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Effect of plasma immersion on crystallinity of V_2O_5 film grown by dc reactive sputtering at room temperature

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Abstract

Vanadium oxide thin films were grown at room temperature by direct current reactive sputtering. To investigate the effect of plasma immersion on the crystallinity of as-grown film, we immersed samples in plasma during the deposition process. X-ray diffraction (XRD) measurements show that as-deposited thin films immersed in plasma are crystalline, whereas those not immersed in the plasma are amorphous. Images taken with scanning electron microscopy show that the surface of films exposed to plasma have a different morphology to the surface of films not exposed to plasma. The Li-intercalation feature of as-deposited films immersed in plasma shows the typical behavior of crystalline vanadium oxide; such behavior is unsuitable for the cathode of thin film batteries (TFBs). These results indicate that direct current plasma promotes the growth of crystalline vanadium oxide films.

Keywords: Sputtering; Plasma processing and deposition; Vanadium oxide; Crystallization

1. Introduction

Recently, the technology of microelectronic systems has attracted global attention for applications such as medical devices, communication systems, sensors and actuators [1–4]. While the development of microprocessing techniques and materials has produced smaller and more precise electronic devices, it has also induced technical problems. One of the biggest problems for microelectronic devices is the development of optimal micropower sources; for example, thin film batteries (TFBs) and the thin film supercapacitors that drive these devices [5–13]. TFBs have great potential for integrating applications such as smart cards, on-chip power sources and portable electronic devices because they can be incorporated into the same integrated circuit with other electronic elements.

A variety of cathode materials such as $LiCoO_2$, $LiMn_2O_4$, LiV_2O_5 and V_2O_5 have been studied extensively for use in Li-based TFBs (LTFBs). As with Bates et al., we recently fabricated TFBs with $LiCoO_2$, $LiNiO_2$, and V_2O5 cathode thin films, as well as with an $Li_{3.3}PO_{3.9}N_{0.17}$ solid electrolyte [14–19]. Among the *studied* cathode materials, *amorphous* V_2O_5 has a wide potential range, high energy density (147 mA h/g at the cut-off voltage of 2.5 V) and good cycling performance. As a result, it is useful for fabricating LTFBs. However, the crystalline phase of V_2O_5 undergoes phase transformations during the processes of intercalation and de-intercalation, and consequently forms irreversible γ- and ω-phases [20]. These irreversible phases induce a poor cycling performance, decrease the capacity of LTFBs and lessens the lifetime of LTFBs. On the other hand, no phase transformations occur in amorphous vanadium oxide during Li intercalation. Therefore, regardless of the deposition method, amorphous V_2O_5 thin film is the only adequate material that can be used to manufacture LTFBs with a high cycling performance.

Many deposition methods have been studied for the preparation of the V_2O_5 thin film. Sputtering has proven to be the best method because of its high deposition rate.

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Compared with chemical vapor deposition, the sputtering method is also simpler.

We now report our observations of the crystallinity, microstructure and electrochemical properties of V_2O_5 thin film grown by direct current (dc) reactive sputtering as a function of plasma immersion.

2. Experimental details

We used the dc reactive sputtering method under the same plasma power and atmosphere conditions to grow vanadium oxide thin films on (100) Si wafers with Pt current collectors, while varying the target–substrate distance. Sample 1 was immersed in plasma but not sample 2. As confirmed by the naked eye, sample 2 made no contact with the plasma. Therefore, the plasma did not affect the crystallinity of sample 2. We then used dc sputtering to deposit the Pt (2000 Å)/Ti (300 Å) current collector layers, where the Ti layer was an adhesive layer between the Si layer and the Pt layer. After the vacuum chamber was evacuated to 6.67×10^{-4} Pa, the vanadium oxide thin films were deposited by using a 4 in.-metal vanadium target with a purity of 99.7%.

