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PREPARATION AND PROPERTIES OF THIN FILM REVERSIBLE CATHODE MATERIALS

### FINAL REPORT

Bruce Dunn and R. F. Bunshah Department of Materials Science and Engineering

July 1985

Contract/Grant Number: DAAG29-82-K-0145

University of California, Los Angeles School of Engineering and Applied Science Los Angeles, CA 90024

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### 1. FOREWORD

This report pertains to the research undertaken and accomplished over the period June 1, 1982 - May 31, 1985. The technical materials mentioned herein were more fully described in the five (5) previous semi-annual progress reports submitted to ARO. The progress achieved over the final project period of 5 months (January 1, 1985 - May 31, 1985) is included in this report. The experimental work during this time primarily involved electrochemical measurements, and the results are contained in the appropriate section of this report.

At the time of this writing, there were a few items in progress associated with project. They are as follows;

- A small number of electrochemical measurements are continuing. These experiments are either confirming in nature or of a more prolong duration (i.e., cell cycling). This work is being used to satisfy and complete a student's M.S. thesis.
- 2. The M.S. thesis of Mr. D. A. Zehnder is in preparation. The date of completion is scheduled for September 1985.
- 3. A manuscript based on the thesis of Mr. Zehnder (but not necessarily on the experiments in progress) is also in preparation. The paper will be submitted as part of the conference proceedings for the International Conference on Solid State Ionics in August 1985.

Items (2) and (3) above are listed in the text of this report for the sake of completeness. The fact that they are in preparation is clearly identified. Upon completion, these items will be sent to ARO in accordance with the usual procedures.

Finally, the authors of this report are very grateful to the U.S. Army Research Office for the support of this research project and for their continued support of our work on thin film cathode materials.

### 2A. STATEMENT OF THE PROBLEM STUDIED

The overall objective of the research was to synthesize reversible cathode materials in thin film form. Such materials had not been previously prepared as thin films and it was unknown whether (a) vapor deposition approaches could be used to synthesize compounds with highly anisotropic structures and (b) whether such materials would display fundamentally different properties as a thin film compared to the bulk material. Thin films also offer some interesting possibilities for secondary lithium batteries including a shorter path length for ion and electron transport and movel cathode structures. The reversible cathode material titanium disulfide ( $TiS_2$ ) was emphasized because considerable information concerning the preparation, structure and properties of the bulk material was available to provide valuable comparisons with the thin films. The breadth of the research program included the preparation of thin films by vapor deposition processes, the characterization of the structural and chemical nature of the films and the investigation of their transport properties and electrochemical behavior.

### 2B. SUMMARY OF THE MOST IMPORTANT RESULTS

### a. Film Synthesis and Characterization

- 1. A. reversible cathode material with a highly anisotropic structure has been prepared as a thin film (2 to  $5\mu m$  thick) using vapor deposition processes.
- 2. The ARE process (activated reactive evaporation) offers considerable flexibility in controlling the chemistry of the film, the resulting crystal phase and the microstructure of the film.
- 3. Under optimized conditions, nearly stoichiometric films  $(Ti_{1.04}S_2)$  can be produced. The films may also show preferential orientation, with the basal planes of TiS<sub>2</sub> parallel to the plane of the substrate.
- 4. The films are of high quality. They are free of pin holes and defects and adhere extremely well to a variety of glass and ceramic substrates.

### b. Transport Properties and Electrochemical Behavior

This category is further divided depending upon whether the property of the film is similar or not to the corresponding bulk material.

