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TiS_2 and TiS_3 Thin Films Prepared by MOCVD

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Thin films of TiS_2 and TiS_3 have been prepared by thermal chemical vapor deposition by reacting $TiCl_4$ and a series of sulfur sources [hexamethyldisilthiane ($(CH_3)_3Si{-}S{-}Si(CH_3)_3$), *t*-butyl sulfide ($(CH_3)_3C{-}S{-}C(CH_3)_3$), and *t*-butyl disulfide ($(CH_3)_3C{-}S{-}S{-}C(CH_3)_3$)]. Thin films of TiS_3 were prepared by reacting $TiCl_4$ and TBDS at a deposition temperature less than 260°C. As the deposition temperature was increased, TiS_2 also formed within the deposited film, until at temperatures greater than 400°C only TiS_2 was formed. The use of the other sulfurizing sources resulted in the deposition of only TiS_2 throughout the temperature range studied (200–550°C). The morphology of the TiS_2 films varied remarkably with deposition temperature. At low temperatures the films were very dense and X-ray diffraction indicated that the films were deposited preferentially with the crystallographic "*c*" axis perpendicular to the substrate. As the temperature increased above 300°C, a porous honeycomb structure was deposited with the crystallographic "*c*" axis parallel to the substrate. © 1992 Academic Press, Inc.

Introduction

Transition-metal sulfide thin-film preparations have been extensively studied in recent years. These thin-film materials have interesting electrochemical properties and can offer distinct advantages over the traditional powder electrode.

TiS_2 has a layer-type structure with Van der Waals gaps between sulfur layers and is regarded as a potential rechargeable cathode materials (*1–3*). TiS_2 allows intercalation and removal of guest ions without forming and breaking chemical bonds within the host in the discharging and charging processes. In an electrochemical cell the discharge current density may be limited by the relatively low ionic diffusion rate of guest ions within a bulk electrode, thus increasing the polarization of the electrode. It is believed that thin-film electrodes having large surface area and perhaps a distinct morphology can reduce the electrode polarization and improve electrode performance.

Kanehoui and his co-workers as well as Takehara *et al.* have prepared TiS_2 thin films by plasma-enhanced and thermal CVD from the reactions between $TiCl_4$ and H_2S (*4–7*). They prepared orientated TiS_2 thin films with the crystallographic "*c*" axis parallel to the direction of the substrate. They found this *c*-axis-orientated thin-film cathode showed improvements in electrochemical performance over a bulk TiS_2/Li cell. However, the use of $TiCl_4$ and H_2S as synthetic reagents has severe limitations, specifically, the reaction between these compounds is very slow even at temperatures greater than 500°C.

We believed that modifications in deposi-

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tion conditions would change the thin-film morphology dramatically, and that a rapid low-temperature deposition reaction would allow us a wide choice of reaction variables. In order to prepare titanium sulfide thin films at low temperatures a variety of sulfurizing agents were examined (hexamethyldisilthiane (HMDST), *t*-butyl disulfide (TBDS), and *t*-butyl sulfide (TBS)) in gas-phase reactions with $TiCl_4$. All of these reagents reacted rapidly with $TiCl_4$ at low temperature and allowed for the preparation of thin-film titanium sulfides.

Previous low-temperature liquid-phase reactions had indicated that the following general reactions took place (*8*, *9*):

$$TiCl_4 + 2(CH_3)_3Si{-}S{-}Si(CH_3)_3 \rightarrow TiS_2 + 4Si(CH_3)_3Cl \quad (1)$$

$$TiCl_4 + (CH_3)_3C{-}S{-}C(CH_3)_3 \rightarrow Ti_3S_4 + C(CH_3)_3Cl + \text{by-products} \quad (2)$$

$$TiCl_4 + (CH_3)_3C{-}S{-}S{-}C(CH_3)_3 \rightarrow TiS_2 + C(CH_3)_3Cl + \text{by-products.} \quad (3)$$

However, since the conditions for the gas-phase synthesis would be substantially different, we could not predict a priori either the phases prepared or the rates for the various reactions. In this work we have studied the titanium sulfide phases prepared, as well as the thin-film orientation and morphology as a function of deposition temperature and sulfur source. Our goal was to develop a rapid, efficient process for the thermal preparation of TiS_2 films.

