# Chemical Vapor Deposition of Titanium Disulfide

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Chemical vapor deposition of $TiS_2$ was examined. $TiS_2$ was deposited on a quartz substrate above 300 °C from a gas mixture of $TiCl_4$, $H_2S$, and Ar. Maximum deposition rate was attained at 700—800 °C for a 0.7 gas flow ratio $H_2S/(TiCl_4+H_2S)$ irrespective of temperature. Crystal morphology and composition were strongly affected by temperature and gas compositions. Well-formed $TiS_2$ crystals were grown either at 600 °C or from a gas mixture of low flow ratio 0.2 of $H_2S/(TiCl_4+H_2S)$. Single phase of $TiS_2$ was deposited in the temperature range 400—850 °C.

There are several non-stoichiometric compounds in the system Ti–S. Of these, titanium disulfide has a $CdI_2$-type structure and is of interest as a dry-lubricant,[1] catalyst,[2] electrical contact operating under friction,[3] reversible electrode,[4] and cathode material for electric vehicle propulsion.[5,6]

Titanium disulfide has been prepared by the reaction between the elements,[7–10] reaction of titanium with hydrogen sulfide,[9,11] titanium dioxide with hydrogen sulfide and carbon,[12] and by chemical transport technique in closed ampoules,[13–18] and in open flow system.[19] Single crystals of titanium disulfide have so far been prepared only by chemical transport in a closed system.

The aim of the present study is to examine the growth conditions of titanium disulfide crystals by the chemical vapor deposition in an open flow system. Over-all reaction used is as follows, unless otherwise stated.

$$TiCl_4 + 2H_2S = TiS_2 + 4HCl. \quad (1)$$

## Experimental

*Materials.* Commercial GR grade titanium and chlorine were used without further purification. Hydrogen was dehydrated by passing over calcium chloride and phosphorus pentaoxide, successively. Argon and hydrogen were also dehydrated by passing through concentrated sulfuric acid. Titanium tetrachloride was prepared *in situ (vide infra)*.

*Growth Apparatus and Procedure.* The apparatus is shown in Fig. 1. A quartz tube, outer dia. 7 mm, length 70 mm, was used as a substrate, into which a silicon carbide heater was inserted. The substrate was held in a vertical quartz tube, inner diam. 19 mm, heated with a nichrome heater from the outside. Titanium tetrachloride was prepared by chlorination of titanium sponge at 350—400 °C and carried by argon into the upper inlet of the reaction tube. Hydrogen sulfide was introduced through an uppermost inlet and allowed to mix with the stream of titanium tetrachloride just above the substrate. The surface temperature of the substrate was measured with an infrared thermometer (Japan Sensor Co., Model TSS-2P) through an observation window. The temperature had been calibrated with a chromel-alumel thermocouple. The flow rate of titanium tetrachloride was calculated from that of the chlorine stream to a bed of titanium sponge assuming full conversion.

*Analysis of Crystals.* Titanium content in the crystals was determined by the gravimetric method. A collection of crystallites was pulverized, weighed, and oxidized to titanium dioxide in an air flow at 1000 °C for an hour. Non-stoichiometry number $x$ of $TiS_x$ was calculated by the following equation:

$$x = \frac{W_{TiS_x} - W_{TiO_2}\dfrac{A.W.\ (Ti)}{M.W.\ (TiO_2)}}{A.W.\ (S)} \Bigg/ \frac{W_{TiO_2}\dfrac{A.W.\ (Ti)}{M.W.\ (TiO_2)}}{A.W.\ (Ti)}$$

$$= \frac{1}{32.06}\left(79.90\frac{W_{TiS_x}}{W_{TiO_2}} - 47.90\right),$$

where $W_{TiS_x}$ and $W_{TiO_2}$ are weights of titanium disulfide sample and its oxidized product, respectively, and $A.W.$(i) and $M.W.$(j) are the atomic weight of element i and the molecular weight of compound j, respectively.

*Thermoelectric Power.* With use of silver conducting paint, a plate-like crystal of titanium disulfide was contacted to two copper plates (3×5 mm) separated 1 mm from each other, one of which was heated by a nichrome heater. The temperature difference of two sides of the crystal was measured with a 100 μm dia. chromel-alumel thermocouple. Thermoelectric power was measured in an argon atmosphere.

