Polarity Independent Resistive Switching in MoS₂ Nanosheets and PEO based Nanocomposite Films

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To,

Prof. Safa Kasap

The Editor-in-Chief

Journal of Materials Science: Materials In electronics

Sub: Submission of the original manuscript.

Dear Professor,

Please find herewith our manuscript entitled “**Polarity independent resistive switching in MoS₂ nanosheets and PEO based nanocomposite films**” for the possible publication in *Journal of Materials Science: Materials In Electronics*. I would like to declare on behalf of my co-authors that this manuscript is original, unpublished and not being considered for publication elsewhere.

In this work, we reported the preparation of MoS₂ nanosheets by liquid phase exfoliation method and investigated the resistive switching memory characteristics in poly (ethylene oxide) (PEO) and MoS₂ nanosheets based nanocomposite films. We observed nonpolar or polarity independent resistive switching in the nanocomposite films. Though MoS₂ nanosheets based two-terminal devices are known to show nonpolar resistive switching, we are reporting the same for the first time in MoS₂ based nanocomposite films. During both the bipolar and unipolar operations, the biasing direction is observed to control the current conduction mechanism which is further elaborated in the manuscript.

We are looking forward to the reviewing process for further improvement, if any, in our manuscript and possible publication.

Thanking you in advance.

Sincerely,

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Declarations

I declare on behalf of my co-authors that this manuscript is original, unpublished and not being considered for publication elsewhere.

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Polarity independent resistive switching in MoS₂ nanosheets and PEO based nanocomposite films

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Abstract:

Here, we report the exfoliation of bulk MoS₂ (molybdenum disulfide) into few layer nanosheets and then prepared nano-composite films with poly (ethylene oxide) (MoS₂-PEO). We observed non-polar or polarity independent bistable resistive switching memory in two-terminal devices with Indium tin oxide (ITO) and aluminum (Al) as bottom and top electrode. In both bipolar and unipolar operations, it is observed that the biasing direction controls the current conduction mechanism. When positive bias is applied at the top Al electrode, the low resistance state (LRS) conduction is Ohmic type. But in opposite biasing condition, LRS conduction is space charge controlled. The current-voltage characteristics of the bipolar and unipolar switching are distinctly different in terms of their RESET process. In bipolar, the RESET process is very sharp whereas in unipolar operation it is staggered and step-wise.

Keywords:

Liquid phase exfoliation, MoS₂ nanosheets, polymer nano-composites, non-polar resistive switching.

1. Introduction

Recently, MoS₂ in its two dimensional (2D) form as monolayer or as few-layer nanoplatelets has drawn considerable interest for many nanoelectronic applications including areas like resistive switching memory, transient electronics, bioelectronics etc [1,2]. Specifically, its resistive switching characteristics are quite diverse owing to its unique properties such as tunable band gap and charge confinement effects. There are reports suggesting that MoS₂ nanoflakes showing both bipolar and unipolar resistive switching memory characteristics in the same device [1 and 3]. Moreover, MoS₂ also with different device architectures can show typical memristive switching and neuromorphic computing operations [4 and 5]. To further advance the application potential in the field of flexible and wearable electronics, two-dimensional MoS₂ nanosheets are lately investigated in nanocomposite films with different polymer hosts. MoS₂ nanoflakes in polymer hosts like PVA, PMMA and PVP are mostly showing bipolar resistive switching and WORM type memory operations [6-8]. The switching mechanism could be redox or charge-trapping type. However, unlike the case of bare MoS₂, there are no reports of observing both unipolar and bipolar resistive switching in the polymeric nanocomposites of MoS₂ nanosheets. Resistive switching devices showing both unipolar and bipolar resistive switching properties are known as polarity independent or nonpolar resistive switching devices. The nonpolar resistive switching devices offer the advantage of flexibility in peripheral circuit design and high storage density in comparison to the conventional bipolar resistive switching memories [9]. Here, in this work we are reporting the observation of nonpolar resistive switching memory in MoS₂ nanosheets based poly (ethylene oxide) (PEO) composites.

