

## 졸겔법을 응용한 이황화티탄늄의 합성에 관한 연구

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(1997. 1. 7 접수)

### Modified Sol-Gel Processing for Titanium Disulfide

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(Received January 7, 1997)

**요 약.** 육방형 이황화 티탄늄의 분말과 박막을 졸-겔법을 변형시켜 제조하였다. 여러 가지 용매하에서 이소프로폭시화 티탄늄과 황화 수소와의 반응에 의해 전구체의 침전을 유도한 후 이것을 황화 수소 분위기에서 열처리를 하면 분말이 얻어지는 반면 2-메톡시에톡시화 티탄늄과의 반응은 안정한 전구체 용액을 주므로 이것을 스핀 코팅하여 열처리하면 박막을 얻을 수 있다. 이러한 분말과 박막의 형태 변화를 열처리를 하면서 전자 현미경과 분말 X-선 회절기를 통해 살펴보았다.

**ABSTRACT.** Powders and thin-layers of a hexagonal titanium disulfide phase have been successfully prepared by modifying the sol-gel process. The reaction of titanium isopropoxide with hydrogen sulfide causes the precipitation of a precursor which was converted to the disulfide on heat-treatment in  $H_2S$  at various temperatures depending on the solvent adopted, whereas that of titanium 2-methoxyethoxide with  $H_2S$  produces a stable solution which was spin-casted onto silicon substrates followed by thermolysis to give thin films. Upon heat-treatment in  $H_2S$ , the disulfides show interesting morphological variations in the form of their powders and thin films, which were characterized by SEM and X-ray diffractometer.

### INTRODUCTION

The use of synthetic chemistry to improve the properties of inorganic materials has become a major trend in recent years; such materials encompass ceramics, metals and polymers.<sup>1-3</sup> Increasingly, research in the field of advanced ceramics has focused on the exploration of new routes to non-oxide compositions, such as carbides, nitrides, borides and sulfides. New synthetic routes based on chemical methods involve growth processes and may result in materials with a homogeneity, shape, composition, or purity not otherwise obtainable. A particular development in recent work is the use of molecular precursors; such species can often be obtained in high purity by distillation, and may be varied by substitution to control reactivity. One of the methods is sol-gel process.<sup>4</sup> The main advantages of this method are that the start-

ing materials may be synthesized in highly pure forms, and there is uniform mixing of the reacting elements on a molecular or even atomic level. Much of the chemical bonding required in the final material is often already in place in the reactants. On the other hand, the presence of large amounts of ligands originally incorporated to lend air, moisture, or thermal stability to precursor organometallics, frequently results in low yields on a mass basis. However, most of the information available in this method is the application for the synthesis of glasses, ceramics, thin films and fibers of oxide materials, and the use of the sol-gel process for the preparation of sulfide materials is relatively scarce.

Titanium disulfide has been identified and studied extensively as an active cathode material in Li based rechargeable batteries.<sup>5</sup> This is mainly

due to a high reversibility of the intercalation reaction, its good electronic conductivity, and high current capacity. The battery performance of  $\text{TiS}_2$  as a cathode can be further improved if the morphology and surface area can be optimized and the material can be synthesized in high purity.<sup>6</sup> Conventionally  $\text{TiS}_2$  has been prepared by the direct reaction of the elements at temperatures above  $700^\circ\text{C}$ .<sup>6,7</sup> The reaction requires long processing times (2 to 4 d) and yields powder with a low surface area. With the improvements and advantages of chemical processes, powders have been produced using vapor phase reactions, inorganic and organic sulfidizing agents and low temperature chemical precipitation reactions employing  $\text{TiCl}_4$ .<sup>7-10</sup> The products, however, contain chlorine as an impurity which could lead to the corrosion of cell wall in batteries. There is therefore a need to explore an alternative route which will circumvent these problems and also provide the thin-layers of  $\text{TiS}_2$ . One of alternative routes is the sol-gel process which has well studied and utilized metal alkoxides as starting materials. Although the use of metal alkoxides for the synthesis of the oxide is well known, the applications of alkoxides for the synthesis of sulfides are relatively unexplored since Vecht and Quddus have reported the preparation of alkaline earth sulfides by using alkoxides in 1976 for the first time.<sup>11-15</sup>

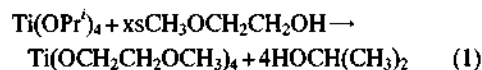
Here we describe the use of titanium alkoxides for the synthesis of titanium disulfide by modifying the sol-gel process, that replaces  $\text{H}_2\text{O}$  with  $\text{H}_2\text{S}$  as a precursor for the network of  $\text{TiS}_2$ .