Experimental

Materials

The titanium source, titanium(IV) chloride ($TiCl_4$) (Aldrich Chemical Company, 99.9995%), was used as obtained. The sulfur sources: (a) hexamethyldisilthiane $(CH_3)_3Si{-}S{-}Si(CH_3)_3$ (HMDST) (Fluka Chemical Company) was fractionally distilled and collected within a boiling range of 160 to 161°C; (b) tert-butyl sulfide $(CH_3)_3C{-}S{-}C(CH_3)_3$ (TBS) (Aldrich Chemical Company) was fractionally distilled and collected within a boiling range of 148 to 149°C; and (c) tert-butyl disulfide $(CH_3)_3C{-}S{-}S{-}C(CH_3)_3$ (TBDS) (Aldrich Chemical Company) was fractionally distilled and collected within a boiling range of 200 to 201°C.

Reactor Design

In the TiS_2 and TiS_3 thin-film preparations, $TiCl_4$ and the organic sulfur sources will react with each other even at room temperature. For the purpose of preventing the expected prereaction of $TiCl_4$ and sulfur reactant near the inlet cold zone, a glass tube was used to inject the sulfur source into the reaction area (Fig. 1). The length of the glass tube could be extended or reduced as required. $TiCl_4$ was put in front of an Ar carrier gas. The Ar gas would dilute and carry this $TiCl_4$ vapor into the reactor.

Thin-Film Preparations

The flow of $TiCl_4$ was controlled by a mass flow meter. The sulfur source vapor pressure was controlled by changing the temperature of the source liquid. The $TiCl_4$ reactant was heated to approximately 55°C to obtain sufficient vapor pressure. This $TiCl_4$ vapor went through a mass flow meter which was also heated to 55°C and mixed with Ar gas (the argon flow rate was also controlled by a mass flow meter) which diluted and carried this vapor into the reactor. The $TiCl_4$ vapor will interact with the sulfur source within the reaction zone and form a titanium sulfide thin film on the substrate surface. By changing the reaction temperature, pressure, and flow of each reactant, we were able to study reaction parameters for preparing thin-film TiS_2 or TiS_3.

Thin-Film Analysis

The phases produced (TiS_2 and TiS_3) were verified by X-ray diffraction (Philips XRD

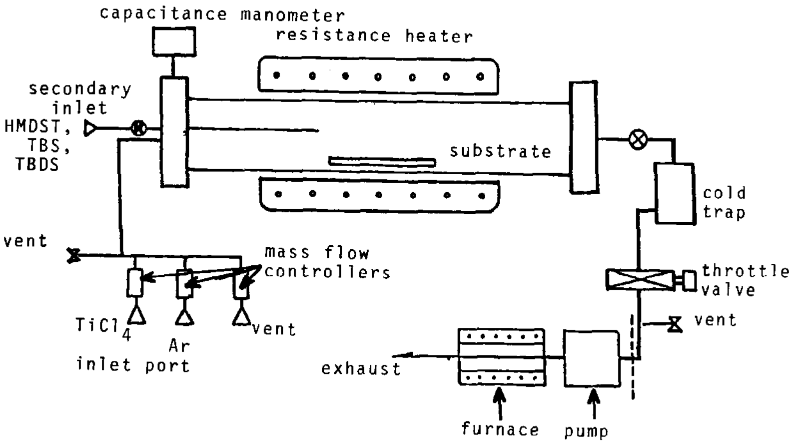

FIG. 1. Schematic diagram of reactor for TiS_2 thin film preparations.

3100 Diffractometer). The orientated TiS_2 thin films were characterized by X-ray diffraction and transition electron microscopy (Hitachi H-800, within accelerating voltage of 200 keV).