### Properties similar to the bulk material

- 1. For as-deposited films of  $\text{TiS}_2$ , the electrical resistivity values at room temperature and the temperature dependence of the resistivity (increasing resistivity with increasing temperature) are in good agreement with the behavior reported for bulk  $\text{TiS}_2$ .
- 2. The films are electrochemically active. Prior to the actual testing, however it is best to "condition" the film by lithiating it. The lithiation is accomplished by a chemical approach and vastly improves the electrochemical performance. Similar procedures are frequently employed for bulk materials.
- 3. The films are able to electrochemically intercalate and de-intercalate lithium. The operating voltage range (2.7V to 1.7V) is comparable to that of the bulk material and cycling occurs at the  $\mu$ A/cm<sup>2</sup> level. No long term cycling studies were performed.
- 4. The electrochemical measurements gave no evidence of interfacial anomalies or phase transformations.
  <u>Properties different than the bulk material</u>
- 5. The diffusion coefficient for lithium was some  $10^2$  to  $10^3$  times less than the bulk material.
- 6. The diffusion coefficient for lithium varied as a function of the lithium content of the  $TiS_2$  film. The diffusion coefficients were highest over the voltage range 1.8V 2.3V and substantially lower for those films with x < 0.1 (for the composition  $Li_xTiS_2$ ). In contrast, bulk  $TiS_2$  exhibits no such variation in the lithium diffusion coefficient over the complete range 0 < x < 1.

7. The different transport properties for the TiS<sub>2</sub> thin films are not altogether unexpected. The materials are titanium rich in their stoichiometry, may exhibit preferred orientation of crystallites and often contain a sizeable fraction of an amorphous phase. Each of these features would serve to impede lithium diffusion as compared to bulk materials.

### 2C. LIST OF PUBLICATIONS AND TECHNICAL ITEMS

### 1. Publications

'Preparation and Characterization of TiS<sub>x</sub> Films Using Activated Reactive Evaporation," by E. Zeira, C. Deshpandey, R. Budhani, H. Doerr, D. Zehnder, R. Bunshah and B. Dunn, submitted to Journal of Vacuum Science and Technology (manuscript attached).

'Transport Properties of Thin Film TiS<sub>2</sub>" by D. Zehnder, C. Deshpandey, B. Dunn and R. Bunshah, in preparation, to be submitted to Solid State Ionics.

### 2. <u>Presentations</u>

"Preparation and Characterization of  $TiS_x$  Films Using the ARE Technique" by E. Zeira et al. Presented at the International Conference on Metallurgical Coatings, San Diego, CA, April 1984.

'Preparation of TiS<sub>2</sub> Films Using the ARE Technique," by E. Zeira et al. Presented at the American Vacuum Society Meeting, Reno, NV, November 1984.

"Transport Properties of Thin Film TiS<sub>2</sub>," by D. Zehnder et al. To be presented at the International Conference on Solid State Ionics, Lake Tahoe, NV, August 1985.

### 3. Theses

"Preparation and Properties of Thin Film Reversible Cathode Materials." M.S. Thesis by E. Zeira, December, 1984.

"Transport and Electrochemical Properties of Thin Film TiS<sub>2</sub>." M.S. Thesis by D. Zehnder, in preparation, to be submitted September, 1985.

## 2D. PARTICIPATING SCIENTIFIC PERSONNEL AND ADVANCED DEGREES AWARDED

- Dr. R. F. Bunshah
- Dr. C. V. Deshpandey
- Dr. B. Dunn
- Mr. D. A. Zehnder (M.S. degree to be awarded, September, 1985)
- Mr. E. C. Zeira (M.S. degree awarded December, 1984)

### APPENDICES

- APPENDIX I: A copy of the manuscript, "Preparation and Characterization of TiS<sub>x</sub> Films Using Activated Evaporation Techniques
- APPENDIX II: The title page and abstract of the M.S. Thesis of E. C. Zeira

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APPENDIX I

Preparation and Characterization of TiS Films Prepared Using Activated Reactive Evaporation Techniques

E. C. Zeira, C. V. Deshpandey, R. C. Budhani, H. J. Doerr, R. F. Bunshah, D. Zehnder and B. Dunn

School of Engineering and Applied Science University of California, Los Angeles, CA 90024

### stract

 $TiS_2$  has been the subject of intense study because of its superior perrmance as a reversible cathode in lithium electrochemical cells. Thin tilms nearly stoichiometric  $TiS_2$  were deposited by evaporating Ti metal in an  $H_2S$ asma. The effect of deposition conditions such as deposition rate,  $H_2S$  paral pressure and flow rate, and substrate temperature on the composition of e  $TiS_2$  films was analyzed using EDAX, while x-ray diffraction and electron ffraction techniques were used to identify the crystalline phases present. the conditions required to synthesize time-grained crystalline  $TiS_2$  films are scussed.

