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PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION OF TITANIUM SULFIDES

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Reaction between $TiCl_4$ and H_2S was performed to deposite titanium sulfide in low-pressure glow discharge. Fine powder of titanium sulfide with submicron diameter was obtained covering the deposited film on the substrate. It had a composition around $Ti_{1.2}S_2$. The phases in the product was investigated in relations to applied rf power and substrate temperature.

There has been growing interest in using low-pressure glow discharges to promote chemical reactions.1) An electron temperature can be raised to high even if a gas temperature is low in a glow discharge. This nonequilibrium nature of the plasma leads to a dissociation of gas and a deposition of film at much lower temperatures than are possible with pyrolytic chemical vapor deposition. The crystal growth can be suppressed due to a nonequilibrium nature. Many applications have been made on the formation of amorphous silicon which is used in solar cell. Plasma-enhanced CVD is now getting to be applied to the formation of oxides, nitrides and carbides. However, there has been a very limited number of reports on sulfide formation.

Titanium disulfide is a promising candidate for the cathode material of lithium intercalation secondary battery.2) The compound has a wide range of titanium excess nonstoichiometry. Titanium trisulfide, TiS_3, is also present in titanium-sulfur system.

In the present investigation, the deposition of titanium sulfide was performed in low-pressure glow discharge.

After the evacuation of reaction vessel down to the pressure lower than 1 Pa, titanium tetrachloride was introduced on a stream of Ar gas at 10 ml/min under a continuing evacuation. It was supplied at the flow rate of 1.4×10^{-4} mol/min. After the introduction of H_2S, rf was applied to the parallel-plate type plasma-CVD reactor, model BP-1, fabricated by Samco International Co., Ltd. The temperature of glass substrate was changed in the range between 300 and 450 °C. The duration of reaction was between 10 min to 1 h . rf power was changed by controlling a plate current. The products were characterized by XRD, TEM, and TG-DTA. Discharging property was also investigated on lithium battery.

Figure 1 shows the relative arrangements of introduction tubes to electrodes in the reaction vessel. The volume of vessel is 10^{-2} m^3. The diameters of upper and lower electrodes are 8 cm and 10 cm. The distance between the electrodes is 3 cm. Substrates were put on the lower electrode. Extremely thin and brown film was deposited in case of (a). Its presence was not detectable by XRD. Flow rate of H_2S was 5 ml/min. The value was equivalent to 2.0×10^{-4} mol/min.

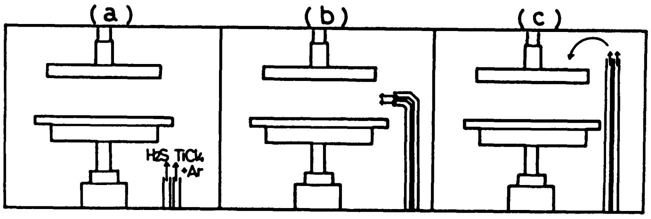

Fig. 1. Ways to introduce raw material gas into a reaction vessel of plasma-enhanced chemical vapor deposition

The ends of the introduction tubes were turned toward the space between the electrodes as shown in Fig. 1(b) in order to supply starting materials as much as possible in amount to the reaction place. The thickness of deposited film was not uniform. It was thicker at a place closer to the tube end. XRD of the film having a thickness of 1.5 μm showed only a broad 001 diffraction line of hexagonal titanium disulfide.

In order to supply raw materials uniformly, the tubes were extended for their ends to be placed above the upper electrode as shown in Fig. 1(c). A flow rate of H_2S was increased to 10 ml/min. Total vapor pressure was c.a. 5×10^{-4} atm in the vessel. The phases in the products depend on a magnitude of current applied to generate rf (I) and a substrate temperature (T) as shown in Fig. 2 where I and T respectively represent these parameters. Black fine powder was obtained with the deposited film due to the increased supply of raw material. Nonstoichiometric compound, TiS_{2-x}, could be obtained at higher T and at larger I than the conditions where TiS_3 could be prepared. Their XRD lines were very broad because crystal growth of the product was suppressed in nonequilibrium reaction. The observed XRD lines were only those for 001, 101 and 110 of TiS_2 and those for 001 and 210 of TiS_3. At 300 °C of the substrate temperature,

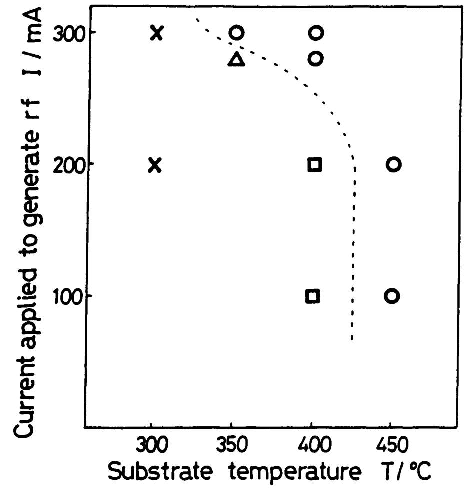

Fig. 2. Titanium sulfides obtained at different conditions of substrate temperature and applied current to generate rf. The symbols, ○ and △, indicate only a single phase TiS_2 and TiS_2 containing a small amount of TiS_3 respectively as the deposited film and powder. At the conditions represented by ×, the deposited film was TiS_3 and the fine powder was a mixture of TiS_2 and TiS_3. At the conditions represented by □, the films were mixtures of TiS_2 and TiS_3 and the fine powders were TiS_2.