Results and Discussion

In attempting TiS_2 thin-film preparations, a gold-colored thin film was prepared at a deposition temperature of 230°C from the reaction of $TiCl_4$ with HMDST. The reaction parameters are described in Table I. The X-ray diffraction pattern of this gold-colored thin film showed only one diffraction peak, corresponding to (001) TiS_2. Electron diffraction of a film grown on NaCl and then floated off showed a series of diffraction peaks which positively identified this gold-colored thin film as TiS_2 (Table II). The X-ray pattern of the thin gold-colored film which shows only one diffraction peak indicates that this thin film is preferentially orientated with the crystallographic *c* axis perpendicular to the direction of the substrate. A series of TiS_2 thin films with different orientations were prepared by changing the deposition temperature. The reaction parameters are described in Table I. Figure 2 shows the X-ray patterns of those films prepared at different deposition temperatures. The deposition temperatures were varied from 200 to 260°C. At deposition temperatures below 250°C, only one diffraction peak was found in the spectra, corresponding to the (001) reflection of TiS_2. This indicates that these films are orientated at a direction with the *c* axis perpendicular to the substrate. At 260°C, two diffraction peaks were obtained in the pattern, corresponding to (101) and (110) reflections of TiS_2. This indicates a modification in the prefered orientation of the film with the *c* axis now either parallel or close to parallel to the direction of the substrate. Since the Van der Waals gap of thin films is orientated either perpendicular or close to perpendicular to the direction to the substrate, this kind of thin film is believed to improve the lithium intercalation process by increasing the active edge surface.

Several substrates were used during the thin-film deposition processes. The TiS_2 thin films showed remarkable adhesion on substrates such as glass, aluminum foil, stainless steel foil, and titanium foil. The thin-film growth rate showed almost no temperature dependence of deposition from 200 to 260°C,

TABLE I

REACTION PARAMETERS FOR PREPARING TiS_2 AND TiS_3 THIN FILMS FROM $TiCl_4$ AND DIFFERENT SULFUR SOURCES

Flow of $TiCl_4$ (sccm)	Flow of Ar (sccm)	HMDST (heating temp.) (°C)	TBS (heating temp.) (°C)	TBDS (heating temp.) (°C)	Rn. Press. (Torr)	Rn. Temp. (°C)
3	10	41			5	200
3	10	41			5	230
3	10	41			5	250
3	10	41			5	260
3	10		38		5	250
3	10		38		5	260
3	10		38		5	300
3	10		38		5	400
3	10		38		5	500
3	10			48	1.5	260
3	10			48	1.5	300
3	10			48	1.5	350
3	10			48	1.5	400

and we obtained values greater than 6 μ/hr. This lack of temperature dependence on growth rates indicates that the growth is mass-transfer controlled. This is perhaps not surprising since this reaction occurs very rapidly in solution even at room temperature. Thin-film TiS_2 with geometric surface areas of 600 cm^2 were easily prepared on Al foil substrates.

In order to solve the price and odor problems of HMDST, alternative sulfur sources (TBS & TBDS) were used. A black thin film was prepared from the reaction of $TiCl_4$ and TBDS at a deposition temperature of 260°C. The deposition parameters are described in Table I. The X-ray diffraction pattern shows that this film was TiS_3 rather than TiS_2. As the deposition temperature was raised to 300 or 350°C, a mixture of TiS_2 and TiS_3 was present in the film. The X-ray diffraction pattern of thin films prepared at 300 and 350°C shows that at higher deposition temperatures TiS_2 was the favored phase. When the deposition temperature was raised to 400°C, a gold-colored film of TiS_2 was obtained (Fig. 3).

