(A) A few layer synthesis of VS$_2$ nanosheets and investigation of their field emission properties.

This chapter is about the synthesis, physico-chemical characterization and field emission investigation of a few layer VS$_2$, a promising member of transition metal di-chalcogenide family. A few layer metallic VS$_2$ nanosheets were synthesized employing a simple hydrothermal method.

4(a) 1. Introduction:

Amongst the various TMDs, VS$_2$ is a highly conductive material consisting of triple layer stack of metal V sandwiched between two S layers giving a layered structure with an interlayer spacing of 5.76Å (S-V-S). Two common polymorphs of VS$_2$ are hexagonal (2H) and trigonal (1T), where the letter indicates crystal structure and digit refers to the number of S-V-S units. Although both the crystal structure are thermodynamically stable, but with decreasing no. of layers 2H system is found to be more stable. A 1T phase changes to 2H phase on moving from bulk to monolayer and vice-versa. Thus the phase changes with layer thickness or temperature. Owing to metallic nature (zero band gap [1-7]) of VS$_2$, it could be a potential candidate for various field emission based devices. Fig.4(a).1 shows the crystal structure of different phases of VS$_2$.

![Crystal structure of VS$_2$](image)

**Figure 4(a).1:** Crystal structure of VS$_2$
4(a) 2. Experimental:

Synthesis of VS$_2$ nanosheets:

VS$_2$ nanosheets were synthesized by a simple hydrothermal route with ortovanadate as vanadium precursor and thioacetamide was used as sulphur source. In a typical synthesis experiment, 90mM of sodium orthovanadate (Na$_3$VO$_4$) and 18 mM of thioacetamide (C$_2$H$_5$NS) were dissolved in 120 ml distilled water and stirred at room temperature for 1 hr. The solution was transferred to teflon lined stainless steel autoclave and heated to 160$^0$C for 24 hrs. Then the system was brought to cool at room temperature and the resultant, in the form of black precipitate, was washed several number of times with DI water and dried in vacuum for 10 hrs at 60$^0$C. During hydrothermal reaction, hydrolysis of thioacetamide generates HS$^-$, which acts as a reductant to reduce V$^{5+}$ into V$^{4+}$ and VS$_2$ layered structures are formed.

4(a) 3. Characterisation:

4(a) 3.1 X-Ray diffraction (XRD):

Fig.4a.2 depicts typical X-Ray diffraction (XRD) pattern of VS$_2$ sheets.

![XRD pattern of VS$_2$ sheets](image)

**Figure 4(a).2:** XRD pattern of VS$_2$ nanosheets using hydrothermal method

The XRD analysis shows the presence of highly crystalline hexagonal structure [a= 3.21 Å, c= 5.77 Å, powder diffraction file (PDF) no. 36-1139] without any impurities. The growth direction of
VS$_2$ nanosheets is mostly along (001) and (101) directions. Higher intense peak along (101) suggest the preferred growth direction of protruding edges of VS$_2$ sheets along it.

4(a) 3.2 X-ray photoelectron spectroscopy (XPS):

The elemental composition, chemical and electronic state of the elements were confirmed using X-ray photoelectron spectroscopy (XPS). The X-ray photoelectron spectroscopy (XPS) confirms the reduction of V$^{5+}$ to V$^{4+}$ [5-7]. The peaks observed at 516.32 eV and 524 eV are attributed to V2p$_{3/2}$ and V2p$_{1/2}$, which are characteristic of the V$^{4+}$ oxidation state and not V$^{5+}$ oxidation state, indicating the formation of pure VS$_2$ phase. The peaks at 160.6 eV and 161.7 eV can be indexed to S2p$_{3/2}$ and S2p$_{1/2}$ of S$^{2-}$ respectively [8].

