

Thio sol–gel synthesis of titanium disulfide thin films and powders using titanium alkoxide precursors

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Abstract

Titanium alkoxides react at room temperature with H₂S to form an amorphous titanium alkoxy-sulfide precursor which can be converted to TiS₂ by heat-treatment in a flowing H₂S gas stream. The reaction of titanium isopropoxide (Ti(OPrⁱ)₄) with H₂S in *n*-butylamine solvent has been studied using infrared spectroscopy (FTIR), gas chromatography/mass spectroscopy (GC/MS), XRD and EDAX measurements. Based on these studies, it is shown that a partially sulfidized alkoxy precursor forms through the partial replacement of some alkoxy groups by hydrosulfide moieties. The alkoxy-hydrosulfide is believed to form following a thiolysis–condensation mechanism similar to the hydrolysis–condensation process that occurs during the oxide sol–gel reaction. The alkoxy-hydrosulfide species then undergoes complete sulfidization at 800 °C in a stream of H₂S to yield pure, hexagonal TiS₂ in either film or powder forms. Crown Copyright © 2007 Published by Elsevier B.V. All rights reserved.

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1. Introduction

Transition metal dichalcogenides have been studied extensively as an important class of materials that exhibit a wide range of electronic and optical properties [1]. For example, titanium disulfide has been identified as an active cathode material in lithium based rechargeable batteries [2]. This is mainly due to a high reversibility of the ion intercalation reaction, their high electronic conductivity, and large current capacity. The battery performance of TiS₂ as a cathode can be further improved if the morphology and surface area can be optimized and the material synthesized in high purity [3]. As computer, medical and other devices become smaller, there is a need to produce smaller storage batteries to power these devices. The layers

of the TiS₂ lattice exhibit a strong tendency to intercalate lithium into the crystal matrix up to a Li:Ti stoichiometry of 1:1, without any phase changes. This intercalate also possesses good electronic conductivity and a high reversibility of the intercalation reaction. The performance of the sulfide as a cathode material depends on the efficacy of the intercalation reaction, which depends on a number of factors such as morphology, particle size and defect composition. To maximize diffusion of the lithium ions into TiS₂, a large surface area is required such as in a thin film or fine powder form. In such an application it is highly desirable that the thin film of TiS₂ have a crystallographic orientation such that the *c*-axis is parallel to the plane of the substrate. In such an orientation, pores in the crystals are perpendicular to the plane of the substrate and are optimum for the intercalation of lithium, which constitutes the primary discharge reaction in the lithium battery [4a]. Use of stoichiometric TiS₂ is imperative for battery use as metal rich titanium sulfide has titanium located in the

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van der Waals gap which can reduce the ability to intercalate [4b,c]. All these factors are strongly influenced by the methods and processing conditions used to synthesize the material.

Conventionally, TiS_2 has been prepared by the direct reaction of the elements at temperatures above 1000°C [5]. This process requires a long processing time and yields a low surface area powder. Several vapor phase reactions have also been investigated to synthesize TiS_2 powders and thin films, the most common being the reaction of TiCl_4 with H_2S or other sulfur sources, including tert-butylthiol and bis(trimethylsilyl)sulfide [6,7]. More recently, the CVD of a single source precursor [$\text{Ti}(\text{S Bu}^t)_4$] was reported to result in the formation of amorphous films of TiS_2 at low temperature [8]. Room temperature chemical precipitation routes, mostly using chlorides and various inorganic [9] and organic [10] sulfidizing agents have also been successfully implemented to synthesize fine particles of TiS_2 . These precipitates are often contaminated by chloride ions and inorganic by-products of the reaction.

Metal alkoxides are characterized by highly reactive alkoxo (RO^- , $\text{R} = \text{alkyl}$) groups which make the metal atoms susceptible to nucleophilic attack [11]. These compounds undergo hydrolysis in the presence of water, followed by condensation polymerization reactions which leads to the formation of the corresponding metal oxide. The hydrolysis and condensation reactions in solution can be controlled to a great extent by the use of an acid or a base catalyst, leading to the formation of either a polymeric gel or a fine powder [12]. Melling and colleagues [13] have demonstrated the applicability of alkoxides for the synthesis of sulfides by reacting germanium alkoxide with H_2S .