TiS_3 films were deposited with the fine powder mixtures of TiS_2 and TiS_3. TiS_3 can be obtained at lower temperature than the preparation temperature of TiS_2 by the classical method using sealed tube.3) High rf power means high preparation temperature.

This assumption could also be confirmed by the compositional variation estimated from the value of c-lattice parameter of the deposited TiS_{2-x} nonstoichiometric compounds. Tentative c-parameters calculated from 001 diffraction line were 5.87 Å and 5.85 Å respectively for the film deposited under the conditions of I = 300 mA and 280 mA at T = 400 °C. It has been known that nonstoichiometric TiS_{2-x} containing more amount of Ti can be obtained at higher temperatures and have larger c-lattice parameters.2) The c-parameters of the present products are larger than 5.75 Å, which was reported for TiS_{2-x} obtained by usual methods. The product might be a polytype of Ti_2S_3 having a diffraction line at d = 5.82 Å (ASTM 32-1377).

The deposited films had smaller values of c-lattice parameter than the obtained fine powders. The values were 5.87 Å for film and 5.89 Å for fine powder at the conditions of I = 300 mA and T = 400 °C, and were 5.81 Å for film and 5.86 Å for fine powder at I = 100 mA and T = 450 °C. The potential of substrate, which is floating potential with respect to ground, is lower than plasma potential.4) The electron temperature can be related to these potentials. The difference of c-lattice parameter between film and powder might be related to the potentials where the products were formed. The powder was formed in the space between electrodes where a high plasma potential was generated. The film was deposited on the substrate having a low floating potential.

Aggregation of platy crystals was observed by TEM observation as shown in Fig. 3. The average particle size of the plate was about 40 nm and the thickness was less than 10 nm. The size of crystallite was estimated as about 5 nm from the broadening of XRD line indexed as 001. Chemical analysis showed that the fine powder obtained at I = 100 mA and T = 450 °C had a composition of $Ti_{1.19}S_2$. Figure 4 shows the discharging of Li/1M $LiClO_4$ in THF/$Ti_{1.19}S_2$ cell at 0.5 mA/cm^2. The behavior was quite different from that of the stoichiometric TiS_2 prepared in the usual method. A rapid potential drop could be observed for TiS_2 before the full utilization was attained. However the cell using fine powder could discharge continuously to the full utilization

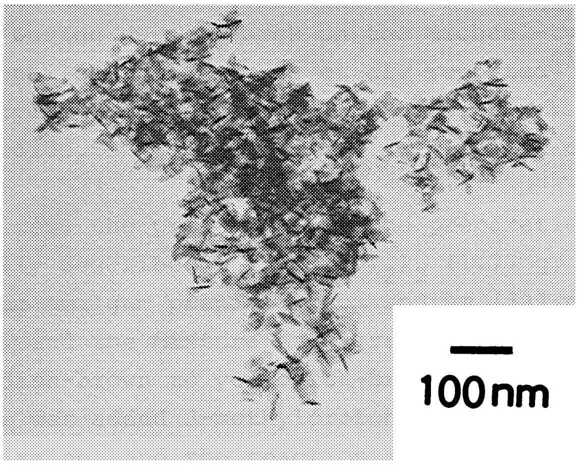

Fig. 3. TEM picture of TiS_2 fine powder.

due to the large surface area of the cathode material.

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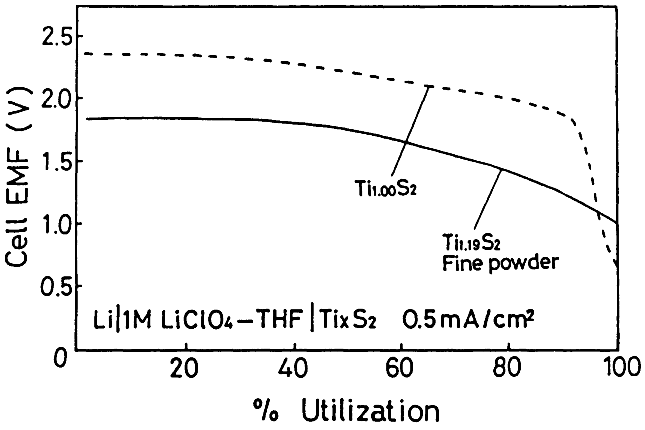

Fig. 4. Discharging of lithium battery using fine powder of $Ti_{1.19}S_2$ as cathode. A dotted line corresponds to the case using stoichiometric TiS_2 having average particle size of 13 μm prepared by an usual method.

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