### Introduction

The phenomenon of fast ion transport in solids has led to the study of veral new types of rechargeable battery systems which are capable of posssing high energy densities (1,2). The use of lithium as an anode material particularly attractive and numerous ionic conductors have been considered reversible cathode materials for lithium batteries. It is generally lieved that a successful cathode should incorporate the anode element into s structure. Intercalation reactions are ideal for this purpose since the ocess involves the insertion of a guest species into the host lattice thout causing structural alteration. The reversible nature of this reaction s enabled transition metal dichalcogenides (among other materials) to be ed successfully as cathodes in electrochemical cells. In addition to reverbility, solid state cathode materials should also exhibit a number of other operties including good electronic and ionic conductivities, a large free ergy of reaction with lithium, a wide composition range and appropriate ructural stability with intercalated lithium, and chemical stability in ganic electrolytes (2).

Transition metal dichalcogenides have received considerable attention r reversible cathode applications. These materials characteristically exhit inversed structures in which alternate layers of anions are held together weak van der Waals forces. The van der Waals gap between layers offers ficient vacant sites to permit a wide composition range of intercalated thium as well as convenient pathways for rapid lithium diffusion. Titanium

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Figure 111





Figure 1

### Figure Captions

- Figure I: Atomic Percent Sulfur vs. Flow Rate
- Figure II: Atomic Percent Sulfur vs. Deposition Rate
- Figure III: Atomic Percent Sulfur vs. Substrate Temperature
- Figure IV: X-Ray Diffraction Patterns for TiS Samples From Figure 1

### TABLE I

Phases present in films based on electron diffraction analysis.

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2

| Dep. Rate     | H <sub>2</sub> S flow | Subst. temp | Phase  |
|---------------|-----------------------|-------------|--|
| o<br>540A/min | 580 SCCM              | 400°C       | Ti S <sub>2</sub>                                  |
| o<br>540A/min | 680 SCCM              | 400°C       | $Ti_2S_3 + TiS_2$                                  |
| o<br>540A/min | 780 SCCM              | 400° C      | Ti <sub>2</sub> S <sub>3</sub>                     |
| o<br>540A/min | 600 SCCM              | 350°C       | <sup>Ti S</sup> 2 + <sup>Ti</sup> 3 <sup>S</sup> 4 |
| o<br>540A/min | 600 SCCM              | 500°C       | Ti <sub>2</sub> s <sub>3</sub>                     |
| o<br>540A/min | 600 SCCM              | 600°C       | Ti <sub>3</sub> S <sub>4</sub>                     |

| VI. References | • |
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### IV. Conclusions

Various titanium sulfide phases, including a nearly stoichiometric TiS 2 phase, were deposited using the ARE technique. The phases, film stoichiometry and structure were found to be quite sensitive to deposition conditions.

The flow rate of the  $H_2S$  gas, combined with the evaporation rate of titanium, were found to have the most profound effects on the percent sulfur and phases found in the films. These parameters were found to be inversely related to one another and hence, a maximum in the percent sulfur was realized. Different phases were produced corresponding to the amount of sulfur (determined by the flow rate of the gas and the  $H_2S/H_2$  ratio) and the amount of Ti available tor the reaction. A high evaporation rate and a low  $H_2S$  flow rate gave the low sulfide phase while a lower evaporation rate at a higher flow rate gave the higher sulfide phase. The temperature of the substrate influenced the films to a lesser degree. An optimum condition was found to cover a wide range of temperatures (300~440°C). Hence, less precise control over this parameter was needed. This situation occurred since the substrate temperature was not the sole source of the kinetic energy. The plasma also contributed to the kinetic energy of the constituents, making the species more energetic and thereby activating the reaction.

