Development of High-Performance Bismuth Sulfide Nanobelts Humidity Sensor and Effect of Humid Environment on its Transport Properties

Muhammad Faheem Afsar,†§ M. A. Rafiq,‡ Arifa Jamil,† Sajid Fareed,† Fizza Siddique,† A. I. Y. Tok,§ and Muhammad Masood ul Hasan‡

†Department of Physics and Applied Mathematics and ‡Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, Nilore, Islamabad 45650, Pakistan
§School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

ABSTRACT: Orthorhombic phase bismuth sulfide (Bi₂S₃) nanobelts were prepared via liquid–solid phase reaction method. Bi₂S₃ nanobelts were observed to be preferentially oriented along the (101) plane. Direct band gap (2.95 eV) and characteristic wavelength (λmax = 342 nm) were extracted through UV–visible spectroscopy. Specific surface area (9.8 m²/g) and pore size (2.5–120 nm) were evaluated through Brunauer–Emmett–Teller (BET) analysis. Relative humidity (RH) sensing properties were studied in the range of 11–97% RH at ambient conditions. The response of the sensor increases linearly with increase in RH. Fast response time (8–10 s) and recovery time (15 s) were observed. Reproducible and large response was also observed between 11 and 97% RH. Small hysteresis (<5%) and long-term stability during 30 days were confirmed. As a function of frequency, capacitance, alternating current conductivity, and electrical complex modulus in the frequency range of 20–2 MHz were studied at 11–97% RH. The sensing mechanism was also studied.

1. INTRODUCTION

Most important physical quantity among the measurable physical quantities is RH. Measurement and control of humidity (water vapors) in industries, textiles, electronics, pharmaceuticals, processing of chemicals, food, and laboratory work is very important. Also in semiconductor industry, the control of humidity is very important for the manufacture of extremely refined integrated circuits. To have a healthy surrounding, it is fundamental to screen, identify, and control the surrounding humidity by advance humidity sensors. Therefore, the requirements for healthy environmental conditions have prompted the advancements in humidity sensors by the utilization of chemical and physical characteristics of hybrid, inorganic, or organic materials. Advancement in humidity sensory systems involves the improvement of transducer performance, for example, principle of mechanism, structure design, fabrication technologies, and sensing elements. Humidity sensor-producing technologies are driven by modern signal-conditioning techniques; fast postprocess, low-cost, and low-power micro- and nanoelectronic hybrid circuits, and improvements in miniaturization technologies. The requirement for product reliability and enhancement of quality are essential for commercial competitiveness. Besides, it is vital to know the level of effectiveness of every sensor identified with its sensing mechanism and calibration circumstances. Scaling down of sensor devices offers various points of interest, for example, batch fabrication, low hysteresis, and integration/packaging alongside the reductions in cost.

For miniaturization of sensor devices, nanostructured materials play a key role due to their high surface-to-volume ratio, small size, and unique photoelectric, chemical, and sensing properties. To date, assortment of one-dimensional nanostructured solar cells, ultraviolet detectors, transistors, and chemical sensors has been reported. One-dimensional metal sulfide/oxide nanostructures have gained much consideration due to their exceptional properties. Among them, Bi₂S₃ with direct band gap (1.3 eV) finds several applications in humidity sensors, gas sensors, infrared spectroscopy, optoelectronic devices, electronic devices, and thermoelectric devices. For the synthesis of Bi₂S₃ nanostructures, different methods have been used, for example, solvothermal/hydrothermal microwave irradiation, and chemical deposition. However, these synthesis processes are complicated with a low production yield. In this paper, we used...
a liquid–solid phase reaction method to produce crystalline Bi$_2$S$_3$ nanobelts at relatively lower temperature (190 °C). This method is easy and generally used to produce several nanomaterials at low cost on a large scale.

Humidity sensors constructed with metal sulfide nanostructures have been extensively reported. However, most of them have long response/recovery time and large humidity hysteresis. In this paper, synthesis of Bi$_2$S$_3$ nanobelts through liquid–solid phase reaction method, structural characterization, evaluation of texture coefficient, optical properties, BET surface area analysis, humidity sensing properties, and effect of humid environment on the transport properties were
examined. Furthermore, synthesis through liquid—solid phase reaction method, evaluation of texture coefficient, humidity sensing properties, and effect of humid environment on the transport properties were explored for the first time for Bi₂S₃ nanobelts. Results show that optimized Bi₂S₃ nanobelts RH sensors possess high response in humid environment, fast response/recovery time, good recyclability, and good stability compared to other metal sulfide nanostructures reported in the literature.28,29 The schematic diagram of a homemade RH sensing setup is shown in Figure 1.