2. Experimental Details

The bulk MoS₂ powders and Poly (ethylene oxide) ($M_w \sim 100,000$) were purchased from Alfa Aesar and Sigma-Aldrich. Dimethylformamide (DMF) was used as solvent for liquid phase exfoliation of MoS₂ due to good wettability and miscibility of MoS₂ in DMF [10] and was bought from Merck. ITO (indium tin oxide) coated PET (polyethylene terephthalate) substrate was purchased from Sigma-Aldrich. According to the reports given for good yield of MoS₂, we followed grinding assisted liquid phase exfoliation [11]. Following liquid phase exfoliation method, MoS₂ nanosheets were prepared from the bulk MoS₂ in DMF medium. The detail experimental procedure was already reported in our previous work [12]. The exfoliation of MoS₂ into few layer nanosheets was confirmed from atomic force microscopy and the average layer thickness of MoS₂ nanosheets is 5 nm. The composite solution of MoS₂ nanosheets and PEO are deposited on to ITO coated PET substrate by spin coating method. We studied the current-voltage characteristics in MoS₂-PEO nanocomposite films with device structure as ITO/MoS₂-PEO/Al where Al works as the top electrode.

2.1. Preparation of MoS₂ and PEO nanocomposites

To prepare nanocomposite films with PEO, initially 600 mg of PEO was added to 10 ml of DMF and stirred at 60°C for 2 hours in a magnetic stirrer. Then 1 wt. % of exfoliated MoS₂ was added to the solution of PEO and stirred for 12 hours at 300 rpm to get a homogeneous mixture. The nanocomposite films were prepared by solution cast method. They were dried at 50°C on a hot plate followed by evacuation at 40°C for 6 hours. To observe current-voltage characteristics in the composite films, two terminal devices were prepared on ITO coated PET substrate. The solutions of MoS₂ nanosheets and PEO in DMF were deposited by spin-coating on ITO surface at 4000 rpm for 1 min. The prepared films were then dried at 50°C for 6 hours in a vacuum furnace followed by deposition of top aluminum electrode having diameter (~100 µm) by using thermal evaporation technique using a stainless steel shadow mask.

3. Results and Discussions

3.1. Structural characterization

Fig. 1 presents the X-ray diffraction (XRD) pattern of prepared nanocomposite film made up of MoS₂ nanosheets dispersed in the PEO host. Bragg peaks corresponding to both 2H-MoS₂ and PEO are observed in the XRD pattern. The diffraction peaks at 14.8°, 32.65°, 36.1°, 39.8° and 44.6° are assigned to (002), (100), (012), (103) and (006) planes of MoS₂ respectively [8,13]. The (120), (112) and (222) peaks of PEO are observed at 19.05°, 23.2° and 26.4° [14, 15] respectively indicated by (*) mark. Further, we separately investigated the (002) peak of MoS₂. The average crystallite size was calculated to be ≈ 8 nm by using Debye-Scherrer formula.

3.2. Film morphology

The surface morphology of the nanocomposite film was investigated using optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Fig. 2(a) shows that the PEO and MoS₂ nanosheets grown into spherulites with lots of interfacial amorphous region. A magnified spherulite is presented in the inset showing radial lamellar structures. Further, the SEM image in Fig. 2(b) clearly shows the lamellar structures with emergence of some micropores or free volume along the growth direction of lamella.

AFM images of exfoliated MoS₂ and MoS₂-PEO nano-composite films are shown in Fig. 2 (c) and (d). For AFM, exfoliated MoS₂ nanosheets in the solution form were drop casted on to a glass substrate. During the drying stage, MoS₂ nanosheets agglomerate to form bigger particles. Hence, from the height profile of the AFM images, layer thickness is calculated. We observed that the average layer thickness of MoS₂ nanosheets is ~ 5 nm. The surface roughness of the MoS₂ nanosheets dispersed PEO nanocomposite film is shown in Fig. 2. (d). The average roughness is ~ 15 nm with some big spike in heights due to some MoS₂ agglomerates present on the surface.

3.3. Thermal analysis

Fig. 3 shows differential scanning calorimetry (DSC) curves of PEO and PEO-MoS₂ nanosheets composite films during the heating process 0 to 100°C. The DSC curve show crystalline melting temperature (T_m) of PEO and PEO-MoS₂ films at around 67.8°C and 67.2°C respectively. The melting enthalpy (ΔH_m) is evaluated by considering the area under the melting peak. The melting enthalpy (ΔH_m) can be related to crystallinity fraction in the films by comparing it with that of the 100% crystalline PEO film by using the equation as:

$$\chi_c = \left(\frac{\Delta H_m}{\Delta H_m^o} \right) \times 100$$

Where ΔH_m is the melting enthalpy measured in the experiment, $\Delta H_m^o = 203$ J/g which is the melting enthalpy of 100% crystalline PEO [16, 17]. It is observed that the percentage of crystallinity fraction (χ_c %) has increased significantly up to 59.34 % in PEO-MoS₂ films in comparison to 17.34 % as that of calculated for pure films. This suggests that the MoS₂ nanosheets have influence on the crystallization kinetics of the PEO. The exact nature of the influence depends upon two competing phenomena namely nucleation to spur crystallization and confinement effect to hinder it. There are reports that nanostructured materials like carbon nanotube and MXene at lower loading aids crystallization process [18, 19]. Hence, we suppose 1 wt.% of MoS₂ nanosheets in the PEO matrix improves the crystallinity fraction.