## Results and Discussion

*Effects of Substrate Temperature.* Deposition rates of titanium disulfide crystals plotted against the temperature of substrate are shown in Fig. 2. The sum of the flow rates of titanium tetrachloride and hydrogen sulfide, and total gas flow rate were kept at 0.4 and

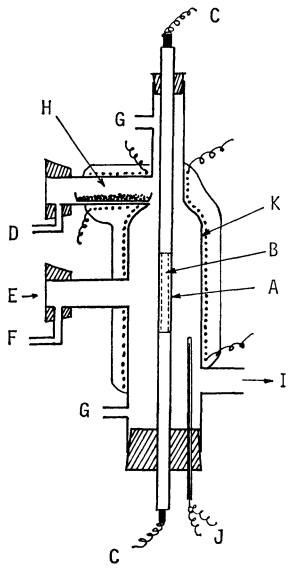


Fig. 1. Apparatus. A) Substrate (quartz, 7 mm o.d., 70 mm long), B) SiC heater, C) electrodes (graphite), D) $Cl_2$, Ar inlet, E) window for observation, path of the optical pyrometer, F) Ar inlet , G) $H_2S$ inlet, H) Ti sponge, I) gas outlet, J) CA thermocouple, K) reaction tube (quartz tube, 19 mm i.d.).

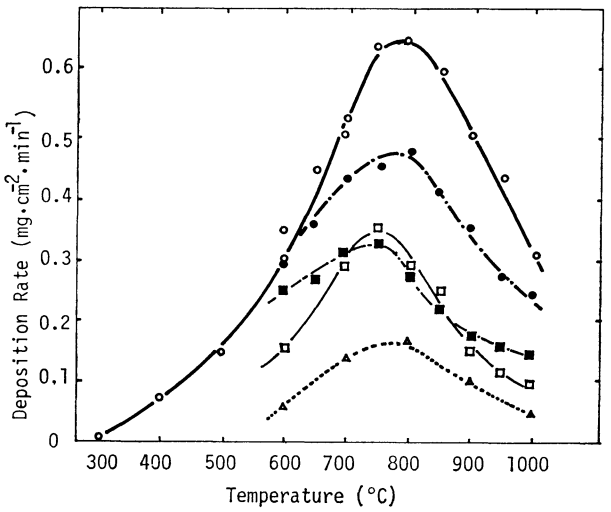


Fig. 2. Effect of substrate temperature on the deposition rate. Reaction time: 15 min, $H_2S+TiCl_4$: 0.4 cm³/s, total flow rate: 6.0 cm³/s, $H_2S/(TiCl_4+H_2S)$: (■) 0.9, (●) 0.8, (○) 0.7, (□) 0.5, (△) 0.3.

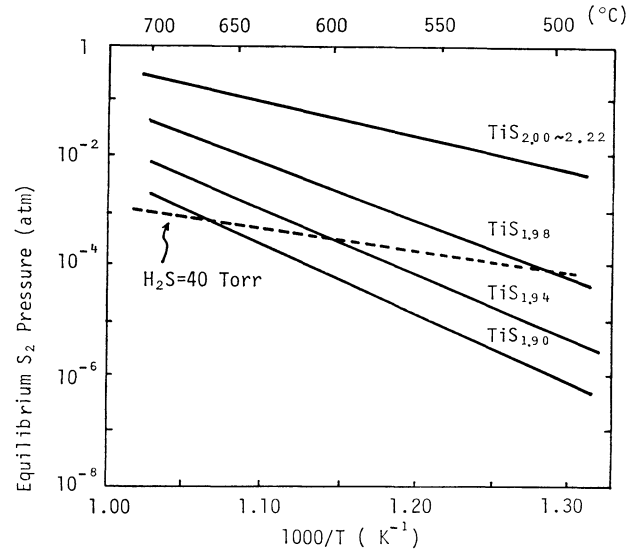


Fig. 3. Equilibrium partial pressure of sulfur *versus* temperature. (——) Partial pressures of sulfur equilibriated with nonstoichiometrical titanium disulfide quoted from Ref. 24, (----) partial pressure of sulfur formed by dissociation of $H_2S$.

