

# Structural Evolution and Electrochemical Performance of Sputter-Deposited Cu<sub>6</sub>Sn<sub>5</sub> Thin-Film Anodes

K.-F. Chiu,<sup>a,\*,z</sup> K. M. Lin,<sup>a</sup> H. C. Lin,<sup>b</sup> W. Y. Chen,<sup>a</sup> and D. T. Shieh<sup>c,\*</sup>

<sup>a</sup>Department of Materials Science and Engineering, Feng Chia University, 407 Taichung, Taiwan <sup>b</sup>Department of Materials Science and Engineering, National Taiwan University, Taiperi, Taiwan <sup>c</sup>Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan

 $Cu_6Sn_5$  thin-film anodes have been prepared by magnetron cosputtering, and the electrochemical properties of the deposited films in relation to lithium have been investigated. Structural evolution of the  $Cu_6Sn_5$  thin films was induced by in situ substrate bias, which then resulted in different electrochemical properties. The crystallinity of the deposited thin films can be well controlled under precise substrate bias. Films deposited with substrate bias ranging from 0 to -80 V showed nearly amorphous structure, with nanosized particles on the surface. These films exhibited typical electrochemical properties of nanocrystalline  $Cu_6Sn_5$ . As the substrate bias became more intense, polycrystalline  $Cu_6Sn_5$  films formed. At a bias of -150 V, highly crystallized  $Cu_6Sn_5$  films were obtained. The postcycled X-ray diffraction spectra indicated a  $Li_2CuSn$  phase in the film made with -150 V bias. This phase was associated with the intercalation process normally found in the high-temperature-phase  $\eta$ - $Cu_6Sn_5$ . The results show that in situ bias is able to induce phase transformation of  $Cu_6Sn_5$  ( $\eta'-Cu_6Sn_5 \leftrightarrow \eta-Cu_6Sn_5$ ) without thermal annealing. The nonbias-deposited films showed electrochemical characteristics of the low-temperature  $\eta'-Cu_6Sn_5$  phase, whereas the -150 V bias-deposited films showed properties of the high-temperature  $\eta-Cu_6Sn_5$  phase.

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Recently, lithium-ion batteries, especially for multifunction portable electronic devices, have been of great interest. Many researchers have focused on searching for new electrode materials and for further understanding of the redox processes in the electrode materials. Among them, alloy-type anode materials have been widely studied due to their large specific capacities. However, the alloy anodes generally show poor cycling properties, due to their large volume changes during lithiated/delithiated processes; this has limited their practical applications. Recently, the possibility of modifying the properties of Sn anodes has motivated investigation of Snbased alloys and intermetallic compounds,  $M_x Sn_y$  (M: inactive element), such as Cu–Sn,<sup>1-5</sup> Ni–Sn,<sup>6-8</sup> and Fe–Sn.<sup>9,10</sup> During chargedischarge cycles, the elemental Li reacts with M<sub>x</sub>Sn<sub>y</sub> compounds and forms brittle Li-Sn alloys, which are embedded in the M matrix. The relatively ductile, inactive M matrix of such compounds is able to endure large stresses caused by significant expansions and contractions of volumes.

Among these anode materials, Cu<sub>6</sub>Sn<sub>5</sub> anode materials show unique electrochemical characteristics. Different crystal phases, i.e.,  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub> and  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub>, exhibit different reactions with lithium. A well-crystallized  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> phase obtained by high-temperature annealing (~400°C) reacts with lithium by an intercalation/ deintercalation process, whereas the nanocrystalline or amorphous  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub> phase alloys and dealloys with lithium during cycling.<sup>2,5</sup> However, typical weight capacity of Cu<sub>6</sub>Sn<sub>5</sub> is around 200 mAh/g,<sup>2,5</sup> which is approximately 56% of the theoretical capacity. Although it is lower than the capacity of the current graphite anodes (~372 mAh/g), the specific volumetric capacity of Cu<sub>6</sub>Sn<sub>5</sub> is as high as 1656 mAh/mL, which is two times higher than that of graphite. The high specific volumetric capacity and the intercalation characteristics make the Cu<sub>6</sub>Sn<sub>5</sub> anodes of potential interest in lithium-ion batteries.

