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Cu-doped Silicon Film as Anode for Lithium ion Batteries Prepared by Ion-beam Sputtering

*Zhongsheng Wen**, *Feng Tian*

Institute of Materials and Technology, Dalian Maritime University, Dalian 116026, China
*E-mail: zswen5@gmail.com

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Cu-doped silicon film was prepared by Ionion-beam sputtering in the work. The facilitation of doping Cu for the electrochemical performance of silicon film as anode materials for lithium ion batteries was demonstrated. Although the thickness of deposited Cu-doped silicon film was up to 10 μm, much thicker than the reported ones, excellent electrochemical performance was obtained. The results demonstrated that the coulombic efficiency of the 10 μm silicon composite film could be up to 80% although free of conductive and binder additives. The capacity retention after 100 cycles could be up to 93.8 % of that for the second cycle. Microcracks were observed on the surface of silicon film electrode after cycling, but no obvious exfoliation was found even after 300 cycles. The continuous maintenance of the electronic contact might be the main reason for the stable electrochemical cyclability of silicon film electrodes. Co-deposited Cu by sputtering makes the dimensional size of silicon film extended to micrometer scale without deteriorating its cycling performance.

Keywords: silicon composite film, Cu doping, lithium ion batteries, ion-beam sputtering

1. INTRODUCTION

Lithium ion batteries (LIBs) have been developed speedily and applied widely in recent years for their attributes of environment-friendly property, high power and energy density properties. However, it is very difficult to make a further breakthrough on the electrochemical performance of LIBs only by technical modification due to the intrinsic capacity limitation of both conventional anode and cathode materials used in commercialized batteries. To find new alternative electrode materials with high capacity is inevitably a feasible way to improve the performance of LIBs.

Materials that could be alloyed with lithium electrochemically, e.g. Si, Sn, Ag, were considered as promising candidates for next-generation anode materials for LIBs [1-3]. Of all known alloyed anode materials, silicon is an attractively alternative anode material due to its highest specific capacity up to 4200mAh/g and moderate lithium insertion voltage [1, 3]. As one of the most promising candidates, however, silicon is also confronted with disastrous volumetric changes caused by the contrast differences in lattice size caused by lithium ionic inserting and extracting at high mole ratio, resulting in structure ruins and subsequently fading in cycling performance. This is akin to the other alloy anode materials [2].

To decrease the dimension of silicon active center has been proved to be a feasible way to improve the electrochemical performance of silicon [3-10]. Generally, electrodes composed of one dimensional silicon nanowires were produced mostly from vapor deposition and could deliver a large capacity for the high mechanical properties of nanowire structure [6, 8, 10]. However, for silicon nanowire electrode, the electric contact of silicon center to its substrate merely depends on the interface between silicon nanowire and substrate, which is similarly a kind of point contact, so the interface is relatively too weak to resist against the volume changes during lithium inserting and de-intercalating. Compared to one dimensional silicon nanowires or silicon nanotubes, Si nano-films composed of two-dimensional nanostructures showed promising results in cycling life despite yielding less capacity than that of silicon nanowires [7, 11, 12, 13-15]. Silicon film electrodes have a relatively strong interface enhanced by the large contact area between active materials and substrates. It has been reported that Si film with the thickness less than 1200 Å possessed a long cycling life and high capacity [12]. However, the electrochemical performance of silicon film would decline dramatically with the increase in the thickness of silicon film, due to the issues of electron conductivity [12]. That is, enhanced electrochemical performance was gained within ultra thin silicon at the cost of less load density on current collectors. The low mass load of silicon electrode essentially impaired the capacity advantages of silicon anode.

