Path Way For Electrical Conduction In ZnO Based ternary Nanocomposite Room Temperature Ethanol Sensors

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PATH WAY FOR ELECTRICAL CONDUCTION IN ZnO BASED TERNARY NANOCOMPOSITE ROOM TEMPERATURE ETHANOL SENSORS

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Abstract

In the present investigations, the samples such as zinc oxide, tin oxide, vanadium oxide and their ternary combinations prepared by hydrothermal route were characterised using the state-of-the-art facilities and were systematically analysed. The interface properties between the grain and grain boundaries of these oxides were studied using Conductive atomic force microscopic (CAFM) studies. From the detailed investigations on topography and I-V characteristics, it is revealed that, zinc-tin-vanadium oxide nanocomposite with smaller barrier height of 0.189 eV exhibited pronounced response magnitude of 98.96 % at a faster rate of 32 s at room temperature. The outstanding ethanol sensing property of the ternary nanocomposite is attributed to the hierarchical morphology with large surface area, the formation of heterojunction at the interface, tuning the schottky barrier height, depletion layer manipulation and the electronic effects.

Keywords: ternary nanocomposite; CAFM; barrier height; ethanol; room temperature

1. Introduction

Continued attention on metal oxide semiconductors (MOS) such as; ZnO [1], In₂O₃ [2], SnO₂ [3], MoO₃ [4], V₂O₅[5] and WO₃[6] nanostructures of different shapes and sizes reveals optimistic properties for application in short wavelength optoelectronic devices and sensors [7]. Research on MOS is also highly inspired by various desirable traits such as improved sensitivity [8], enhanced adsorption ability [9], extensive catalytic activity [10] and high thermodynamic stability [11] towards the analyte gases. Yet obtaining all of these characteristics using a single metal oxide has proved to be difficult. However, reports are available on coupling these different MOS in appropriate proportion to form heterostructures. These heterostructure nanocomposites favours enhanced functional properties compared to their individual metal oxide counterparts in

sensing gases like LPG, NO₂, H₂, NH₃ and so on[12]. This might be due to the formation of junctions at the interface of the heterostructure and thereby shortening the electron transport distance [13-17]. The synergistic effect of these nanocomposites has paved the platform to explore them as novel materials as high performance gas sensors.

Among various volatile gases, ethanol is used in various fields such as chemical industry, medicine and food industry [11, 18]. Ethanol being a hypnotic gas causes severe harmful effect on environment due to its toxic nature. Hence, monitoring and controlling the production of ethanol and their usage in industries and laboratories, there is a need to deploy sensors integrated with electronic systems to avoid accidents as well as health risks [19]. Among various MOS, loosely arranged zinc oxide (ZnO)nanorods of flat end shape [20], tin oxide (SnO₂) nanoparticles [21] and elongated nanostructured vanadium oxide (V₂O₅) [22] have been identified as room temperature ethanol sensors. ZnO and SnO₂with reduced dimensions provide more active sites for the adsorption of gases [23] and V₂O₅, due to its high work function with semiconducting properties shows charge recombination [24], generation and transportation in many device applications. Stable sensing performance towards ethanol at room temperature could be improved by hybrid nanostructures [25]. There occurs Fermi-level mediated charge transfer effects and synergistic behavior of different components which could contribute for the enhanced ethanol sensing at room temperature. The mechanism behind the sensing of ethanol by heterojunction nanocomposites is: the depletion layer could be further depleted by the adsorption of oxygen gas onto the surface, which contracts the conduction channel by extracting electrons from the conduction band of the semiconductor and enhances the response towards the analytes [26]. The semiconductor with a lower Fermi energy acts as a metal in a Schottky junction. At that point, introducing foreign analytes at the heterointerface could alter the conductivity in

various ways depending on the types of analyte and heterointerface [15]. The addition of a second constituent will undoubtedly change the resistance just by a rule-of-mixtures such that adding a more conductive material will increase the conductivity. Literature reports on, binary and ternary nanocomposite using these mentioned individual oxides and their investigations on band bending are available [15, 27].

To explore further, the interface properties between zinc oxide, tin oxide and vanadium oxide and to analyse the path way conduction mechanism in the ternary nanocomposite, conductive atomic force microscopy (CAFM) has been employed. Therefore, in this present work, for the first time, ZnO, SnO₂ and V₂O₅ were investigated for the topography and local conducting property using conducting atomic force microscopy. The conduction mechanism in ethanol sensing with respect to the potential barrier height established between the interface layers of the prepared samples are thoroughly investigated.

