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cure temperatures provides the possibility for thin films with even more stable second-order nonlinearity.

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Registry No. (BTDA)(DDM) (copolymer), 25038-84-0; (BTDA)(DDM) (polyamic acid SRU), 56802-71-2; (BTDA)(DDM) (polyimide SRU), 26913-87-1.

Low-Temperature Atmospheric Pressure Chemical Vapor Deposition of Titanium Disulfide Films

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Titanium disulfide (TiS_2) has attracted considerable technological attention, due to its favorable attributes as a cathode material in lithium batteries[2,3] and, to a lesser extent, for its application as a component in lubricating coatings for titanium alloys.[4] Recent emphasis on the development of thin-film lithium batteries has underscored the need for high-purity, crystallographically oriented, stoichiometric coatings.[3] TiS_2 films have been largely prepared by chemical vapor deposition (CVD) routes involving titanium tetrachloride and hydrogen sulfide,[3] although radio frequency (rf) sputtering[5] and sulfurization of titanium metal[6] have been demonstrated to provide coatings. All of these strategies possess inherent limitations, including a wide range of titanium to sulfur stoichiometries, high deposition temperatures (400-800 °C), and concomitant substrate restrictions. Since lithium battery performance has been shown to be critically dependent upon the crystallographic orientation of the TiS_2 cathode film,[3a,b] any process that will be of use in battery applications must provide a suitable orientation. Herein we report a new atmospheric pressure CVD process for titanium disulfide films which relies upon the reaction of titanium tetrachloride with organothiols at temperatures as low as 200 °C.[7] This procedure affords stoichiometric TiS_2 coatings with crystallographic orientations that are optimum for use in lithium batteries. The facility of the film formation indicates that a remarkably efficient carbon-sulfur bond cleavage is operant. Importantly, the low-temperature nature of this process should greatly expand the range of substrates upon which TiS_2 films can be deposited.

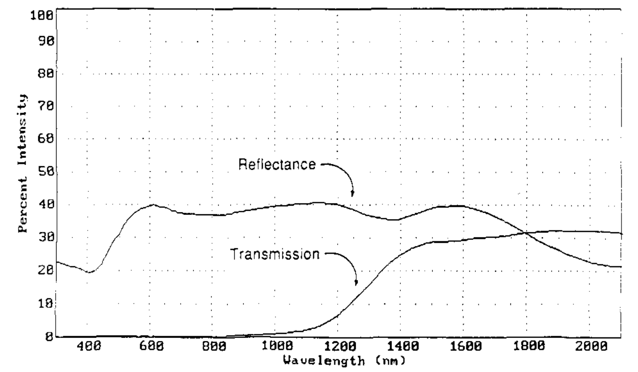

Figure 1. Reflectance/transmission spectra of a film prepared at 500 °C.

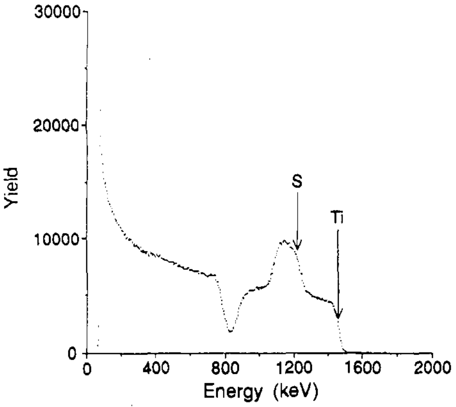

Figure 2. Rutherford backscattering spectrum of a film prepared at 300 °C.

Adhesive, highly reflective gold-colored films of TiS_2 could be deposited on glass, silicon, and stainless steel substrates in the temperature range 200-600 °C using the atmospheric pressure CVD reaction of titanium tetrachloride and *tert*-butylthiol in a horizontal hot-walled reactor. Deposition rates for films grown at 400 and 600 °C under these conditions were 247 and 280 Å s^{-1}, respectively.[8] Other organothiols (e.g., ethanethiol, 2-butanethiol, 1-propanethiol) were equally effective at providing films between 200 and 600 °C, but their volatilities were either too high or too low for convenient use. Dimethyl sulfide and dimethyl disulfide both failed to afford films with titanium tetrachloride in the temperature range 200-600 °C.[9]

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[1] (a) Wayne State University. (b) Ford Motor Co., Glass Division.

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[8] These deposition rates are unoptimized. Presumably, higher rates could be achieved in a cold wall reactor.