This study is focused on the exploitation of the unique electrochemical characteristics of  $Cu_6Sn_5$  thin films. In this research,  $Cu_6Sn_5$  thin films have been prepared by cosputtering of Cu and Sn targets with in situ substrate bias. The substrate bias modifies the films' crystal structures and therefore the films' electrochemical properties. The results show that in situ bias is able to induce phase transformation of  $Cu_6Sn_5$  ( $\eta'$ - $Cu_6Sn_5 \leftrightarrow \eta$ - $Cu_6Sn_5$ ) without thermal annealing.

## Experimental

The Cu<sub>6</sub>Sn<sub>5</sub> thin films were prepared by magnetron cosputtering and deposited on stainless steel substrates using pure Sn and Cu (99.99%) targets (2 in. in diameter). The power sources for Sn and Cu targets were radio frequency (rf) and dc power supplies, respectively. Figure 1 shows the sputter system. The substrate holder was located between the targets, and the distance between the targets and substrate was 11 cm. The working gas was 99.99% pure argon and the gas flow was 15 sccm during sputtering. The working pressure was maintained at 1.33 Pa for all deposition processes. The power levels applied on the Sn and Cu targets were 25 and 30 W, which resulted in the stoichiometric composition of Cu<sub>6</sub>Sn<sub>5</sub> thin films. The currents on the substrate holder were monitored and used as an indicator for the precise control of the deposition process under different substrate bias. Cu<sub>6</sub>Sn<sub>5</sub> films were deposited with different levels of negative substrate bias, namely: -20, -40, -60, -80, -100, -120, and -150 V. For the films deposited without substrate bias (0 V), the substrates were simply grounded. The deposition time was controlled to obtain the same film thickness ( $\sim 120 \text{ nm}$ ) for different bias conditions. The atomic ratios of Sn and Cu were measured by an inductively coupled plasma-atomic emission spec-



Figure 1. Apparatus of the dual-gun sputter system.

<sup>\*</sup> Electrochemical Society Active Member.

<sup>&</sup>lt;sup>z</sup> E-mail: kfchiu@fcu.edu.tw



Figure 2. Currents measured on the substrate holder at different negative substrate bias.

trometer (ICP-AES). The films' crystallography was characterized by X-ray diffraction (XRD) using a Rigaku D/MAX2500 X-ray diffractometer with Cu K $\alpha$  radiation (wavelength 1.5405 Å). The surface morphology was observed by a JOEL JSM-6700 field-emission scanning electron microscope (FESEM).

The deposited films were packed in coin cells (size no. 2032) with the following configuration: Li foil  $|1 \text{ M LiPF}_6$  in ethylene carbonate and ethyl methyl carbonate mixed solution (volume ratio 1:2)| Cu<sub>6</sub>Sn<sub>5</sub>. The Li foil was also used as the reference electrode. All cells were assembled in an Ar-filled glove box. The charge-discharge and cycle life tests were performed using an electrochemical work station (Jiehan ECS-5000, Taiwan). The cells were charged (lithiated) and discharged (delithiated) at constant current density of 50  $\mu$ A/cm<sup>2</sup> between voltage ranges of 0 and 2 V at a constant temperature of 25°C.

#### **Results and Discussion**

Different substrate biases were applied to attract ions from the plasma to the substrate. These ions contributed to the current flow through the substrate holder. The currents, measured as a function of different negative substrate bias on the substrate holder, are shown in Fig. 2. The currents (i.e.,  $Ar^+$  flux) increase with the substrate bias, which means that negative bias accelerates positive argon ions ( $Ar^+$ ) toward the substrate. These ions bombard on the growing films with energy equal to the difference between the plasma potentials and bias voltages. The increased ion-flux bombardment provides extra energy for grain growth and greatly influences the film crystallography and morphology. However, if a negative bias is too extreme, it may also cause damage to the films.

