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RAPID COMMUNICATION

Influences of annealing on lithium-ion storage performance of thick germanium film anodes

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Abstract
A high performance germanium (Ge) based anode is achieved through an appropriate air annealing post-treatment. Annealed Ge is fabricated by sputtering of Ge onto a stainless steel (SS) current collector and then annealed in air. It shows high specific and volumetric capacities of 1186 mA h g^{-1} and 5887.4 mA h cm^{-3}, respectively, at the rate of 812 mA g^{-1} up to 50 cycles. These specific and volumetric capacities are approximately a factor of 20 higher than those from as-deposited Ge on the SS substrate. In addition, the annealed Ge has a higher initial Coulombic efficiency of 90.8% than the as-deposited Ge of 81%. The improved performance of the annealed Ge can be attributed to the enhanced adhesion of annealed Ge film to SS substrate through interdiffusion at the SS/Ge interface due to the annealing post-treatment.

Introduction

Germanium (Ge) as a lithium-ion battery anode has a theoretical specific capacity of 1624 mA h g^{-1} ($Li_{22}Ge_5$) or 1384 mA h g^{-1} ($Li_{15}Ge_4$). As Ge has a high bulk density [1] of 5.3234 g cm^{-3}, Ge has a high theoretical volumetric capacity of 8643 mA h cm^{-3} ($Li_{22}Ge_5$) or 7367 mA h cm^{-3} ($Li_{15}Ge_4$). The theoretical

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specific and volumetric capacities of Ge are much higher than those of widely used graphite anode of 372 mA h g^{-1} and 830 mA h cm^{-3}, respectively [2]. However, as Ge undergoes a huge volume change (~260%) [3] during lithiation/delithiation that induces the structure disintegration and/or delamination of loaded Ge from the current collector, Ge based anodes typically show a very poor cycling performance. Mainly because of this problem, the application of Ge as Li-ion battery anode is unfeasible.

Several approaches have been used to overcome this challenge. First approach was to alleviate the stress by reducing the dimensions of Ge to nano-scale such as Ge nanowires [4,5], Ge nanotubes [6], porous nanostructure [7-9], etc. However, Ge nanostructures tend to have a lower density, leading to a small volumetric capacity. Second approach was to introduce a buffering matrix to coat Ge [10-12] or to be coated by Ge [13], Ge composite [14], etc. Depending on the ratio of active Ge to the buffer matrix, the theoretical specific capacity of the composite might be significantly decreased. Third approach was to deposit Ge film directly onto a current collector [15-17]. Graetz [15] deposited 60-250 nm thick amorphous Ge on a planar nickel current collector and showed a specific capacity of 1700 mA h g^{-1} at the rate of 375 mA g^{-1} up to 60 cycles. Laforge [16] showed that 200 nm thick amorphous Ge with n-type doping had a specific capacity of ~1460 mA h g^{-1} at the rate of 100 μA cm^{-2} up to 180 cycles. Recently, Rudawski [17] applied ion-beam treatment to 140 nm thick Ge film and achieved a specific capacity of ~1500 mA h g^{-1} at the rate of 649.2 mA g^{-1} up to 25 cycles. However, as their Ge thickness was only 140 nm, the areal capacity was limited to ~0.1 mA h cm^{-2} [17] which is not favorable for commercial purpose [18].

It is well observed that the cycle performance of Ge based anodes depends on the thickness of loaded Ge onto the current collectors. When Ge thickness is higher than a critical thickness, the cycle performance degrades because of the pulverization and/or delamination of the Ge film.

Herein, we investigate the electrochemical performance of 760 nm thick Ge film on a stainless steel (SS) current collector. Air annealing post-treatment is examined as a simple technique to improve the performance of the thick Ge film anode. The effect of titanium nitride (TiN) diffusion barrier layer at SS/Ge interface is also studied.

We have fabricated the following samples: as-deposited Ge (73, 126, 183, 358 and 760 nm Ge thickness), as-deposited TiN/Ge (126 and 760 nm Ge thickness), annealed Ge (760 and 1530 nm Ge thickness) and annealed TiN/Ge (126 and 760 nm Ge thickness). The details of the sample preparation, physical and electrochemical characterization can be found in the Supporting information.