2. Experimental details

Analytical grade (AR) chemicals were used for the experiment and were used as such without further purification. Initially, 0.1 M aqueous solution of zinc chloride (ZnCl₂) was taken and stirred well. During constant stirring, 0.1 M glyoxalic acid was added. Then, ammonium hydroxide was added dropwise and the pH was adjusted to 9 under stirring. The gel was obtained and it has been transferred into an autoclave and was kept in an oven at 160°C for 3 h. Aerogel obtained was collected and it is washed with absolute ethanol and deionized water. The powders obtained were dried in air and calcined at 600 °C and named as ZnO. Similarly, SnO₂ and V₂O₅ were obtained by changing the suitable precursors as tin chloride (SnCl₂.2H₂O) and vanadium chloride (VCl₃) respectively. The same protocol is followed to obtain the binary and ternary combination of these individual oxides by taking equimolar mixture of the corresponding

precursors and the final samples obtained were named as ZT (zinc - tin nanocomposite), ZV (zinc - vanadium nanocomposite), TV (tin - vanadium nanocomposite) and ZTV (zinc - tin - vanadium nanocomposite) and the stepwise procedure is given in Fig. 1.

Fig. 1: Preparation of zinc-tin-vanadium oxide (ZTV) nanocomposite using hydrothermal method

3. Characterization Techniques

The structural property of all the samples was analysed by recording X-ray Diffraction pattern using PANalytical X'Pert PRO diffractometer. The morphology of the samples was obtained from ZEISS ultra-field emission scanning electron microscopy (FESEM). Brunauer–Emmett–Teller (BET) based on the nitrogen adsorption–desorption isotherm is used for determining the specific surface area and size of the pores for all the samples. To analyse the compositional differences in the electrically conducting and non-conducting oxides, imaging of all the samples were performed using Scanning Probe Microscopy (SPM, NTEGRA NT-MDT Russia).

Topography and current maps were obtained in contact mode using a conducting cantilever (force constant of 2.5 N/m and radius of curvature 25 nm with a PtIr coated tip).

4. Results and Discussion

4.1 Structural studies

All the samples were subjected to X-ray Diffraction and the patterns have already been reported [13]. The peaks obtained in the X-ray diffraction pattern of the individual oxides were indexed and compared with the standard ICDD File of ZnO (36-1451), SnO₂(41-1445)and V₂O₅ (41-1426) respectively. The weak intensity for the peaks of both SnO₂ and V₂O₅ indicated the poor crystallinity of the samples. Similarly, XRD pattern of ZT corresponds to ZnO, SnO₂ and Zn₂SnO₄ (ICDD, 24-1470) and ZV identifies ZnV₂O₆ (ICDD No: 23-0757) and ZnV₃O₈ (ICDD No: 71-0731) phases along with hexagonal wurtzite ZnO and orthorhombic V₂O₅ structures. The peaks obtained for TV nanocomposite matches with tetragonal rutile structured SnO₂ and orthorhombic structured V₂O₅. In a similar fashion, we observe distinct peaks of SnO₂, ZnV₂O₆, ZnV₃O₈ and Zn₂SnO₄from our ZTV sample.

4.2 Morphological Studies

Figure 2(a)-(c) depicts the FE-SEM images of ZnO, SnO₂ and V₂O₅ nano morphology respectively. ZnO nanorods have a length of 380 nm and a 95 nm diameter with hexagonal facets (70 nm).The SnO₂ is formed as nanoparticles with uniform grain size of around 50 nm and V₂O₅ revealed micro flakes with grain boundaries between and 5 nm sized uniform nanoparticles were distributed over the flakes. Spectral analysis form EDAX spectra are available in supplementary documents to reveal no trace of impurities and confirmed the phase purity of as prepared nano particles. The nanorods, nanoparticles and flakes with surface area of 123.9 m²/g, 118.8 m²/g and 116.5 m²/g respectively [13] could have the ability to provide more surface active sites to

enhance the adsorption of ethanol molecules over the surface so as to increase the sensitivity in our earlier studies. The nitrogen adsorption-desorption isotherm obtained for all the samples exhibited type IV with type H3 hysteresis loop for the relative pressure P/P_0 in the range of 0.1 – 1 which indicated the presence of mesoporous structure [13]. Among the three samples, ZnO nanorods possessed large surface area compared to SnO_2 and V_2O_5 and the pore size of about 11.8 nm confirms the mesoporous nature of these samples [13].

