Effect of ion irradiation on nanoscale TiS$_2$ systems with suppressed Titania phase

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Abstract. Titanium disulfide (TiS$_2$), being an important of the transition metal dichalcogenide, (TMDC) family, has drawn numerous interest owing to exhibition of tunable band gap as well as high carrier mobility. In this work, we highlight preparation of TiS$_2$ nanopowder with minimal TiO$_2$ content and also demonstrate modified properties upon swift heavy ion irradiation on TiS$_2$ nanoparticles dispersed PVA films. Different properties of the irradiated samples have been characterized through diffraction, microscopic and spectroscopic techniques. As a result of irradiation, due to agglomeration of particles, the grain size is found to increase. We could also observe a red shift after irradiation with increasing fluence, leading to easy flow of electron from valence to conduction band, which shows that conduction of electrons is more in case of irradiated films compared to the pristine one and thus there may be a possibility of using the irradiated samples in various optoelectronic devices.

1. Introduction

In the recent years, 2D materials like graphene have received a great deal of attention among the researchers due to their wide range of electronic and optical properties [1]. However, due to the lack of band gaps, the electronic devices made from graphene cannot be effectively switched on and off and have low turn on and off time ratios [1]. There is a need to overcome these limitations using other layered structures. This leads to the exploitation of other 2D materials, such as, transition metal dichalcogenides (TMDC) which possess sizable band gaps and thus can be promising for electronic and optoelectronic components [1]. Moreover the band gap of these materials can be tuned by tuning their dimensions and thus making them versatile for their use in different applications [2]. TMDCs have generalised formula MX$_2$, where M is a transition metal element (group IV or group V), and X is a chalcogen [3]. Among the TMDCs, titanium disulphide (TiS$_2$) has been identified as an active cathode in lithium-based rechargeable batteries [4]. These materials are layered structures of the form S-Ti-S unit, the sulphur atoms in two hexagonal planes separated by a plane of Ti atoms. The Ti-S bonds are bonded covalently whereas the adjacent S-Ti-S layers are bonded through the weak Vander Waals forces. The properties like high conductivity as well as high lithium diffusion rates have made TiS$_2$ to perform as a stable and high electrode material with long life cycle [5]. As, it may be noted, that TiS$_2$ can also serve as an efficient catalysis for hydrogenation, and as a hydrogen storage material...
The study of TMDCs including TiS$_2$ is gaining momentum owing to its versatility and being regarded as an alternative to the zero gap graphene based material. All materials possess structural defects and due to these defects, materials possess several interesting properties [7]. Tuning of defects within TMDC devices serves as an alternative method to vary electronic and optoelectronic properties [8]. These may be tuned through irradiation effects. Ion irradiation, apart from defect formation and alteration, also cause several other significant changes, which include track formation in material, implantation etc [9]. Bombardment with ions brings in changes in the electronic, optoelectronic properties, apart from structural morphology. Irradiation with charged particle beams allows precise control of defect generation by altering beam conditions and exposure dose [8]. Kim et al. have shown the use of a high energy proton beam to introduce trap states in the back gate dielectric of a MoS$_2$ thin-film transistor [10]. Tongay et al. have used $\alpha$-particle irradiation to generate vacancies in TMDCs, which give rise to new emission peaks with enhanced photoluminescence intensity [11]. Fox et al. have demonstrated the use of a focused helium-ion beam to pattern MoS$_2$ as well as preferentially sputter sulfur atoms [12]. The local tuning of opto-electronic properties of mono and few-layer TMDCs can provide an excellent opportunity to realize sharp homojunctions similar to conventional p-n, p-i-n, or p-n-p junctions, which are critical to many device architecture [8].

Among all other TMDCs, TiS$_2$ is very less stable as it gets oxidized easily and forms TiO$_2$. Therefore the preparation of TiS$_2$ needs no exposure of oxygen. The synthesis of TiS$_2$ at room temperature has not been made till now. In this work, we made several attempts to synthesize TiS$_2$ nanoscale system with reduced titania phase. The synthesized nanoparticles were first dispersed in a matrix and then bombarded with the 80-MeV nitrogen ion at different fluencies. The modified structural, morphological and optical properties are discussed.