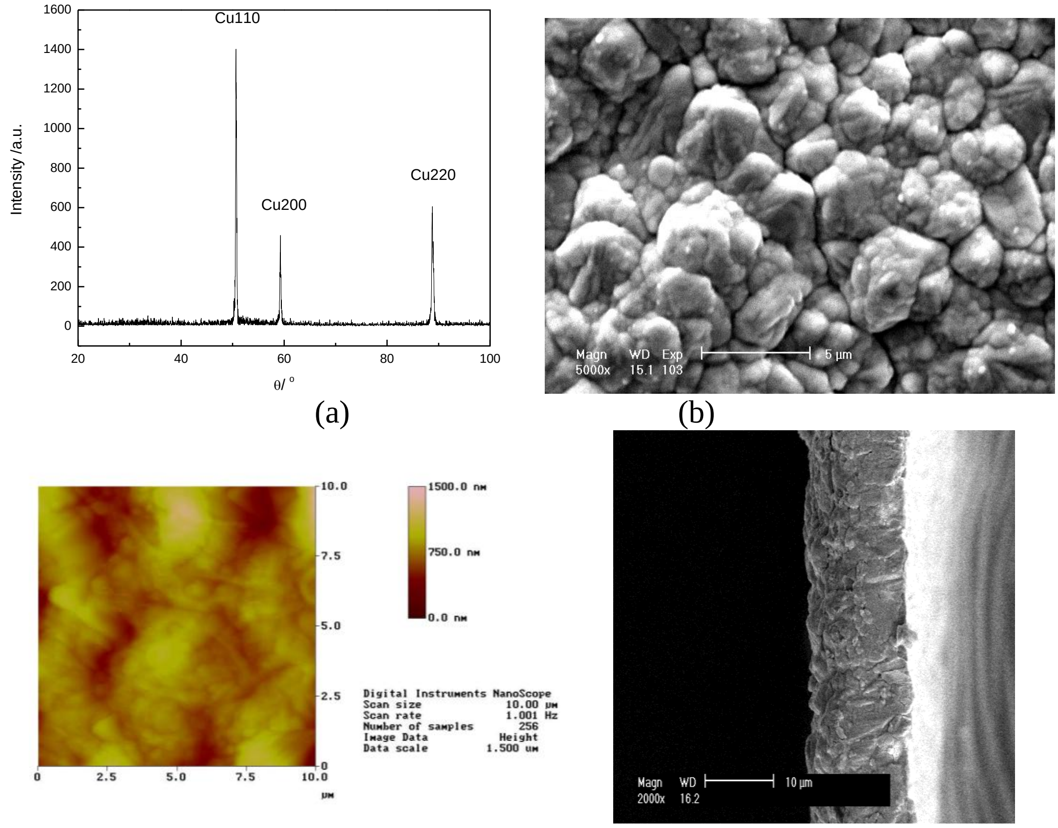
It is speculated the modification of the conductivity could make silicon film get through the limitation of nano-scale thickness maintaining good electrochemical performance. We report here a silicon film doped with Cu prepared by Ionion-beam sputtering. Doped Cu could improve the electronic conductivity of silicon film and promote the utilization efficient of Si active center. Although the thickness of deposited silicon film was up to 10 μm, much thicker than the reported ones, excellent electrochemical performance was gained. The results demonstrated that the coulombic efficiency of the silicon composite film free of conductive and binders could be up to 80%. The capacity retention after 100 cycles could be up to 93.8 % of that for the second cycle. Microcracks were observed on the surface of silicon film electrode after cycling, but no obvious exfoliation was found even after 300 cycles. The continuous maintenance of the electronic contact might be the main reason for the stable electrochemical cyclability of silicon film electrodes.

2. EXPERIMENTAL

Cu foils with thickness of 25 μm were used as the substrates. Cu foils were cleaned by ion beam sputtering to remove oxides on its surface before depositing. The target, which is negatively biased with respect to the plasma potential, was composed of n-type silicon target (15cm×10cm) mounted with Cu stripes (3cm in width) across. The ion beam was triggered at 2.5KV and the beam current was controlled at 40mA. Cu-doped Si film was deposited onto surface-cleaned Cu foil for 15min unless stated otherwise. The morphology and thickness of the deposited sample were identified by Atomic Force Microscope (AFM) and Scanning Electric Microscope (SEM). The crystal structure of samples was detected by X-ray Diffraction (XRD).

2025 coin cells, in which the deposited substrate was mounted as the working electrode and Li foil acted as both reference and counter-electrodes, were assembled to test the electrochemical performance in 1M LiPF6/EC+DMC (1:1 in volume) electrolyte solution. The electrochemical behavior of the cells was investigated by constant current charging-discharging measurement within the stable voltage window of 0.02-1.5V. Cyclic Voltammograms was tested at the scan rate of 0.05mV/s.