6.0 cm³/s, respectively (linear velocity at room temperature, 2.4 cm/s). The deposition rate reached a maximum at 700—800 °C. The temperature range 700—800 °C corresponding to that of maximum growth rate has been used in chemical vapor transport.[17] Saeki,[18] Biltz *et al.*,[19] and Winn and Steele[20] reported on the equilibrium partial pressure of diatomic sulfur over the non-stoichiometric titanium disulfide. The pressure[20] is shown in Fig. 3, together with that of diatomic sulfur formed in dissociation of hydrogen sulfide in the case of inlet partial pressure of hydrogen sulfide of 40 Torr. Although the pressure of titanium disulfide is very low[21] in comparison with the disulfur pressure in the temperature range of the present work, the equilibrium sulfur pressure increases steeply with

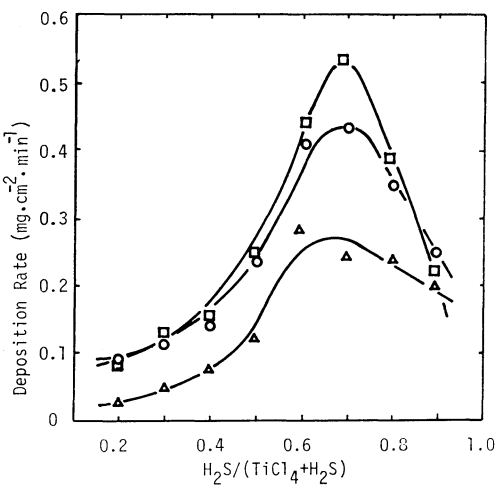


Fig. 4. Effect of gas flow ratio of $H_2S/(TiCl_4+H_2S)$ on the deposition rate. Reaction time: 15 min, $TiCl_4+H_2S$: 0.4 cm³/s, Ar: 5.6 cm³/s, substarte temperature: (△) 600 °C, (○) 700 °C, (□) 800 °C.

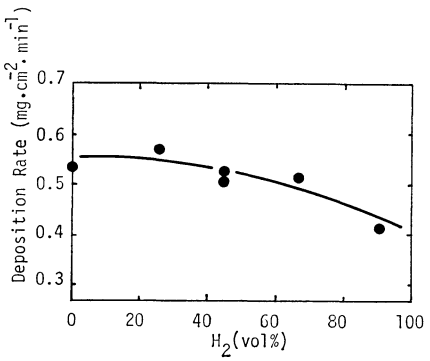


Fig. 5. Effect of hydrogen flow rate on the deposition rate. Reaction time: 15 min, $H_2S$: 0.1 cm³/s, $TiCl_4$: 0.1 cm³/s, $H_2+Ar$: 2.2 cm³/s, substrate temperature: 800 °C.

the increase of the sulfur content in titanium disulfide and with the increase of temperature especially above 800 °C. Thus, the decrease of the deposition rate above 800 °C can be attributed to the degradation of titanium disulfide to a lower sulfide phase and disulfur. The maximum deposition efficiency of titanium disulfide with respect to the feed of titanium tetrachloride was estimated to be about 20 per cent.

*Effects of Gas Composition and Flow Rate.* The effects of gas flow ratio $H_2S/(TiCl_4+H_2S)$ ("$H_2S$" ratio hereafter) on the deposition rate of titanium disulfide, with substrate temperature used as parameter, are shown in Fig. 4. The deposition rate increases with increase in the $H_2S$ ratio, reaching a maximum at the ratio of *ca.* 0.7, which is roughly in agreement with the stoichiometrical ratio (0.67) of Reaction 1. The optimum $H_2S$ ratio shifts to the lower value when hydrogen is introduced in the input gas. For example, $H_2S$ ratio corresponding to the maximum deposition rate varies to 0.5 when hydrogen is introduced up to 80 per cent. The deposition rates of titanium disulfide increase with increase in the sum of the flow rates of titanium tetrachloride and hydrogen sulfide, attaining