TABLE II

IDENTIFICATION OF TiS_2 FROM TEM

Intensity	*d* Values (measured)	*d* Values (reference)	*hkl*
3	2.95	2.948	100
Weak	2.61	2.6182	101
1	1.70	1.7024	110
Weak	1.43	1.4272	201
Weak	1.10	1.0927	211
2	0.98	0.9829	300
Weak	0.85	0.8516	220

TBS was subsequently used as a sulfur source in TiS_2 thin-film preparations. By following the deposition conditions described in Table I, a gold-colored film was obtained from $TiCl_4$ and TBS at a deposition temperature of 260°C. The X-ray diffraction pattern of this gold-colored film shows two diffraction peaks which correspond to (101) and (110) reflections of TiS_2. This particular orientation is almost identical to the one that was obtained from $TiCl_4$ and HMDST at the deposition temperature of 260°C. The thin-

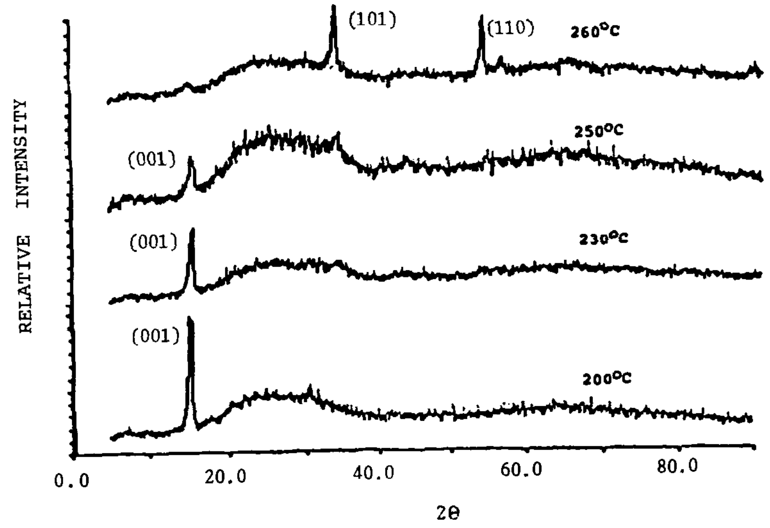

FIG. 2. XRD patterns of TiS_2 thin films prepared at different deposition temperatures.

film adhesion quality (on glass, Al foil, stainless steel foil, and Ti foil) are the same as those of TiS_2 thin films prepared from $TiCl_4$ and HMDST. A series of TiS_2 thin films were prepared from $TiCl_4$ and TBS, following the deposition conditions as described in Table I but at different deposition temperatures (e.g., 250, 300, 400, and 500°C). In this reaction the growth rate is temperature-dependent with the rate increasing substan-

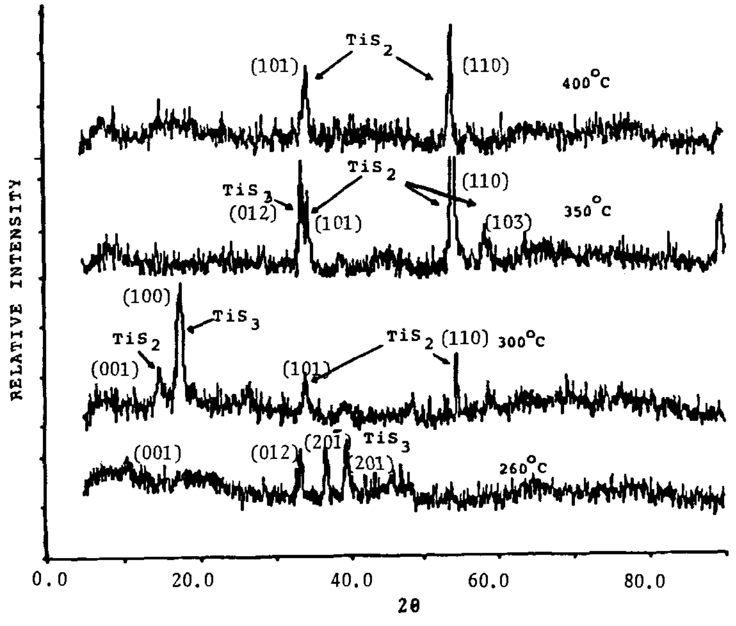

FIG. 3. $TiCl_4$ + *t*-butyl disulfide → TiS_2 (or TiS_3) (at different deposition temperatures).