![Figure 4(a.3): (a,b) XPS of VS$_2$ nanosheets using hydrothermal method](image)

4(a) 3.3 FESEM:

Fig. 4(a.4) shows the high magnification field emission scanning electron microscope (FESEM) images of flower like VS$_2$ nanosheets morphology and intercrossed sheet structures stacked layer by layer with the thickness ~10-100 nm and length in the range of ~1-5 μm. Furthermore, the Si substrate is observed to be completely covered with the VS$_2$ nanosheets possessing rough morphology along with nearly vertical alignment.
Figure 4(a).4 FESEM images of few-layer VS$_2$ nanosheets. Inset shows the magnified image of VS$_2$ nanosheets

4(a) 3.4 TEM:

The morphology and the crystalline nature of the as synthesized VS$_2$ nanosheets were further confirmed using TEM and HRTEM and shown in Fig. 4a.5.

Fig. 4(a).5 (a) shows the low magnification TEM image. The HRTEM image shown in Fig.4(a).5(b) of an edge of a VS$_2$ sheet clearly shows that layered VS$_2$ consists of a few layers (5-6 layers) with an interlayer spacing of 0.57 nm, which is in good agreement with the (001) plane of VS$_2$. Inset of Fig. 4(a).5(b) shows the fast Fourier transform (FFT) of the electron diffraction pattern of a few layers of VS$_2$. The diffraction pattern obtained by FFT confirms the presence of pure hexagonal phase of VS$_2$. 
Figure 4(a).5: TEM analysis of VS$_2$ sheets (a) low magnification image, (b) high resolution TEM image and inset of (b) fast Fourier transform of the electron diffraction pattern of a few layers of VS$_2$.

4(a) 4. Growth Mechanism:

Fig. 4(a).6 shows the schematic of growth mechanism of VS$_2$ flower like nanosheets using hydrothermal method. During the hydrothermal process, hydrolysis/dissociation of thioacetamide and Na$_3$VO$_4$ occurs. The sulfur generated from the dissociated thioacetamide promotes to form pristine VS$_2$ sheets during the hydrothermal process. Formation of flower-like morphology of VS$_2$ is believed to be involved two steps: an initial nucleating stage and crystal growth stage involving Ostwald ripening process, which is known for the growth of metal sulfide flower-like structure[9].

In the initial stage, various functional groups such as –NH$_2$, -COOH and –SH present in the reaction vessel reacts with V$^{4+}$ ions to form V-S complex and then they decompose to form VS$_2$ nuclei for later growth [10]. In the second stage, the flower-like structures would have formed as a result of the Ostwald ripening and self-assembly of the VS$_2$ sheets.
Figure 4(a).6: Schematic of hydrothermal growth process of VS$_2$ nanosheets.

4(a) 5. DFT calculations:

The band gap of the VS$_2$ nanosheets was estimated by Density Functional Theory (DFT). The DFT calculations were performed using the ABINIT [11] software, which is a plane-wave pseudopotential implementation of density functional theory [12,13]. V and S atoms were treated using norm-conserving Troullier-Martin pseudopotentials [14] with plane wave cutoff energies of 30.0 Hartree. For the two-dimensional systems, a 12x12x1 k-point grid was used for sampling in reciprocal space. A vacuum energy level was introduced approximately 15 Å to separate periodic images along the z-direction. For VS$_2$ systems, an in-plane lattice constant of 3.22 Å was used. The orientation of the VS$_2$ unit cells along strained graphene substrates are shown in Fig. 4(a).7 (a, b).

# The DFT calculations were done by the C.S. Raout et al. at IIT Bhubaneshwar and is not claimed as part of the work presented in the thesis, but is used for the completeness of the work.
The work function is defined as the energy required to remove an electron from the chemical potential (Fermi Energy) of a crystal to the vacuum region. We calculate this quantity in two steps; first by self-consistently calculating the Fermi energy and then by calculating the electrostatic potential along the non-periodic direction. Far from the surface of the crystal, the vacuum potential converges to a constant value and this is used as the value of the vacuum potential. The work function is thus defined as:

\[ \phi = V_{\text{vac}} - E_F \]  

In each case, convergence with respect to the thickness of the vacuum layer was performed and we've found that the value of the work function converges for around 15-20 Å of vacuum.