Fig. 2: FE-SEM image of (a) ZnO nanorods, (b) SnO_2 nanoparticles and (c) V_2O_5 fine nanoparticles (d) ZT reduced nanorods (e) ZV rough surfaced nanorods and (f) TV nanoparticles

FE-SEM image of the ZT composite in Fig. 2(d) depicted both the smaller spherical and larger hexagonal structured nanoparticles clouded among the irregular nanorods. The nanorods in the matrix of the nanoparticles could increase the surface area and it might provide more surface active sites ($156.7\text{m}^2/\text{g}$) for the adsorption of gas molecules. Unlike the smooth surface of ZnO

nanorods (observed in ZnO phase), in ZV composite as in Fig.2(e), V_2O_5 nanoparticles got attached over the nanorods resulting in surface irregularity leading to the specific surface area of ($151.6 \text{ m}^2/\text{g}$). In the vanadium loaded tin oxide as in Fig. 2(f), the reduction in the grain size of SnO_2 may be due to the presence of V_2O_5 and resulted in surface area of ($128.5 \text{ m}^2/\text{g}$). EDAX spectra of the three binary oxides are available in supplementary. The adsorption – desorption isotherm of ZT, ZV and TV exhibited the type IV – H3 hysteresis loop and from the pore size distribution plot the existence of mesoporous structure was identified in all the samples. From the Table 1, it was noted that ZT possessed larger surface area compared to ZV and TV nanocomposite.

Morphology	Sample	Specific surface area (m^2/g)	Avg. pore size (nm)
Nanorods	ZnO	123.9	11.8
	ZT	156.7	11.8
	ZV	151.6	11.8
Nanoparticles	SnO_2	118.8	11.8
	V_2O_5	116.5	11.8
	TV	126.5	11.8
Flower like microstructures and spherical nanoparticles	ZTV	167.3	8.3

Table 1: Morphological impact on the specific surface area and pore size values of the samples

FE-SEM image of the nanocomposite ZTV exhibited hierarchical flower like microstructure with enormous petals and minute pores (Fig. 3 (a and b)). The flower like microstructure is composed of nanoflakes extending axially from the center. The respective EDAX analysis (Table. 2) on the individual flake indicated the presence of excess amount of Zn than Sn and V [13]. In addition, the composite also exhibited spherical nanoparticles with 11 nm diameter in which excess Sn is

identified from its elemental composition. The ternary oxide also exhibited type IV-H3 hysteresis loop as in Fig.3(c). Further, the pore size distribution plot (Fig. 3 (d)) revealed the existence of maximum number of pores with less than 10 nm diameter. The surface area and average pore size determined from BET and BJH for ZTV were 165.7 m²/g and 8.3 nm respectively

Fig. 3: (a)-(c) FE-SEM image and (d) N₂ adsorption – desorption isotherm and (e) Pore size distribution plot of ZTV

Element (%. at.)	O K	V K	Zn K	Sn L
Surface of the flake	65.00	11.72	13.86	9.41
Surface of the spherical particles	76.33	7.13	7.46	9.09

Table 2: Elemental distribution

Among the detailed analysis, it is revealed that the elongated nanostructures [15] especially ZTV exhibits the largest surface area with pore size of 8.3 nm. This could attribute to the best sensing performance experienced by ZTV towards ethanol at a faster rate even at room temperature.

4.3 Gas sensing analysis

The prepared samples were tested for ethanol sensing property at room temperature using the gas sensing apparatus [13]. The sensitivity was calculated for all the samples using the formula in equation (1) -

$$\text{Sensitivity} = \frac{|R_{\text{air}} - R_{\text{ethanol}}|}{R_{\text{air}}} \times 100 \quad \dots(1)$$

which is described as the ratio of the modulus of magnitude of change in resistance upon exposure to ethanol vapour to that of in air without vapour. The response time and recovery time was is defined as the time needed to reach 90% and 10% of the base line resistance after the injection and removal of ethanol respectively.