## EXPERIMENTAL

Commercial chemicals(Aldrich), titanium isopropoxide( $\text{Ti}(\text{OPr}^i)_4$ ), 2-methoxyethanol and hydrogen sulfide gas, were used as received without further purification. All solvents were freshly distilled; tetrahydrofuran(THF) and benzene from Na/benzophenone,  $\text{CS}_2$  and toluene from  $\text{CaH}_2$ . All manipulations of reactants and products were accomplished under nitrogen or argon atmospheres.

Titanium 2-methoxyethoxide was prepared by

the alcohol exchange reaction of titanium isopropoxide with excess 2-methoxyethanol:



Excess(2~3 times) 2-methoxyethanol was added to titanium isopropoxide and the resulting mixture was refluxed for 2 h and all solvents were distilled off. Light golden titanium 2-methoxyethoxide was collected.

**Titanium disulfide powders.** Titanium alkoxides were dissolved in THF, benzene, toluene and carbon disulfide, respectively, and hydrogen sulfide gas was bubbled through it with flowing rate of 40 cc/min at room temperature as shown in Fig. 1. As soon as  $\text{H}_2\text{S}$  was passed, the colorless Ti solution turned red, and black precipitates were observed after 10 min in THF, benzene and toluene, and 20 min in  $\text{CS}_2$ , respectively. The bubbling was continued for 2 h to ensure completion of the reaction, and reaction vessels were sealed and isolated overnight. The precipitate was collected, washed thoroughly with each of solvents and dried under vacuum at room temperature for 4 h, after which it was perceived to be pyrophoric

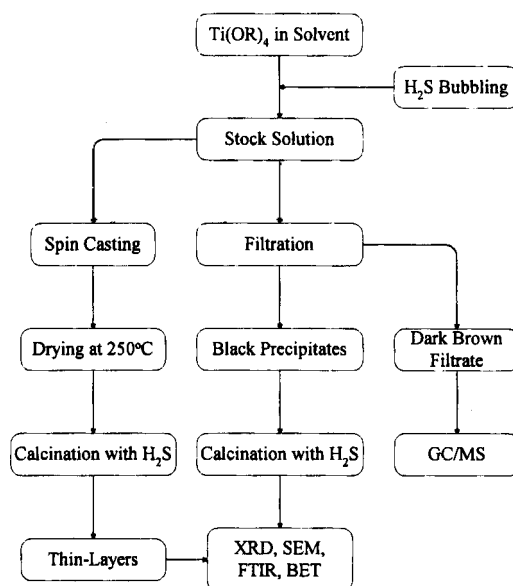


Fig. 1. Schematic diagram showing the procedure of the powder and the thin film of  $\text{TiS}_2$ .

and therefore very air sensitive. The dried precursor powder was heat-treated in flowing  $\text{H}_2\text{S}$  with rate of 40 cc/min at 500, 600, 700, 800 and 900 °C for 6 h.

**Thin films of titanium disulfide.** The precursor solutions of titanium alkoxides were prepared by modifying the method of  $\text{TiS}_2$  powder illustrated above. Titanium alkoxides (OR=isopropoxide and 2-methoxyethoxide) were dissolved in THF and  $\text{CS}_2$ , and then  $\text{H}_2\text{S}$  gas was bubbled through the solution at room temperature, respectively. The bubbling was continued just before the black precipitate was formed.

