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Titanium Disulphide Thin Film Prepared by Plasma-CVD for Lithium Secondary Battery

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Abstract: Titanium disulphide fine power and preferred oriented thin film were prepared by plasma-CVD. The fine powder product was an aggregate of plate-like crystallites of some 10 nm in width, and less than 10 nm in thickness. Crystalline orientation of TiS_2 in the film was investigated in relation to deposition rate and film thickness. The preferred orientation of the TiS_2 basal plane perpendicular to the substrate was obtained on films with a thickness of more than ~ 10 μm at a deposition rate of $\sim 4\times 10^{-3}$ g/cm^2·h. Both the fine powder and the preferred orientation resulted in large discharge capacities in a lithium battery cathode application. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Applications of ceramic thin film have attracted increasing attention. It is very important to orient crystals in these films for the characteristics of the crystals to be emphasized. Plasma-CVD has been applied to prepare several kinds of high-tech ceramic materials. The method has been useful in obtaining thin film coatings and also fine powders of refractories. TiS_2 is one of the most promising candidates for the lithium secondary battery cathode.[1] Lithium ions are intercalated in the TiS_2 crystal lattice forming Li_xTiS_2 ($0\leq x\leq 1$). The reaction energy is released as electrical energy from the battery. The lithium ion has to diffuse in the TiS_2 crystal lattice during the reaction. A large surface area is necessary to obtain a high current density. The Li intercalation occurs along the TiS_2 layer, and it is difficult to intercalate Li^+ from a direction perpendicular to the host layer. The battery charge and discharge occur with lithium intercalation and deintercalation. It seems to be very important that the very fine TiS_2 powder orients its layer plane perpendicular to the lithium anode surface in order to enhance current density. In the discharging process, most of the lithium ions are electrostatically absorbed on the TiS_2 film surface if TiS_2 crystals orient their layer planes parallel to a substrate, as schematically shown in Fig. 1(a). If the crystals stand perpendicularly, as shown in Fig. 1(b), the Li^+ is easily intercalated to the TiS_2 inter-layer space in an applied electric field.

Chemical vapour deposition of titanium disulphide has been investigated in a classical way using an electrical furnace. The products formed in a quartz substrate were large TiS_2 crystals (~ 100 μm thick) having relatively random orientation. It is not easy to obtain stoichiometric TiS_2 due to the presence of the non-stoichiometric titanium-rich compositional range $Ti_{1+x}S_2$ and also the higher sulphide TiS_3. The non-stoichiometry x of $Ti_{1+x}S_2$ increases with an increase in firing temperature. TiS_3 is obtained under high sulphur pressure and at lower temperature than the preparation conditions of TiS_2.[2] It is important to set up an optimum temperature and sulphur pressure to obtain stoichiometric TiS_2. The chemical diffusion constant of sodium ion in TiS_2 was very much reduced with the non-stoichiometry. However, a recent investigation showed that the diffusion constant of Li^+ was not much reduced, but the amount of the intercalated Li^+ decreased.[3] A large amount of non-stoichiometry is unfavorable, but a trace amount may be permitted for the battery application. Application of plasma-CVD seems very useful in obtaining TiS_2 fine powder and its preferred oriented thin film.[4–6]

In the present investigation, a plasma-CVD reactor of parallel-plate type was used to obtain TiS_2 fine powder and its preferred oriented thin film. The products were characterized by X-ray diffraction, SEM, TEM, etc., and they were applied for the lithium secondary battery cathode.

2 EXPERIMENTAL

A reaction vessel of 10^{-2} m^3 was evacuated and then $TiCl_4$ (99.9% pure) was supplied at a rate of 4.9×10^{-5}–1.7×10^{-3} mol/min, with Ar carrier at a flow rate of 10 cm^3/min. H_2S (99.9% pure) was introduced at a rate of 5–100 cm^3/min. The reaction was performed by applying a high frequency (13.56 MHz) with an electric power of 10–125 W for a duration of 2–60 min. Prior to the deposition, the substrates were etched with Ar for 30 min, with a substrate temperature (Ts) of 300 °C and rf power of 50 W. The supply rate of $TiCl_4$ was controlled by changing the temperature of the $TiCl_4$ reservoir. The products were characterized by XRD, TEM and SEM. 1M $LiClO_4$–tetrahydrofuran (THF) was used as an electrolyte-solvent in the lithium battery. Discharge and charge were performed at a constant current of 0.15 mA/cm^2, in the range 2.7–1.5 V.

