Development of All-solid-state Thin-film Secondary Battery for MEMS and IoT Device

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Abstract. All-solid-state thin-film secondary battery (TFB) has come to recognized as one of the key enabling technologies for stand-alone MEMS/sensor devices which are indispensable for internet-of-things (IoT) solution. This paper presents on anode material development for TFB. Silicon is promising candidate to replace metallic lithium due to high heat-resistant and even high theoretical specific capacity. In this work, the effect of titanium addition on sputtered silicon electrode performance was investigated in order to improve not only mechanical damage but also resistivity.

1. Introduction
Li-ion secondary batteries have particularly high energy density, and there has been a steady increase in the demand for Li-ion secondary batteries especially for consumer electronics. However, they even have the risks of expansion, liquid leakage, and fire caused by organic liquid electrolyte. To resolve these problems intrinsically, all-solid-state batteries with solid electrolyte has been proposed and developed. Among all-solid-state batteries, TFBs are produced by thin-film deposition technology which has special advantages that are not only safe as their being all-solid-state but also thin, small, lightweight and flexible [1, 2]. As solid electrolyte, glass lithium phosphorus oxynitride (LiPON) has been commonly used due to advantages of no grain boundary, less electronic conductivity, isotropic property, and electrochemical stability [3], and therefore, TFBs also have the features such as less self-discharging property and long cycle-life.

Owing to the above features, it is expected that TFBs can be employed in various application such as RF-ID tag, smartcard, wearable device as well as IoT device with microprocessor, MEMS sensor, wireless communication, and power supply components. Especially, IoT device is essential to realize a smart society of the future, however its power management is becoming one of the fatal issues. To achieve the stand-alone power supply, the integration with TFB and energy harvesting device is proposed by some research groups [4, 5].

To fabricate a smart IoT device, each component must be integrated onto the same substrate or chip using solder-reflow and through-silicon via (TSV), which are the one of the enabling technologies to high-density packaging [6]. However, Li which is currently the most used as an anode material in TFB has low melting point as around 180 deg.C and cannot be employed for high-density packaging due to including high-temperature ambient (e.g. maximum temperature is 250 deg.C). Meanwhile, Si which is extensively studied as anode material in bulk-typed Li-ion battery is a promising candidate to replace Li due to not only its high specific capacity (834 μAh cm⁻²μm⁻¹ for Li₁₅Si₄ that represents the highest lithiated phase) but also low electrode potential. Nevertheless, there is an issue of drastic volume expansion of Si electrode during lithiation (up to around 280%) and causes mechanical breakage [7, 8].
Our previous work has shown that amorphous and porous Si electrode suppresses to capacity fading due to relaxation of mechanical damage [9], however sputtered Si was high resistivity. It has also reported that providing an inactive framework that Ni, Cu, Fe and Ti are well known, is one possible way to alleviate the expansion issue [10]. In this work, the effect of Ti addition on sputtered Si electrode performance was investigated in order to improve not only mechanical damage but also resistivity.

2. Experimental

2.1. Preparation of Si-Ti alloy film

Si-Ti alloy film was prepared by co-sputtering with boron-doped Si target whose resistivity is below 0.02 Ωcm and Ti sputtering target. The size of both sputtering target size was 4-inch diameter. Ti composition within the film was adjusted by changing applied power to Ti target while fixing that of Si target. This time, DC power of Si target was fixed to 1000 W and RF power of Ti target was set to 0, 90, 200, and 450 W, Ar was used as sputtering gas, and process pressure was adjusted to high pressure at 3.0 Pa for low film-density. Prepared film was characterized by SEM, XRD, four-terminal sensing, and ICP-AES.

2.2. Fabrication of Li/LiPON/Si_{1-x}Ti_{x} half-cell

Each layer was deposited by sputtering and evaporation; 20 nm Cr and 100 nm Ni as cathode current collector, 200 nm Si_{1-x}Ti_{x} as cathode, 2 μm LiPON as solid electrolyte, 4 μm Li as anode, and 100 nm Ni as anode current collector, and finally half-cell was completed by encapsulation with UV curable resin and barrier lid. Cross-sectional schematics is shown in figure 1(a). The actual capacity of Si_{1-x}Ti_{x} electrode was checked by CC discharging (0.03 mA const., < 50 mV).