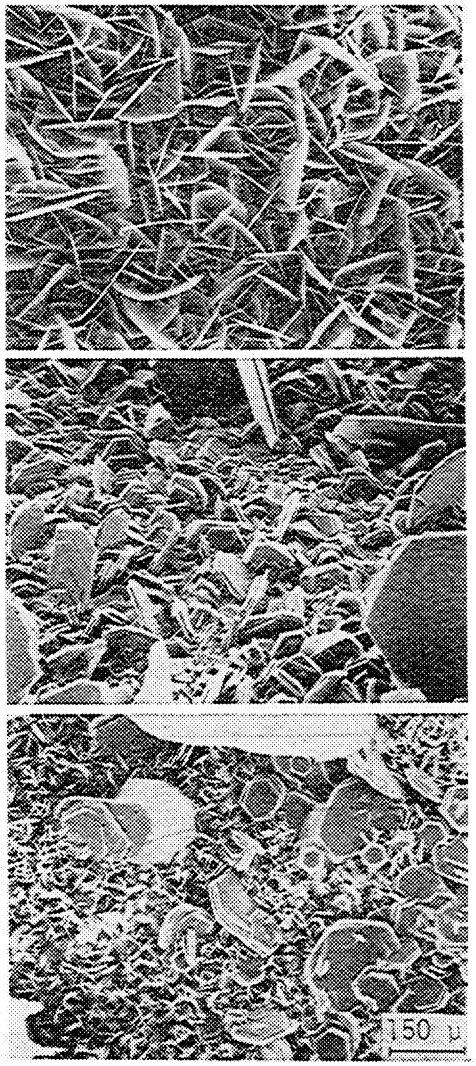


Fig. 6. Morphologies of $TiS_2$ crystals (1). $H_2S/(TiCl_4+H_2S)$: 0.2, substrate temperature: (A) 600 °C, (B) 800 °C, (C) 1000 °C.

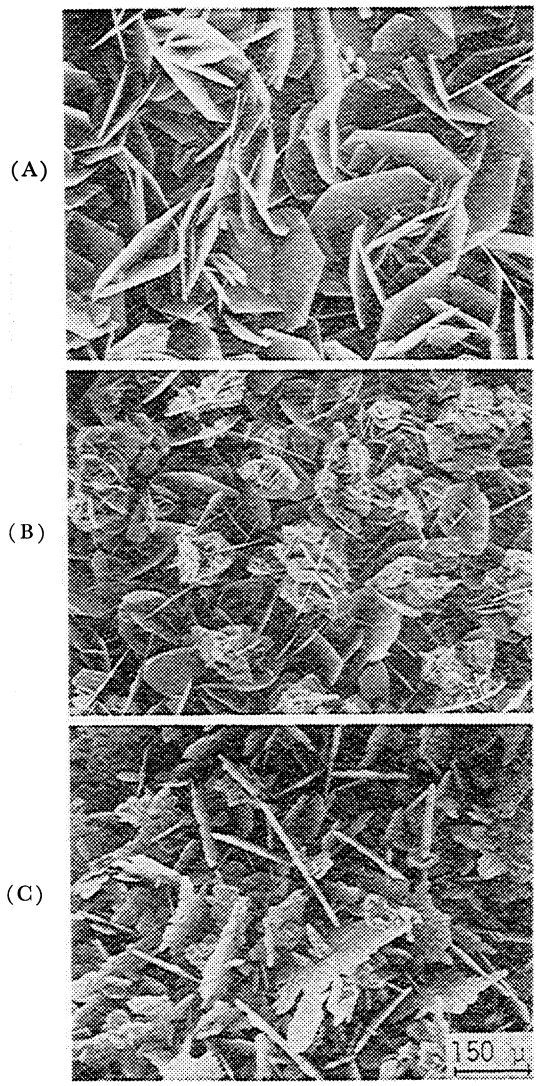


Fig. 7. Morphologies of $TiS_2$ crystals (2). $H_2S/(TiCl_4)$: 0.5, substrate temperature: (A) 600 °C, (B) 800 °C, (C) 1000 °C.

a constant value for the flow rate above 0.2 $cm^3/s$, irrespective of substrate temperature. Introduction of hydrogen resulted in negative effect on the deposition rate of titanium disulfide as shown in Fig. 5, probably due to the depression of the dissociation of hydrogen sulfide. The dissociation degree of hydrogen sulfide is estimated to be 7.4 per cent at 800 °C.[22]

*Effect of Growth Time.* The deposition rate of titanium disulfide became roughly constant after an induction period of 3—5 min. Hexagonal plate-like crystals of average diagonal of 2 mm having mirror faces were formed after an hour growth.