From the detailed analysis, it has been observed that the sensitivity of ZTV is considerably better than the individual oxides at a faster adsorption - desorption rate. This might be due to the large surface area and the synergistic effect. Moreover, the gas sensing mechanism [3] for n-type semiconductor nanocomposites can be explained based on the change in resistance which is

caused by the adsorption and desorption of gas molecules over the surface of the sensing layer. When the oxides are surrounded by air, oxygen molecules will get adsorbed on the surface and hence it generates chemisorbed oxygen species by capturing electrons from the conduction band of the nanocomposites. Hence, depletion region will be formed on the surface of the nanocomposite which in turn results in the increase of sensor resistance. The oxygen adsorption reaction kinematics could be described in the following equations [3, 7] -

Later, when the nanocomposite ZTV is subjected to the exposure of ethanol at room temperature, the vapor molecules will react with the adsorbed oxygen species and form CO_2 and H_2O . This in turn promotes the re-injection of the trapped electrons back to the depletion layer. Therefore, the width of the depletion layer gets decreased and so the sensor resistance gets decreased further. Fig. 4(a), (b) and (c) shows the reaction mechanism of individual ZnO nanorods, SnO_2 nanoparticles and V_2O_5 nanoflakes. The net reaction mechanism between

ethanol and ionic oxygen species can be written as -

Fig. 4: Ethanol sensing mechanism in individual oxides (a) ZnO, (b) SnO₂ and (c) V₂O₅

4.4 AFM analysis and Electrical Conductivity Studies

The information about the topographical and the nano scale properties of all the samples were provided by the C-AFM technique [17]. The current flow between the conductive tip and sample is carried out initially. The cantilever deflection is monitored further as the tip scans over the surface. Topography images of all the samples were recorded to provide more information about the structural peculiarities. The conductive tip of a nanoprobe is used to provide the I-V measurements of the selected region of the samples.

4.4.1 Individual oxides

Topography image of ZnO in Fig. 5 (a) shows nanorods clustered as bundles with length 1 μm and diameter less than 100 nm. From the CAFM image, the non polar faces are found to be more conducting and there are no visible grain boundaries from the topographic image of ZnO. The current maps are simultaneously recorded as in Fig. 5(d) along with the topography using C-AFM for a bias voltage of 1 V. Current image of ZnO shows similar feature of the topographic image. Based on the bias voltage, bright and dark regions appeared in the current image as in Fig. 5(g) corresponding to the high and less conductive current zones respectively. The maximum current value observed is around 60 pA. Uniform conductance has been occurred on

the edges of the nanorods [18]. The corresponding height profile of ZnO with respect to the position of the probe on ZnO surface is depicted in Fig. 5(g).

Fig. 5: (a) – (c) AFM image of ZnO, SnO₂ and V₂O₅, (d) – (f) Current maps of ZnO, SnO₂ and V₂O₅, (g) - (i) Height and the corresponding current profile of ZnO, SnO₂ and V₂O₅ respectively.

Conductive Atomic force microscopy was performed meticulously to study the surface topography in a small scale. CAFM topography of SnO₂ in Fig. 5(b) shows fine grains with spherical shaped nanoparticles of uniform distribution with grain size around 50 - 100 nm. Slightly bigger grains of 200 nm were also obtained. In the grain boundary region, conductivity is less [19]. In the topographical image, SnO₂ nanoparticles seem to be compact, dense without much vacant sites (gap) in between them. Nanoaggregates of SnO₂ nanoparticles are

formed upon crystallization at higher calcination temperature [20]. The height and current profile has been depicted in Fig. 5(h). The current map recorded as in Fig. 5(e) in the corresponding scan direction shows maximum current value of 0.5 nA at the curvature of the particles.

C-AFM image in Fig. 5(c) shows flakes like morphology with lateral dimension of 0.5 μm . These flakes are stacked diagonally to form bundles with clear lateral view. With respect to the bias voltage of 1 V, maximum current value of the bright zones around 600 pA were observed for the side of the V_2O_5 bundles as in Fig. 5(i). The corresponding line profile for the topography and the current image is also depicted in Fig. 5(f).