2. Experimental: Materials And Methods

2.1. Synthesis of TiS$_2$ nanoparticles and sheets

As for synthesis, TiCl$_4$ (LobaChemie, 99.5% pure) as the titanium source and Na$_2$S as the sulphur source while tetrahydrofurane (THF) (THF, Rankem, 99.7% pure) was taken as the solvent knowing that a polar solvent is free from oxygen and water [13]. The as-received, Na$_2$S is first dried at 150°C in vacuum for some hours to remove the surface adsorbed water and making Na$_2$S perfectly anhydrous. Then 1.2 g of the anhydrous Na$_2$S is taken in 10 ml of THF and is subjected to magnetic stirring at a temperature of 50°C. After about 30 minutes, 1 ml of TiCl$_4$ is added to the solution under stirring and left undisturbed for 12h at room temperature. The precursor is then centrifuged (~5000 rpm) and washed with methanol and THF for several times and dried in vacuum. The powder obtained is then labeled as $S_i$. While preparing the sample, care was taken to avoid direct exposure to air oxygen in it. The synthesis steps are illustrated in the block diagram shown in figure 2.
2.2. Irradiation of the synthesised nanoparticles
Polyvinyl Alcohol (PVA) was selected to disperse the TiS$_2$ nanoparticles so as to protect against particle agglomeration and environmental attack [9]. For the irradiation purpose, TiS$_2$ nanoparticles were dispersed in PVA films (50% volume dispersion) and then casted on laboratory glass slides. The sample so prepared is labeled as sample $S_2$. The samples were irradiated in the Material Science chamber under a high vacuum (pressure of $10^{-6}$ mbar) condition and using 80 MeV-N$^{4+}$ ion beams (with a beam current of 1 pnA, particle-nanoampere), available at the 15UD tandem pelletron accelerator of Inter University Accelerator Centre, New Delhi. The ion beam fluence was measured by integrating the ion charge on the sample ladder, which was insulated from the chamber. The ion fluence was varied as $5 \times 10^{11}$ ions/cm$^2$, $5 \times 10^{12}$ ions/cm$^2$ and $5 \times 10^{13}$ ions/cm$^2$ and accordingly the samples were named as $S_3$, $S_4$ and $S_5$. The schematic diagram of the ion beam falling on the films is shown in figure 3.

3. Characterisation Techniques Employed
To exploit information as regards structural and crystallographic phase, x-ray diffraction (XRD) study was carried out by employing a MiniFlex Rigaku X-ray diffractometer equipped with a CuKα source ($\lambda=1.543$ Å). Morphological analysis was carried out both by scanning electron microscopy (JEOL, 6390LV), Field emission scanning electron microscopy (MIRA II LMH from TESCAN), with a resolution of 1.5 nm at 30 kV was employed to study the irradiated films at a better magnification. It has a secondary electron (SE) and a backscattered electron (BSE) detector for imaging. An energy dispersive X ray detector has also been installed in this system for elemental analysis and transmission electron microscopy (FEI, Tecnai). The elemental analysis was performed through the energy dispersive x-ray spectroscopy (EDX) (INCA PentaFET3 with 133 keV resolution from OXFORD) attached to the SEM machine To study the optical properties, we have employed the UV–Visible absorption spectroscopy (UV 2450, Shimadzu Corporation).