Thin films were deposited by spin casting (Photoresist spinner, Headway Research EC/PM) on the platinized silicon substrates (Pt/Ti/SiO<sub>2</sub>/Si). The precursor solution was syringed through a filter (0.45  $\mu\text{m}$ ) onto the substrate, and spinning was started immediately. The conditions (3500 rpm and 30 s) of spin-casting were same for all species. After deposition, the thin films were dried at about 250 °C on a hot plate for 1 min to remove residual solvents. They were then heat-treated in flowing  $\text{H}_2\text{S}$  at 800 and 900 °C for 6 h, respectively.

**Characterization.** The flow chart in Fig. 1 describes the characterization of titanium precursors, powders and thin-layers of titanium disulfide. Titanium 2-methoxyethoxide was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and the filtrate of the mixture solution was analyzed by gas chromatography/mass spectrometry (HP, GC/MS 5890/5971). An infrared spectrum of each powder sample was obtained in the range of between 4000 and 500  $\text{cm}^{-1}$ , and 500 and 250  $\text{cm}^{-1}$  wavenumber in a KBr pellet using FT-IR spectrometer (Perkin Elmer System 2000), respectively. Powder X-ray diffraction patterns of the powder and the thin film from  $2\theta=20^\circ$  to  $90^\circ$  were acquired on a X-ray diffractometer with Cu  $\text{K}\alpha$  radiation (Rigaku, D/Max), and the powder and the thin layers were observed by scanning electron microscopy (Hitachi, S2400). The surface areas of the as-prepared and the calcined powder were measured by the Brunauer, Emmett and Teller, BET method (Fisons, Sorptomatic 1999).

## RESULTS AND DISCUSSION

**Titanium disulfide powders.** All the as-prepared powders were amorphous and X-ray diffraction patterns collected on the heat-treated powders obtained from different solvent systems and sol-gel derived  $\text{TiO}_2$  are shown in Fig. 2(a) to (e). In all solvent systems adopted and sol-gel derived  $\text{TiO}_2$  from  $\text{Ti}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$ , crystalline  $\text{TiS}_2$  (hexagonal phase) was observed after calcining at 900 °C for 6 h in a  $\text{H}_2\text{S}$  environment to obtain yields (81% in THF, 31% in  $\text{CS}_2$ , 26% in benzene and 27% in toluene, respectively) based on Ti. However, there is also the appearance of oxide,  $\text{TiO}_2$  (rutile phase). The X-ray patterns of the powders from THF and  $\text{CS}_2$  systems show single hexagonal  $\text{TiS}_2$  phase with relatively higher yields, but the X-ray patterns from benzene and toluene systems also show hexagonal  $\text{TiS}_2$  phase and small amounts of rutile  $\text{TiO}_2$  phase. It is also interesting to note that the powder from the reaction of the

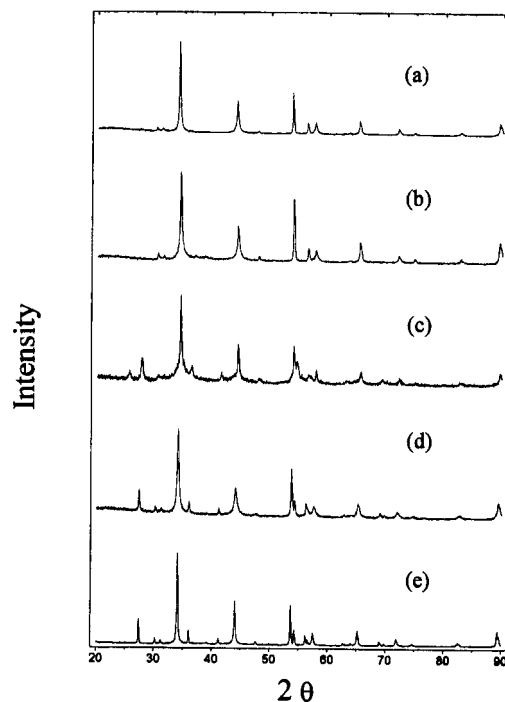


Fig. 2. XRD patterns of powders prepared in (a) THF, (b)  $\text{CS}_2$ , (c) Toluene, (d) Benzene and (e) sol-gel derived  $\text{TiO}_2$  from  $\text{Ti}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$  was converted to  $\text{TiS}_2$  followed by calcination under  $\text{H}_2\text{S}$  at 900 °C for 6 h.