*Effects of Temperature and Gas Composition on Crystal Morphology.* The morphology of titanium disulfide is affected by substrate temperature and $H_2S$ ratio as shown in Figs. 6, 7, and 8. Thin plate-like crystals up to 1 μm thick grew vertically to the surface of the substrate at 600 °C. The growth rate in direction *c* is very low as compared with that in direction *a*. However, at a low $H_2S$ ratio such as 0.2, crystals grew appreciably in direction *c*, hexagonal crystals of 20 μm thick being obtained (Figs. 6B and 6C). Under a high $H_2S$ ratio (Figs. 7B and 7C) or high substrate temperature (Figs. 8B and 8C) secondary deposition is apt to take place. Strotzer *et al.*[23] reported on the color-change of the Ti–S system compounds in connection with the sulfur content. The crystals grown in the present study were golden-yellow independent of the substrate temperature and gas compositions.

*Effects of Temperature and Gas Composition on Crystal Compositions.* X-Ray diffraction profiles of titanium sulfides grown at various temperature with the $H_2S$ ratio kept at 0.7 are shown in Fig. 9. Peaks of titanium trisulfides ($TiS_3$) and sesquisulfide ($Ti_3S_4$) are found only on the profiles of the crystals grown below 350 °C and at 1000 °C, respectively (Figs. 9C and 9D). On the profiles of crystals grown at 400—850 °C, only the peaks of titanium disulfide are seen irrespective of the $H_2S$ ratio (Fig. 9B).

Titanium disulfide is a well-known non-stoichiometric compound. From the results of gravimetric analysis of titanium in relation with growth temperature and $H_2S$ ratio, the atomic ratio of sulfur to titanium (S/Ti) in crystals was determined as shown in Fig. 10. The

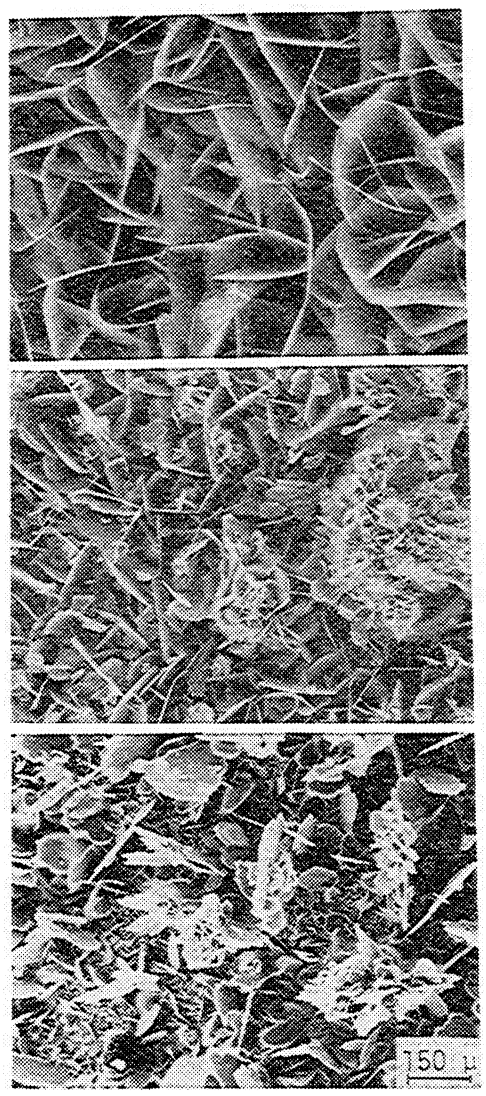


Fig. 8. Morphologies of $TiS_2$ crystals (3). $H_2S/(TiCl_4+H_2S)$: 0.8, substrate temperature: (A) 600 °C, (B) 800 °C, (C) 1000 °C.