4. Results And Discussions
4.1. Structural and elemental analyses
The diffractogram of the pristine samples ($S_1$, $S_2$) and the irradiated samples($S_3$, $S_4$, $S_5$) at different fluences are shown in figure 4. In sample $S_1$, the diffraction peaks positioned at $2\theta \sim 15.30^\circ$, $34.31^\circ$, $44.34^\circ$, $53.51^\circ$ and $65.35^\circ$ characterize hexagonal phase of TiS$_2$ (figure 4(a)) (JCPDS card no. 74-1141) [6]. Most of the crystallites are believed to have preferential orientation along the (011) plane.
A suppressed NaCl peak at ~31.80° is also seen. Moreover, a small peak at 48.20° corresponds to the anatase phase of TiO$_2$ [14]. On the other hand for the TiS$_2$/PVA system ($S_t$), the peaks for TiS$_2$ are observed at 2$\theta$ ~15.35°, 34.12°, 44.15° and 65.25° along with the characteristic crystalline peak of PVA is observable at 2$\theta$ ~20.30° [15] (figure 4(b)). With irradiation, all these peaks are found to shift towards a higher angle and decrease in the full width half maxima FWHM value with increasing the ion fluence (figure. 4(c) and 4(d)). But, no additional peak has been observed as a result of irradiation. The peaks shifting towards higher angle suggests an increase in the average crystallite size as well as decrease in microstrain in the irradiated films [16]. An observable decrease in the FWHM value reveals the increase in crystallinity which can also be witnessed by the increase of the peak intensity as we go on increasing the ion fluence. The increase in the grain size can be explained by the fact that with the impact of high energetic ion on to the PVA films the polymer gets destroyed, allowing TiS$_2$ nanoparticles free from encapsulation (figure. 4(b)). These irradiation induced free particles can agglomerate and make a bigger particle and thus increasing the grain size [17].

![Figure 4](image)

**Figure 4.** (a) XRD pattern of the sample $S_1$, (b) XRD patterns of the samples $S_2$ (i), $S_3$ (ii), $S_4$ (iii) and $S_5$ (iv), (c) shifting of the (011) peak, (d) plot showing variation of peak shift and FWHM with ion fluences

| Ion fluence (ions/cm$^2$) | Peak position, 2$\theta$ (degree) | FWHM, $\beta$ (degree) | Microstrain ($\epsilon$) ($\times 10^{-3}$) | Lattice parameters (Å) | Crystallite size, d (Å) |
|--------------------------|----------------------------------|-----------------------|---------------------------------|----------------------|----------------------|
| 0                        | 34.12                            | 0.972                 | 4.05                            | a = 3.48, c = 5.71  | 85.18                |
| $5 \times 10^{11}$       | 34.26                            | 0.915                 | 3.81                            | a = 3.46, c = 5.67  | 90.43                |
| $5 \times 10^{12}$       | 34.39                            | 0.854                 | 3.55                            | a = 3.45, c = 5.65  | 96.92                |
| $5 \times 10^{13}$       | 34.51                            | 0.772                 | 3.24                            | a = 3.43, c = 5.63  | 106.33               |

**Table 1:** Physical parameters obtained through XRD analysis
Using single line fitting and Debye-Scherrer formula \( d = \frac{0.9 \lambda}{\beta \cos \theta} \), where, \( \lambda \) is the wavelength of the x-ray source, \( \beta \) is the full width at half maxima (FWHM) in radians and \( \theta \) is the Bragg’s angle, the average crystallite size, \( d \) is estimated to be \( \sim 85.18 \) Å for the sample \( S_2 \), whereas for the irradiated samples, the crystallite is found to increase with increase in ion fluence. The average crystallite size was found to be 90.43 Å, 96.92 Å and 106.33 Å for \( S_3 \), \( S_4 \) and \( S_5 \) respectively. The lattice parameters for each of the sample have been calculated and are given in the Table 1. We have also calculated the microstrain (\( \varepsilon \)) present in the films by the relation, \( \varepsilon = \frac{\beta \cos \theta}{4} \). From the calculation, the microstrain was found to decrease with increase in ion fluence. The value of FWHM, microstrain and the average crystallite size for the unirradiated and the irradiated samples are summarized in the table 1.

4.2. **Morphological analyses through electron microscopy imaging**

Figure 5 shows the TEM and SEM micrograph of a thin sliced specimen of the sample \( S_1 \). The development of TiS\(_2\) nanosheets along with foldings is apparently realized from the micrograph shown in figure 5(a). A magnified image is also shown in figure 5(b). It highlights multilayer, bilayer sheets. The TEM image figure [5(d)] shows that the interlayer separation of TiS\(_2\) ~0.567 nm, which is in good agreement with the literature value for the (001) of TiS\(_2\) [18]. The selected area electron diffraction pattern (SAED) is shown in figure 5(c).