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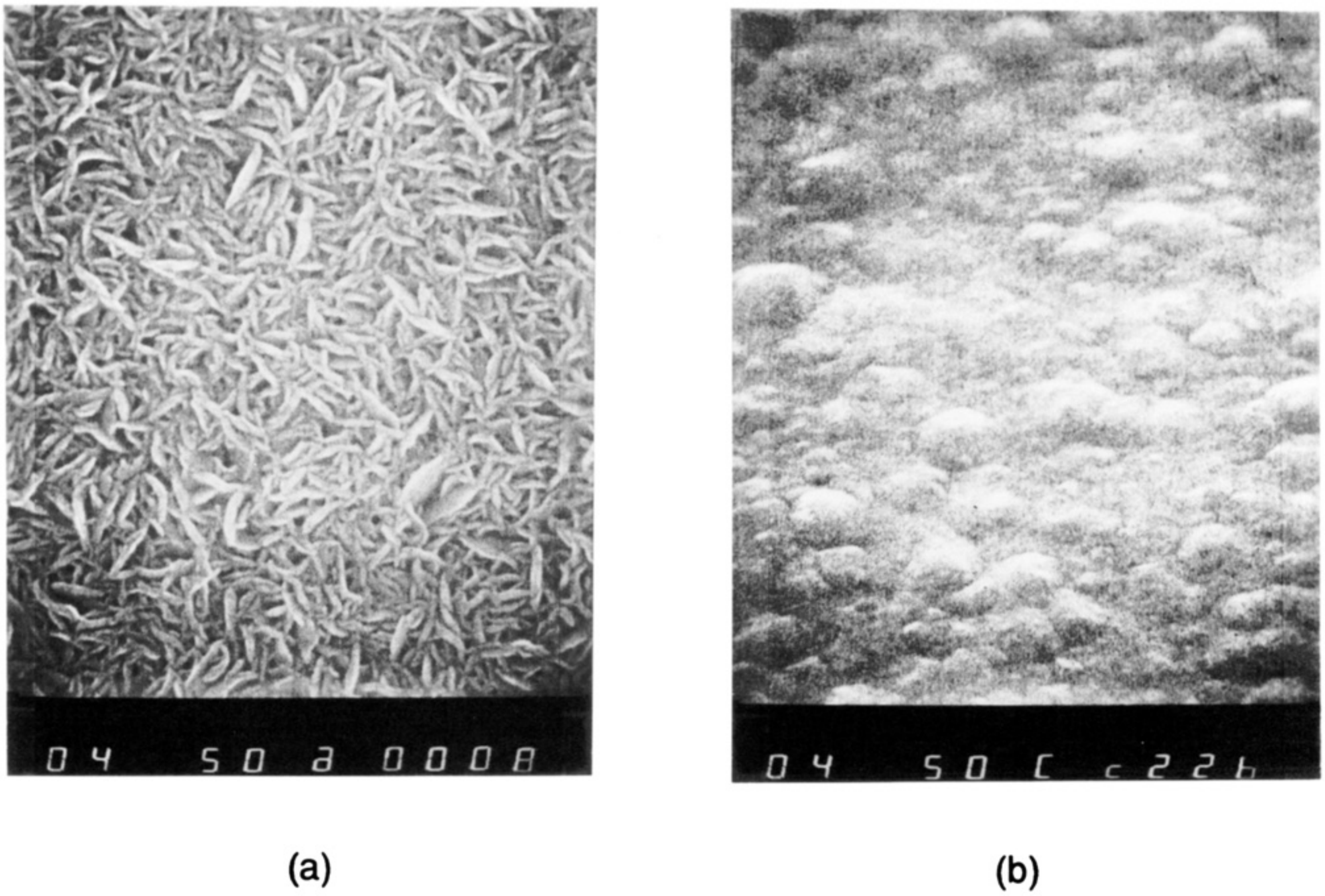

Figure 3. Scanning electron micrographs of TiS_2 films prepared at 300 and 500 °C.

Successful fabrication of the films required that the gaseous thiol stream be introduced to the reaction zone for 1–2 min prior to the introduction of the gaseous titanium tetrachloride. If this "sulfur pretreatment" was not performed, then only a thin film of mixed titanium dioxide (anatase) and titanium disulfide resulted, as determined by X-ray diffraction. The films produced using organothiols adhered extremely well to glass substrates and could not be removed upon vigorous rubbing with a Kimwipe. By contrast, films prepared under analogous conditions using hydrogen sulfide[3] adhered poorly to glass and were easily removed from the substrate by rubbing. Moreover, the surface finish (i.e., reflectivity) of films prepared from *tert*-butylthiol was consistently higher than those made from hydrogen sulfide.

