\eta'$ - $\text{Cu}_6\text{Sn}_5$  phase ( $d=1.482$  Å, (22–6)) in Figure 5(a) disappeared, but #2 and #3 rings which match with diffraction of  $\eta$ - $\text{Cu}_6\text{Sn}_5$  ( $d=2.519$  Å,

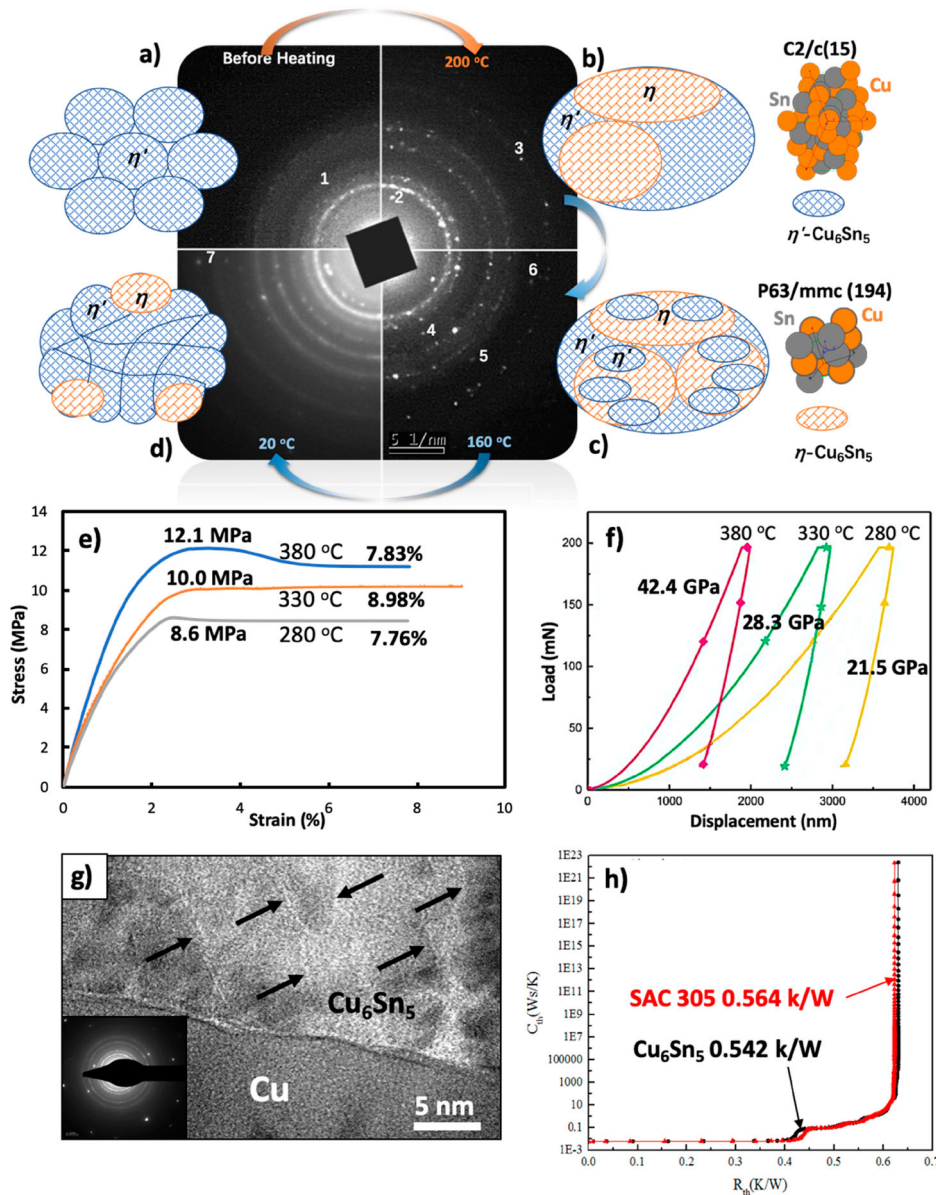


**Figure 5.** a ~ d) The diffraction pattern and schematic crystal evolution during phase transformation between high temperature  $\eta$ - $\text{Cu}_6\text{Sn}_5$  and low temperature  $\eta'$ - $\text{Cu}_6\text{Sn}_5$ . a) Before heating, b) heated to 200 °C, c) cooled down to 160 °C, and d) fully cooled down to 20 °C. e) Tensile test results of sintered  $\text{Cu}_6\text{Sn}_5$  NPs. f) Nanoindentation results. g) TEM image of the interface between the sintered  $\text{Cu}_6\text{Sn}_5$  and Cu substrate. h) The relationship between heat capacity and thermal resistance of SiC MOSFET device connected by  $\text{Cu}_6\text{Sn}_5$  NPs and SnAgCu305 solder.

