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Effects of Fe layer on Li insertion/extraction Reactions of Fe/Si Multilayer thin Film Anodes for Lithium Rechargeable Batteries

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ABSTRACT

The influences of the thickness and microstructure of Fe layer on the electrochemical performances of Fe/Si multilayer thin film anodes were investigated. The Fe/Si multilayer films were prepared by electron beam evaporation, in which Fe layer was deposited with/without simultaneous bombardment of Ar ion. The kinetics of Li insertion/extraction reactions in the early stage are slowed down with increasing the thickness of Fe layer, but such a slowdown seems to be negligible for thin Fe layers less than about 500 Å. When the Fe layer was deposited with ion bombardment, even the 300 Å thick Fe layer significantly suppress Li diffusion through the Fe layer. This is attributed to the dense microstructure of Fe layer, induced by ion beam assisted deposition (IBAD). It appears that the Fe/Si multilayer films prepared with IBAD show good cyclability compared to the film deposited without IBAD.

Keywords: Fe/Si multilayer films, Anode, Thin films, Lithium rechargeable batteries, IBAD

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1. Introduction

In recent years, intensive studies have been conducted on thin-film microbatteries as a power source for microsystems.[1,3)] Concurrently, there has been considerable interest in finding new materials to replace the existing lithium metal anode.[4,10)]

Silicon is one of the best candidates for the anode material but it has a drawback of poor cycle life due to a dramatic volumetric variation during cycling. It could be overcome by using a multiple-layer thin film comprising a silicon (Si) layer and a transition metal (M) layer.[12,13)] At this point, it should be noted that the metal (M) is thermodynamically immiscible with lithium. This drives us to the question whether the metal (M) layer can act as a diffusion barrier against Li penetration during Li insertion/extraction reactions of the multilayer film electrode. Moreover, Since the Li penetration could be affected by the microstructure and the thickness of the metal (M) layer, the investigation of those effects is very important for developing the understanding on the electrochemical characteristics of M/Si multilayer thin film anodes.

In general, the microstructures of thin film are dependent on deposition methods and conditions. It has been also reported that the ion bombardment of growing film increases the ad-atom mobility at the surface and thus changes film morphology, microstructure, defect concentration and preferred orientation.[14)]

This work examines the effects of the thickness and the microstructure of Fe layer on the Li insertion/extraction reactions of Fe/Si multilayer thin film anodes, in which the microstructure of the Fe layer is controlled by ion-beam assisted deposition (IBAD) method.

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2. Experimental

The Ti (150 Å)/Si (400 Å)/Fe (0-1500 Å) multilayers have been prepared to examine the effects of Fe layer on the electrochemical performance, particularly the Li insertion/extraction reaction kinetics of the Si phase. The films were deposited on Ni substrate by using electron beam evaporation. For some samples, the Fe layer was deposited with simultaneous bombardment by Ar ion at 120 eV ion energy and 0.13 mA/cm^2 ion density. The concurrent Ar ion bombardment of the growing film was provided by Kaufmann ion source which was installed in the side flange of the chamber allowing the Ar ion bombardment to impinge on the substrate at an angle of 45°. A faraday cup ion probe was used to measure the ion current density. The films were deposited successively without breaking vacuum.

All depositions were performed at room temperature. The film thickness was controlled by the evaporation time and was checked during the deposition by a quartz-crystal thickness monitor. The thickness of as-deposited films was confirmed by using a surface profilometer.

To evaluate the electrochemical performance of the multilayer films, 2016 coin-cell hardware was used. The cells comprised a lithium metal electrode and a multilayer film electrode that were separated by a separator. The electrolyte was 1 M $LiPF_6$ in a 1 : 1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), provided by PANAX ETEC Co., Korea. The cells were cycled galvanostatically at current densities ranging between 30 and 400 μA/cm^2 within the potential range of 0.0 −1.2 V versus Li/Li$^+$.

3. Results and Discussion

Fig. 1 shows the second discharge (Lithium insertion)-charge (Lithium extraction) curves for the films of the Ti/Si/Fe structure at 90 μA/cm^2, in which the thickness of the Fe layer varied between 0 and 1500 Å. For the films with a Fe layer less than 500 Å thick, the discharge-charge curves seem to be essentially identical, but with thicker Fe layers, a capacity loss is observed. This trend is clearly illustrated in Fig. 2, which shows the dependence of the charge capacities of the films of the Ti/Si/Fe structure on current densities as a function of the Fe layer thickness. The capacity falls off with increasing current density, as is always observed for electrode materials of lithium-ion batteries. However, when the thickness of Fe layer is less than 500 Å, the effect of the Fe layer on the capacity loss appears to be negligible.