4.4.2 Binary oxides and Ternary oxides

C-AFM topography image of ZT nanocomposite shown in Fig. 6(a) corresponds to the nanorods of length around 0.5 μm and diameter around 50 nm. The decrease in the dimension of the nanorods is clearly visible which is in consistent with the FE-SEM image of the ZT nanocomposite shown in Fig. 6 (a). From the AFM image it is understood that the rod is more conducting and the length of the nanorods are of 100 nm and diameter around 60 - 75 nm. Here, the grain boundaries are not conducting. The corresponding current image as in Fig. 6(e) obtained from CAFM depicted the bright and dark zones along the edges in the lateral view. In the AFM image big and small grains are visible. The maximum current value obtained for pure ZnO is 40 pA and pure SnO_2 is 0.5 nA respectively. But in the case of ZT nanocomposite the maximum current obtained along the lateral dimension is around 1.5 nA which is little more than the individual oxides. This might be due to the synergistic effect of the nanocomposite and is also attributed to the formation of the secondary phase Zn_2SnO_4 . These results are in accordance with the XRD analysis obtained for the ZT nanocomposite. Fig. 6(i) depicted the corresponding height and current profile of ZT nanocomposite.

Fig. 6: (a) – (d) AFM image of ZT, ZV, TV and ZTV, (e) – (h) Current maps of ZT, ZV, TV and ZTV, (i) - (l) Height and the corresponding current profile of ZT, ZV, TV and ZTV respectively

In the case of ZV nanocomposite, the topographic image obtained from CAFM is shown in Fig. 6(b) shows densely packed rough surfaced nanorods. In the current map Fig. 6 (f), the bright zones are appeared along the denser region with current of 1.5 nA which is comparatively larger compared to the corresponding individual oxides. The large current flow is observed for the

nanocomposite when compared with individual ZnO and V₂O₅ which might be due to the formation of zinc vanadate phases along with the individual phases. The height and current profiles of ZV nanocomposite is depicted in Fig. 6(j). The distribution of nanorods is random and the domains are piezo activated.

C-AFM image of the TV nanocomposite in Fig. 6(c) shows smaller spherical shaped nanoparticles with grain size of about 25 nm - 50 nm. The current flow (1.2 nA) as in Fig. 6 (g) through the composite is less compared to other two binary systems. This might be due to the absence of any secondary phases and also due to the morphological impact [Fig. 6 (k)]. That is, ZT and ZV possess nanorods while TV possess nanoparticles. Composites with elongated nanostructures provide large flow of current because of larger surface area which in turn favours the gas sensing probability.

In the case of ZTV nanocomposite, clusters of nanoparticles with size of around 25 - 50 nm are observed from the topographic image (Fig. 6(d)). The corresponding current maps of ZTV also reveals the hollow flower like structures with bright edges and dark centers Fig. 6(h). Maximum current of 12 nA is observed as in Fig. 6(l).

From the detailed study, among all the samples, ZTV is the most conducting material (Table .3) which is mainly due to the similar topographical image with spherical shaped nanoparticles with smaller grain size compared to pure SnO₂ [21]. The synergistic effect and the nanocomposite formation [22] further would have contributed for better conductance of ZTV. Here in ZTV, grain boundary regions are more conducting. In the case of ZTVnanocomposite, the enhanced sensitivity is mainly due to their electrical transport mechanism, which is different from that of the individual metal oxide sensors. It has been analysed that the barriers between the metal oxide grains on the nanocomposites dominate the sensor resistance [23, 24, 28]. Electrons travel

through the metal oxide grains into the nanocomposites and then conduct in between them. The process of adsorption mainly occurs at the surface of the grains. Because the size of the metal oxide grains in the nanocomposites are very small, a large fraction of the atoms are present at the surface and almost all the adsorbed species are active in producing a surface depletion layer for the small grains of nanocomposites (Fig7(a) and (b)). Moreover, the depth of the electron-depletion surface layer [29] due to oxygen ionosorption, has the impact on the particle size and henceforth the sensing performance of ZTV nanocomposte.

Fig.7: Conduction mechanism in nanocomposite (a) and elongated zinc vanadate nanostructures and spherical shaped SnO_2 nanoparticles in ZTV nanocomposite contribute for enhanced ethanol sensing mechanism (b)

Sample	ZnO	SnO_2	V_2O_5	ZT	ZV	TV	
Morphology	Nanorods	Nanoparticles	Nanoparticles	Nanorods	Nanorods	Nanoparticles	Flower like microstructures and spherical nanoparticles
Current (nA) at 1V	0.06	0.5	0.6	1.5	2.5	1.2	18