V. Acknowledgements

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produces the observed maxima in %S displayed in Fig. 1 and Fig. 2. Our experiments show that ratio of  $H_2S/H_2$  in the plasma controls the stoichiometry of the films. Detailed analysis of this behavior based on emission spectroscopic studies of the plasma will be presented in a subsequent publication.

### B. Phases present in the deposit

The effects of deposition conditions on the phases present in the films are indicated in Table I. Fig. 4 shows X-ray diffraction patterns for films deposited under three different conditions as indicated by the letters a,b,c displayed in Fig. 1. The large peak at  $2\theta \approx 22^{\circ}$ C is diffraction from the Vycor substrate. In sample (a), the  $TiS_2$  phase has a very small grain size and electron diffraction suggests a (100) preferred orientation. Structure of the film is not obvious from the X-ray results (Fig 4-a). Sample b (Fig. 4-b) shows a larger grain size (note the intensity of the peaks) and still exhibits a (100) preferred orientation. In addition two more peaks appear in the diffraction patterns corresponding to the (101) reflection of  $Ti_2S_3$  and the (110) reflection of  $TiS_2$ . This suggests that sample (b) contains two phases,  $Ti_2S_3$ and  $TiS_2$ . Abendroth et al.<sup>(8)</sup> have also reported the existence of a two phase region of TiS<sub>2</sub> and Ti<sub>2</sub>S<sub>3</sub> below 500°C. Sample (c) (Fig. 4-c) shows the pattern of  $Ti_{2}S_{2}$  single phase film. Based on these results, one may conclude that for a given deposition rate and substrate temperature, the phases present in the films depend on  $H_{2}S$  flow rate. A similar dependence of the phases present in the films is observed with substrate temperature as indicated in Table 1.

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 $500^{\circ}$ C, the equilibrium sulfur pressure above TiS<sub>2</sub> rises dramatically with temperature. For example, at  $500^{\circ}$ C, the sulfur pressure above TiS<sub>2</sub> is 76 torr and climbs to about 7 atm. at  $600^{\circ}$ C. Since the working pressure in the chamber does not exceed 1 X  $10^{-2}$  torr, one would expect to see a decrease in the sulfur content of the films at temperatures above  $500^{\circ}$ C. At temperatures below  $300^{\circ}$ C, the rate of reaction is slower due to desorption of sulfur from the substrate. Desorption occurs because of the high vapor pressure of sulfur. H<sub>2</sub>S and HS at relatively low temperature. Thus, the mean residence time of these species (S, H<sub>2</sub>S, HS) on the substrate is very short at such temperatures. Consequently, these species desorb from the substrate prior to reacting with Ti, leaving sulfur deficient films. This combination of features explains why there are sulfur deficient films at high and low temperature, with a maximum at  $400-425^{\circ}$ C.

Apart from the rate of arrival of Ti and S on the substrate, the experimental conditions which determine the species present in the plasma contribute significantly to the observed variation in the %S as shown in Figs. 1 and 2. During the deposition process, the plasma dissociates the  $H_2S$  molecule and leads to the formation of species such as  $H_2S^+$ ,  $HS^-$ ,  $H_2$  and  $S_2$ . The type of species produced depends on electron-molecular collisions (defined in terms of collision cross-section) that take place in the region between the source and the substrate. For a given energy (anode potential, 100-110V in our case) the collision cross-section depends on the number of  $H_2S$  molecules present and the electron density (number of electrons/unit vol). The number of  $H_2S$  molecules is related to  $H_2S$  flow rate whereas electron density is related to evaporation rate which controls the number of secondary electrons in the plasma. It is this relationship between the  $H_2S$  flow rate and evaporation rate which

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expected that the deposition rate curve would exhibit a distinct maximum in \$S, analogous to that observed in Fig. 1 for  $H_2S$  flow rate. However, we believe that the flow rates used were too high to produce a maximum for the deposition rates employed.