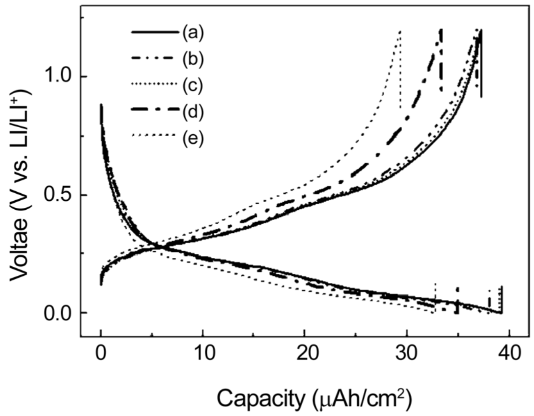

Fig. 1. The second discharge (Lithium insertion)-charge (Lithium extraction) curves for the films of the Ti/Si/Fe structure at 90 μA/cm^2 with the thickness of the Fe layer of : (a) 0, (b) 300, (c) 500, (d) 1000, (e) 1500 Å.

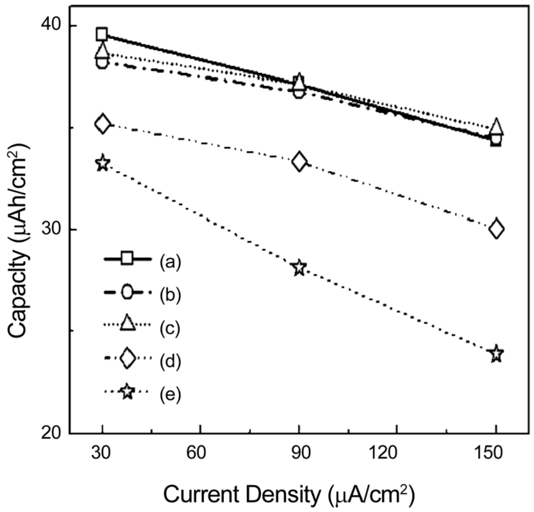

Fig. 2. The dependence of the charge capacities of the films of the Ti/Si/Fe structure on current densities for the Fe layer thickness of : (a) 0, (b) 300, (c) 500, (d) 1000, (e) 1500 Å.

Since the microstructure of the Fe layer can have an influence on the diffusion of lithium ion through Fe layer, we investigated the effect of microstructural modification by using ion beam assisted deposition (IBAD) on the Li insertion/extraction reactions of the Fe/Si film. Fig. 3 shows the discharge-charge curves at the second cycle for Ti/Si/Fe films, in which the 300 Å thick Fe layer was deposited with/without concurrent ion bombardment. In

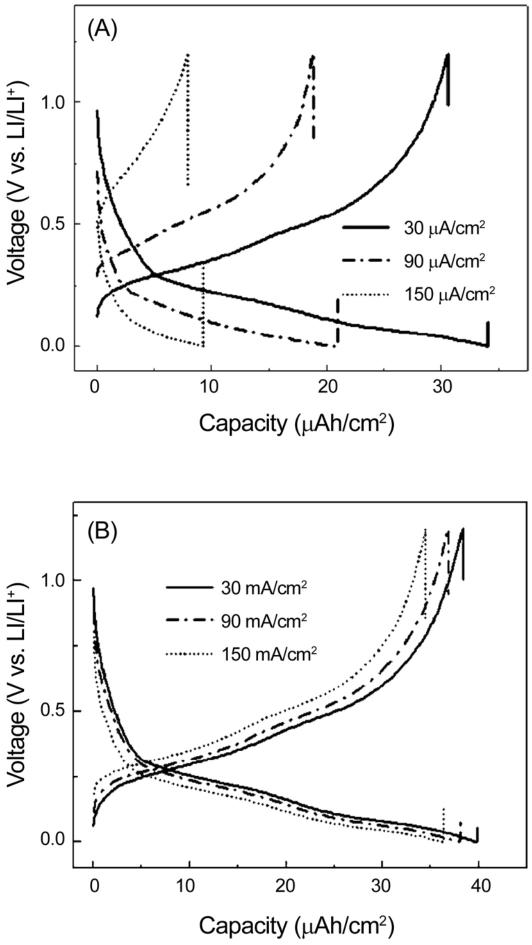

Fig. 3. The second discharge-charge curves for the Ti/Si/Fe films, in which the 300 Å thick Fe layer was deposited (a) with / (b) without concurrent ion bombardment.

contrast with the film prepared without IBAD, the multilayer film with Fe layer prepared by IBAD shows a drastic capacity loss with current density. This indicates that even though the thickness of the Fe layer is in the range of 500 Å, the lithium diffusion through Fe layer might be slowed down by applying IBAD process and as a result the Li insertion/extraction reactions of the Si/Fe multilayer film would be suppressed.