Results and discussions

As-deposited Ge has a stable cycle performance when Ge thickness is less than critical thickness. Figure 1 shows that the specific capacities for as-deposited Ge (73 nm) and as-deposited Ge (126 nm) were 1476.4 and 1304.1 mA h g^{-1}, respectively. The corresponding mass loading was only 0.032 and 0.066 mg cm^{-2}. Thus, the areal capacity was 0.047 and 0.086 mA h cm^{-2} for as-deposited Ge (73 nm) and as-deposited Ge (126 nm), respectively. The cycle performance was found to degrade when the thickness of loaded Ge was ≥ 183 nm. As-deposited Ge with thickness of 183, 358 and 760 nm had the specific capacities of 594.9, 150 and 56.6 mA h g^{-1}, respectively, at the rate of 812 mA g^{-1} at 50 cycles.

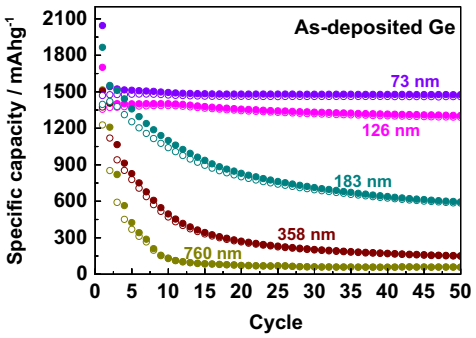

Figure 1 Specific capacity vs. cycle of as-deposited Ge (73, 126, 183, 358 and 760 nm) at the rate of 0.5 C.

In the following study, we investigate the effect of air annealing on the electrochemical properties of 760 nm thick Ge with mass loading of 0.377 mg cm^{-2}. X-Ray Diffraction (XRD) and Raman spectra showed no difference between the annealed Ge (760 nm) and the control sample of as-deposited Ge (760 nm). The broad XRD peak at ~27° and the Raman peak at about 273 cm^{-1} can be attributed to amorphous germanium in both as-deposited and annealed Ge [19], see Figure S4. Scanning Electron Microscopy (SEM) images showed that the annealed Ge had a little higher oxide than the as-deposited Ge due to an air annealing process (Figure S5).

Figure 2a shows that the electrochemical performance of annealed Ge (760 nm) was much better than the as-deposited Ge (760 nm). The as-deposited Ge had specific capacities of 1514.1 mA h g^{-1} and 1226.3 mA h g^{-1} during first lithiation and first delithiation, respectively. The Coulombic efficiency was 81%. In contrast, the annealed Ge had specific capacities of 1374.8 mA h g^{-1} and 1247.6 mA h g^{-1} during first lithiation and delithiation, respectively. The Coulombic efficiency of annealed Ge was 90.8%, much higher than the as-deposited Ge and comparable to the highest Coulombic efficiency reported so far [20]. The as-deposited Ge had a poor cycle performance. It had a specific capacity of 56.6 mA h g^{-1} up to 50 cycles at the rate of 0.5 C (1 C=1624 mA h g^{-1}). In contrast, the annealed Ge had an improved cycle performance with a specific capacity of 1186 mA h g^{-1} up to 50 cycles at 0.5 C rate. To test the rate capability, different lithiation and delithiation rates were used as shown in Figure 2b. The annealed Ge shows an excellent specific capacity of 1308.8, 1261.2, 1215.4, 1153.5 and 1043.3 mA h g^{-1} at 0.1, 0.5, 1, 2 and 4 C, respectively. In contrast, the as-deposited Ge could only withstand a maximum rate of 2 C. The as-deposited Ge had a poor specific capacity of 186.4, 51.3, 22.6 and 8.1 mA h g^{-1} at 0.1, 0.5, 1 and 2 C, respectively. When the rate was tuned back to 0.1 C, the annealed Ge showed a significant recovery with a specific capacity of 1302.1 mA h g^{-1}, while the as-deposited Ge only showed a specific capacity of 60.0 mAhg $^{-1}$. Figure 2c shows that the annealed Ge had achieved a cycle life for up to 100 cycles with a specific capacity of 1178.5 mA h g^{-1} at the rate of 1 C.