The sulfur content of the films showed an increase with substrate temperature up to about 400°C and then decreased somewhat when temperature was increased further. A typical variation in %S with substrate temperature for a constant deposition rate and  $H_{\gamma}S$  flow rate is shown in Fig. 3.

The observed variation in %S shown in Figs. 1, 2 and 3 indicates that there exists a cefinite relationship among the deposition parameters (i.e., deposition rate, flow rate and substrate temperature) which controls the stoichiometry of the films. To obtain a high sulfur content in the films, there must be a specified number of Ti and S atoms arriving at the substrate and a sufficient amount of energy to activate the reaction. The number of titanium and sulfur atoms arriving at the substrate (per unit area per unit time) for a given pressure are directly proportional to the evaporation rate and H<sub>2</sub>S partial pressure, respectively. At the same time the activation energy is dependent on the plasma conditions (which influences the kinetic energy of the depositing species) and the substrate temperature. Since plasma conditions were kept relatively constant during each experiment, the activation energy was primarily dependent on the substrate temperature. This is illustrated in Fig. 3 which shows that the sulfur content in the film varies with the substrate temperature. At the high temperature end of the graph, the percent sulfur decreases slightly. This phenomenon has also been observed in a number of prior investigations involving the preparation of  $TiS_2^{(1-3)}$ . Above

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soda-lime glass and quartz substrates developed cracks on cooling due to thermal expansion mismatch.

### B. Film Characterization

The films were analyzed for sulfur content (in atomic percentage) using Energy Dispersive Analysis (EDAX). A TiS<sub>2</sub> standard was used for calibration. The Scanning Electron Microscope (SEM) was also used to study the film surface morphology. Phase identification and lattice parameters were determined using JEOL CX STEM in the diffraction mode. The electron diffraction results were confirmed by X-ray diffraction techniques using a Norelco X-ray diffractometer and a buinier X-ray camera.

### III Results and Discussion

The tilm composition was found to be influenced by the  $H_2S$  flow rate, substrate temperature and deposition rate. The variation in S in the film with respect to these parameters (keeping the other conditions constant) is shown in Fig. 1-3 respectively.

It can be seen from Fig. 1 that the  $H_2S$  flow rate plays a dominant role in establishing the sulphur content in the film. The amount of sulphur in the film varies as much as 30% between the minimum (200 cc/min) and maximum (800 cc/min) values of the flow rate. The dashed line shows that a higher deposition rate causes the maximum to be shifted towards a greater flow rate.

As shown in Fig. 2 the deposition rate did not produce a very pronounced effect on %S in the films for the range of flow rates investigated. It was

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process, high energy species such as ions and high energy neutrals generated by neutral atom-ion collisions enhance . We reactivity of the condensing species, i.e. the "activity" of the process. Hence compounds can be formed at relatively low pressures of the reactive gas<sup>(7)</sup> as well as at low deposition temperatures. Considering this advantage, we have investigated the synthesis of  $11S_2$  by the ARE technique where Ti was evaporated in a  $H_2S$  plasma. The effect of deposition conditions such as deposition rate,  $H_2S$  flow rate and pressure, and substrate temperature on composition and structure of the film was investigated. The results of this investigation are reported below.