3. RESULTS AND DISCUSSION



(a) (b)

(c) (d)

Figure 1. (a) XRD profile of Cu-doped Si film deposited on Cu substrate. (b) AFM image of Cu-doped Si film sample. (c) SEM image of the surface of Cu-doped Si film sample. (d) SEM image of the cross section of Cu-doped Si film

Different from other silicon film deposited, thicker silicon films were prepared in this paper with reference to the commercialized anode. Typical diffraction peaks of crystalline Cu were found by

XRD analysis, whereas no obvious diffraction peaks of silicon were found (figure 1a). We changed the substrate to nickel film to deposit silicon on it under the same depositing conditions so as to verify if the Cu diffraction was from substrate, and the diffraction results agree well with that of the samples deposited on Cu substrates. This demonstrated the amorphous silicon and the crystalline Cu were deposited under the experimental conditions. It was deduced that silicon was deposited accompanied with the deposition of Cu particles, and the existence of sputtered Cu could impede the growth of silicon seed reversely, so the deposited Si here presented amorphous state. The morphology of as-prepared sample was shown in figure 1b and 1c. The deposited film consists of micro clusters with a size range of a few micrometers (figure 1b), corresponding with the morphology of the surface of Cu foil substrate. AFM image shows the coarse surface of the deposited film and the height of the clusters is less than 1.5 μm (figure 1c). AFM image and the cross section image (figure 1d) also demonstrated that the connected micro clusters were composed of finer clusters with columnar structure along the depositing direction, presenting the typical character of physical vapor deposition under high power. The thickness of as-prepared film is about 10 micrometers (figure 1d). Normally, thicker silicon film could impede the diffusion of lithium ions and electrons for its semi conductive property, and this is the reason that the thickness of the reported silicon film was usually controlled at nanometer scale. In our case, highly dispersed copper was deposited simultaneously with silicon, so it is possible to get highly dispersed Cu in the active film, and thus improve the conductivity of silicon film could be improved.