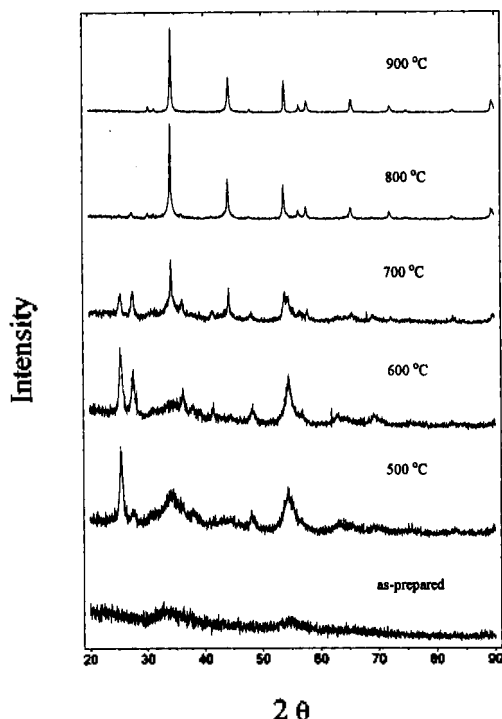


Fig. 3. XRD patterns of as-prepared powder and powders prepared in THF followed by calcination at 500, 600, 700, 800, and 900 °C for 6 h.

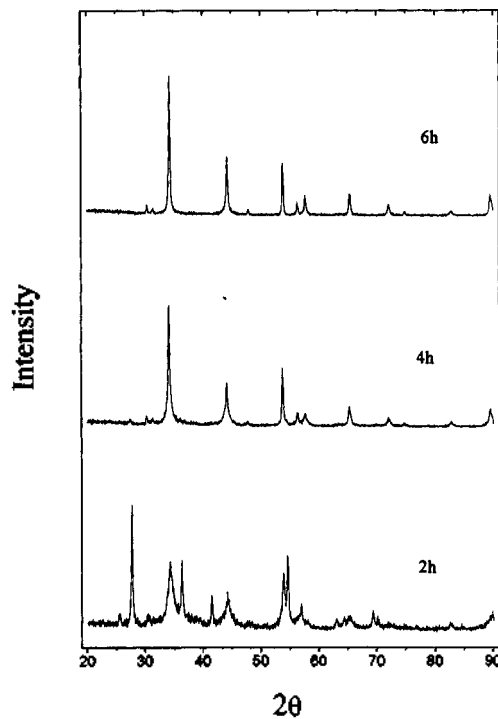


Fig. 4. XRD patterns of powders prepared in THF followed by calcination at 900 °C for (a) 6 h, (b) 4 h, (c) 2 h.

sol-gel derived  $\text{TiO}_2$  amorphous particles from  $\text{Ti}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$  with  $\text{H}_2\text{S}$  has still rutile phase, which indicates that if the network already has been formed by oxygen atoms between Ti atoms, it is difficult to convert  $\text{Ti-O-Ti}$  to  $\text{Ti-S-Ti}$  completely during the relatively short reaction time. Therefore we can choose THF and  $\text{CS}_2$  as solvents for the synthesis of  $\text{TiS}_2$  from the reaction of titanium alkoxides with  $\text{H}_2\text{S}$ .

Fig. 3 shows the X-ray patterns of the THF system with respect to different calcined temperatures. Hexagonal  $\text{TiS}_2$  phase was seen to form after heat-treating at 700 °C with rutile  $\text{TiO}_2$  phase, whereas it was observed to produce completely after calcining at 800 °C. But the formation of single  $\text{TiS}_2$  phase was also dependent upon the time of heat-treatment. It was observed after calcining at 900 °C for only 2 h and completely formed for 4 h as shown in Fig. 4.