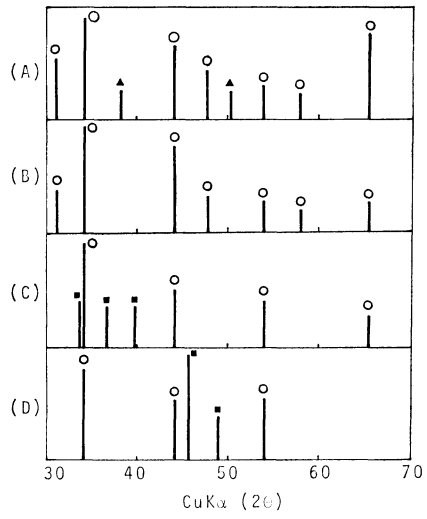


Fig. 9. X-Ray diffraction profiles.
$H_2S/(TiCl_4+H_2S)$: 0.7, substrate temperature: (A) 1000 °C, (B) 700 °C, (C) 350 °C, (D) 300 °C, (○) $TiS_2$, (▲) $Ti_3S_4$, (■) $TiS_3$.

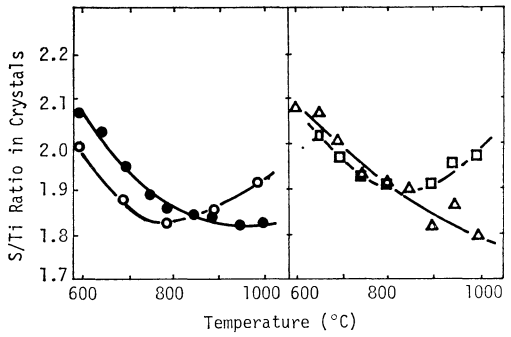


Fig. 10. Effects of temperature and gas composition on crystal composition. $H_2S/(TiCl_4+H_2S)$: (○) 0.2, (●) 0.4, (△) 0.6, (□) 0.8.

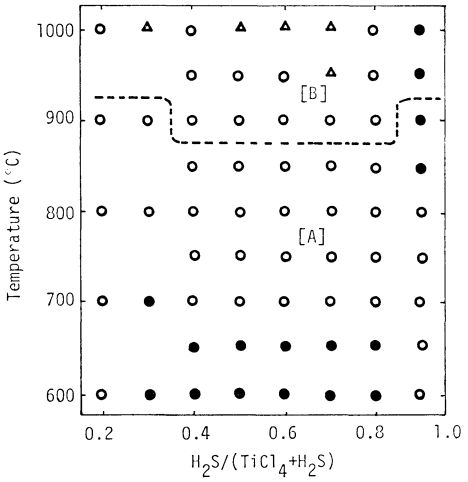


Fig. 11. Deposition region of $TiS_2$. (●) S/Ti>2.00, (○) 1.81≤S/Ti≤2.00, (△) S/Ti<1.81; [A] single $TiS_2$-phase, [B] mixed phase of $TiS_2$ and $Ti_3S_4$.

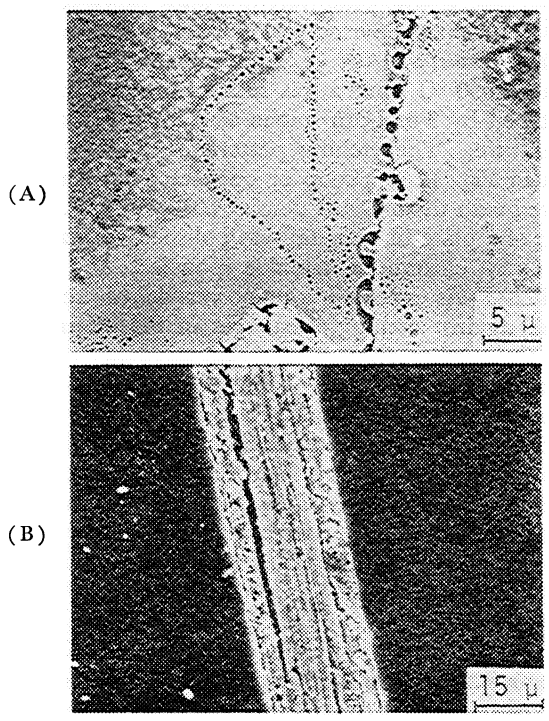


Fig. 12. Etching patterns. (A) Surface, (B) cross section.