![TEM images](image)

**Figure 5.** TEM images of sample (a) \( S_1 \) (b) Higher magnification image of \( S_1 \), (c) SAED pattern of the sample \( S_1 \), (d) interlayer spacing and (e,f) SEM images of the sample \( S_1 \)

The diffused, yet distinguishable diffraction ring patterns suggest polycrystalline nature of the product along with the small amount of single crystalline content. The rings represent the (001), (011) and (012) planes of the synthesized TiS\(_2\) sample.

The SEM micrograph of the sample \( S_1 \) is shown in figure 5(e). One can visualize micron-to submicron size distribution of TiS\(_2\) particles (figure 5 (e)). Typically, the average size of the unclustered particles ranges between 50 nm- 200 nm. At a higher magnification, some of the particles appeared to be in agglomerated form, with a diverse morphology, and having dimension < 2 \( \mu \)m. The agglomerated particles tend to form hexagonal prism-like conformation owing to the hexagonal phase
of TiS$_2$ [3, 6]. The presence of Ti and S in the sample $S_1$ can be witnessed from the EDX micrograph shown in figure 5(f). The FESEM micrographs of the samples $S_2$ and $S_4$ are shown in figure 6 (a, b, c, d).

It is found that with irradiation, the PVA film got damaged Fig. 6(a, c) and the size of the TiS$_2$ particles are enhanced Fig. 6(b, d) in the sample $S_4$ compared to $S_2$. The enhancement of the particle size is due to agglomeration of the TiS$_2$ nanoparticles.

The EDX spectrum of the pristine sample ($S_1$) reveals a proportionately high intense S peak along with Ti peak and suppressed Na and Cl peaks (Fig. 6(e)). Quantitatively, Ti to S atomic percentage ratio is nearly 1:2, as desired for the development of TiS$_2$. Whereas, the evidence of presence of C, O, Ti and S can be assured from the EDX spectrum of the irradiated sample (Fig. 6(f)).

4.3. UV-Visible optical absorption spectroscopy analysis

The UV Vis spectra of the pristine and irradiated samples are shown in figure 7.

Figure 7: FESEM images of the samples (a,b) $S_2$, (c,d) $S_4$ and EDX micrographs of the samples (e) $S_2$, (f) $S_4$
It is found that the pristine sample shows an absorption peak at 596 nm which is ascribed due to $M_2^- \rightarrow M_1^+$ of TiS$_2$ transition [19]. With an increase in the fluence, a red shift in the absorption edge is occurred which leads to the decrease in the bandgap of the TiS$_2$ film. The optical band gap $E_g$ can be calculated using the Tauc’s relation for direct and allowed transition [20]

$$\alpha h \nu = A (h \nu - E_g)^{1/2}$$

where, $h \nu$ is the energy of the photon and $A$ is the system dependent parameter. From the Tauc’s plot (shown inset) the bandgap of the unirradiated sample ($S_1$) was found to be 2.85 eV and the value was observed to decrease with increase in the ion fluence. The value of the bandgaps are found to be 2.34 eV, 1.97 eV and 1.79 eV for the samples $S_2$, $S_3$ and $S_4$ respectively. The decrease in the band gap of the irradiated sample may be due to the increase in the crystallite size of the samples [21]. It can be easily understood that with decrease in the band gap the transfer of electrons from the valence band to conduction band can easily take place. Thus the conduction of electrons will be more in the irradiated films than the pristine one and thus there may be a possibility of using the irradiated samples in various optoelectronic devices [22].

5. Conclusions
We have synthesized TiS$_2$ with reduced titania phase by a simple chemical route and characterized the samples with different characterization techniques. The obtained TiS$_2$ particles are dispersed on PVA and casted on a laboratory glass slide. The resultant TiS$_2$/PVA films were irradiated using 80 MeV N$^{4+}$ ions at different fluences. The irradiated films were characterized using XRD, EDX, SEM and UV Vis spectroscopy. Due to irradiation, the agglomeration of the TiS$_2$ particles took place and the grain size was found to increase as evident from XRD and SEM analysis. A gradual decrease in the band gap with increase in ion fluence was observed from the Tauc’s plot which is the result of the increase in the grain size of the TiS$_2$ particles.

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