### II. Experimental Procedure and Measurement Techniques

The films were deposited by evaporating Ti using an electron beam source in a  $H_2S$  plasma. The plasma was generated by accelerating the electrons thermionically emitted from a thoriated tungsten filament towards an anode plate maintained at 110 volts positive d.c. potential. The plasma was confined to the area between the substrate and the source using ceramic bar magnets arranged in a cylindrical configuration around the source. The  $H_2S$  flow rate was controlled by a flow meter while the required pressure ( $\approx 2X10^{-3}$  torr) was maintained by throttling the high vacuum valve. The deposition rate was measured using a quartz crystal located near the substrate and connected to a AIR(U) iemescal (Model FDC-8000) thickness monitor. Substrates were located 12" above the source and were heated by quartz infrared lamps. The substrate temperature was monitored by a chromel-alumel thermocouple attached to the back of the substrate. A variety of substrates were used including soda-lime glass, quartz, polycrystalline alumina, and sapphire wafers. Alumina and sapphire substrates were found to give the best results. Films deposited onto

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disulfide (TiS<sub>2</sub>) is probably the most widely investigated transition metal dichalcogenide as it successfully fulfills most of the requirements for rever-sible cathode operation in lithium secondary batteries.

The conventional method of synthesizing  $\operatorname{TiS}_2$  is by direct reaction of the elements at elevated temperature  $(600^{\circ}\mathrm{C})^{(3,4)}$ . Standard pressed-powder cathodes are then prepared from this material. Although the performance of these cathodes is quite good, there are certain areas where improvements in the properties of  $\operatorname{IiS}_2$  would be highly desirable. The application of thinfilm vacuum deposition methods to the fabrication of reversible cathode materials appears to offer several advantages. The use of thin films reduces the path length of charge transport, thus improving the kinetics of ion transport and lowering the electronic resistance. Thin film deposition techniques also offer novel microstructures, less contamination and they enable new battery configurations to be considered.

Synthesis of  $\operatorname{TiS}_2$  using vacuum deposition techniques was first reported by Perry<sup>(5)</sup>. Ti films about 3000 Å thick were prepared by sputtering and subsequently heat-treated at 630°C in a H<sub>2</sub>S ambient. The films produced were found to be Ti<sub>1.005</sub>S<sub>2</sub>. However this technique does not differ significantly from the direct reaction method mentioned earlier. More recently, Kanehori et al.<sup>(6)</sup> prepared TiS<sub>2</sub> films by (VD methods. In this case the microstructure consisted of narrow platelets which were fairly porous. Bather low diffusion coefficients for lithium were reported. In contrast to prior work, the Activated Reactive Evaporation (ARE) process<sup>(7)</sup>, which is extensively used to synthesize refractory compounds, transparent conductors, and superconducting compounds, appears to be an ideal technique for the synthesis of TiS<sub>2</sub>. In this

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APPENDIX 11

UNIVERSITY OF CALIFORNIA Los Angeles

Preparation and Properties of Thin Film Reversible Cathode Materials

A thesis submitted in partial satisfaction of the requirement for the degree Master of Science in Engineering

by

Eitan Chaim Zeira

1984

### ABSTRACT OF THE THESIS

### Preparation and Properties of Thin Film Reversible Cathode Materials

by:

Eitan Chaim Zeira

Master of Science in Engineering University of California, Los Angeles, 1984 Professor R. F. Bunshah, Committee Co-Chair Professor Bruce S. Dunn, Committee Co-Chair

The binary phase of  $TiS_2$  has been the subject of intense study because of its superior performance as a reversible cathode in lithium electrochemical cells. This film deposition offers several advantages over the conventional method in preparing this cathode material. In this investigation, this films of  $TiS_2$  were prepared using the Activated Reactive Evaporation (ARE) technique.

The films were deposited by evaporating Ti metal in an  $H_2S$  plasma. The effect of deposition conditions such as evaporation rate,  $H_2S$  flow rate and substrate temperature on the composition and structure of the films was studied. The films were characterized by X-ray diffraction, electron diffraction, energy dispersive X-ray analysis (EDAX), and scanning electron microscopy.

It was found that the ARE process can be used to deposit films of  $TiS_2$ . The  $H_2S$  flow rate and the evaporation rate of titanium were found to be the more significant parameters that determine the composition and structure of the films.

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