(002) and  $d = 0.806 \text{ \AA}$ , (304), respectively) showed up. Meaning, after heating the specimen up to 200 °C,  $\eta$ - $\text{Cu}_6\text{Sn}_5$  was detected, revealing partial high temperature phase transformation from  $\eta'$ - $\text{Cu}_6\text{Sn}_5$  to  $\eta$ - $\text{Cu}_6\text{Sn}_5$ . During cooling, after reducing the temperature from 200 °C to 60 °C (from Figure 5(b) to Figure 5(c)), #4 diffraction ring (which was the same as #1 as in Figure 5(a)) reappeared. Thus,  $\text{Cu}_6\text{Sn}_5$  NPs experienced phase transformation from  $\eta$  to  $\eta'$  while they went through  $\sim 180^\circ\text{C}$  in the cooling process. But still, there were some diffraction patterns (#5 and #6) detected representing  $\eta$ - $\text{Cu}_6\text{Sn}_5$  after cooling down, as

the phase transformation has not been fully accomplished during the cooling process. After the sample was totally cooled down to 20 °C, the diffraction rings became more clear and integrated, indicating better crystallization and more new grains generated. Diffraction spot #7 of  $\eta'$ - $\text{Cu}_6\text{Sn}_5$  with a very small  $d$ -spacing appeared, indicating enhanced crystallization. Thus, by carefully comparing the diffraction pattern before, during and after heating and cooling, we witnessed the reversible phase transformation from low temperature  $\eta'$ - $\text{Cu}_6\text{Sn}_5$  to high temperature  $\eta$ - $\text{Cu}_6\text{Sn}_5$  and then back to  $\eta'$ - $\text{Cu}_6\text{Sn}_5$ .

Combining the phase transformation observed in Figure 5, the grain refinement mechanism of  $\text{Cu}_6\text{Sn}_5$  can be summarized as:

- (i) while heated through  $186^\circ\text{C}$  to a higher temperature,  $\text{Cu}_6\text{Sn}_5$  coarsened and some  $\eta'$ - $\text{Cu}_6\text{Sn}_5$  transformed into  $\eta$ - $\text{Cu}_6\text{Sn}_5$  (schematic in Figure 5 (a) to (b));
- (ii)  $\eta$ - $\text{Cu}_6\text{Sn}_5$  and  $\eta'$ - $\text{Cu}_6\text{Sn}_5$  both grow larger during continuous heating and the first cooling stage before reaching the PTT (Figure 5 (b));
- (iii) once cooled down through PTT,  $\eta$ - $\text{Cu}_6\text{Sn}_5$  turned into  $\eta'$ - $\text{Cu}_6\text{Sn}_5$ , and it is a polymorphic phase transition process, leading to fast (seconds to minutes) and dramatic grain differentiation, surface reconstruction and spontaneous grain refinement (Figure 5 (c));
- (iv) during further cooling process, more  $\eta$ - $\text{Cu}_6\text{Sn}_5$  turned into  $\eta'$ - $\text{Cu}_6\text{Sn}_5$ , with more extreme small grains generated (Figure 5 (d)). The kinetics behavior of phase-transformation-induced grain refinement is described in the supplementary information.