The morphologies of the as-prepared powder

and heat-treated powders are shown in Fig. 5. As can be seen, the as-prepared powder is composed of agglomerates of spherical particles with diameter of about 1  $\mu\text{m}$ . The size and morphology of the aggregate was observed as similar as that of the as-prepared powder increasing calcined temperatures up to 600 °C. However, the SEM micrograph of the powders heat-treated at 700 °C shows interesting difference in morphology. There are couples of needlelike shapes of  $\text{TiS}_2$  up to 5  $\mu\text{m}$  length. When the particles were calcined at 800 °C, their morphological features completely changed from spherical agglomerates to smaller needlelike shapes and platelets. These results are well correspondent to those of X-ray patterns.

Surface area measurements of the powder calcined at 800 °C prepared in  $\text{CS}_2$  and THF gave 45.29 and 10.94  $\text{m}^2/\text{g}$ , respectively, and such high surface area materials might have a significant influence on the electrochemical characteristics of

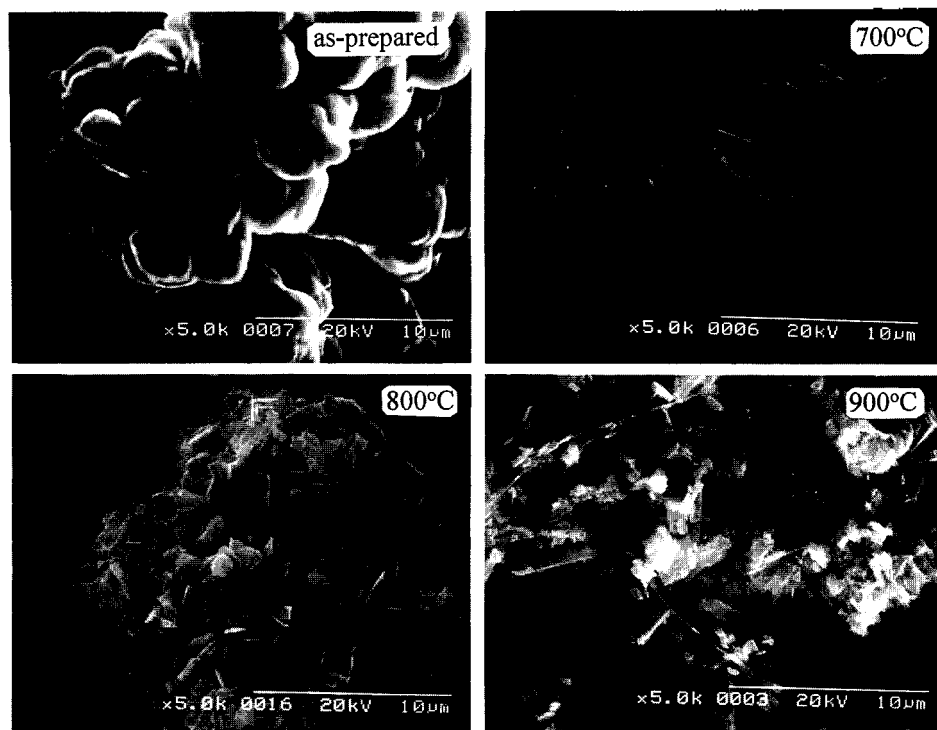


Fig. 5. SEM photomicrographs of powders (a) as-prepared, and calcined at (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C for 6 h.

cathode materials. Studies on the electrochemical behavior of these powders will be done soon.

**Thin films of titanium disulfide.** Thin-layers of  $\text{TiS}_2$  were obtained by spin casting the precursor solution onto silicon substrates followed by thermolysis under hydrogen sulfide atmosphere. Fig. 6 shows XRD patterns of the thin-layers on platinized silicon substrates (Pt/Ti/SiO<sub>2</sub>/Si) after calcining at 900 °C for 6 h under the H<sub>2</sub>S atmosphere, depending upon bubbling time (0 h, 4 h and 8 h) of the sulfidization of the precursor. A hexagonal  $\text{TiS}_2$  phase was observed with unidentified phases and peaks of the substrate. The unknown peaks could be formed from the reaction of the substrate elements with H<sub>2</sub>S at such a high temperature. The possible formation of rutile  $\text{TiO}_2$ , anatase  $\text{TiO}_2$ , hexagonal  $\text{TiS}$ , cubic  $\text{TiS}_2$ , and monoclinic  $\text{TiS}_3$  phases may be excluded in the absence of a large relative intensity of the peaks of each phase.