3 RESULTS AND DISCUSSION

Fine black powder was obtained on a thin film deposited on a glass substrate. The powder portion of the total deposit (film and fine powder) was dependent both on the reaction pressure and on the deposition site on the lower electrode. The powder was obtained in high yield under a pressure of 120 Pa at the electrode centre, where the plasma density was high. Its deposition rate had a maximum value of $\sim 5\times10^{-3}$ g/cm^2·h at the centre of the reactor electrode, and rapidly decreased along the radial direction. The following investigations were performed on the products obtained at the centre.

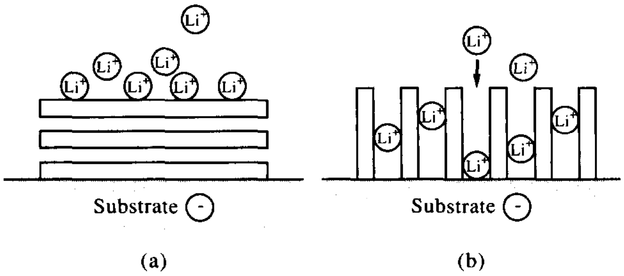


Fig. 1. Schematic representation for the cathode reaction in a Li/TiS_2 thin film battery.

The variety of product phases characterized by XRD depended both on the magnitude of the rf power and also on the substrate temperature. Figure 2 depicts a formation diagram obtained at a reactant ratio of $[H_2S]/[TiCl_4] \approx 3$. TiS_2 powder was obtained on thin films of TiS_2 or of TiS_2 contaminated with a small amount of TiS_3 at reaction conditions represented by the circles and squares, respectively. At conditions depicted by the triangle and crosses, the powders were mixtures of TiS_2 and TiS_3. TiS_2 had been prepared above 600 °C by a classical method.[2] TiS_2 fine powder was obtained on a substrate heated up to 450 °C in the present plasma-assisted CVD. The preparation temperature for TiS_2 was reduced with the application of plasma. The real composition of the TiS_2 described above was a non-stoichiometric $Ti_{1+x}S_2$. TiS_2 has a titanium-excess non-stoichiometric composition range, where the c-lattice parameter expands from 0.5695 nm with the increasing titanium content.[1] The powder deposited at 450 °C and 12 W had the shortest c-parameter (0.584 nm) among the products in Fig. 2. Thermogravimetry showed its composition to be $Ti_{1.19}S_2$.

3.1 *TiS_2 fine powder*

Stoichiometric TiS_2 had been synthesized from the reaction of $TiCl_4 + 2H_2S \rightarrow TiS_2 + 4HCl$ in a closed reaction system. A molar ratio of 2 for H_2S to $TiCl_4$ might be sufficient to attain a stoichiometry of TiS_2. The present products had titanium-excess non-stoichiometry because H_2S was removed faster than $TiCl_4$ from the reaction vessel during the continuous evacuation during the reaction. The H_2S flow was increased under the most favorable

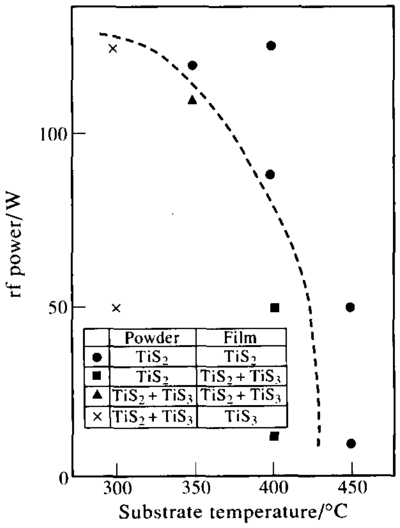


Fig. 2. Formation diagram of titanium sulphide powder and thin film.

conditions of 450 °C and 12 W. The lattice parameter *c* continuously shrank with the increasing [H_2S]/[$TiCl_4$] reactant ratio. The stoichiometric composition $Ti_{1.0}S_2$ with *c* = 0.570 nm was attained in the powder product with a reactant ratio of 27. Titanium disulphide crystallizes in a hexagonal CdI_2-type crystal lattice. Crystallite sizes of the fine powder were estimated from the broadening of the XRD(001) line to be about 5 nm, and a value of about 18 nm was obtained from the (110) line. X-ray diffraction peaks for Ti_2S_3 overlap with many of these for TiS_2. However, the present product was not contaminated with Ti_2S_3 because the strongest 104 diffraction line of Ti_2S_3 (JCPDS 35-1135) was not observed. TEM observations showed an aggregation of plate-like crystallites of about 40 nm in width and about 10 nm in thickness, as shown in Fig. 3.