**Figure 4(a),7:** (a) The unit cell orientations of VS\(_2\). (b, c) The out-of-plane electrostatic potential and work function for VS\(_2\).
A schematic representation of the VS$_2$ unit cell as seen from above is shown in Fig.4(a). The hexagonal symmetry is reminiscent of graphene, although VS$_2$ actually contains three separate layers (S-V-S) each covalently bonded to one another. The work function as calculated self-consistently for an isolated single layer of VS$_2$ was found to be 6.01 eV, and the electrostatic potential in the out-of-plane direction is plotted in Fig.4(a). 7b. The two potential energy minima correspond to energy wells between V and S atoms, while the potential converges to a nearly constant value of 4.58 eV far away from the surface. This number is taken to be the vacuum potential when calculating the work function.

When VS$_2$ is confined to a single monolayer, the electronic band structure remains metallic with a single band crossing the Fermi level. The metallic states are due to the d-like states in the vanadium atoms, as shown in the angular-momentum resolved partial density of states in Fig. 4(a). 7 c. The numerical value of the Fermi Energy is -1.43 eV, which together with the vacuum potential gives a work function of 6.01 eV = 4.58 eV – (-1.43 eV). This is the first report which describes the work function calculation of VS$_2$.

4(a) 6. Field emission investigation:

For field emission measurements the VS$_2$ nanosheets powder was sprinkled over carbon tape and pasted on copper stub acting as anode. Prior to FE measurements, a preconditioning in terms of removal of any asperities and/or contaminants via ion bombardment was done by keeping the emitters at 1kV for about 5 min. The plot of the field emission current density ($J$) versus applied electric field ($E$) recorded at base pressure of ~ 1x10$^{-8}$ mbar for VS$_2$ nanosheets is shown in Fig. 4(a).8(a). The turn-on field defined as the field required to draw an emission current density of 1μA/cm$^2$, was found to be 4.1 V/μm. With increasing applied voltage, the emission current density was found to increase rapidly and an emission current density of 293.2 μA/cm$^2$ was drawn at an applied field of 7.62 V/ μm. The $J$-$E$ curves reveal that, after the turn-on field, the emission current rapidly increases with increase in the applied field, indicating that the emission is due to quantum mechanical tunelling of electrons as per the F-N theory.
Figure 4(a).8: Field emission from few-layered VS$_2$ nanosheets. (a) Applied electrical field as a function of emission current density. (b) F-N plot showing linear behaviour indicating emission current from the metallic emitter.

Fig. 4(a).8b represent the corresponding F-N plot [a plot of $\ln (J/E^2)$ versus $1/E$] of the emitters. The VS$_2$ sheet field emitter exhibit almost linear F-N plot behaviour over the entire applied field range, indicating metallic behaviour. The field enhancement factor ($\beta$) provides a quantitative idea of the
degree of enhancement in the electric field at the emitter edges due to their nanometric dimension. In the present case, $\beta$ is calculated from the slope of the F-N plot, as defined in equation 1

$$\beta = \frac{-6.8 \times 10^3 \phi^{3/2}}{m}$$

(1)

where $m$ is slope of F-N plot. The value of workfunction of the emitter ($\phi$), estimated from density functional theory (DFT) calculations is 6.07eV for VS$_2$. The $\beta$ values calculated from equation (2) are found to be 2484 for VS$_2$ field emitters. The high value of $\beta$ not only facilitates availability of large number of emission sites (confirmed from the emission image) but also enhances the emission current density from the emission site, at the given applied field. In addition to the emission competence, stability of the emission current is one of the decisive parameters from the application point of view. We have tested the emission current stabilities of the VS$_2$ emitters at base pressure of $\sim 1 \times 10^{-8}$ mbar. Fig. 4a.9 depicts the emission current versus time (I-t) plots of the VS$_2$ emitter recorded at the different preset values, 1 and 10 $\mu$A/cm$^2$. The emission current exhibits good stability at the lower preset value (1 $\mu$A/cm$^2$). At higher preset value (10 $\mu$A/cm$^2$), the stability is observed to be poor, characterized by excursion superimposed with spike like fluctuations. The excursions in the emission current followed by stabilization at higher value may be attributed to cleaning of the emitter surface due to residual gas ion bombardment. Since we have used as-prepared emitter, it is expected that in the initial stage of stability measurement, desorption of the adsorbed species from the emitter surface will give more fluctuations, which eventually die out as the emitter surface becomes cleaner due to residual ion bombardment.
Figure 4(a-9): Field emission current stability (a) at preset value of 1\(\mu\)A and 10 \(\mu\)A for a period of about 3 and (b) long term stability at 1 \(\mu\)A indicating good emission current stability.