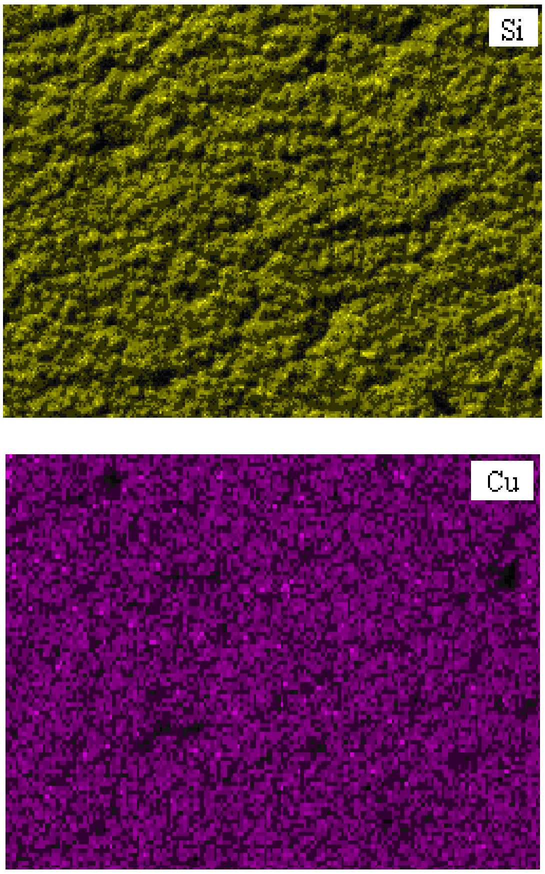
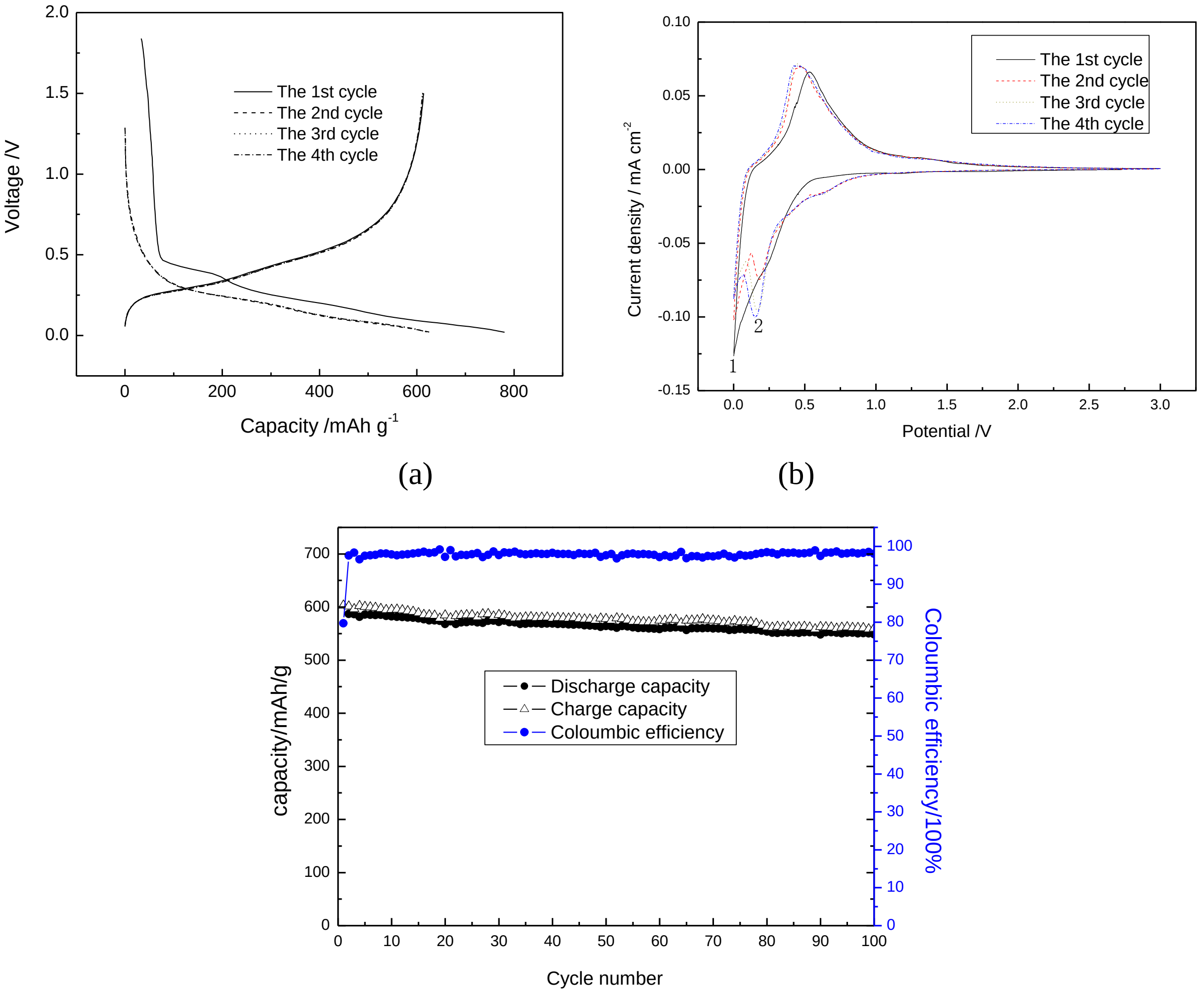


Figure 2. The element map of as-prepared Cu-doped film

To verify the distribution of silicon and Cu, element map was detected by energy spectrum. The element maps of as-prepared Cu-doped film are shown in figure 2. Silicon and Cu could be found dispersed uniformly in the film. Highly dispersion of conductive in silicon host could improve the conductivity property of Si active center, which is the fundamental factor to fabricate diffusion tunnels for lithium ions and electrons. A phenomenon that should not be ignored is that Cu-Si compound was not found although Cu and Si were sputtered at the same time. No big cluster of copper or silicon was found. Generally, it is easy to gain crystalline silicon film by physical vapor deposition. In this case, large amount of copper was deposited simultaneously with silicon at high rate. The high deposition power and the existence of copper should be the main reason of the formation of amorphous silicon.



(a) (b)

(c)