Figure 4 shows the discharging behaviour of Li/1M $LiClO_4$ in THF/$Ti_{1+x}S_2$ cells. A utilization of 100% corresponds to the discharged electricity necessary to obtain $LiTiS_2$ by the Li intercalation into TiS_2. A rapid potential drop was observed for the cell using a coarse powder of $Ti_{1.00}S_2$ prepared by the sealed-tube method before full utilization was attained. The $Ti_{1.19}S_2$ fine powder cell could be discharged continuously to full utilization. It generated a slightly lower voltage than the $Ti_{1.00}S_2$ cell described above. The voltage reduction is mainly attributed to its non-stoichiometry. The cell interior resistivities may not differ so much: lithium ionic diffusivity is not greatly affected by the non-stoichiometry.[3] These cells were discharged at a current density of 0.5 mA/cm^2. A relatively flat discharge curve was also observed for the cell using $Ti_{1.0}S_2$ fine powder, in spite of a higher current density of 1.5 mA/cm^2. Its generated voltage was slightly lower than that of $Ti_{1.00}S_2$ due to the higher current density. The cell was cycled in voltage limits between 2.7 and 1.5 V. Its discharge capacity continuously decreased to ~40% after the 50th discharge–charge cycle.

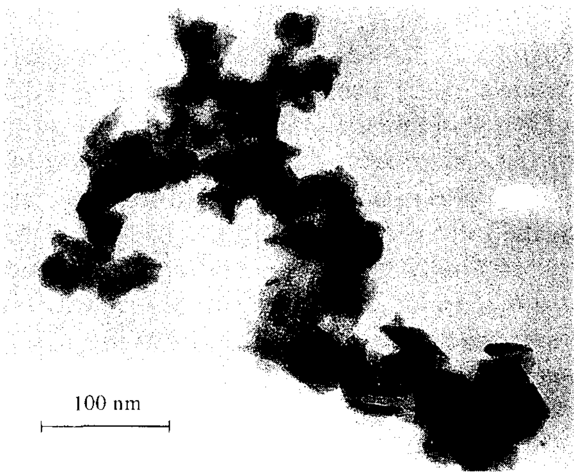


Fig. 3. TEM photograph of TiS_2 fine powder.

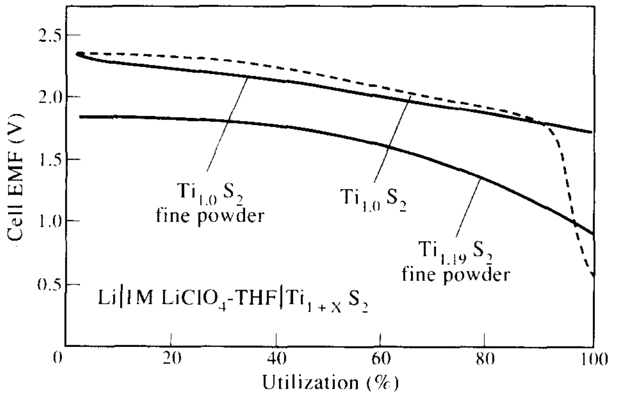


Fig. 4. Discharge curves of $Ti_{1+x}S_2$/Li batteries. Full and dotted lines represent lithium battery discharges using fine powder prepared by plasma-CVD and coarse powder prepared by the classical method, respectively.

3.2 Preferred oriented TiS_2 film

The products were mainly films without contamination of powder when the deposition rate was slower than 7.5×10^{-3} g/cm^2·h. The preferred orientation of the *c*-plane parallel to the substrate became stronger with a decrease of the deposition rate to 2.2×10^{-4} g/cm^2·h. Almost perfect preferred orientation was attained at a rate of 2.2×10^{-4} g/cm^2·h.