The precursor solutions were prepared by the reaction of  $\text{Ti}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$  with H<sub>2</sub>S at room

temperature. It is of interest to observe that the black precipitates were not formed during the sulfidization reaction of titanium 2-methoxyethoxide with hydrogen sulfide gas in THF even for 8 h, and the resulting dark red solution was very stable for 6 mon under the argon atmosphere. Little difference between Fig. 6(a) and (b) indicates that the time of sulfidization of the alkoxide with H<sub>2</sub>S may be convergent. However, the sulfidization reaction of titanium isopropoxide with hydrogen sulfide gave black precipitates within 10 to 20 min depending on a solvent. A titanium atom is coordinated with four oxygen atoms in the case of the isopropoxide, whereas a Ti atom is coordinated with six O atoms via a bidentate ligand  $\text{OCH}_2\text{CH}_2\text{OCH}_3$  in the case of the 2-methoxyethoxide.<sup>16</sup> It indicates that the Ti of the former is much more vulnerable to attack of H<sub>2</sub>S than that of the latter. The more sulfidization of the 2-methoxyethoxide with H<sub>2</sub>S results in the easier formation of a hexagonal  $\text{TiS}_2$  phase as increasing time of the sul-

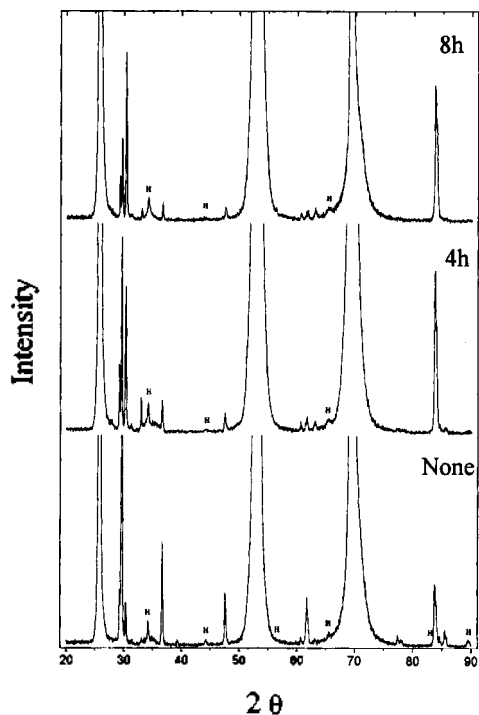


Fig. 6. XRD patterns of thin films with respect to bubbling time for (a) 0 h, (b) 4 h, (c) 8 h. H indicates the hexagonal phase of  $TiS_2$ .

fidization.

Fig. 7 shows SEM photomicrographs of a layer crystallized at  $900\text{ }^\circ\text{C}$  and illustrates the unique nature of the microstructure. There are similar morphological features among the micrographs which show needlelike shapes and platelets that indicate the formation of a hexagonal  $TiS_2$  phase. But some difference between Fig. 7(b) and (c) indicates that the sulfidization of the alkoxide would be needed. This result is correspondent with those of  $TiS_2$  powders as shown in Fig. 5. However, these micrographs also show sparse features which indicate that the reason why their XRD patterns have a variety of phases could be explained as shown in Fig. 6. The elements of the substrate may be reacted with  $H_2S$  at elevated temperatures during the thermolysis, resulting in the occurrence of the unidentified XRD traces.