A typical field emission image photographed at a current density of 50 \(\mu\)A/cm\(^2\) and 100 \(\mu\)A/cm\(^2\) is shown in Fig. 4(a).10. The emission image recorded at the onset of current stability measurement. All these features propose \(\text{VS}_2\) as a promising field emitter candidate for vacuum micro-nanoelectronic devices.
Figure 4(a).10: Field emission micrographs of a few layered VS$_2$ nanosheets at a current density of (a) 50 μA/cm$^2$ and (b) 100 μA/cm$^2$

4(a) 7. Conclusion:

- A few layered VS$_2$ nanosheets has been synthesized by a simple hydrothermal route with sodium orthovanadate and thio-urea as precursors.
- The structural morphology, crystalline nature and elemental composition was confirmed using FESEM, TEM/HRTEM, XPS etc.
- The field emission properties of VS$_2$ nanosheets have been investigated at a base pressure of 1x10$^{-8}$ mbar.
- The low turn-on field value and relatively fair long term stability, makes it a promising candidate for field emission based devices.
References:

(B) Synthesis and field emission investigation of VS₄-RGO.

This part of the chapter 4 deals with the synthesis of VS₄ nanosheets via hydrotehrmal method. VS₄ can be obtained only when appropriate amount of graphene oxide (GO) was added to the solution of orthovanadate and thioacetamide. Thus GO acts as a template for the synthesis of VS₄.

4(b) 1. Introduction:

Vanadium tetrasulphide VS₄, another vanadium sulfide analogous to VS₂, is a narrow band gap (~ 1.3 eV) semiconductor. This linear-chain compound has alternating bonding and nonbonding contacts between the vanadium centers. The vanadium is octa-coordinated, which is a typical form for this metal. Its one dimensional chain structure consisting of V and S₂ moiety. Each V is bridged by two S₂ moieties to form a chain. These chains are then packed in such a way that each chain is surrounded by six such chains [1,2].

As stated in the earlier section, various 2D materials such as graphene, GO and layered MoS₂ sheets have recently shown their enhanced field emission properties and thus inspired for investigation of other layered structured material as possible field emitters [3,4]. The recent report on the morphological and structural changes of the vanadium sulfide in the presence of GO during hydrothermal reaction, has increased desire to explore its field emission properties[2]. It is expected that unique morphologies of the VS₄ nanostructures can exhibit promising field emission properties. This chapter deals with field emission study on VS₄-RGO nanocomposite. The promising field emission behaviour exhibited by the VS₄-RGO nanocomposite are attributed to the unique morphology characterized by the sheet edges of few atomic thickness, coupled with the improved electrical properties of the composite. In addition, density functional theory (DFT) calculations have been performed using first principle to show that the enhanced field emission properties of the are due to the overlapping nature of the electronic structure of the VS₄-RGO composite system.

4(b) 2 Experimental:

4(b) 2.1 Synthesis of GO Solution:

GO was synthesized vai modified Hummers’ method using natural graphite powder [7]. In a typical experiment 1 g of K₂S₂O₈ (Sigma Aldrich, ≥99.0%) with 2 g of graphite powder (SP-1, Bay carbon) and 1 g P₂O₅ (Sigma Aldrich, 99.99%) were taken in 8 mL of H₂SO₄ (Merck Chemicals, 98%) and heated at 80°C. A dark-blue mixture was obtained which was allowed to cool to room temperature, followed by stirring for 6hrs. The mixture was then filtered, washed, and dried in vacuum at ambient temperature overnight. Thus obtain preoxidized graphite was then subjected to oxidation by gradually adding 6 g of KMnO₄ (Sigma Aldrich, ≥99.0%) to 46 mL of H₂SO₄ at 0°C. The mixture was then stirred at 35 °C for 2 h, and further 92
mL of distilled water was added. After 15 min, 280 mL of distilled water and 5 mL of H$_2$O$_2$ (SAMCHUN pure chemical, 34.5% extra pure) solution was added to terminate the reaction. A yellow coloured solution was obtained. This mixture was filtered and washed with 500 mL of HCl (SAMCHUN pure chemical, 10 wt %) solution. In order to remove excess HCl, the resulting graphite oxide was suspended in 200 mL of distilled water again, followed by dialysis (dialysis membrane: Spectrum Laboratories, MWCO-12–14,000). The graphite oxide is exfoliated by a high-pressure homogenizer at 15,000 psi. The nonexfoliated graphite oxide was removed by centrifugation at 3500 rpm for 10 min.