Table 3: Current values at constant voltage of all the samples

4.5 I -V Characteristics of individual, binary and ternary systems

Atomic Force Microscopy is a powerful versatile tool for the electrical characterisation of the nanojunctions. The platinum coated silicon tip has been used as a point electrode and the electrical characterisation has been performed in the contact mode while a fixed bias is applied between the conductive probe and the substrate. The electrical contact area between the AFM tip and the sample surface depends on the mechanical properties of the tip and the surface of the sample as well as loading force. In C-AFM, both the surface topography and the load current passing through the sample were measured simultaneously. With this tool, I-V measurements of a selected region can be performed using the conductive tip of a nanoprobe. Though poor mechanical stability of the tip and conductance fluctuation is observed in C-AFM, this tool is still advantageous in nanometer scale compared to conventional electrode evaporation techniques [30].

The thermionic emission current–voltage relation of a Schottky diode [31, 32] is given by

$$I=I_0[e^{\frac{qV}{nKT}}-1] \quad \dots\dots\dots (8)$$

where I_0 is the saturation current, q is the electronic charge, V is the applied voltage, n is the ideality factor, k is Boltzmann's constant and T is the temperature in K. The saturation current I_0 [33, 34] is defined by

$$I_0 = A A^* T^2 e^{\left[\frac{-q \Phi_{SB}}{KT}\right]} \quad \dots\dots\dots (9)$$

where A , n is the theoretical Richardson constant ($32 \text{ A/m}^2 \text{ K}^2$ for ZnO, $120 \text{ A/m}^2 \text{ K}^2$ for SnO₂ and $50.3 \text{ A/m}^2 \text{ K}^2$ for V₂O₅), A is the diode area and Φ_{SB} is the zero bias barrier height or schottky barrier height. Φ_{SB} is calculated using the following relation -

$$I_o = A A^* T^2 e^{\left[\frac{-q \phi_{SB}}{KT}\right]} \dots \dots \dots (10)$$

4.5.1 Individual oxides

The typical I–V characteristic curve for ZnOnanorods has been recorded and is shown in Fig. 8(a). The tip-to-sample contact on the top surface of ZnOnanorods and the curve depends on surface conditions as well as measurement parameters. The I–V characteristics curve shows a turn-on voltage of 4V for the forward bias and a reverse bias breakdown voltage of -10V. The analysis of the I–V characteristics curve in terms of Schottky barrier formation has also been performed and the schottky barrier height, band gap, resistance, surface area, sensitivity, response and recovery time were calculated and shown in Table 3. The corresponding SBH has been estimated as 0.587 eV. The SBH obtained for ZnOnanorods is smaller than those values of 0.61–0.96 eV reported in the literature for the ZnO[33, 34]. The lower Schottky barrier height contributes to the reasonably higher currents obtained in the literature. This indicates the active conductive regions of ZnO nanorods.

The I–V characteristic curve for SnO₂ nanoparticles observed is shown in Fig. 8(b).The I–V characteristics curve shows a turn-on voltage of 6 V for the forward bias and a reverse bias breakdown voltage of -1V. SBH of SnO₂ nanoparticles has been calculated as 0.545 eV which is in accordance with the already reported values such as 0.6015 eV and 0.5073 eV with respect to the size of the grains [35, 36]. It is evident from the literature that SnO₂ nanoparticles with a grain size of around 18 nm and 52 nm possess smaller barrier height.

Fig.8: *I–V characteristic curve of individual oxides (a) ZnO, (b) SnO₂ and (c) V₂O₅*

From the I-V plot (Fig. 8(c)) of V₂O₅, the barrier height has been calculated as 0.439 eV [37]. The barrier height value obtained for the prepared V₂O₅ flakes lie close to the value obtained for V₂O₅ nanorods. The I–V characteristics curve shows a turn-on voltage of 0.1 V for the forward bias and a reverse bias breakdown voltage is not observed till -10 V.

Compared to ZnO, SnO₂ and V₂O₅, from CAFM measurements, it is identified that SnO₂ is said to be more conducting holding 0.5 nA of current. V₂O₅ possess slightly more conductive nature when compared to ZnO.