Crystalline orientation also changed with the film thickness. Deposition rate was kept almost constant in the range 3.1–4.1×10^{-3} g/cm^2·h. A thin film of 2.3 μm thickness showed an intense 001 X-ray diffraction line, as shown in Fig. 5. The 001 peak disappeared and an intense 110 line was observed for a film of 13.5 μm thickness. These results suggest that the TiS_2 basal plane is parallel to the substrate in a thin film. With increasing film thickness, the TiS_2 layer gradually stands up, and it is perpendicular to the substrate in films which are > 10 μm thick. The surface texture of the 2.3 μm

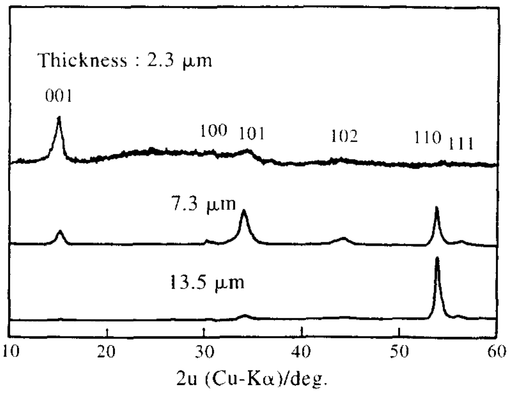
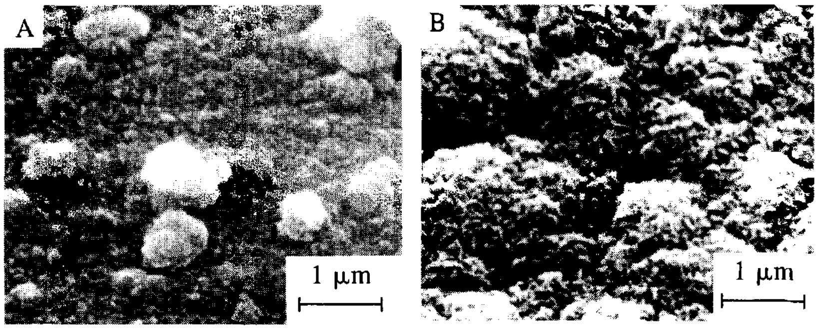
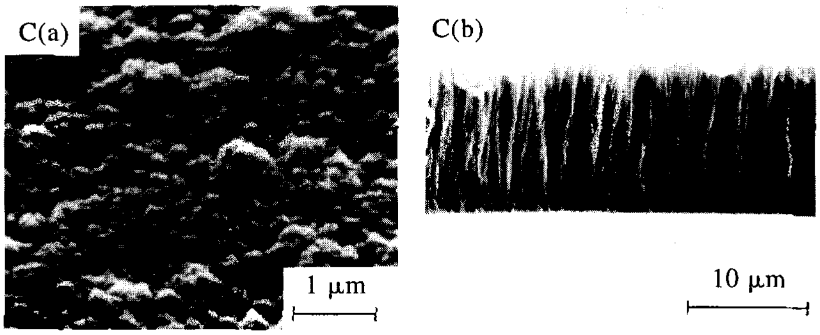


Fig. 5. X-ray diffractograms of TiS_2 thin film with various film thicknesses.



Film surface
thickness : 2.3 μm

Film surface
thickness : 7.3 μm



Film surface
thickness : 13.5 μm

Cross-section
thickness : 13.5 μm

Fig. 6. SEM observation of surface and cross-sectional textures for TiS_2 thin film with various film thicknesses.

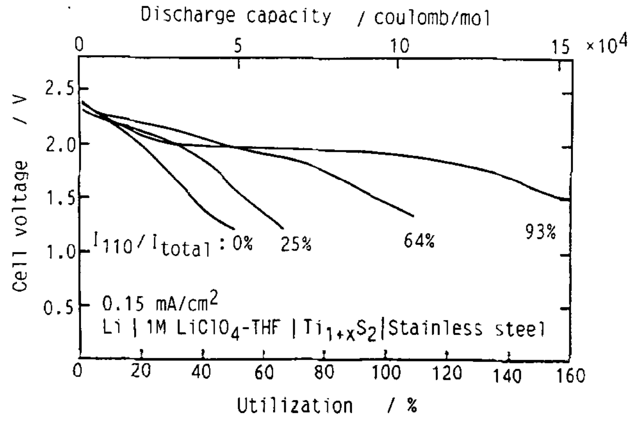


Fig. 7. Discharge curves for the lithium batteries using TiS_2 thin film with different crystal orientation as the cathode.

