Abstract

Preliminary results on the photoelectrochemical properties of polycrystalline TiS$_3$ layers grown on titanium substrates are shown. At first glance, TiS$_3$ layers are composed by needles of bluish-black colour, but scanning electron microscopy (SEM) images show rough surfaces formed by a large number of thin ribbon shaped structures. Ribbons are formed by monoclinic TiS$_3$, as identified by X-ray diffraction patterns, with crystallite size of about 80nm. S/Ti stoichiometric ratio of 2.9 (±0.1) was estimated by energy dispersive x-ray analyses. Photocurrent measurements in an aqueous solution containing SO$_3^{2-}$ ions have been taken at different bias potential under white illumination (I$_{ph}$-V curve) and under different photon energies at 0.2V(Ag$^+/AgCl$) (photocurrent spectral response). The most significant results from these measurements are the anodic photocurrent, hinting n-type conductivity what agrees well with previously reported transport data, and the two direct transitions, at 1.1 and 1.6 eV, obtained from the photocurrent spectral response.

Keywords: Titanium sulphides; TiS$_3$; Photocurrent spectral response; Metal Trichalcogenides.

1. Introduction

In recent years titanium-sulphur compounds (TiS$_x$) have attracted the interest of the scientific community due to their potential applications: cathodes in batteries, hydrogen storage and thermoelectric energy conversion devices [1-3]. Among them, bulk titanium trisulphide (TiS$_3$) seems to be a promising material to be used in photovoltaic and thermoelectric applications [4-5].

TiS$_3$ is a semiconducting compound belonging to the family of trichalcogenides of group IV transition metals (MX$_3$) which are characterized by a quasi-one-dimensional structure. These MX$_3$ layer compounds crystallize in fibrous strands or filamentary ribbon-shaped structures [6-7]. Concerning the physical properties of TiS$_3$, available data are scarce and from bulk material. TiS$_3$ is shown as a n-type semiconductor with a band gap energy of 0.9 eV [8]. Electrical and transport properties have been reported showing high values of thermoelectric coefficient (-0.7
mV/K) [9], Hall mobilities between 10-50 cm²/V·s, donor densities about 10¹⁸-10¹⁹ cm⁻³ and conductivities of 10-20 (mΩ·cm)⁻¹ at ambient temperature [10].

The aim of this work is to investigate the photoelectrochemical response of polycrystalline TiS₃ in aqueous solution. Some results on TiS₃ single crystals photoresponse in aqueous media have been previously reported in a paper by Gorochov et al. [11] concluding that the material is unstable in aqueous acidic and basic solutions but it could be partially stabilized in presence of I₂/I⁻. Here, preliminary results on the photoelectrochemical behavior of polycrystalline TiS₃ grown on titanium substrates are shown. Aqueous electrolyte containing reducing species as SO₃⁻ is used in order to prevent the decomposition suggested by Gorochov.

2. Experimental

Titanium trisulphide layers have been obtained by direct sulphuration of Ti discs (⌀=10 mm) in a vacuum sealed ampoule at 550°C with sulphur powder during 20 hours. Prior to this, Ti discs had been etched in HNO₃:HF (30:4 wt%) for 1 minute, washed in distilled water and finally dipped in ethanol. Heating rate was 0.4±0.05°C/min and the cooling process took place in ambient conditions. Sulphur pressure into the ampoule during the treatment at 550°C was that corresponding to the sulphur vapour pressure at this temperature (4 bars) [12].

Glancing angle X-ray diffraction patterns were taken in a Panalytical X’pert Pro X-ray diffractometer with CuKα radiation (λ=1.5406Å) and a fixed incidence angle of 1.7°. The morphology, composition and microstructure of the films were investigated by SEM (Scanning Electron Microscopy) and EDX (Energy Dispersive Analyses of X-ray). A Scanning Electron Microscope (Hitachi, S-3000N) attached with an EDX analyser (Oxford Instruments, Inca X-sight) to measure the sample stoichiometry were used. Photoelectrochemical measurements were done in a single-compartment three electrode conventional photoelectrochemical cell with a platinum counter electrode and a Ag⁺/AgCl electrode as the reference one. Electrolyte was an aqueous solution of 1.0 M Na₂SO₃ purged with N₂ gas before the measurements. A 150W Xe lamp is used as a light source which is coupled to a Bausch and Lomb monochromator when monochromatic light is needed. Photocurrents have been measured at different bias potential under white illumination (I_p-V curve) and under different photon energies at 0.2V (Ag⁺/AgCl) (photocurrent spectral response). The potential of the working electrode was controlled by an EG&G PAR Potentiostat.

3. Results and discussion

At first glance titanium sulphide layers seem to be formed by groups of bluish-black colour needles. Close inspection of the, scanning electron micrographs showed that they are formed by a large number of thin ribbon-shaped structures that can be seen in Fig. 1 at two magnifications.

Figure 1: SEM micrographs of polycrystalline TiS₃ grown on Ti discs sulphurated at 550°C under sulphur atmosphere.
As it can be observed the sizes of the ribbons vary between 2 and 8 μm of width and their length appears to be higher than 100 μm. The third and lowest dimension has been investigated by TEM and it was concluded that most of the ribbons have thicknesses between 100-200 nm [13]. Film stoichiometry, determined by EDX, gives values of S/Ti= 2.9 ± 0.1.