2.3. Fabrication of Si_{1-x}Ti_{x}/LiPON/LiCoO_{2} full-cell

All layers were deposited by sputtering; 20 nm Ti and 100 nm Pt as cathode current collector, 3 μm LiCoO_{2} as cathode, 2 μm LiPON as solid electrolyte, 600 nm Si_{1-x}Ti_{x} as anode, and 100 nm Ni as anode current collector. Only LiCoO_{2} layer was annealed at 600 deg.C for crystallization, and finally full-cell was completed by encapsulation. Cross-sectional schematics is shown in figure 1(b). The battery capacity was checked by CCCV charging (0.3 mA const., > 4.1 V / < 0.03 mA) and CC discharging (0.3 mA const., < 2.5 V) and impedance property was checked at 25 deg.C by AC impedance measuring method. Frequency was swept from 50 mHz to 1 MHz and amplitude voltage was set to 10 mV.

3. Result and discussion

Figure 2 shows cross-sectional SEM image of sputtered Si_{1-x}Ti_{x} films. The microstructure of each film seems columnar shape and its grain size observes almost same. Ti composition (x) of each Si_{1-x}Ti_{x} film was estimated to (a) 0, (b) 0.033, (c) 0.115, and (d) 0.296 analyzed by ICP-AES, and it also confirmed that each film observes amorphous state determined by XRD (figure not shown). Figure 3 shows the resistivity of sputtered Si_{1-x}Ti_{x} film. The resistivity of sputtered Si (x = 0) indicates high and a value close to pure Si (3.97×10^{5} Ωcm) in spite of using boron-doped Si sputtering target. This means
that boron is volatilized and almost removed during sputtering. In addition, resistivity is drastically reduced by adding Ti up to around 0.1, and then slightly reduced.

Figure 4 shows the discharge curves of fabricated half-cell and the actual capacity of each amorphous Si$_{1-x}$Ti$_x$ electrode is observed 482 (x = 0), 479 (x = 0.033), 434 (x = 0.115), and 205 μAh cm$^{-2}$μm$^{-1}$ (x = 0.296). It is found that capacity reduces with increasing Ti composition, however the capacity of Si$_{0.704}$Ti$_{0.296}$ is less than half that of Si. It might be considered that excessive and inactive Ti disturbs Li-ion diffusion as well as lithiation and causes significant decrease of capacity.

Figure 5 shows 1st discharge curves of fabricated full-cell. The capacity of each cell is 43.6 (x = 0), 40.8 (x = 0.033), and 38.9 μAh cm$^{-2}$μm$^{-1}$ (x = 0.115). Despite the same LiCoO$_2$ film thickness in each full-cell, differences in capacity are seen. Figure 6 shows nitny plot of fabricated full-cell in state of fully charge. The resistance of full-cell mainly consists of electrolyte and interface component and first and second semi-circle represent LiPON and electrolyte/electrode (LiPON/LiCoO$_2$ and LiPON/Si$_{1-x}$Ti$_x$) interfacial resistance, respectively. It is found that internal resistance with Si$_{1-x}$Ti$_x$ electrode indicates lower than that with pure Si electrode and it reduces from 170 to 140 Ω. Figure 7 shows the capacities under the each current condition from 0.02 to 5.7 mA cm$^{-2}$. It is found that power performance of full-cell with Si$_{1-x}$Ti$_x$ electrode is improved comparing to that with pure Si electrode, and higher current can be output up to 5.7 mA cm$^{-2}$. According to impedance result, Ti within Si electrode may play a role in improving not only electrode resistivity but also interfacial resistance (LiPON/Si$_{1-x}$Ti$_x$) reduction by Ti mutual diffusion.
4. Conclusion

We investigated the effect of Ti addition on sputtered Si electrode performance for improving all-solid state thin-film secondary battery with high-temperature tolerance. By adding Ti, the capacity of full-cell (Si$_{1-x}$Ti$_x$/LiPON/LiCoO$_2$) trends to reduce, whereas power performance is improved and high continuous current can be output up to 5.7 mA cm$^{-2}$.

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