Detailed analyses were carried out on the films produced from *tert*-butylthiol at 300 and 500 °C. Figure 1 shows the reflectance/transmission spectra for a film produced at 500 °C. The spectrum is consistent with the material being either a semimetal or a semiconductor with a high density of states in the gap.[10] The resistivity of a film grown at 600 °C on glass was 394 $\mu\Omega$ cm.[11] Characterization using Rutherford backscattering spectroscopy (RBS) revealed a homogeneous composition throughout and a stoichiometry of $Ti_{1.0\pm0.05}S_{2.0\pm0.05}$. Figure 2 shows the RBS spectrum of a film grown at 300 °C. No carbon or chlorine contamination was observed in the films.[12,13] The density of the 300 °C film (from RBS) was 2.81 g/cm^3, which is 87% of the density of bulk TiS_2 (3.22 g/cm^3).[14] Scanning electron micrographs of surfaces of the 300 and 500 °C films are shown in Figure 3. The 300 °C film consisted of small, narrow platelike crystals that grew at 45–90° angles to the plane of the substrate. By contrast, the 500 °C film was nearly featureless.

All of the X-ray diffraction peaks corresponded to those of hexagonal TiS_2. The 300 °C film showed three peaks corresponding to the (001), (101), and (110) orientations, with the (101) peak predominating. However, corresponding films prepared at 500 and 600 °C showed exclusive (001) orientation. The (001) and (110) orientations place the *c* axis parallel to substrate,[3a] which are useful crystallographic orientations for use as cathodes in lithium batteries.[3b]

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(9) Schleich has reported that *bulk* titanium disulfide can be synthesized by treatment of titanium tetrachloride with *tert*-butylthiol, di-*tert*-butyl sulfide, and di-*tert*-butyl disulfide, followed heating at >200 °C: Bensalem, A.; Schleich, D. M. *Mater. Res. Bull.* **1988**, *23*, 857. By contrast, the CVD reaction of titanium tetrachloride with dimethyl sulfide and dimethyl disulfide described herein failed in the temperature range 200–600 °C. The fact that sulfides and disulfides provide bulk titanium disulfide but not films suggests different mechanisms for the two processes.

(10) For a discussion of the semimetal versus semiconductor properties of TiS_2, see: Perry, P. B. *Phys. Rev. B* **1976**, *13*, 5211.

(11) For comparison, the resistivity of bulk titanium disulfide has been reported to be 1400 $\mu\Omega$ cm: Conroy, L. E.; Park, K. C. *Inorg. Chem.* **1968**, *7*, 549.

(12) Film thicknesses were 1100 Å (300 °C) and 7900 Å (500 °C). RBS simulations of both the 300 and 500 °C films showed oxygen at the silicon/film interface. No attempt was made to remove surface oxygen from the silicon wafers; surface oxides are undoubtedly the origin of the oxygen contamination. We will discuss attempts to eliminate the interfacial oxygen in a forthcoming full paper.

(13) Initial X-ray photoelectron spectroscopy (XPS) studies corroborate the low carbon incorporation observed by RBS. Results for a 300 °C film deposited on glass (atom percent): Ti, 36.4; S, 50.8; C, 1.24; O, 11.48. The high oxygen content in the XPS spectrum may arise from surface oxidation of the film. Alternatively, the oxygen contamination may originate from the glass substrate upon which the film was deposited. Studies to probe these issues are in progress.

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In summary, we have developed a new atmospheric pressure CVD process for TiS_2 thin films of high purity, which relies upon the reaction of titanium tetrachloride with volatile organothiols. Several important properties of these coatings (e.g., adhesion, surface finish, density) are superior to those obtained using hydrogen sulfide as the sulfur source. In particular, the crystallographic orientation of the films is ideal for use as cathode materials in lithium batteries. The low carbon content implies that an efficient carbon–sulfur cleavage is operant. Such bond breaking is remarkable in view of the robust nature of carbon–sulfur bonds in thiols (66–74 kcal/mol[15]). The reaction of titanium tetrachloride with organothiols to afford TiS_2 can be contrasted with the thermal decomposition of tetrakis(*tert*-butylthiolato)titanium(IV), which produces TiS coatings.[16] The combined results imply that it may be advantageous to utilize carbon-substituted element precursors in chemical vapor deposition schemes, since our films contained low carbon contamination.[17] We are continuing to work on the delineation of TiS_2 film properties, evaluation of single-source precursors, and titanium–sulfur chemistry of relevance to the CVD processes. These studies will be published in due course.

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Registry No. TiS_2, 12039-13-3; Si, 7440-21-3; *tert*-BuSH, 75-66-1; stainless steel, 12597-68-1.

