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# Twisted nanocolumns for LIBs via phi-sweep method in ion assisted e–beam deposition

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ABSTRACT

In this work, twisted nanostructured silicon-copper (with 19%at. copper) thin film is fabricated by glancing angle deposition phi-sweep process of ion beam assisted electron beam evaporation method. The thin film delivers 977 mAh $g^{-1}$ after 100 cycles, when cycled with 100 mA $g^{-1}$ rate and performs 280 mAh $g^{-1}$ at 2.5 A $g^{-1}$ rate. The morphological and the compositional particularities of the electrode might govern this noticeable cycle performance: Gaps among the nanostructures accommodate large volume changes and provide easy access to lithium ions for reacting with silicon to deliver high capacity. Plus, the direct connection of nanostructures to the current collector displays short lithium travelling distance promoting lithiation kinetic. Moreover, small intermetallics creating electronic conductive pathways enhance the reversibility. And finally, 5 min ion assisted deposition increases the adhesion of the film while avoiding possible delamination, hence quick failure of the electrode in the early stages of cycling.



## 1. Introduction

Silicon (Si) as a new generation anode material that offers high theoretical capacity (3579 mAhg$^{-1}$ at room temperature) and safe working potential. Moreover, it has high abundance in the earth's crust, environmentally friendly and non-toxic behaviors [1]. But, upon cycling Si performs drastic volume changes (>300%) causing pulverization and electrical disconnections finally quick failure in cycling [2]. Plus, its low electrical conductivity and low lithium (Li) diffusion coefficient retard lithiation kinetic leading a poor rate performance [3]. Possible gateways to overcome these disadvantages are first, engineering Si electrode into nanostructures (inducing porosities in the electrode) and second incorporating some metals along with Si [4–7].

Recently, possible uses of M-Si (M: Cu, Ag, Ni) nanowires, nanorods, structured thin films as electrodes for lithium ion batteries (LIBs) are investigated and the results are found to be promising [8–10]. It is possible to deposit structured M-Si based thin films using thin film deposition techniques. Among other deposition techniques, glancing angle deposition method via electron beam evaporation process (GLAD) becomes remarkable as it helps to make composite, structured electrodes in one step without needs of binders or additives. In GLAD, the substrate position is continuously/intermittently manipulated (azimuthal rotation ($\phi$)) during the evaporation while the angle ($\alpha$) between the incident evaporated particles and the substrate surface normal (being typically > 70°) creates highly oblique flux resulting porous, low-density thin films with a directional columnar structure. Herein, with the help of the azimuthal rotation ($\phi$) various structures including free standing vertical posts, chevrons, zigzag, and helices could be structured [11,12].

In this study, the substrate has been rotated with a constant rate intermittently and at each outer extreme of the sweep curve, the substrate is paused for a period of time to have a constant film growth. This process has been named as “phi-sweep method” [13,14].

To our knowledge, first in literature, ion assistance (IAD) has been adopted to phi-sweep method to produce highly adherent co-deposited SiCu twisted nanostructures as an anode for LIB. An optimization is made for Cu/Si atomic ratios to benefit the advantages of Cu atoms (promotes the adhesion of the film to Cu foil due to its glue effect and the reversibility of the lithiation reaction)

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without losing the specific capacity (due to the electrochemically inactive behavior of Cu versus Li) [15]. The typical twisted morphology has been made by rotating the substrate with $60^0$ step sizes, to avoid sharp active edges (which is expected to represent potential preferential sites for lithiation). The possible use of this film as negative electrode has been evaluated based on galvanostatic and electrochemical test results.

## 2. Experimental

During GLAD, two quartz-crystal microbalances (QCMs) were used independently to monitor the deposition rates and film thicknesses of Cu (0.09 nm $s^{-1}$) and Si (1 nm $s^{-1}$) separately. The schematic of the experimental setup was given in our previous work [16].

Cu foil (99.99% purity, 1.5-mm thickness) and Si wafer were cleaned with acetone and ethanol before loading into the vacuum chamber. Then, the substrates were loaded with $85^0$ versus the surface normal of graphite crucibles. Si and Cu chunks (having the purity of >99.95%) were placed in the crucibles, respectively. Once the chamber was locked, it was vacuumed by turbomolecular pump down to $8 \times 10^{-5}$ Pa.

Before the beginning of the deposition, sputtering was applied for 5 min using 900 eV $Ar^+$ (from a Kaufman ion source) around $10^{-2}$ Pa, with a gas feeding of 8 sccm. In sputtering, the incident angle of $Ar^+$ to substrate normal was $35^0$. Then, once the sputter was finished, the shutters were released, and the deposition was started. To promote the adhesion of the film, $Ar^+$-assisted deposition was made at 250 V and 23 mA for the initial 5 min of the deposition. After that, the Ar feeding and ion gun were stopped and 30 mA current beam, 40 V discharge and 100 V accelerator voltage were applied in the rest 11 min of the evaporation.