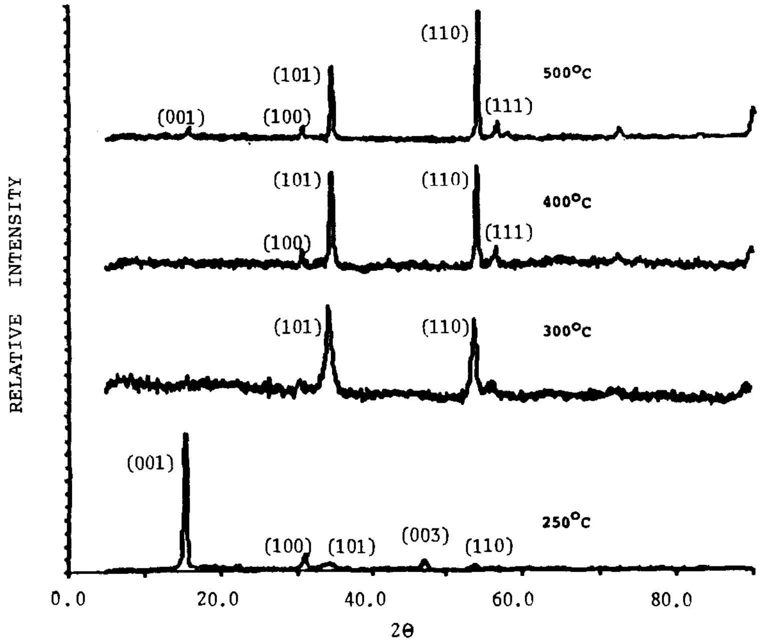

FIG. 4. $TiCl_4$ + *t*-butyl sulfide → TiS_2 (at different deposition temperatures).

tially with temperature (approximately a 10-fold increase in growth rate is observed in increasing the temperature from 250 to 550°C). In our previous liquid-phase reactions we observed substantially slower reactions when *t*-butyl sulfide or *t*-butyl disulfide react with $TiCl_4$. Quartz, Al foil, Ti foil, stainless steel foil, carbon fiber, titanium fiber, and stainless steel fiber were used as substrates. The X-ray diffraction patterns of the films prepared at different deposition temperatures are shown in Fig. 4. Modifications in orientation, as observed by X-ray diffraction, are easily followed. Films were also examined by scanning electron microscopy. Figures 5 and 6 show SEM photographs of the films prepared at 250 and 500°C. The total change of thin-film morphology is clearly seen from these SEM figures. Figure 7 shows the side view of the thin film deposited at 400°C, showing not only the thickness of the film but also the orientated particles in the film. Growth rates at 400°C in excess of 20 μ/hr were easily obtained by proper selection of conditions. A detailed study of the electrochemical properties of these films will appear in a future publication (*10*).

Conclusion

This study demonstrates that titanium sulfide thin films may be rapidly grown by chemical vapor deposition over a wide range of temperatures by selection of active sulfurizing sources. TiS_3 was deposited only when *t*-butyl disulfide was used as the sulfurizing sources. In order to stabilize TiS_3 relative to the decomposition, $2TiS_3 \rightarrow 2TiS_2 + S_2$, it is necessary that a sufficient sulfur vapor pressure exist in the reactor. Previous studies have shown that the partial pressure of sulfur over TiS_3 can be described by the following relationship: $\log P_{(\mathrm{mmHg})} = 10.42\ (\pm 0.42) - 6850/T\ (\pm 340)$ (*11*). Using this empirical relationship and substituting 673