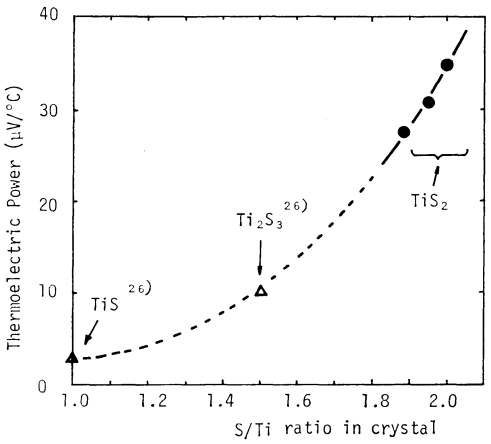


Fig. 13. Thermoelectric power of $TiS_2$ crystal.

atomic ratio of S/Ti decreases with increase in temperature, attaining a maximum of 1.83—1.90 at *ca.* 800 °C and increasing above 800 °C, except for that of crystals grown from a gas mixture of the $H_2S$ ratio 0.6. Crystals having a high atomic ratio of 2.07—2.09 were grown at 600 °C with $H_2S$ ratio of 0.4—0.7. Rimmington and Balchin,[17] Jeannin,[24] and Bartran[25] reported the limit of atomic ratio of S/Ti for titanium disulfide phase as 1.96—1.89, 1.98—1.81, and 2.00—1.50, respectively. Deposition limits of the single phase of titanium disulfide are shown in relation with growth temperature and gas flow ratio in Fig. 11, in which compositions of crystals are divided into three regions according to the phase limits.[24]

The lattice parameters of titanium disulfide crystals of S/Ti of 1.98 were determined to be 3.407 Å for *a* and 5.712 Å for *c*. The former agrees with those of $TiS_{1.96\pm0.03}$.[17] However, the latter is higher than those reported by Rimmington and Balchin[17] and lower than that reported by Norrby and Franzen.[28]

*Etching Patterns.* A titanium disulfide crystal grown at 850 °C from a gas mixture of $H_2S$ ratio 0.5 was etched by 3 mol/dm³ nitric acid for 5 min at room temperature. The etching pattern on a (001) face is shown in Fig. 12A. Loop or open etch-pit arrays are observed with the order of density $10^2$—$10^3$/cm². Cross section of a plate-like crystal was polished with abrasive paper and chromium trioxide powder, and etched (Fig. 12B). As expected, a plane vertical to the *c*-plane is weak against etching, cleavages of 0.5—2 μm thick being observed.

*Thermoelectric Power.* The thermoelectric power of titanium disulfide crystal is shown in Fig. 13 together with that reported on the titanium sulfides. Thermoelectric power of the crystals of S/Ti ratio 2.00 and 1.89 are 35 and 28 μV/°C at 20 °C, respectively, increasing linearly with increasing temperature. The thermoelectric power of the titanium sulfides was reported by Dubrovskaya and Oranesyan[26] to be 3.4 μV/°C (TiS) and 10 μV/°C ($Ti_2S_3$) and McTaggart[27] to be 200 μV/°C ($TiS_{1.95}$) and 600 μV/°C ($TiS_3$) on the pressed samples of fine powder. Thermoelectric power of the titanium sulfides increases with increase in sulfur content irrespective of the crystallographic nature, as in the Zr–S system.[27]

## Conclusion

Crystals of titanium disulfide were grown by chemical vapor deposition in an open flow system.

1) Deposition rate reached a maximum at 700—800 °C. The flow ratio $H_2S/(TiCl_4+H_2S)$ near that of reaction stoichiometry, 0.67, resulted in the maximum rate irrespective of temperature.

2) Titanium trisulfide and sesquisulfide were found among the disulfide deposits below 350 °C and at 1000 °C, respectively.

3) It was found that well-formed hexagonal crystals grow either at low temperature such as 600 °C or from a gas mixture of a 0.2 flow ratio of $H_2S/(TiCl_4+H_2S)$.

4) Atomic ratio of S/Ti in grown crystals decreased to 1.83—1.90 with increase of temperature up to 800 °C.

5) Thermoelectric power of the crystals with the S/Ti ratios 2.00 and 1.89 was determined to be 35 and 28 μV/°C at 20 °C, respectively.

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