3.4. Electrical characterization

The current-voltage characteristics of the two terminal devices prepared as the sandwich structure of Al/MoS₂-PEO/ITO are shown in Fig. 4. Both bipolar and unipolar resistive switching was observed. In the positive bipolar resistive switching (BRS) mode, the memory cell was initially in the high resistance state (HRS) (OFF state). As we swept the voltage from 0 to 4 V, an abrupt increase in current was observed at a voltage of ~ 3.44 V where the current is limited by the compliance of 0.1 mA, switching the memory cell into low resistance state (LRS) (ON state). This is known as SET/WRITE process. Again as we swept the voltage from 0 to -3 V, a drastic decrease in current was observed at ~ -2.04 V. This completes the cycle of switching back to the HRS (OFF state) and the process is known as RESET/ERASE. At a compliance current of 0.01 mA by changing the voltage polarity of SET/RESET process, similar switching behavior was observed in case of negative BRS mode where the memory cell was SET at ~ -2.7 V and RESET at ~ 1.6 V while sweeping the voltage from 0 to -4 V and 0 to 2 V respectively as shown in Fig. 3 (b). In case of positive unipolar resistive switching (URS) mode, while sweeping the voltage from 0 to 3 V, the memory cell was switched from HRS to LRS at a voltage of ~ 2.76 V and the compliance current (CC) was fixed at 0.1 mA. Now to RESET the memory cell, same voltage sweep was applied and the cell was switched from LRS to HRS at a voltage of ~ 1.02 V. Similar RS characteristics was observed in case of negative URS mode by applying negative voltage sweep where the CC was fixed at 0.01 mA and the memory cell was SET at ~ -3.3 V and RESET at ~ -0.94 V.

A comparison between bipolar and unipolar operations in the cells suggests that the SET process in both the cases is sharp and observed mostly at $|V_{\text{SET}}| \sim 3$ volts. In contrast, the RESET voltages in both the operations are quite different. While for both the bipolar operations in Fig 4. (a) and (b), the $|V_{\text{RESET}}| \sim 2$ volts, in unipolar switching the $|V_{\text{RESET}}|$ varies in a range of 1 to 3 volts. Moreover, RESET process in bipolar and unipolar operations are strikingly different. The RESET or ERASE process is very sharp in the bipolar switching whereas it is staggered and step-wise in the case of unipolar.

To further understand the switching mechanism, the I-V characteristics for bipolar and unipolar operations are replotted in Fig. 5 and 6 in log-log scale. The Fig. 5 (a) shows the SET process of bipolar operation. The slope of the I-V curve observed to rise in three steps with slope rising from 2.24 to 3.77 and then the cell reaches the LRS. The slope value more than 2 confirms that the conduction mechanism during the SET process is due to trap-controlled space charge limited current (TC-SCLC) [20]. In the LRS the slope is ~ 1 indicating ohmic type conduction in LRS. The inset shows the linear relationship between $\ln(I)$ and $V^{0.5}$ in the region between 0.04 V to 0.12 V. This suggests that the electrons are injected at the Aluminium-composite film interface by Schottky emission [20].

During the RESET process, the log-log plot of the I-V characteristic is depicted in Fig. 5. (b). Starting from 0 volt up to the RESET voltage (2.2 V) the slope remains one due to the ohmic conduction process. As the RESET occurs at 2.2 V, the maximum slope observed is 1.29 indicating the de-trapping process of electrons from the trap sites of the composite films. For the bipolar switching operation where SET is observed in negative bias as shown in Fig. 5 (c), the HRS current is again TC-SCLC. But the LRS current is not the ohmic like the previous case. The LRS slope decreases gradually from 2.36 to 1.56 and hence, indicating SCLC [21]. This is the major difference between these two bipolar operations. The log-log plot of the unipolar operation along the both the polarities are presented in Fig. 6. The operation done in the positive bias side as shown in Fig 6 (a) and (b) show HRS and LRS currents are governed by TC-SCLC and ohmic mechanism. Whereas in the negative bias side shown in Fig 6 (c) and (d), the LRS is non-ohmic rather governed by SCLC mechanism similar to the bipolar operation with SET process observed in negative bias side. So, we infer that in both bipolar and unipolar operations, the LRS conduction mechanism is either ohmic or SCLC type depending solely on the biasing direction. This may be due to the asymmetric electrode combinations used in the memory cells. The top aluminium electrode is oxidizable