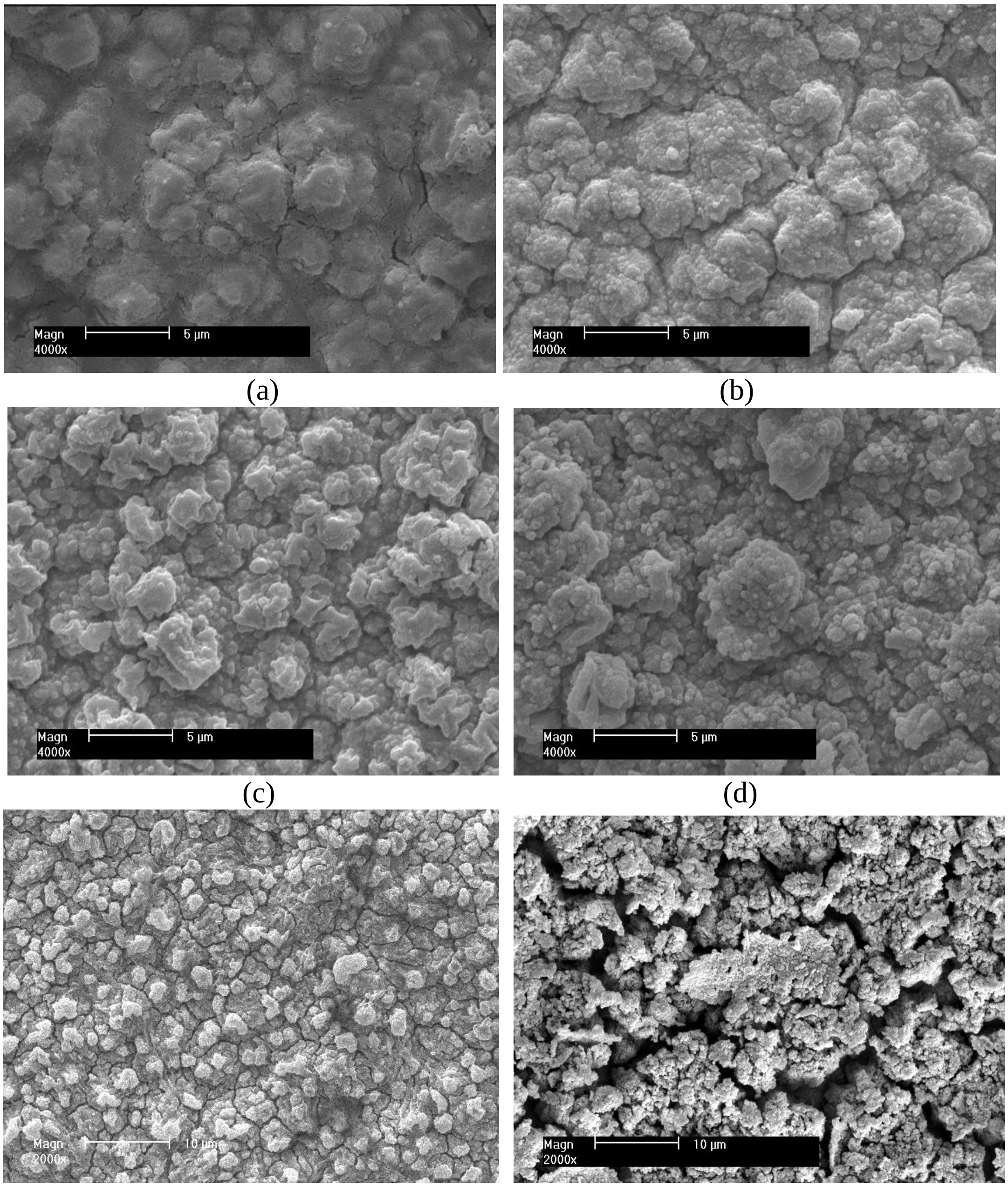
Figure 3. The electrochemical performance of as-prepared film anode: a) The charging-discharging profiles. b) The cyclic voltammetric curves. c) The cycling performance.

The electrochemical performance of as-prepared Cu-doped silicon film as anode was investigated in detail, shown in figure 3. The first discharging capacity is 775mAh/g, and the reversible capacity of the first cycle is 620mAh/g (figure 3a). Although the reversible capacity is relatively low comparing with pure silicon for Cu doping, the charging-discharging profiles present highly reproductive character except for that of the first discharging, indicating highly reversibility on cycling. It is worth noting that the thickness of silicon film applied in this experiment was above 10 micrometer, much higher than the suggested value mentioned in other reports. Silicon film in same thickness but free of Cu was also prepared under same experimental conditions. The first discharging capacity of the latter could be up to 1800 mAh/g, but fading dramatically in few cycles. This demonstrated again that the dope of Cu could definitely enhance the electrochemical reversibility of thick Si film. In addition, the amorphous silicon could avoid the crystal transformation and hence alleviated the irreversible trapping of lithium ions by the dangling bonds produced by structure collapse, resulting in the increase of coulombic efficiency on cycling.