Bulk  $\text{Cu}_6\text{Sn}_5$  is generally brittle intermetallic compound, with tensile fracture strength estimated as  $1.13 \pm 0.04$  Pa and average tensile strain of  $\sim 1\%$  [28]. By dramatically reducing the grain size to less than 4 nm in the bulk, the mechanical property of nanocrystalline  $\text{Cu}_6\text{Sn}_5$  was significantly changed. As shown in Figure 5(e), the  $\text{Cu}_6\text{Sn}_5$  NPs were sintered at 380, 330 and  $280^\circ\text{C}$  respectively, and the ultimate strength reached 12.1, 10.0 and 8.6 MPa. The elongation was remarkably increased from  $\sim 1\%$  to as much as 7.83%, 8.98% and 7.76% respectively. Figure 5(f) is the nanoindentation test results. The Young's Modulus of regular  $\text{Cu}_6\text{Sn}_5$  bulk is  $\sim 119$  GPa [21]. However, the modulus was reduced to 42.4, 28.3 and 21.5 GPa, respectively, while sintered at above temperatures. Such a behavior indicates that the elasticity of the sintered  $\text{Cu}_6\text{Sn}_5$  nanocrystalline bulk material was much enhanced compared to the conventional  $\text{Cu}_6\text{Sn}_5$  bulk. Also, higher processing temperature leads to relatively higher strength and Young's Modulus, but with a relatively lower elongation. This is understandable as a higher temperature processing may lead to a relatively larger grain size. However, the ductility is still much better than that of the brittle bulk material.

Figure 5(g) is the TEM image of the interface between the sintered  $\text{Cu}_6\text{Sn}_5$  and Cu substrate; the arrows are pointing to the grain boundaries, confirming that the grain size of the sintered  $\text{Cu}_6\text{Sn}_5$  is indeed less than 5 nm. There is no obvious presence of pores in the

sintered microstructure. The connection at the interface was solid at atomic level, indicating a very robust interconnection has been realized. The diffraction pattern in the inset proved that  $\text{Cu}_6\text{Sn}_5$  was stable without decomposing or transforming into other Cu-Sn crystal structures.

Figure 5(h) compares the steady thermal resistance of joints made by  $\text{Cu}_6\text{Sn}_5$  NPs and conventional SAC305 solder (a lead-free alloy solder containing 96.5% tin, 3% silver, and 0.5% copper). It is confirmed that the thermal conductivity  $K$  of nanocrystalline  $\text{Cu}_6\text{Sn}_5$  is very good, even comparable with that of a conventional Sn based solder ( $K = 0.542$  K/W vs  $0.564$  K/W).

The polymorphic phase transition process of  $\text{Cu}_6\text{Sn}_5$ , especially occurring at lower temperatures where diffusional coarsening is minimal, is the key factor leading to spontaneous grain refinement. It allows the resultant alloy to consist of extremely fine nanograins of less than 4 nm. The cooling part of the thermal cycling always restores the nanograin size regardless of thermal exposure history, making this proposed concept to be the first demonstration to *stabilize* the ultra-fine nanograin structure with its own spontaneous behavior. This dramatic, order of magnitude grain refinement to such a small nanometer size regime can be applicable for some other alloy systems having polymorphic phase transformations, such as  $\text{Fe}_4\text{Al}_{13}$ ,  $\text{Ti}_{50}\text{Zr}_{50}$ ,  $\text{Al}_2\text{O}_3$ ,  $\gamma$  and  $\gamma'$  phase of Cu-Al, etc.

## Conclusions

We report here a new phase transformation-induced path to spontaneous formation of extremely fine, sub-4 nm nanograin structure. Temperature-increase during *in-situ* transmission electron microscopy (TEM) resulted in a substantial grain growth of  $\text{Cu}_6\text{Sn}_5$  from sub-10 nm to tens of nanometers, while inducing partial phase transformation from  $\eta'$ - $\text{Cu}_6\text{Sn}_5$  to  $\eta$ - $\text{Cu}_6\text{Sn}_5$ . During cooling, the grain growth continued at the beginning. However, it spontaneously switched to grain refinement mode while cooling through  $\sim 180^\circ\text{C}$ , by the phase transformation from  $\eta$ - $\text{Cu}_6\text{Sn}_5$  back to the low temperature phase  $\eta'$ - $\text{Cu}_6\text{Sn}_5$ , ending up with an extremely small average nanograin size of  $\sim 2.5$  nm. The cooling part of the thermal cycling always restores the nanograin size regardless of thermal exposure history, making this proposed concept to be the first demonstration to *stabilize* the ultra-fine nanograin structure with its own spontaneous behavior. The Young's Modulus of nanocrystalline  $\text{Cu}_6\text{Sn}_5$  was significantly reduced by a factor of at least three to less than 42.2 GPa, and the elongation was remarkably increased eight-fold up to 8.98%.

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## Disclosure statement

No potential conflict of interest was reported by the author(s).

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