2. RESULTS AND DISCUSSION

Figure 2a shows the X-ray diffraction (XRD) pattern of Bi₂S₃ nanobelts, acquired using Cu Kα X-rays with wavelength of 1.5418 Å. The pattern matches with PDF card number 00-006-0333 (space group Pbmm and space group # 62), and no impurity peak is present. The Bi₂S₃ nanobelts are of orthorhombic phase with lattice constant parameters a, b, and c equal to 11.14, 11.32, and 3.97 Å, respectively. The density (ρ) and volume of the unit cell (V) are 6.81 g/cm³ and 501.52 Å³, respectively. These values of a, b, c, ρ, and V are in close agreement with those given in the PDF card number 00-006-0333 (a = 11.15 Å, b = 1.130 Å, c = 3.98 Å, ρ = 6.78 g/cm³, and V = 501.59 Å³). To understand the degree of preferred orientation for different crystalline planes, texture coefficient \( T_{C(hkl)} \) was determined using25–27

\[
T_{C(hkl)} = \left( \frac{I_{(hkl)}^{obs}}{I_{(hkl)}^{th}} \right)^n \left( \frac{1}{n} \sum_{i=1}^{n} \frac{I_{(hkl)}^{obs}}{I_{(hkl)}^{th}} \right)^{-1}
\]

(1)

where \( I_{(hkl)}^{obs} \) is the intensity extracted from XRD pattern of Bi₂S₃ nanobelts, \( I_{(hkl)}^{th} \) is the intensity written in the reference PDF card, and n is an integer corresponding to the number of diffraction peaks under consideration. \( T_{C(hkl)} \leq 1 \) for randomly distributed planes, and it is >1 for preferentially oriented planes.25–27 The calculated values of \( T_{C(hkl)} \) for Bi₂S₃ nanobelts planes are listed in Table 1. For the (101) plane, \( T_{C(101)} = 1.839 \) >1. Therefore, for Bi₂S₃ nanobelts, it is the preferentially oriented plane. Figure 2b shows the scanning electron microscopy (SEM) image of Bi₂S₃ nanobelts with average thickness ~25 nm. The energy-dispersive spectroscopy (EDS) image shown in Figure 2c contains Bi and S peaks confirming the composition and purity of Bi₂S₃ nanobelts. Figure 2d shows the low-resolution transmission electron microscopy (TEM) image of Bi₂S₃ nanobelts. The nanobelts have average thickness ~25 nm and length ~80 to ~300 nm. The inset of Figure 2c shows the high-resolution TEM image with a d-spacing of 0.504 nm along the (120) plane.

The UV–visible absorption spectrum with characteristics wavelength (\( \lambda_{max} = 342 \) nm) of the Bi₂S₃ nanobelts is shown in Figure 3a. Using this spectrum, an (\( \alpha h\nu \))² versus \( h\nu \) plot was constructed and is shown in Figure 3b. The x-intercept of the graph provides the direct band gap of Bi₂S₃ nanobelts. The Bi₂S₃ nanobelts have a higher direct band gap value (2.95 eV) compared to the bulk Bi₂S₃ 34 and in good agreement with those reported in the literature.4,35 This increment in band gap is another evidence for the formation of Bi₂S₃ nanobelts that are useful as humidity sensors due to their larger surface area.

The textural property of Bi₂S₃ nanobelts is further considered by the nitrogen (N₂) adsorption–desorption estimation. Figure 3c,d shows the N₂ adsorption–desorption isotherms and pore size distribution plots corresponding to the Barrett–Joyner–Halenda (BJH) method, respectively. Mesoporous materials characteristic isotherms (type IV) were recognized in Bi₂S₃ nanobelts. In light of the BJH technique and adsorption of N₂ isotherm, the estimation of pore size dispersal shows that a comparatively narrow pore size dispersal centers at 39.7 nm. For RH sensing, porous structures provide more passages for water vapor to travel into the sample, enhancing its adsorption capacity. Also high BET specific surface area with large active centers and adsorption pathways would be necessary for a good RH sensor.36–38 The BET specific surface area of Bi₂S₃ nanobelts is 9.8 m²/g. This may be one of the reasons for Bi₂S₃ nanobelts displaying good RH sensing properties.