Figure 3a-e shows the surface morphologies of the deposited films as a function of substrate bias. The nonbiased and low-biased (0-60 V) films exhibit similar morphologies, and only the nonbiased sample is shown here (Fig. 3a). For the nonbiased sample, the film surface is composed of nanosized primary particles (5–10 nm), which aggregate into clusters of 50–80 nm (Fig. 3a). The clusters loosely disperse on the film surface, and the spaces between the clusters can be clearly observed. As the bias increases to -80 V (Fig. 3b), the sizes of the clusters shrink slightly and become more uniform. The film surface is denser because the -80 V bias is able to induce ion bombardment with enough energy to result in the rearrangement of adatoms and the formation of a denser and smoother surface. This is known as the atomic peening effect.<sup>11,12</sup>

As the bias exceeds -100 V (Fig. 3c), individual particles with much greater sizes form on the surface, and the morphology is completely different. At -120 V of bias (Fig. 3d), the surface particles grow into large structures, and some neckings form between particles. At -150 V (Fig. 3e), the particle size can be as large as



Figure 3. Surface morphologies of the films deposited with substrate biases of (a) 0, (b) -80, (c) -100, (d) -120, and (e) -150 V.

 $\sim$  100 nm. This evolution of surface morphology can be attributed to the bias-induced ion bombardment, which provides extra energy input during film growth. The extra energy enhances grain growth, and the physical ion bombardment results in redistribution of the surface adatoms, which fills the space between surface grains.<sup>12</sup> As a consequence, the film morphology is composed of large grains with unclear boundaries (Fig. 3e).

Figure 4 shows the XRD patterns of  $Cu_6Sn_5$  thin films deposited with different substrate biases. The crystallinity changes are correlated with the surface morphologies. The nonbiased and low-biased films exhibit low-intensity diffraction peaks, indicating nearamorphous features of the films. As the substrate bias increases to -80 V, the crystallinity of  $Cu_6Sn_5$  thin films is gradually enhanced.



Figure 4. XRD patterns of the films deposited under different substrate bias.

For films deposited with higher bias (-100, -120, and -150 V), the films are well crystallized and exhibit formation of large grains on their surfaces (Fig. 3c-e). The evolution of crystalline formations can again be attributed to the bias-induced ion bombardment during film growth. For deposition under a bias so extreme as to be outside the scope of the present study, such as -180 V, the severe ion bombardment causes etching of the films, and no net-deposition can be obtained. The diffraction patterns of the low-temperature-phase  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub> and high-temperature-phase  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> are very similar. However, these two crystallographic phases have different electrochemical properties and can be clearly distinguished by electrochemical tests.

In the present research, three kinds of films are used for electrochemical tests: films with nanosized particles and X-ray amorphous features (0 V films), films with medium grain sizes and diffraction peak intensities (-100 V films), and films with large grains and well-crystallized features (-150 V films). Figure 5a-c shows the 1st, 2nd, and 5th charge/discharge curves for Cu<sub>6</sub>Sn<sub>5</sub> films deposited at 0, -100, and -150 V bias. At the first charge, the capacity of the 0 V film exceeds the theoretical capacity of  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub> (608 mAh/g). The extra capacity might be due to the formation of a solid-electrolyte-interphase (SEI) layer, which is produced as the active elemental Sn reacts with the electrolyte at the first charging step. The reversible capacity for the 0 V film achieves 587 mAh/g, which is close to the theoretical capacity of  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub>. The -100 and -150 V films exhibit relatively lower reversible capacity compared with that of 0 V films. The higher capacity of 0 V films can be attributed to their nanosized features (Fig. 3a), which result in larger surface area and activity. The curves of these films (shown in Fig. 5) also exhibit slightly different potential plateaus. More detailed information can be obtained from the dQ/dE curves as shown in Fig. 6. Extreme bias (-100 and -150 V in Fig. 6b and c) deposited films show high intensity redox peaks due to better crystallization. Figure 6c clearly shows that a reduction peak (marked by a dashed line) near 0.4 V has developed for the -150 V biasdeposited film. In addition, the sharp reduction peak near 1.25 V at the first cycle for the 0 V deposited film (Fig. 6a) is not recorded in the films deposited at -100 and -150 V (Fig. 6b and c), where two distinctive peaks appear around 1.25 V. This suggests that the reactions during the first charge-discharge cycle differ between the nano/ amorphous Cu<sub>6</sub>Sn<sub>5</sub> and the highly crystallized Cu<sub>6</sub>Sn<sub>5</sub>.