Fig. 4 shows the differential capacity curves (dQ/dV versus potential), as obtained by differentiating the discharge-charge curves of Fig. 3 with respect to the potential. For comparison, the differential capacity of the Fe-layer free Si thin film electrode is also presented (Fig. 4(c)). For the sample with Fe film prepared by IBAD, the potential separation between the redox peaks increased significantly with current density, while when the Fe layer was deposited without IBAD the peak separation was little changed in the range of current densities investigated. It is worthwhile to note that the dQ/dV curves feature of the latter sample is similar to that of Fe-layer free Si thin film. Considering that such a peak separation is indicative of the insertion and extraction process of lithium being associated with an overvoltage due to the bulk transport, we can see that the lithium insertion and extraction process of Fe/Si multilayer films is significantly affected by microstructural characteristics of Fe layer, as induced by IBAD process. It has been demonstrated that a concurrent ion bombardment during deposition resulted in the dense microstructure, in particular, in grain boundaries.[15] Microstructural defects such as grain boundaries and voids would be the preferential pathway for Li diffusion in a Fe layer. Therefore, the suppressed Li insertion/extraction reaction in samples with Fe film deposited by IBAD as illustrated in Fig. 3 and 4, is attributed to the dense microstructure of Fe layer.

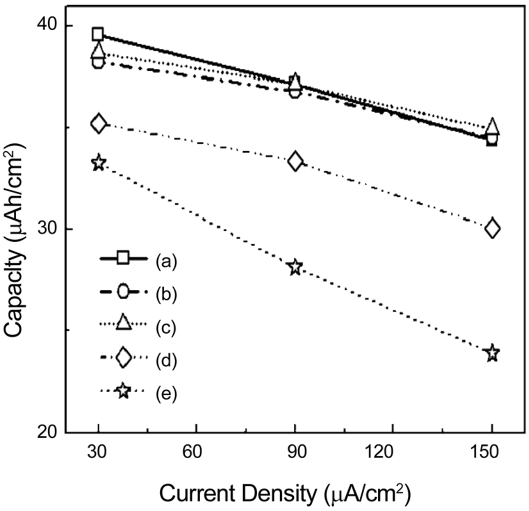

Fig. 4. The differential capacity curves (dQ/dV versus potential) of Fig. 3 curves, in which the 300 Å thick Fe layer was deposited (a) with/(b) without concurrent ion bombardment and (c) the differential capacity plotof the Fe-layer free Si thin film electrode.

The results for Fe/Si single stack films mentioned above show that the rate of lithium diffusion through the Fe layer appears to be similar in the thickness range of 500 Å, and thus the Li insertion/extraction rate capability of Fe/Si single stack film electrode behaves similarly. Then, we have tried to investigate the Li insertion/extraction rate capability of Fe/Si

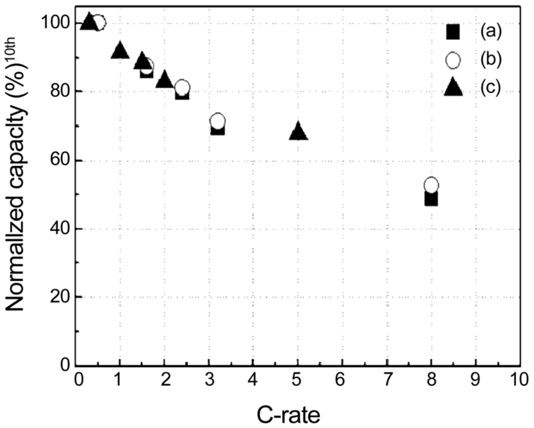

Fig. 5. The discharge capacities of the Fe/Si multilayer film electrodes, specified at Table 1, as a function of discharge rate.

multiple stack films with different stacking structure as given in Table 1. Fig. 5 shows the discharge capacities of the Fe/Si multilayer film electrodes as a function of discharge rate. The capacity falls off with increasing discharge rate as in general trend. However, it is revealed that the rate capability of those Fe/Si multilayer films is essentially identical for experimental conditions investigated, although the multilayer stacking structures, such as the number of a multiple layer, the total thickness of Si layer, and the thickness of Fe layer, are different from each other. This indicates that there is a critical value of the thickness and number of Fe layer, below which the Li insertion/extraction kinetics of Fe/Si electrodes are not significantly affected by Fe layer even for the Fe/Si multiple stack films.