**4(b) 2.2 Synthesis of VS$_4$/RGO Hybrids:**

Under the similar experimental conditions, as that for VS$_2$ sheets, RGO was added in different concentration for the synthesis of VS$_4$/RGO hybrids. To the mixture of sodium orthovanadate and thioacetamide, GO solution of 5 mg/mL was added and a total volume of the solution was adjusted to 120 mL for all reactions. The solution was transferred to a 150-mL Teflon-lined stainless steel autoclave, heated up to 160 °C, and kept for 24 h. After cooling naturally, the product was filtered, washed with DI water, and dried in vacuum at 60 °C for 6 h. During the hydrothermal process, VS$_4$ were formed on GO, and GO was transformed to RGO. By adding different volumes of 5 mg/mL GO solution (2.4, 6, 12, 24, 48, and 96 mL), to the mixture of sodium orthovanadate and thioacetamide, VS$_4$/RGO hybrids with different amounts of RGO was obtained. The actual amounts of RGO in the final VS$_4$/RGO hybrids products were estimated from carbon contents (wt %) by elemental analysis: 0.3 wt % for 2.4 mL, 0.75 wt % for 6 mL, 1.5 wt % for 12 mL, 3 wt % for 24 mL, 6 wt % for 48 mL, and 12 wt % for 96 mL of 5 mg/mL GO solution. The final carbon content of the composite was estimated to be ~3 wt%.

The optimized experimental conditions for the synthesis of pure VS$_4$ phase, requires addition of GO (≥60 mg) to a mixture of 1 mM Na$_3$VO$_4$ and 5 mM C$_2$H$_5$NS in a total volume of 120 mL DI water. For amount less than GO ≤30 mg, a mixed phase of VS$_2$ and VS$_4$ was obtained. Thus within the same reaction mixture, the VS$_4$ phase grows only on the GO support, while VS$_2$ phase is formed without any support. With RGO as a template various nanomaterials have been synthesized, where RGO controls the morphology of the nanoform [8-10]. The chemical interactions and bonding between RGO and nanomaterials, helps to control nucleation and growth rate of the nanoform. In the present case chemical composition of the nanoform is changed which is in contrast with the earlier results, where GO helps to control morphology only.
4(b) 3. Results and discussion:

4(b) 3.1 XRD:

Fig. 4(b).1 depicts typical X-Ray diffraction (XRD) pattern of the as-synthesized VS₄-RGO nanocomposite. The appearance of a set of well defined diffraction peaks in the XRD pattern confirms its crystalline nature. All the observed diffraction peaks are indexed to monoclinic VS₄ phase with lattice constants, a= 12.10, b= 10.29, c= 6.78 Å (JCPDS no. 21-1434). The characteristic diffraction peak due to RGO (typically observed at 26°) was not observed in the XRD spectrum. This may be due to the presence of very thin layer of RGO in the composite [5,6]. Furthermore, a small intensity diffraction peak observed around 26° has been indexed to (200) plane of VS₄ phase, thus the characteristic diffraction peak of RGO might have overlap with this peak.