thick thin film showed that plate-like crystals were deposited, keeping their basal plane parallel to the substrate, as depicted in Fig. 6(A). Flat basal planes were observed even in the coagulated particles with a diameter of 0.5 μm. The film surface had small homogeneous ridges on the film which were ~ 10 μm thick, as indicated in Fig. 6(B) and (C(a)). The plate-like TiS_2 crystals stand perpendicularly to the substrate forming a columnar texture, as shown in the cross-sectional picture of Fig. 6(C(b)). TiS_2 crystallites easily grow in their (001) plane, which is their closest packing plane. In the beginning of the deposition process, mostly (001) plane-preferred oriented TiS_2 crystallites cover the whole substrate surface. Once the TiS_2 crystallites cover the whole substrate surface, a small portion of the crystallites (having a slight misorientation of (001) orientation from the substrate surface) grow continuously in their own (001) plane. With increasing film thickness, the ratio of TiS_2 (110) plane-preferred orientation gradually increases because the gas species are supplied along the direction perpendicular to the substrate. The easy growing direction of the crystal coincides with the gas supplying direction above.

Lithium battery performance was studied on the TiS_2 thin film prepared under various conditions. Figure 7 represents discharge curves for the batteries where the TiS_2 film was deposited on stainless steel. One mole of TiS_2 can reversibly intercalate one mole of Li^+. A 100% utilization in the abscissa corresponds to the discharge capacity to obtain $LiTiS_2$. The value of I_{110}/I_{total} tentatively represents the degree of preferred orientation. A larger discharge capacity was observed for the battery using TiS_2 film with a high I_{110}/I_{total} percentage. The film having a TiS_2 crystal basal plane perpendicular to the substrate seems to show a large discharge capacity, probably because Li intercalation occurs easily when a Li^+ ion is supplied along the TiS_2 basal plane, as shown in Fig. 1(b). The films deposited on carbon substrate showed the same tendency as that observed for stainless steel. TiS_2 crystalline orientation changed

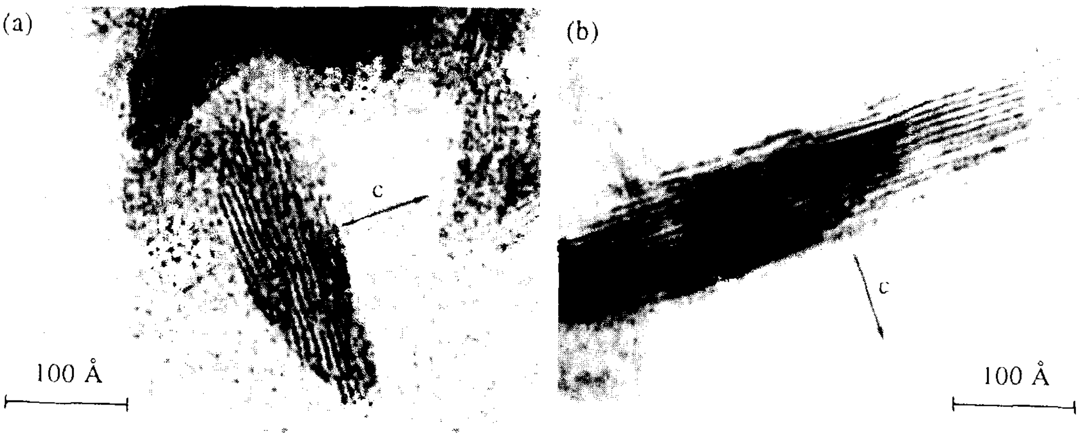


Fig. 8. TEM photographs of TiS_2 fine powder prepared by plasma-CVD in high magnification.

with its deposition rate and also with the film thickness. The discharge capacity was correlated to TiS_2 crystallite orientation.

Transmission electron micrography showed that TiS_2 prepared by plasma-CVD had a higher density of crystalline defects than that for TiS_2 obtained by a reaction between Ti and S at high temperature. Figure 8 shows transmission electron micrographs of TiS_2 fine powder prepared by plasma-CVD in high magnification. The stripe lines corresponding to the TiS_2 (001) plane are not straight, discontinuous or unclear anywhere. The distance between the lines is not uniform. There are many kinds of crystalline defects. The high density of these defects is a characteristic of plasma-CVD TiS_2 and it may contribute to the unexpectedly large discharge capacity of the lithium battery.

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