**Evolution of  $TiS_2$  powder and Thin-layer from titanium alkoxides.** Fig. 8 shows FT-IR spec-

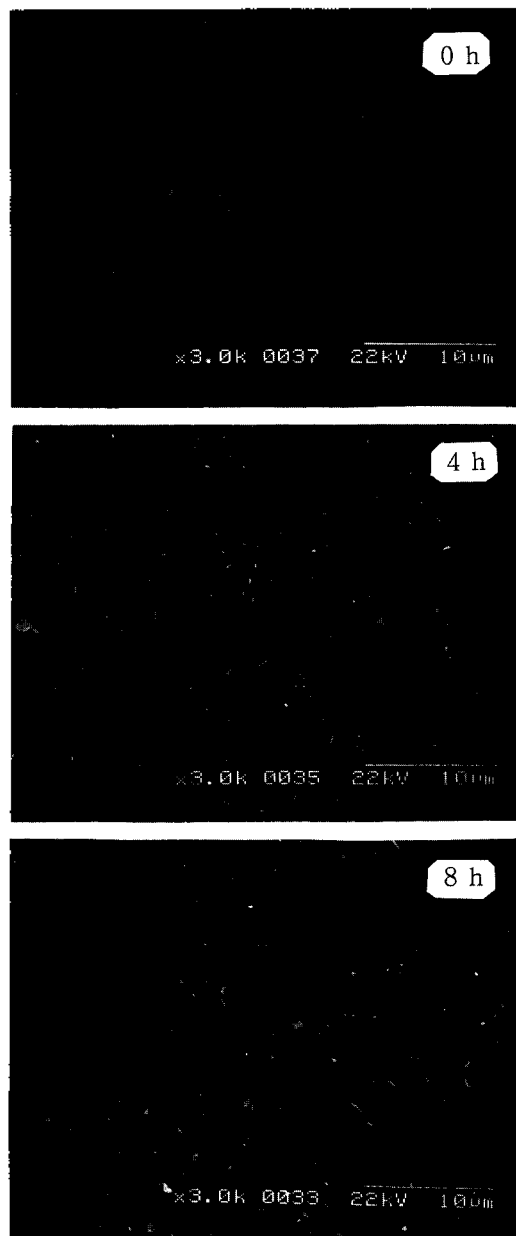


Fig. 7. SEM photomicrographs of thin films with respect to bubbling time for (a) 0 h, (b) 4 h, (c) 8 h.

trum of as-prepared powders from the reaction of  $Ti(OPr)_4$  with  $H_2S$ , which indicates that the precipitates contain isopropoxy groups. Bands at  $1377$ ,  $1160$ ,  $1118$  and  $1010\text{ cm}^{-1}$  are characteristic of the isopropoxy groups on titanium.<sup>17</sup> The precipitates and the calcined powders also contain Ti-S

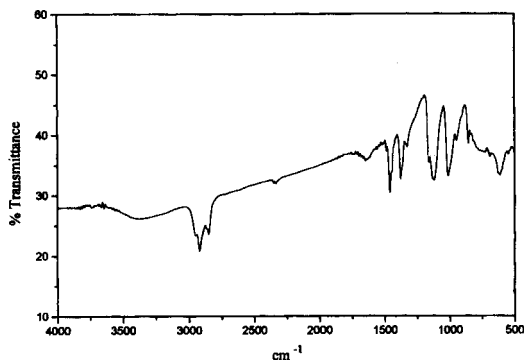


Fig. 8. Infrared spectrum of the as-prepared powder from the reaction of titanium isopropoxide with  $\text{H}_2\text{S}$ .

bondings by the observation of the characteristic vibration at about  $290\text{ cm}^{-1}$  (vs.  $755\text{ cm}^{-1}$  for  $\text{Ti-O-Ti}$ )<sup>18</sup> in Fig. 9. GC/MS analysis performed on the filtrate and the precursor solution showed that alcohols (R=isopropanol and 2-methoxyethanol) were liberated during the reaction. These results therefore suggest a replacement of the alkoxy groups by thiol (SH) groups from  $\text{H}_2\text{S}$ . This substitution reaction seems to be a thiolysis reaction which is similar to the hydrolysis reaction in the sol-gel process.