The excellent reversibility could be confirmed further by cyclic voltammetric analysis (figure 3b). The cathodic process corresponds to lithium insertion and the anodic process corresponds to delithiation. There was an obvious difference between the first and the successive CV cycles. It was speculated that activation process took place during the initial cycling, derived from the phenomenon of separating on the cathodic peaks. It could be deserved found that only one wide cathodic peak appears blow 0.57V on the first-cycle lithiation curve, whereas two separated peaks was found in the successive cycles (figure 3b). It is worth noting that there is a visible peak shift toward negative direction occurring on anodic curves after the first cycle, which was reverse from the trend in other reports on silicon-containing electrode. This should be attributed to the activation of silicon active center and the improvement in the global conductivity by Cu doping on a large scale. After the first and second cycles, the shape of the CV curve became reproducible, which is similar to other reports. That is, the decrease of polarization and the improvement of conductivity could definitely facilitate the improvement of cycling performance of anode film. The charging-discharging profiles are coincidence with the CV curves very well.

As mentioned above, the coulombic efficiency of Cu-doped silicon film could be enhanced by sputtered Cu, and 80% and 98% was gained in the first cycle and the successive cycles, respectively. Whereas silicon film free of sputtered Cu in with the same thickness yielded a coulombic efficiency of only 70% for the first cycle and faded dramatically on cycling. The stable reversible capacity of the former could be 580 mAh/g and exhibited a stable cycling performance to 100 cycles. Figure 3c shows that the retained capacity is 549mAh/g after 100 cycles, 93.8% of that of the second cycle (figure 3c). Cu is an inert phase for lithium inserting and could be stable with an excellent mechanical property of plastic deformation in the circumstance took place in our experiment. In this case, we demonstrated that the sputtered Cu not only improved the conductivity of the Si film, but also acted as a buffering media alleviating the stress caused by lithium ion insertion. In addition, sputtered Cu has better affinity with Cu substrate and this provided the possibility to promote the interface stability during charging and discharging.

To investigate the reason for its good cyclability, film electrode in this case after cycling was taken out and rinsed clean with DMC to explore the morphology. To our surprise that the silicon attached on Cu substrate tightly instead of exfoliating from the current collector that usually observed on silicon electrode with cycling. Figure 4 shows the surface morphology after the first, 2nd, 5th cycles, 10th, 100th and 300th cycle (figure 4a-4f). Cracks were found initially after the first cycle. A hazy solid electrochemical interface (SEI) film seemingly formed on the surface of the film electrode because that the edge of deposited cluster particles became blur. It was deduced that the structure expansion occurring in the film caused the crack for the thick thickness of as-prepared film. Whereas, the amazing results shows that there is no any exfoliation happened even after 100 cycles, attributing to the highly dispersed Cu within silicon film, which connected silicon active point center between each others and kept good electronic contact.



(a) (b) (c) (d) (e) (f)

Figure 4. The morphology of as-prepared film electrode after different cycles: a) the first cycle, b) The 2nd cycle, c)The 5th cycle, d) The 10th, e) The 100th cycle, f)The 300th cycle

The particle refining phenomenon became apparent after 300 cycles (figure 4f), but yet the exfoliation hasn’t been observed. It is deduced that the highly dispersed Cu atoms acted as the joint point for dispersed silicon active center. Carbon-type material once was considered as the promising matrix for silicon [12, 16-18], but its active property and relatively low plastic mechanical properties make it difficult to be applied in the modification of silicon film. Different from carbon, Cu is relatively inert and plastic, it could alleviate the inner stress by plastic deformation once structure expanding and shrinking of silicon active center occurring. It could be the main reason for the enhancement in electrochemical performance of silicon film.

4. CONCLUSION

Cu-doped Si films were successfully prepared by ion sputtering. Excellent electrochemical performance of the film has been demonstrated although with a thickness of two orders of magnitude higher than reported ones. Cu was found beneficial in prolonging the cycling life of silicon film for its mechanically plastic property. The initial coulombic efficiency was 80% and carried 580mAh/g reversible capacity although with high mass load and with a high thickness of up to 10 μm, much higher than reported one. . The retained capacity maintained 93.8% of its first charging capacity. No visible exfoliation was found in the film electrode even after 300 cycles, which should be the main reason for high cyclability. Cu is considered an excellent doped candidate for the modification of silicon film and it makes the dimensional size of silicon film extended to micrometer scale without deteriorating its cycling performance.

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