and can diffuse through as ions when positive bias is applied during either of the bipolar or unipolar operations. Hence, when a SET process is completed or an ON state is achieved by applying positive bias to the top Al electrode, conductive bridge may be formed assisted by electron trapping at MoS₂ sites as well as by electrochemical reduction of Al at ITO electrode. But when the ON state is achieved by reversing the bias or by applying positive bias to ITO side, may be exclusively an electronic effect governed by electron trapping at MoS₂ sites present in the PEO matrix. However, these inferences need further corroboration from other experimental observations. Nevertheless, the MoS₂ nanosheets and PEO composite films offer the tunability in resistive switching memory operations. A better understanding of its switching mechanism will pave the way for more control on switching operations and its parameters.

4. Conclusions

Exfoliated MoS₂ (molybdenum disulfide) nano-sheets were prepared by grinding assisted liquid phase exfoliation method and was made composite with PEO. The nanocomposite thin films show versatile switching operations. Nonvolatile memory is observed with both bipolar and unipolar mode with different biasing directions. This suggests a polarity independent or non-polar resistive switching memory operation achieved in Al/MoS₂-PEO/ITO memory cells. During the switching cycles, the current in HRS is governed by TC-SCLC irrespective of mode of operation (bipolar or unipolar) or biasing direction. But the current in LRS is either ohmic or space charge limited controlled mainly by biasing directions. During bipolar operation, the RESET process is very sharp but in unipolar operation it is a step-wise staggered process.

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References

- [1] R. Ge, X. Wu, M. Kim, J. Shi, S. Sonde, L. Tao, Y. Zhang, J. C. Lee, D. Akinwande, Nano Lett. 18, 434 (2018). <https://doi.org/10.1021/acs.nanolett.7b04342>
- [2] X. Chen, Y. J. Park, M. Kang, S. K. Kang, J. Koo, S. M. Shinde, J. Shin, S. Jeon, G. Park, Y. Yan, M. R. MacEwan, W. Z. Ray, K. M. Lee, J. A. Rogers, J. H. Ahn, Nature Communications 9, 1 (2018). <https://doi.org/10.1038/s41467-018-03956-9>
- [3] X. Zhao, Z. Fan, H. Xu, Z. Wang, J. Xu, J. Ma, Y. Liu, J. Mater. Chem. C 6, 7195 (2018). <https://doi.org/10.1039/C8TC01844H>
- [4] A. A. Bessonov, M. N. Kirikova, D. I. Petukhov, M. Allen, T. Ryhanen, M. J. A. Bailey, Nature Mater. 14, 199 (2015). <https://doi.org/10.1038/nmat4135>
- [5] T. Paul, T. Ahmed, K. K. Tiwari, C. S. Thakur, A. Ghosh, 2D Mater. 6 045008 (2019). <https://doi.org/10.1088/2053-1583/ab23ba>
- [6] M. M. Rehman, G. U. Siddiqui, J. Z. Gul, S. W. Kim, J. H. Lim, K. H. Choi, Scientific Reports 6, 1 (2016). <https://doi.org/10.1038/srep36195>
- [7] S. Bhattacharjee, U. Das, P. K. Sarkar, A. Roy, Organic Electronics 58, 145 (2018). <https://doi.org/10.1016/j.orgel.2018.03.039>
- [8] Z. Wu, T. Wang, C. Sun, P. Liu, B. Xia, J. Zhang, Y. Liu, D. Gao, AIP Advances 7, 125213 (2017). <https://doi.org/10.1063/1.4994227>
- [9] P. Zhuang, W. Lin, J. Ahn, M. Catalano, H. Chou, A. Roy, M. Q. Lopez, L. Colombo, W. Cai, S. K. Banerjee, Adv. Electron. Mater., 1900979 (2019). <https://doi.org/10.1002/aclm.201900979>
- [10] J. Shen, Y. He, J. Wu, C. Gao, K. Keyshar, X. Zhang, Y. Yang, M. Ye, R. Vajtai, J. Lou, P. M. Ajayan, Nano Lett. 15, 5449 (2015). <https://doi.org/10.1021/acs.nanolett.5b01842>
- [11] E. P. Nguyen, B. J. Carey, T. Daeneke, J. Z. Ou, K. Latham, S. Zhuiykov, K. K. Zadeh, Chem. Mater. 27, 53 (2015). <https://doi.org/10.1021/cm502915f>
- [12] P. Pathak, R. Deb, S. R. Mohapatra, Materials Today: Proceedings 24, 2295 (2020). <https://doi.org/10.1016/j.matpr.2020.03.758>
- [13] T. Almaro, M. K. Ram, Electrochimica Acta 235, 623 (2017). <https://doi.org/10.1016/j.electacta.2017.03.102>
- [14] K. K. Kumar, M. Ravi, Y. Pavani, S. Bhavani, A. K. Sharma, V. V. R. N. Rao, J. Membrane Science 454, 200 (2014). <https://doi.org/10.1016/j.memsci.2013.12.022>
- [15] A. Azli, N. S. A. Manan, M. F. Z. Kadir, Advances in Materials Science and Engineering 2015, 1 (2015). <https://doi.org/10.1155/2015/145735>