The sol-gel process is based on the hydrolysis and condensation of metal alkoxide compounds.<sup>4</sup> Hydrolysis replaces the alkoxide groups with hydroxyl groups and subsequent condensation reactions involving the hydroxyl groups produce M-O-M bonds as follows:



It is noticeable that the oxygen atom of M-OH and M-O-M of Eq. (2), (3) and (4) is originated from a water molecule rather than an alkoxide molecule, which was confirmed by  $^{17}\text{O}$  NMR spectroscopy.<sup>19</sup>

It is speculated that the evolution of  $\text{TiS}_2$  from the alkoxide could be happened as following. If  $\text{H}_2\text{O}$  is replaced by  $\text{H}_2\text{S}$  in Eq. (2), the thiolysis reaction occurs:

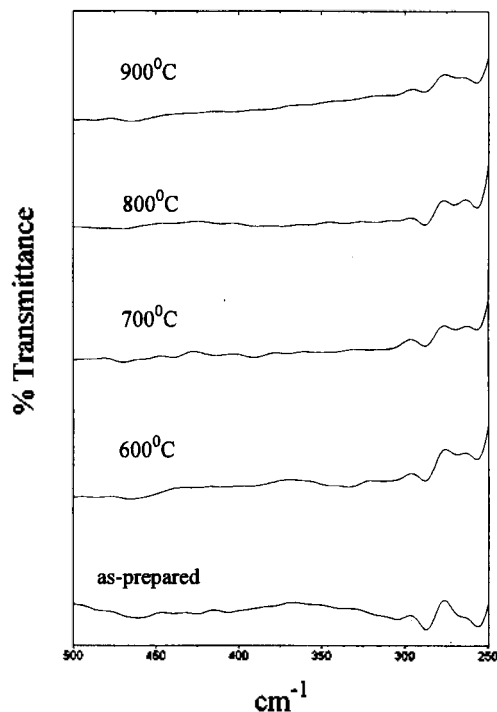
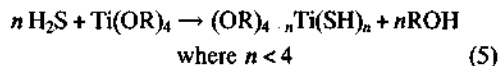
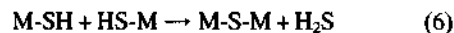
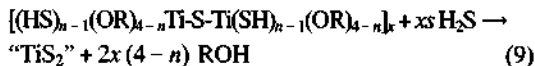


Fig. 9. Infrared spectra of the powders in the wavenumber range of  $500$  and  $250\text{ cm}^{-1}$ .

After the thiolysis, the precipitates could have formed due to the condensation of the alkoxy-thiols by the liberation of  $\text{H}_2\text{S}$  or  $\text{ROH}$  as follows:



The overall reaction can be written as:



However, the thiolysis (Eq. (5)) and the condensation (Eq. (7)) of alcohol groups are less likely because of the polar character of the Ti-O bonds ( $\Delta\chi=2.15$  for Ti-O vs.  $0.67$  for Ti-S).<sup>20</sup> The precursors could contain more alkoxy groups on titanium than those of the sol-gel process, and then should be heat-treated with  $\text{H}_2\text{S}$  to produce  $\text{TiS}_2$ . It was also observed in the conversion reaction of the sol-gel derived  $\text{TiO}_2$  precursor to  $\text{TiS}_2$  by ther-

molysis under the H<sub>2</sub>S atmosphere. It, however, is difficult to be completely converted to the TiS<sub>2</sub> phase because the structure of the precursor has already been composed of the network of Ti-O-Ti. This is in concurrence with the data of TiS<sub>2</sub> powders as shown in Fig. 2(e).

Guiton *et al.* have reported similar thiolysis reactions in the sulfidization of mercaptides and organometallic compounds of zinc such as Zn(SR)<sub>2</sub> and ZnR<sub>2</sub>(R=Bz, Ph, But, Pr and Et) to form ZnS.<sup>12</sup> Bochmann *et al.* have also reported the preparation of TiS by the thermolysis of Ti(SBut)<sub>4</sub>. Work in the thiolysis reaction of Ti(SR)<sub>4</sub> with H<sub>2</sub>S is under way and will be published elsewhere.

**Acknowledgement.** This study was financially supported by NON DIRECTED RESEARCH FUND, Korean Research Foundation and the Basic Science Research Institute Program(BSRI-95-3407) by the Korean Ministry of Education.

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