![XRD spectrum](image)

**Figure 4(b).1:** XRD spectrum of the VS₄-RGO nanocomposite

4(b) 3.2. FESEM:

Fig. 4(b).2 shows the field emission scanning electron microscope (FESEM) images of as synthesized few-layered VS₄-RGO nanocomposite. From the FESEM images it is clear that the composite exhibits a large number of protruding edges on the surface. The lateral and longitudinal lengths of the VS₄ sheets lie in the range of 50 to 100 and 100 to 500 nm, respectively. Apparently, the presence of RGO is not identified in the FESEM images of the nanocomposite, and hence for better structural and morphological understanding, TEM and HRTEM characterization was carried out.
Figure 4b.2: FESEM images of the VS$_4$-RGO nanocomposite

4(b) 3.3. TEM and HRTEM:

Further the crystal symmetry was confirmed using TEM and HRTEM shown in Fig. 4(b).3. The TEM image (Fig. 4(b).3(a) shows sheet structure of VS$_4$ embedded along with a thin layer of RGO. The HRTEM image shown in Fig. 4(b).3(b) shows a d-spacing of $\sim$0.56 nm, which corresponds to that of (110) plane of monoclinic VS$_4$ phase and is consistent with the d-values obtained from the XRD analysis. Inset of Figure 4(b).3 (b) is fast Fourier transform of the electron diffraction pattern of a VS$_4$ sheet.
Figure 4(b).3: (a) TEM image of the VS₄-RGO nanocomposite showing presence of both the VS₄ and RGO nanosheets, and (b) HRTEM images showing (110) lattice planes of VS₄. Inset of Fig.4(b).3 (b) is FFT of VS₄.

4(b) 4. DFT calculations:

The work function for a VS₄ surface with reference to vacuum level in the z-direction was estimated using DFT calculations and is found to be 4.67 eV. For VS₄ systems, the in-plane lattice constants were taken as 3.585 Å (a) and 5.514 Å (b). A vacuum level was added in the z-direction to simulate a monolayer. All unit cells were 20.0 Å in the z-direction. The angles (α, β, γ) were set to (90, 100.8, 90) for VS₄. Interestingly, by placing a monolayer of VS₄ on a graphene substrate at a separation of 3Å, the work function was observed to increase by 1eV, estimating resultant value of 5.82eV. Just as in the case of VS₂ on graphene, we find that by moving the VS₄ closer to the graphene substrate so that the interlayer separation is reduced to 2Å, the value of the work function also reduces from 5.82eV to 5.46eV. These results are summarized in Fig. 4(b).4(a, b, c). The bulk orientation of the VS₄ unit cell is shown in Fig. 4(b).4(d).
Figure 4(b.4): (a, b, c) shows the out-of-plane electrostatic potential and work function for VS₄ with and without a graphene substrate. (d) shows the unit cell orientation of bulk VS₄.

4(b) 5. Field emission:

Field emission properties of VS₄-RGO nanocomposite have been investigated at a base pressure of $1 \times 10^{-8}$ mbar. The VS₄-RGO nanocomposite powder was sprinkled over carbon tape, pasted on the copper stub. Fig. 4(b.5) shows J-E and F-N curve of the nanocomposite.
Figure 4(b).5: (a) Applied electrical field vs. field emission current density (J-E) plot and (b) corresponding F-N plot of VS$_4$ emitters.

The J-E curve (Fig. 4(b).5(a)) shows that, as the applied voltage is increased, the emission current increases very rapidly. The values of the turn-on field and threshold field, required to draw emission current density of 1 and 100 μA/cm$^2$ are observed to be ~2.4 and 3.5 V/μm, respectively. Since, the edges of VS$_4$-
RGO nanocomposite are sharper than VS$_2$ nanosheets, it is reasonable that the nanocomposite exhibit lower turn-on field than VS$_2$ nanosheets.

The corresponding F-N plot [a plot of $\ln (J/E^2)$ versus $1/E$] of the emitters is shown in Fig. 4(b). The VS$_4$ sheet field emitter exhibit almost linear F-N plot behaviour over the entire applied field range, indicating metallic behaviour. The field enhancement factor ($\beta$) provides a quantitative idea of the degree of enhancement in the electric field at the emitter edges due to their nanometric dimension. In the present case, $\beta$ is calculated from the slope of the F-N plot, as defined in equation 1

$$\beta = \frac{-6.8 \times 10^3 \phi^{3/2}}{m}$$

where $m$ is slope of F-N plot.