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Room-Temperature Catalytic Hydrogenation of Aromatic Hydrocarbons Using $[(1,5\text{-COD})RhH]_4$ as a Catalyst Precursor

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There has been intense activity in the synthesis, characterization, and reactivity studies of metal colloids. Metal particles that have sizes in the range 1–50 nm are interesting because they are expected to exhibit unusual catalytic reactivity and selectivity[1] and also quantum confinement effects.[2,3] The typical methods for the preparation of such metal particles are chemical reduction, decomposition of organometallic compounds, and metal atom evaporation to form the so-called small metal atom dispersed (SMAD) catalysts.[4] These materials are often dispersed on high surface area metal oxide supports which aids retention of the dispersion. It has been shown that chemical reduction methods, using $LiBEt_3H$ as reducing agent, can result in the formation of stable colloidal particles in the absence of surfactants in polar organic solvents.[5] Recently, a modification of this approach has been reported using $[NR_4]^+[BEt_3H]^-$, $R = C_8H_{17}$, as a reducing agent, where liberation of a surfactant ($[NR_4]^+$), in situ, resulted in formation of stable colloids containing 1–3-nm-sized metal particles.[6]

We have been interested in developing methods to prepare metal colloids, especially containing rhodium, for catalytic hydrogenation applications.[7–9] In the course of reducing $[(1,5\text{-COD})RhCl]_2$ with $LiBEt_3H$, we observed the formation of $[(1,5\text{-COD})RhH]_4$. This species has been prepared previously by elimination of ethylene from $[(1,5\text{-COD})RhCH_2CH_3]$ above −25 °C,[10] but the reactivity of $[(1,5\text{-COD})RhH]_4$ has not been studied. Here we report the synthesis of $[(1,5\text{-COD})RhH]_4$, its use as a source of 2-nm-sized Rh crystallites under mild conditions, and some preliminary studies of the reactivity of solutions derived from $[(1,5\text{-COD})RhH]_4$ toward the hydrogenation of aromatic hydrocarbons at room temperature.

The compound $[(1,5\text{-COD})RhH]_4$ was prepared by the reaction of $[(1,5\text{-COD})RhCl]_2$ with $LiBEt_3H$ at room temperature in THF under a nitrogen atmosphere.[11] The ^1H NMR characterization data and fluxional behavior were consistent with those reported previously for this compound.[11,12] Solutions of $[(1,5\text{-COD})RhH]_4$ were indefi-

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[11] Slowly, 2 mL of a 1.0 M solution of $LiBEt_3H$ in THF was added to a solution of 0.493 g (1 mmol) of $[(1,5\text{-COD})RhCl]_2$ in 38 mL of THF cooled in an ice bath. The color of the solution changed from yellow to black immediately. The reaction mixture was then stirred at room temperature for 4 h. The volatile components were removed in vacuo and the residue was extracted with five 10-mL portions of *n*-pentane. The volatile components were again removed in vacuo and the crude product was dissolved in 10 mL of benzene. The solution was freeze dried to give 0.22 g (0.26 nmole) of $[(1,5\text{-COD})RhH]_4$ (52% yield). Elemental Anal. Calcd for $C_{32}H_{52}Rh_4$: C, 45.30; H, 6.18%. Found: C, 45.03; H, 6.82%. IR data (KBr disk, cm^{-1}) 2993.0 (m), 2925.5 (vs), 2908.2 (vs), 2867.3 (vs), 2819.9 (vs), 1497.7 (m), 1473.6 (m), 1458.0 (w), 1447.4 (m), 1426.7 (s), 1400.2 (m), 1326.1 (s), 1298.3 (m), 1259.9 (m), 1234.2 (m), 1210.5 (m), 1171.0 (m), 1149.5 (m), 1072.0 (s), 1001.0 (m), 986.0 (m), 932.2 (m), 880.5 (m), 861.6 (m), 840.7 (s), 811.8 (s), 753.8 (w), 682.5 (w), 584.0 (w), 472.3 (m). ^1H NMR (250 MHz, C_6D_6, 20 °C) 4.79 ppm, s, br, 4 H, 1,5-COD; 2.21 ppm, m, br, 4 H, 1,5-COD; 1.70 ppm, m, br, 4 H, 1,5-COD; −11.83 ppm, quint, $^1J_{Rh-H} = 14.4$ Hz, 1 H, H. $^{13}C\{^1H\}$ NMR (62.9 MHz, C_6D_6, 20 °C) 79.3 ppm, d, $^1J_{Rh-C} = 11.1$ Hz, 1,5-COD; 31.9 ppm, s, 1,5-COD. The deuterium-labeled compound, $[(1,5\text{-COD})RhD]_4$, was prepared by the same method using $LiBEt_3D$ as reducing agent. The positions of $\nu(M - H/D)$ were not unambiguously assigned to due to the presence of other overlapping peaks, but believed to be 1260 cm^{-1} for $\nu(M - H)$ and 680 cm^{-1} for $\nu(M - D)$.

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