Recently, Wang et al.<sup>2</sup> reported the electrochemical properties of  $\eta$ - and  $\eta'$ -phase Cu<sub>6</sub>Sn<sub>5</sub> anodes. It was shown that  $\eta'$ -phase Cu<sub>6</sub>Sn<sub>5</sub> reacted with lithium by alloying Li with Sn. For high-temperatureannealed  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub>, it has been suggested that lithium reacts with the Cu<sub>6</sub>Sn<sub>5</sub> anodes by an intercalation process.<sup>1,2,5</sup> The alloying and intercalation mechanisms can be distinguished by the occurrence of the intermediate phase during lithiation. For the alloying process, Li directly alloys with Sn, as shown in Eq. 1

$$22\text{Li} + \text{Cu}_6\text{Sn}_5 \leftrightarrow 5\text{Li}_{4,4}\text{Sn} + 6\text{Cu}$$
[1]

For the intercalation process, Li enters the lattice of  $Cu_6Sn_5$  and forms metastable  $Li_xCu_6Sn_5$  phase (Eq. 2). Full lithiation also results in  $Li_{4.4}Sn$  (Eq. 3)

 $10\text{Li} + \text{Cu}_6\text{Sn}_5 \leftrightarrow 5\text{Li}_2\text{CuSn} + \text{Cu}$ [2]

$$12\text{Li} + 5\text{Li}_2\text{CuSn} \leftrightarrow 5\text{Li}_{44}\text{Sn} + 5\text{Cu}$$
[3]

Because the volume change for intercalation is smaller than the change for the alloying process, the cycling stabilities are expected to be different. Figure 7 and Table I show the cycling performances for thin-film anodes deposited with different biases. Although the thin-film anodes still cannot make full use of the active materials, the performance levels of  $Cu_6Sn_5$  thin films are much better than those of the  $Cu_6Sn_5$  powders, as shown in Table I. In the initial ten cycles, the capacity decreases obviously for the 0 V film, but it maintains a reversible capacity in the following cycles. The capacity dramatically declines to 250 mAh/g (2070 mAh/mL) after the 40th



Figure 5. Charge-discharge curves of the films deposited with substrate biases of (a) 0, (b) -100, and (c) -150 V.

cycle. The capacity fading between the 1st and 50th discharges of the 0 V anode is around 57% (Table I). Although the capacity of the -150 V sample also exhibits rapid fading in the initial cycles, it shows much better long term cycling reliability up to the 50th cycle. There is still a capacity of 200 mAh/g (1656 mAh/mL) after 50 cycles, corresponding to a capacity fading of ~30% (Table I). There is almost no capacity fading between the 10th and 50th cycles, which may be attributed to the different crystallographies of the samples. The 0 V film is amorphous or nanocrystalline; it undergoes an alloying process during charge/discharge cycles. The



Figure 6. dQ/dE curves of the films deposited with substrate biases of (a) 0, (b) -100, and (c) -150 V.

-150 V film has a highly crystallized Cu<sub>6</sub>Sn<sub>5</sub> phase, which may favor the intercalation/deintercalation process. As a consequence, the -150 V sample shows better cycling stability with a lower capacity. Because the film crystallography evolves gradually with increased substrate bias, it is therefore reasonable to expect that some suitable bias between -150 and 0 V may result in a film with two coexisting phases, where part of the film may favor the alloying process and the other part intercalation. Indeed, as shown in Fig. 7, the -100 V film exhibits an initial capacity between the capacity of the 0 V sample and the capacity of -150 V sample and shows a better cycling stability than the 0 V film. Despite having a slightly lower initial discharge capacity than the 0 V film, the -100 V film exhibits higher reversible capacity and the volumetric capacity is as



Figure 7. Discharge capacity as a function of cycle number for the films deposited with substrate biases of 0, -100, and -150 V.

high as 2200 mAh/mL at the 50th cycle. The 0 and -100 V films show a trend of continuous decrease in capacity after 50 cycles. The -150 V shows much better cycling stability after 10 cycles, which may eventually compensate for its low capacity as the cycle number increases.