4.5.2 Binary and Ternary oxides

The I-V plot of ZT nanocomposite is depicted in Fig. 9(a). The I–V characteristics curve shows a turn-on voltage of 7.5 V for the forward bias and a reverse bias breakdown voltage is not observed till -1.5 V. The schottky barrier height calculated for ZT nanocomposite is 0.554 eV which is found to be lower than the barrier height of individual zinc oxide. This smaller barrier height might be attributed to the reduction in the growth of the nanorods due to the formation of the secondary phase Zn₂SnO₄ along with the ZnO and SnO₂ phases [37]. This decreased barrier height paves the way for the faster adsorption and desorption of ethanol molecules on the surface of ZT which gives better sensitivity of 77.93% while ZnO and SnO₂ shows only 51.98 % and 42.92 % respectively.

The I-V plot of ZV nanocomposite is depicted in Fig. 9(b). The I-V characteristics curve shows a turn-on voltage of 3 V for the forward bias and a reverse bias breakdown voltage is not observed till -0.5 V. The schottky barrier height (Table 3) calculated for ZV nanocomposite is 0.389 eV. But for ZnO the barrier height is 0.587 eV and for V₂O₅ the barrier height is 0.489 eV. The much smaller barrier height observed for ZV nanocomposite might be due to the combination of the elongated nanostructures contributed from both the individual oxides [36]. This decreased barrier height could be the reason for the better sensitivity of 72.97 % with response and recovery time as 98 s and 84 s respectively.

Fig. 9: (b) I-V characteristic curve of (a) ZT, (b) ZV, (c) TV and (d) ZTV

The I-V plot of TV nanocomposite is depicted in Fig. 9(c) The I–V characteristics curve shows a turn-on voltage of 5 V for the forward bias and a reverse bias breakdown voltage is not observed till - 5 V. The schottky barrier height shown in Table 4 for TV nanocomposite is 0.512 eV. The sensitivity of TV nanocomposite towards sensing of ethanol at room temperature is 63.99 %.

The I-V plot of ZTV nanocomposite is depicted in Fig. 9(d). The I–V characteristics curve shows a turn-on voltage of 1 V for the forward bias and a reverse bias breakdown voltage is not observed till - 6 V. The schottky barrier height calculated for ZTV nanocomposite is 0.189 eV (Table 4). ZTV nanocomposite exhibits the smallest barrier height when compared to all the individual and binary oxides. It is understood from the Table 2 that the larger current of 18 nA possess smallest band gap due to the porous regions and hence the barrier height is smaller for ZTV.

Sample	Band gap (eV)	Barrier height (eV)	Resistance (Megaohm)	Sensitivity (%)	Response time (S)	Recovery time (S)	Surface area (m/g2)
ZnO	3.30	0.587	16700	51.98	105	130	123.9
SnO2	4.35	0.545	2000	42.92	162	118	118.8
V2O5	2.35	0.439	1700	30.98	156	128	116.5
ZT	4.44	0.554	670	77.93	68	79	156.7
ZV	3.47	0.389	400	72.97	98	84	151.6
TV	4.96	0.512	830	63.99	87	93	126.5
ZTV	1.97	0.189	56	98.98	32	6	167.3

Table 4: Band gap, Barrier height, resistance, gas sensing values and surface area of all the samples

ZTV also experiences smaller resistance of 56 M ohm which also supports the decrease of barrier height. Also, this smaller barrier height [37] with less resistance of ZTV shows the fastest response and recovery of 32 s and 6 s respectively with better sensitivity of 98.93%. The results obtained for ZTV is in accordance with the literature that the metal oxides having smaller barrier height could exhibit good sensitivity at a faster rate towards the test gases.

4.6 Conclusion

In this present work, the topography and the electrical property of ZnO, SnO₂, V₂O₅, ZT, ZV, TV and ZTV were systematically analysed. The local conducting studies have been carried out and from the detailed analysis, it is revealed that, among all the samples, ZTV possess the smallest barrier height of 0.189 eV. Also, the smaller resistance offered by the hierarchical architecture of ZTV and its larger surface area incites ZTV to excel with enhanced ethanol sensing even at room temperature. This unique hierarchical porous architecture also provides beneficial structural advantage in gas diffusion and adsorption, surface chemical reactions and electron transfer which might be due to the obtained smallest potential barrier heights between the grain boundaries. The CAFM and valence band characteristics of the hierarchical ZTV further illustrates and confirms that the small energy barrier of ZTV plays an important factor in the fast-response gas detection. Such local study on the sensor performance of ZTV reported for the first time paves the way for the researchers to fabricate this material as a portable device using MEMS technology.

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