Since the Li insertion/extraction reactions of the Fe/Si single stack films are affected by the microstructure of the Fe layer, we have studied the effect of the microstructural modification of Fe layer caused by IBAD on the Li insertion/extraction reaction of Fe/Si multiple stack films. It should be noted here that the Si layer thickness increased to 2000 Å for the synthesis of high capacity electrodes.

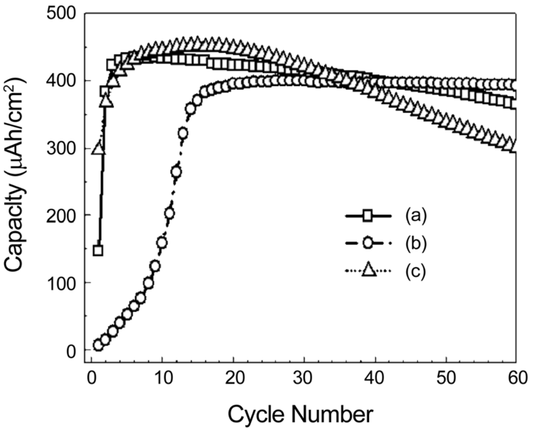

Fig. 6. The capacity versus cycle number of multilayer film electrodes with a contact structure of the Ti(150 Å)/Si(2000 Å)/Fe(300 Å)/Si(2000 Å)/Fe(300 Å)/Si(2000 Å)/Fe(100 Å). The Fe layer was deposited with IBAD for samples (a) and (b), but without IBAD for sample (c). Note that the samples (a) and (c) were cycled at 200 μA/cm², but the sample (b) was cycled at 400 μA/cm².

Fig. 6 shows the capacity vs. cycle number of the Fe/Si multiple stack electrodes, prepared by succeeding deposition of a 2000 Å thick Si layer and a 300 Å thick Fe layer, with a contact structure of Ti/Si/Fe/Si/Fe/Si/Fe, in which a 150 Å thick Ti layer was deposited as an adhesion-promoting layer to enhance the adhesion and the top Fe layer thickness was 100 Å.

As expected, when the Fe layer was deposited by IBAD, the reaction of the Fe/Si multilayer electrode with lithium was retarded in the early stage of cycling and this behavior was more significant at higher current density, while the long-term cycle performance of the Fe/Si multilayer film was improved by applying the IBAD process. At this point, it is necessary to note that the electrode with the Fe layer deposited without IBAD also seems to be a little resistant in the early stage of cycling. This can be attributed to the thick Si layer of 2000 Å, in which the Si layers are cracked during initial several cycles and then react with lithium more easily.

Table 1. The specification of the Fe/Si multi-layer film electrode

Sample	Stackin Sequence	Layer thickness (Å)				Total Thickness (Å)/ Thickness of Si (Å)
		Ti	Si	Fe	Fe (top)	
A	Ti/Si/Fe(7)/Si/Fe	150	80	60	40	1250/640
B	Ti/Si/Fe(4)/Si/Fe	150	128	96	76	1250/640
C	Ti/Si/Fe(7)/Si/Fe	150	128	96	76	1922/1024

The number in brackets indicates the number of Fe/Si stacks in the multilayer films.

4. Conclusions

In this paper, the effects of the thickness and the microstructure of Fe layer on the electrochemical characteristics of Fe/Si multilayer thin film anodes were investigated. The kinetics of Li insertion/extraction reactions, especially in initial cycling, are slowed down with increasing the thickness of Fe layer, which can be, nevertheless, negligible for thin Fe layers less than about 500 Å. However, even 300 Å thick Fe layer, when deposited by IBAD, Li diffusion through Fe layer is significantly suppressed in the early stage of cycling. This is attributed to the dense microstructure of Fe layer, induced by IBAD. The Fe/Si multilayer films prepared with IBAD show good cyclability compared to the film deposited without IBAD. There is a critical value of the thickness and number of Fe layer, below which the Li insertion/extraction kinetics of Fe/Si multilayer films are not significantly affected by Fe layer.

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