Figure 2 shows the XRD patterns of a bare Ti disc and a titanium trisulphide film obtained after sulphuration. The first one shows peaks corresponding to Titanium [14] and the second one can be identified by monoclinic TiS₃ [15]. Crystallite size of 80 ± 4 nm was determined by applying the Scherrer formula to the TiS₃ XRD pattern [16].

As far as we know, there is only one report on the photo- and electrochemical response of this material and it refers to TiS₃ single crystals [11]. In that paper, TiS₃ was measured in H₂SO₄ and NaOH electrolytes, in which it was unstable, and in a I₂/I⁻ solution, where it was stabilized for several days. In this paper, we present photoelectrochemical results of our TiS₃ layers in presence of reduced SO₃²⁻ species in order to avoid the decomposition. Cyclic voltammograms of TiS₃ films in an aqueous solution of 1.0 M Na₂SO₃ at dark and under white light illumination are shown in Fig. 3a beside the photocurrent-potential curve, obtained at each stationary bias voltage, shown in Fig. 3b. In the voltammograms a couple of anodic peaks at about -0.1V (Ag⁺/AgCl) and +0.2 V (Ag⁺/AgCl) can be observed during the positive sweep, instead of a negligible dark current expected from an ideal n-type semiconductor-electrolyte junction. The first one, which is practically unaffected by illumination, could be associated to the oxidation of SO₃²⁻ species through the following reaction

\[
SO₃²⁻ + H₂O → SO₄²⁻ + 2H⁺ + 2e⁻
\]  

Second peak is not as well defined as the first one and disappears under illumination hidden under the photocurrent. The nature of these peaks is not yet clarified and currently under investigation.

Figure 3: (a) Cyclic voltammetry of a TiS₃ film in 1.0M Na₂SO₃. Scan rate: 50mV/s. (b) Two Iph-V curves of a TiS₃ electrode in 1.0M Na₂SO₃ at ambient temperature under white light illumination. Points in red are a magnification (x5) of data at V < +0.1V.
Photocurrent vs. bias potential plot under white light illumination is shown in Fig. 3b. Photocurrent values were obtained at each stationary bias potential. As can be seen the anodic photocurrent starts to be appreciable at about -0.1 V (Ag+/AgCl) and shows a quasi linear dependence on the potential in the range of 0.0 - 0.7 V(Ag+/AgCl).

Photocurrent spectral response of TiS$_3$ photoelectrode in an aqueous solution of 1.0M Na$_2$SO$_3$ at 0.2 V(Ag+/AgCl) is shown in Fig. 4a. From these data the type and energy of interband transitions can be estimated by linear fitting of $(I_{ph}\cdot h\nu)^n$ vs. $h\nu$ where $n$ is ½ or 2 for indirect or direct transition, respectively [17]. The corresponding fitting for $n=2$ is plotted in Fig. 4b, in which at least two linear segments appear. One of them extrapolates at $E_{g1}=1.1$ (± 0.1) eV (close to the TiS$_3$ reported band gap [8]) and the other at $E_{g2}=1.6$ eV.

The earliest reported optical data on transition metal trichalcogenides (MX$_3$ with M=Ti, Zr, Hf) is that from Grimmeiss et al. [8] where optical absorption was performed on single crystals of TiS$_3$, ZrS$_3$, HfS$_3$ and ZrS$_3$. In this paper a direct energy gap value of 0.9 eV was reported for TiS$_3$. Two donor levels at energies of 0.14 eV and 0.04eV below the conduction band were also reported. Later, Brattas et al. [18] obtained a value of 0.83 eV for the energy gap of TiS$_3$ from Diffuse Reflectance Spectra measurements by using an extrapolation method. The values reported in these references are in good agreement for all of the trichalcogenides investigated, however, they are more than 1 eV lower than those reported by Schairer [19] who performed optical absorption measurements on single crystals of ZrS$_3$ and HfS$_3$. At last, an estimation of the energy gap of TiS$_3$ was reported by Gorochov et al. [11] from the onset photocurrent observed in the $I_{ph}$ dependence on photon energy measured in a photoelectrochemical cell in I$_2$/I$^-$ solution. They give a value of 1.0 eV and suggest an indirect transition. From our measurements, two direct transitions can be observed in Fig. 4b: that at the lowest energy (1.1 ± 0.1 eV) agrees well with the direct energy band gap proposed in refs. [8,11,18]; that at the highest energy could be another direct transition, appearing in metal trichalcogenides as those observed by Schairer [19] in ZrS$_3$ and HfS$_3$, but not reported up to now in TiS$_3$.

Figure 4: (a) Photocurrent spectral response of a TiS$_3$ deposit in sodium sulfite solution (1.0M Na$_2$SO$_3$) at 0.2 V (Ag+/AgCl). Photocurrents were corrected for the Xe-lamp photon flux. (b) Plot of $(I_{ph}\cdot h\nu)^2$ - $h\nu$ from the photocurrent data in (a).

4. Conclusions

Ribbon-like films of TiS$_3$ have been grown on Titanium substrates and their photoelectrochemical characterization has been carried out. From this characterization the following conclusions have been reached:

- Polycrystalline TiS$_3$ films show anodic photocurrent hinting n-type conductivity what agrees well with previously reported transport data.
- The onset potential for the photocurrent is close to -0.1V (Ag+/AgCl).
- From the photocurrent spectral response, two direct energy transitions at 1.1 and 1.6 eV have been determined. The first one agrees well with the direct reported energy gap obtained from optical measurements (absorption and diffuse reflectance) with single crystals TiS$_3$.

These results on polycrystalline TiS$_3$ are in a good agreement with those previously reported in single crystals.
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