In deposition, the substrate surface (with inclined surface angle) was swept from one point to another with an angle of $60^0$. At each outer extreme of the sweep curve, the substrate was paused for a period of time (50 s) to grow twisted nanocolumns in the film.

Morphological analyses of the SiCu nanostructured thin film were made by field-emission scanning electron microscopy (FEG-SEM, JEOL JSM 7000 F and JEOL 5410). The composition of the film was determined by energy dispersive X-ray spectrometer (EDS, Oxford). X-Ray diffraction (XRD, Bruker D8 Discover) in a 2θ range of 20-$100^0$ by steps of $0.05^0$ (with CuKα) was used for structural analyses. Half-cells were assembled in 2032-coin cells [16]. Galvanostatic tests were conducted at room temperature in a voltage range of 0.2 V–1.2 V versus $Li/Li^+$ at 100 mA $g^{-1}$ rate (at 10 μA $cm^{-2}$ current density). Then, to evaluate the rate performance of the electrode, the sample was tested at various rates (200, 400, 800 mA $g^{-1}$, 1.6 and 2.5 A $g^{-1}$). Morphological changes after the 3rd, 30th and 100th cycles were also examined under SEM.

Cyclic voltammetry tests were made in the 1st, 2nd, 3rd and 4th cycles between the potential range of 0.2–1.2 V (vs $Li/Li^+$) using a scan rate 0.03 mV $s^{-1}$. EIS analyses were done on the 1st, 2nd, 3rd, 10th and 30th cycled samples in the frequency range of 10 mHz-10 kHz with 10 mV (rms) at discharge potentials of 0.2 V (Gamry PCI4/750). The impedance spectra were analyzed by using a software program, Gamry Framework for fitting the experimental data to an equivalent circuit model.

## 3. Results and discussions

Fig. 1a–b shows the schematic representation of the substrate

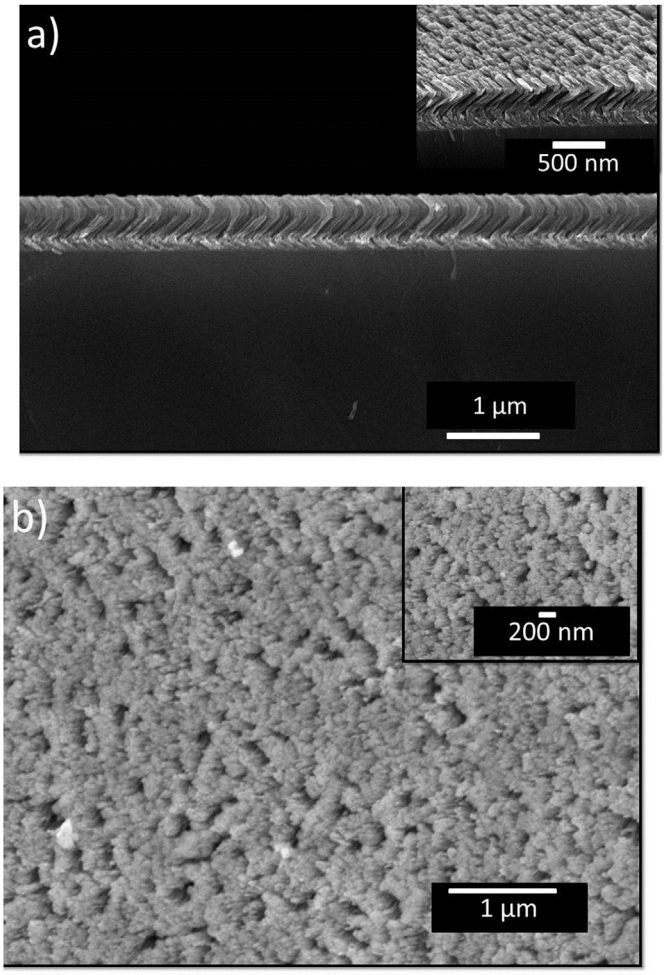


**Fig. 2. a)** Cross section, **b)** surface SEM views of the twisted nanostructured silicon-copper thin film.

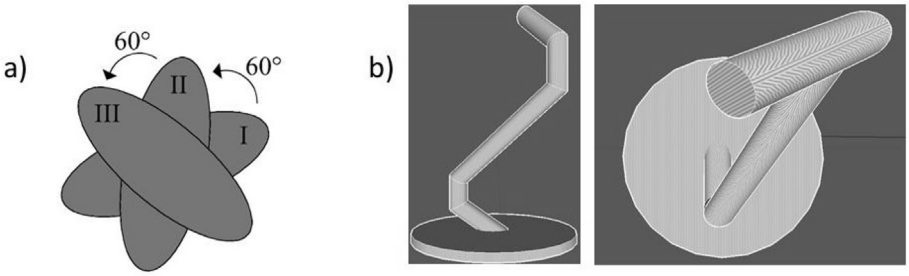


**Fig. 1. a)** Schematic representation of **a)** the substrate positions switching in phi-sweep process, **b)** the twisted nanostructured silicon-copper film growth during the phi-sweep process.