Before growing vanadium oxide thin film, we prepared the metal vanadium target surface with Ar^+ ion plasma to remove the oxide layer and contaminants from the target surface. The treatment lasted for 20 min with a working vacuum of 5 mTorr and a dc sputtering power of 370 W. To avoid contamination of the Pt current collector by particles sputtered from the metal vanadium target during the pre-sputtering process, we positioned two separate shutters ahead of the target and substrate. After the pre-sputtering, the vanadium oxide thin film was deposited at room temperature with a working pressure of 5 mTorr. In both cases of sample 1 and sample 2, the dc sputtering power was 250 W.

Details of the different experimental conditions for sample 1 and sample 2 are as follows. For the dc sputtering process, we used an on-axis sputtering system. For sample 1, the distance between the substrate and the target was 8 cm; for sample 2, it was 10 cm. The results show that sample 1 has a slightly higher growth rate than sample 2. When the O_2:Ar gas ratio is 3:7 (15:35 sccm), the growth rate is 0.335 nm/min for sample 1 and 0.303 nm/min for sample 2.

To investigate the bonding state between the vanadium and oxygen for the as-deposited thin films, we used Fourier transform infrared (FT-IR, Mattson Instruments) spectroscopy. And to confirm the composition of thin film grown by dc reactive sputtering, we used Rutherford backscattering spectrometry (RBS, NEC, 6SPH2, 3MeV). In addition, we used wide-angle X-ray diffraction (XRD, Rigaku, CuK_α) to confirm the crystallinity of the as-deposited thin films, and we used HREM (JEM 2010, 200 kV, 300 mm) to examine the microstructure of the as-deposited thin films. We used scanning electron microscopy (SEM, Hitachi S-4100, 15 kV) to investigate the surface structure of the as-deposited thin films. To measure the thickness of the as-deposited vanadium oxide films, we conducted cross-sectional SEM analysis. To evaluate the electrochemical properties and cycling performance of the as-deposited thin films, we measured the cycles in half-cells; the half-cells were assembled with lithium foils (Cyprus) as counter electrodes and reference electrodes. We used a propylene separator with 1 M $LiPF_6$ in EC:DMC (1:1, Merck) for the electrolyte solution. To test the charge–discharge behavior, we used a constant current and a battery cycler system (WBCS 3000). The current density was 20 $\mu A/cm^2$, and the cut-off voltage ranged from 3.8 to 1.5 V.

3. Results and discussion

Fig. 1 shows the FT-IR absorption bands for the vanadium oxide thin films immersed in plasma (sample 1) and for those not immersed in plasma (sample 2). The absorption bands of the two samples are similar to those obtained by Abello and Benmoussa for the V_2O_5 phase [21,22]. Therefore, the phase of the as-deposited thin film grown by the dc reactive sputtering method is the same as the V_2O_5 phase.

Fig. 2 shows an as-received RBS spectrum and a simulation spectrum obtained by the Rutherford universal manipulation program. The simulation identified the composition as $V_2O_{4.67}$. The RBS spectra show a similar composition of V_2O_5, with and without immersion in plasma. The RBS result shows that the plasma immersion

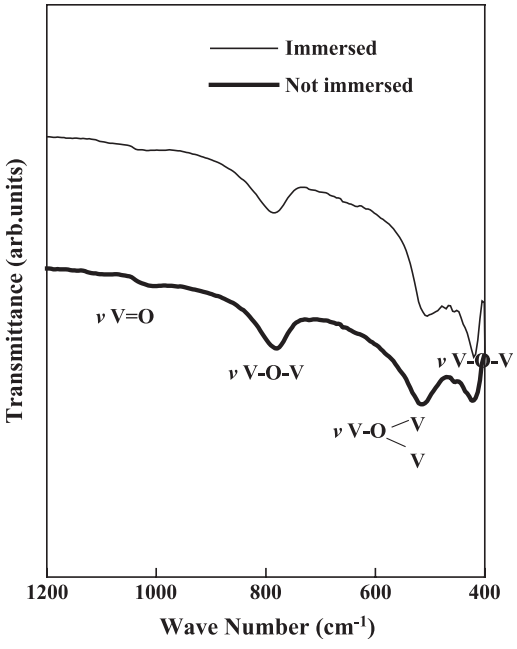

Fig. 1. FT-IR absorption bands for vanadium oxide thin films with immersion of plasma (a) and without immersion of plasma (b).