- [16] J. Gurusiddappa, W. Madhuri, R. P. Suvarna, K. P. Dasan, Materials Today: Proceedings 3, 1451 (2016). <https://doi.org/10.1016/j.matpr.2016.04.028>
- [17] M. I. D. Rosero, N. M. J. Meneses, R. U. Kaffure, Materials 12, 1464 (2019). <https://doi.org/10.3390/ma12091464>
- [18] L. Li, C. Y. Li, C. Ni, L. Rong, B. Hsiao, Polymer 48, 3452 (2007). <https://doi.org/10.1016/j.polymer.2007.04.030>
- [19] Z. Huang, S. Wang, S. Kota, Q. Pan, M. W. Barsoum, C. Y. Li, Polymer 102, 119 (2016). <https://doi.org/10.1016/j.polymer.2016.09.011>
- [20] J. Song, H. Han, B. Peng, Y. Hu, Q. Cui, Z. Lou, Y. Hou, F. Teng, RSC Adv. 7, 54128 (2017). DOI: 10.1039/C7RA11879A
- [21] Y. Cui, H. Peng, S. Wu, R. Wang, T. Wu, ACS Appl. Mater. Interfaces 5, 1213 (2013). <https://doi.org/10.1021/am301769f>

Fig. 1 XRD pattern of MoS₂ doped PEO nanocomposite

Fig. 2 (a) Optical Microscopy and (b) SEM images of MoS₂-PEO composite film; (c) and (d) AFM of exfoliated MoS₂ and MoS₂ doped PEO nanocomposite films respectively.

Fig. 3 DSC thermograph of PEO and PEO-MoS₂ composite.

Fig. 4 (a) and (b) bipolar (SET-RESET in the positive-negative and negative-positive voltage polarities respectively) and (c) and (d) unipolar (SET-RESET in the positive and negative voltage polarities). The inset in (d) shows the schematic diagram of the two-terminal devices.

Fig. 5 Linear fitting for the I - V curve for the (a) SET and (b) RESET process using log-log plot of bipolar switching. The insets in the (a) and (c) show the plot of the $\ln(I)$ vs. $\sqrt{V}$ in a small range of bias, when the voltage scan just started.

Fig. 6 Linear fitting for the I - V curve for the (a) SET and (b) RESET process using log-log plot of unipolar switching. The insets in the (a) and (c) show the plot of the $\ln(I)$ vs. $\sqrt{V}$ in a small range of bias, when the voltage scan just started.

Figures

Figure 1

XRD pattern of MoS₂ doped PEO nanocomposite

Figure 2

(a) Optical Microscopy and (b) SEM images of MoS₂-PEO composite film; (c) and (d) AFM of exfoliated MoS₂ doped PEO nanocomposite films respectively.

Figure 3

DSC thermograph of PEO and PEO-MoS₂ composite.

Figure 4

(a) and (b) bipolar (SET-RESET in the positive and (c) and (d) unipolar (SET-RESET in the positive and negative voltage polarities. The inset in positive-negative and negative-positive voltage polarities respectively) (d) shows the schematic diagram of the two-terminal devices.

Figure 5

Linear fitting for the I-V curve for the (a) SET and (b) RESET process using log-log plot of bipolar switching. The insets in the (a) and (c) show the plot of $\ln(I)$ vs. $\sqrt{V}$ in a small range of bias, when the voltage scan just started.

Figure 6

Linear fitting for the I-V curve for the (a) SET and (b) RESET process using log-log plot of unipolar switching. The insets in the (a) and (c) show the plot of the $\ln(I)$ vs. $\sqrt{V}$ in a small range of bias, when the voltage scan just started.