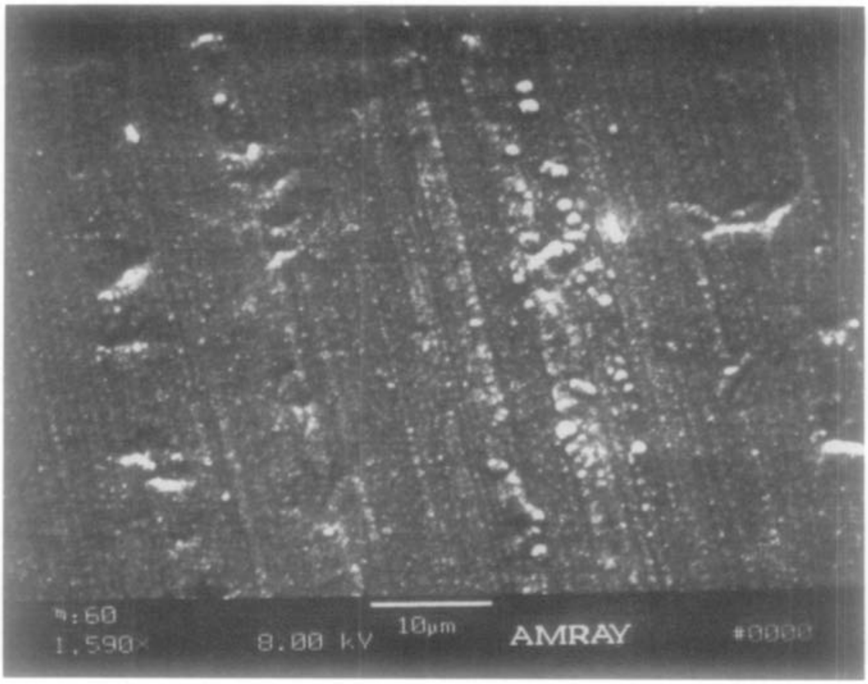

FIG. 5. SEM picture of TiS_2 thin film prepared at 250°C.

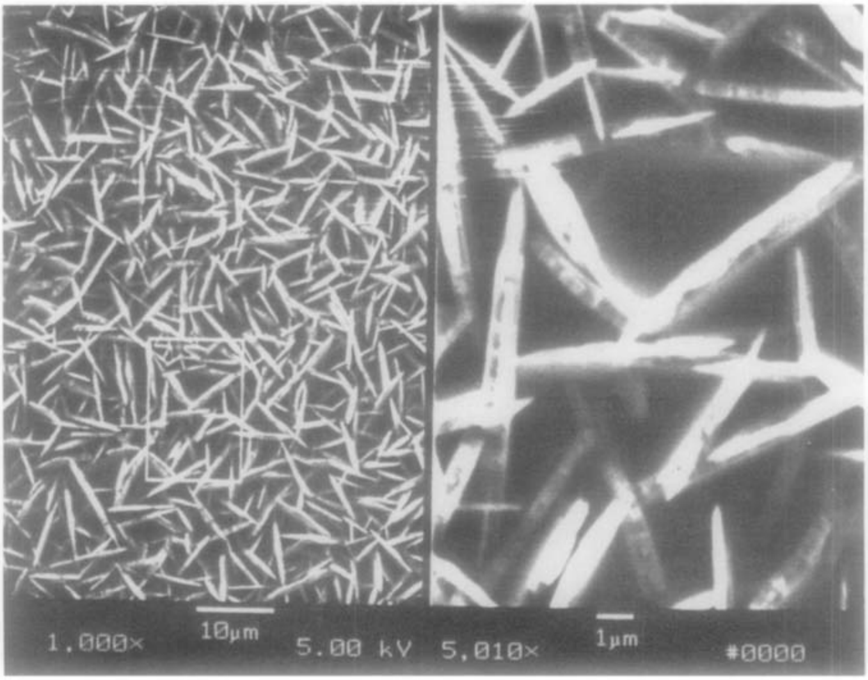

FIG. 6. SEM picture of TiS_2 thin film prepared at 500°C.