The value of workfunction of the emitter ($\phi$), as estimated from density functional theory (DFT) calculations is 4.67 eV for VS$_4$. The $\beta$ value calculated from equation (1) is found to be 2314 for VS$_4$ field emitters. In addition to the emission competence, stability of the emission current was also checked from the application point of view.

Table 4(b).1 shows the comparative values of applied electric field required to draw emission current densities of 1 µA/cm$^2$, 10 µA/cm$^2$, and 100 µA/cm$^2$, respectively. From the table it is clear that the turn-on field for VS$_4$ are closer to RGO and lower than VS$_2$. This can be attributed to the lower work-function values of VS$_4$ (4.67 eV) as compared to VS$_2$ (6.07 eV). The lower work function facilitates tunneling of electrons at lower applied field. Further, high value of $\beta$ also facilitates availability of large number of emission sites (confirmed from the emission image) and enhances the emission current density from the emission site, at the given applied field.
Table 4(b). 1:

<table>
<thead>
<tr>
<th>Field emitter (For a cathode-anode separation of 1000µm)</th>
<th>Turn on field for emission current density J (1µA/cm²) (V/µm)</th>
<th>Field enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS₂</td>
<td>4</td>
<td>2482</td>
</tr>
<tr>
<td>RGO sheets</td>
<td>2.3</td>
<td>2619</td>
</tr>
<tr>
<td>VS₄-RGO</td>
<td>2.4</td>
<td>2314</td>
</tr>
</tbody>
</table>

The emission current stabilities of the VS₄ emitters was tested at two preset values of 1 and 10 µA/cm² and the corresponding I-t curve is shown in Fig. 4(b).6. It is clearly seen that the VS₄ emitter exhibits excellent current stability at 1 µA, as compared to VS₂. The emitter exhibits excellent emission current stability at pre-set value ~ 1 µA, and the current fluctuations are observed to be within ± 10 % of the average value. The excursions in the emission current followed by stabilization at higher value may be attributed to cleaning of the emitter surface due to residual gas ion bombardment. Since we have used as-prepared emitter, it is expected that in the initial stage of stability measurement, desorption of the adsorbed species from the emitter surface will give more fluctuations (shown in the circle), which eventually die out as the emitter surface becomes cleaner due to residual ion bombardment. Furthermore, the I-t plots are observed to be almost identical after repetitive measurements and no degradation in the emission current is observed. The entire set of field emission measurements have been carried out on another VS₄ emitter and the results are found to be similar in nature.

A typical field emission micrograph recorded at a current density of 100 and 1000 µA/cm² is shown in Fig. 4(b).7. A careful observation of the emission images reveals that the emission image of the VS₄ consists of a large number of tiny bright spots with relatively higher brightness and uniformity, as compared to VS₂. The field emission results imply that the VS₄ emitter exhibits superior emission behaviour in terms of low threshold field, delivery of very high current density at relatively lower applied field and excellent long term emission current stability. All these features propose VS₄ as a promising field emitter candidate for vacuum micro-nanoelectronic devices.
Figure 4(b). 6: Long term field emission current stability at 1 and 10 μA indicating fluctuations in stability due to adsorption and desorption of gas molecules.

Figure 4(b). 7. Field emission micrograph of VS₄ at two different current density
4(b) 6. Conclusion:

- VS$_4$-RGO nanocomposite was synthesized by the same precursors as used for VS$_2$, except an addition of GO, entire process remains same.
- GO serves as a template for the synthesis of VS$_4$ nanosheets, and also gets reduce to RGO.
- The field emission properties of VS$_4$ have been investigated at the base pressure of ~1x10$^{-8}$ mbar. The turn on field required to draw a current density of 10μA/cm$^2$ is found to be 2.93 V/μm for VS$_4$, which is remarkably lower than VS$_2$.
- Enhanced field emission behavior is observed for VS$_4$ due to low workfunction and high field enhancement factor associated with surface protrusions.
- In addition, the DFT results show that the enhanced field emission may be compounded by the overlapping electronic structures of VS$_2$ and VS$_4$. Owing to the low turn on field and planar (sheet-like) structure morphology, the VS$_4$ emitter can be utilized for new generation vacuum microelectronics/nanoelectronics and flat panel display applications.
References