The sol-gel process is a promising method for the synthesis of transition-metal dichalcogenides such as TiS_2 . One of the most important advantages of the sol-gel process is that it provides an opportunity to control the microstructure of sulfides for different applications. A thio 'sol-gel' type process has been reported for the synthesis of TiS_2 involving the reaction of titanium alkoxide (e.g. $[\text{Ti}(\text{OPr}^i)_4]$ [14,15] or titanium thiolates [16]) with H_2S gas in solution (e.g. toluene, benzene). However, when alkoxides were used as precursors, the reaction products were mixtures of both metal oxides and metal sulfides, indicating further precautions were needed to eliminate water.

In this paper, we present the synthesis of TiS_2 powders and films using a thio 'sol-gel' process involving the reaction of titanium isopropoxide with H_2S in an amine solvent. The reaction products were characterized by various techniques before and after heat-treatment.

2. Experimental

Titanium isopropoxide ($\text{Ti}(\text{OPr}^i)_4$, Aldrich) was used as received without further purification, *n*-butylamine (BuNH_2 , Aldrich) was dried over KOH pellets. H_2S was used as the sulfidizing agent, obtained by reaction of FeS (Rowe Scientific) with HCl (Rowe Scientific). All reactions

were conducted in glassware dried under vacuum and all manipulations of reactants and products were accomplished under a nitrogen atmosphere.

In a typical preparation, titanium alkoxide (isopropoxide) was dissolved in *n*-butylamine, under a dried nitrogen atmosphere in a glove box. The solvent:alkoxide ratio was 95:5 (vol. %) and hydrogen sulfide (H_2S) gas, dried by passage through a column of CaSO_4 desiccant, was bubbled through the solution at room temperature. As soon as H_2S was introduced, the colorless titanium alkoxide solution turned black, for $\text{Ti}(\text{OPr}^i)_4$. The bubbling was continued for 3 h to ensure complete reaction, and although the solution became viscous, no solid was seen. The solution was stable to precipitation for at least 1 month. Solvent removal from the black solution was achieved with a vacuum pump and the solid obtained was pyrophoric and very air sensitive. The parent precursor solution was used to deposit a thin film by spin coating (3500 rpm and 30 s) on a silicon or quartz substrate under a nitrogen atmosphere. After drying in a stream of nitrogen, the films were heat-treated in flowing H_2S at various temperatures from 600 to 800°C for 6 h, using heating rates of 50 or $75^\circ\text{C}/\text{h}$. The flow chart in Fig. 1 provides a summary of the route to prepare thin film TiS_2 and its characterization.

Elemental analysis of the product was performed with an energy dispersive X-ray analysis (EDAX) attachment on a scanning electron microscope. The yellow oil trapped from the reaction solution was analyzed by gas chromatography/mass spectrometry (Hewlett Packard 5890, GC/MS). The infrared spectrum of a powder sample was obtained between 4000 and 400 cm^{-1} (in a KBr pellet) using a Perkin-Elmer System 2000 FT-IR spectrometer. The Raman spectrum of the as-prepared sample, and TiS_2 obtained after heat treatment at $800^\circ\text{C}/6\text{ h}$, was obtained using a Reinshaw System 2000, equipped with a Peltier cooled charge coupled device (CCD) for detection of Raman scattered light. X-ray diffraction patterns of the powders and thin films, from $2\theta = 10^\circ$ to 90° , were acquired on a D8 Advance X-ray diffractometer (Bruker) using Cu K_α radiation. A Philips XL-30 scanning electron microscope was used to examine the morphology of samples mounted on a graphite surface. TEM images and electron diffraction results were obtained on a Jeol 1010 transmission electron microscope. Samples of TiS_2 powder for TEM examination were prepared by ultrasonication in tetrahydrofuran for 5 min and placing a few drops of the suspension on a carbon grid.

3. Results

3.1. Titanium disulfide powders and film

The as-prepared powder obtained at room temperature was amorphous as indicated by the X-ray diffraction pattern shown in Fig. 2 (a). After heat-treatment and sulfidization at 600°C , hexagonal TiS_2 containing some rutile and anatase phase (TiO_2) was observed. At 700°C , the propor-

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