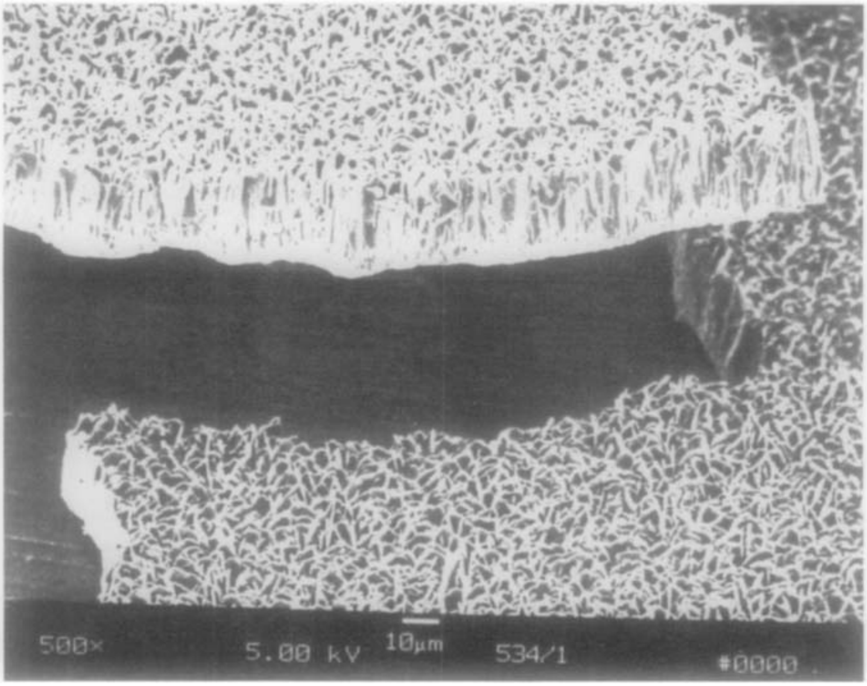

FIG. 7. SEM picture of edge view of TiS_2 thin film.

K, we obtain a value of 1.7 Torr, substantially greater than the total pressure in our reactor and thus certainly favoring the thermal decomposition of TiS_3 to TiS_2. At low temperatures, lower than 260°C, the partial pressure of sulfur over TiS_3 is very low (less than 10 mTorr calculated from the previous formula) and probably is obtained within our reactor. Thus at these temperatures TiS_3 would remain as a stable phase. The preparation of the trisulfide at low temperatures is probably due to the direct reaction between $TiCl_4$ and *t*-butyl disulfide. Although the *t*-butyl disulfide can decompose and generate a partial pressure of sulfur, at temperatures below 250°C we would not expect appreciable reaction rates between TiS_2 and sulfur. Therefore if TiS_2 was formed in this reaction we would expect to find substantial TiS_2 and sulfur in the film. In addition, the direct relationship between the TiS_3/TiS_2 ratio and the deposition temperature maps very well to the decomposition of TiS_3 expected as the temperature increases. It may seem mechanistically reasonable that the S–S pair in the *t*-butyl disulfide is responsible for generating the TiS_3 phase, which also contains an S–S pair.

From an applied perspective the best choice of a sulfurizing agent was *t*-butyl sulfide. This reagent was able to readily react with $TiCl_4$ at low temperatures and yet did not create TiS_3 even at low temperatures (from our perspective TiS_2 was the desired phase). In addition, this reagent is easy to use, moderate in cost, and has limited odor problems (unlike hexamethyldisilthiane).

The morphology of our thin-film TiS_2 prepared from *t*-butyl sulfide could be readily modified by simply changing the deposition temperature. At very low temperature the film is amorphous to X-rays and shows no features by scanning electron microscopy. At moderate temperatures (200–250°C) the film is no longer amorphous to X-rays, indicates preferred orientation (*c* axis perpendicular to substrate), and still shows no features by SEM. At higher temperatures, very crystalline material is deposited in a well structured honeycomb type morphology. After the formation of the honeycomb morphology additional temperature increases result in larger crystallites within the structure. The very good adhesion to a variety of substrates and the rapid growth rates (growth rates greater than 90 μ/hr were obtained) indicate that this process is well suited for preparing TiS_2 thin films of various morphologies.

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