In order to verify the points mentioned above, crystallographic structures of the postcycled films were measured. Figure 8a and b shows the XRD patterns of the postcycled films measured at different cutoff voltages. Because many of the diffraction peaks from different Li<sub>x</sub>Sn alloys directly overlap or have very similar diffraction angles, the possible phases are indexed for each diffraction peak in Fig. 8a and b. At a cutoff voltage of 0 V, all the films are lithiated to Li<sub>x</sub>Sn (Fig. 8a). Almost all the diffraction peaks correspond to highly lithiated Li3,5Sn and Li44Sn phases, except some lowintensity peaks which may belong to Li2 5Sn and Li2 6Sn. Despite the fact that the as-deposited 0 V bias film is amorphous as shown in the XRD data (Fig. 4), it exhibits crystalline phases of lithium alloys  $(Li_xSn)$  when charged to 0.4 and 0 V. This phenomenon was also observed in other Sn-related alloys<sup>13,14</sup> and pure Sn anodes<sup>15</sup> with amorphous features. Because the amorphous Sn-alloy thin films are actually composed of nanosized clusters with very high surface energy, the insertion of lithium into the films provides a driving force and readily results in crystallization of LixSn grains. As a consequence, in their charged states, the films exhibit crystalline Li<sub>x</sub>Sn phases

At the cutoff voltage of 0.4 V, the 0 V film also exhibits diffraction peaks of Li<sub>x</sub>Sn alloys as identified in Fig. 8b, indicating the nature of n'-phase Cu<sub>6</sub>Sn<sub>5</sub>. Li<sub>2</sub>CuSn phase and the unreacted Cu<sub>6</sub>Sn<sub>5</sub> were obtained for -150 V films at the cutoff voltage of 0.4 V and no Li<sub>x</sub>Sn phase was found. The results suggest that the -150 V film reacts with Li through an intercalation mechanism and exhibits the nature of the  $\eta$ -phase Cu<sub>6</sub>Sn<sub>5</sub>. The remaining Cu<sub>6</sub>Sn<sub>5</sub> signals in the XRD spectrum indicate that the grains near the bottom of the film do not react with lithium, which could be due to the large particle size and limited kinetics for lithium insertion. This lack of reaction is also responsible for the low discharge capacity of the -150 V films. As for the -100 V films, diffraction peaks for Li<sub>x</sub>Sn and for Li2CuSn can be found, indicating that two phases coexist. For the 0 V films, all the peaks correspond to Li<sub>x</sub>Sn phases. The expected lattice distortion due to intercalation is beyond the resolution of the XRD measurements used here. The results in Fig. 6-8 correlate with each other and suggest that the mechanisms of lithiation change with increased bias, and a phase transformation of  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub>  $\leftrightarrow \eta$ -Cu<sub>6</sub>Sn<sub>5</sub> may be induced by in situ bias during film deposition.

Table I. Electrochemical performances of the $Cu_6Sn_5$ anodes with different conditions $(C_n)$ . <sup>a</sup>						
	Type of samples	Discharge capacity $C_1 \text{ (mAh/g)}$	Discharge capacity C <sub>10</sub> (mAh/g)	Discharge capacity C <sub>50</sub> (mAh/g)	Capacity retention $C_{50}/C_1$	Capacity retentior $C_{50}/C_{10}$
From Ref. 2	Powder	412(0.00-1.50 V)	~3.20	None	None	None
From Ref. 5	Powder	$\sim$ 580(0.00–2.00 V)	$\sim 150$	$\sim 30$	5%	20%
0 V	Films	527(0.00-2.00 V)	402	250	47%	62%
-100 V	Films	496(0.00-2.00 V)	391	283	57%	72%
-150 V	Films	342(0.00-2.00 V)	221	185	54%	83%

<sup>a</sup>  $C_n$  indicates discharge capacity at *n*th cycle.

<sup>b</sup> Only 20 cycles were shown in Ref. 2.

## Conclusion

It has been shown that Cu<sub>6</sub>Sn<sub>5</sub> films prepared by cosputtering of Sn and Cu exhibit improved cycling stability. During in situ bias



Figure 8. Postcycled XRD patterns of the films deposited with substrate biases of 0, -100, and -150 V and charged (lithiated) to the cutoff voltages of (a) 0 and (b) 0.4 V. The peaks from stainless steel substrates are indicated as SS.

treatment, ion bombardment causes evolution of film morphology and crystallography. As a consequence, the mechanism of lithiation also changes from alloying to intercalation. This change of working mechanism correlates to the performance of electrochemical properties. The 0 V film is an alloy-type anode, showing higher capacity but larger capacity fading during cycling. The -150 V sample is found to react with lithium by an intercalation mechanism, which displays lower capacity but better cycling stability. Suitable bias (i.e., -100 V) results in a film which has both alloying and intercalation properties and which can achieve higher reversible capacity and cycling stability.

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