To evaluate the performance of Bi₂S₃ nanobelts RH sensor, the I–V curves were measured from 11 to 97% RH and are shown in Figure 4a. For each RH level, the I–V curves are linear, indicating Ohmic contact between the Bi₂S₃ nanobelts and Ag electrodes. At 5 V, the current is 10 µA at 11% RH, 19 µA at 32% RH, 28 µA at 58% RH, 50 µA at 76% RH, and 133 µA at 97% RH. Clearly, the current in the Bi₂S₃ increases with increase in RH. The resistance of the sensor calculated at 11% RH is 4.94 × 10⁴ Ω and that calculated at 97% RH is 3.38 × 10⁵ Ω at 5 V. Therefore, the resistance of the sensor at 97% RH is 14 times less than that at 11% RH. The increase in current with increase in RH indicates decrease in resistance of the Bi₂S₃ nanobelts sensor with increase in RH and is shown in Figure 4b. Among other characteristics of the RH sensors, response (R) of the sensor is very important, which in our case is defined as

Table 1. Texture Coefficient Values for Orthorhombic Phase of Bi₂S₃ Nanobelts

| h | k | l | \( I_{ad} \) | \( I_{rad} \) | texture coefficient |
|---|---|---|---|---|---|
| 2 | 2 | 0 | 3852 | 40 | 0.77 |
| 1 | 0 | 1 | 4596 | 20 | 1.84 |
| 1 | 1 | 1 | 11 011 | 95 | 0.93 |
| 0 | 2 | 1 | 2630 | 18 | 1.17 |
| 2 | 3 | 0 | 11 789 | 100 | 0.94 |
| 2 | 2 | 1 | 5819 | 65 | 0.72 |
| 3 | 0 | 1 | 4089 | 35 | 0.94 |
| 2 | 1 | 1 | 2937 | 25 | 0.94 |
| 0 | 3 | 1 | 2522 | 35 | 0.65 |
| 2 | 3 | 1 | 1681 | 16 | 0.84 |
| 0 | 4 | 1 | 1952 | 25 | 0.62 |
| 1 | 4 | 1 | 2767 | 35 | 0.63 |
| 4 | 2 | 1 | 1958 | 10 | 1.58 |
| 5 | 2 | 0 | 1374 | 10 | 1.09 |
| 0 | 0 | 2 | 4326 | 35 | 0.99 |
| 4 | 3 | 1 | 5141 | 55 | 0.75 |
| 0 | 6 | 0 | 1544 | 14 | 0.88 |
| 2 | 5 | 1 | 1848 | 14 | 0.82 |
| 2 | 2 | 2 | 1478 | 14 | 0.85 |
| 3 | 1 | 2 | 3478 | 35 | 0.79 |
| 0 | 6 | 1 | 1104 | 10 | 0.88 |
| 2 | 3 | 2 | 1204 | 8 | 1.20 |
| 4 | 1 | 2 | 833 | 4 | 1.67 |
| 2 | 4 | 2 | 1544 | 16 | 0.77 |
| 7 | 2 | 0 | 1104 | 8 | 1.11 |
| 3 | 4 | 2 | 1204 | 6 | 1.61 |
where RH<sub>i</sub> is the resistance of sensor at 11% RH, which is the lowest RH level and RH<sub>j</sub> is the resistance of the sensor at certain higher RH levels (32, 58, 76, and 97%). All of the values of resistances are calculated at 100 mV. Response and recovery times are very important characteristics of a sensor. Response time is the time in which the sensor's response approaches 90% of the maximum response value after the RH sensor is exposed to a certain RH level (32, 58, 76, and 97%). Recovery time is the time in which the sensor's response approaches 10% of its original value after the RH sensor is exposed to the lowest RH level (11%). For Bi<sub>2</sub>S<sub>3</sub> nanobelts RH sensor, response and recovery time curves at different RHs are shown in Figure 4c. From this figure, we note that the response of RH sensor increases linearly with increase in RH. Its percentage values are ∼0.15, 34, 49, 65, and 81 at 11, 32, 58, 76, and 97%, respectively. A linear relationship between response and RH is shown in Figure 4d. The response and recovery times for Bi<sub>2</sub>S<sub>3</sub> nanobelts were calculated from Figure 4c and are plotted in Figure 4e at 32, 58, 76, and 97% RH with respect to 11% RH. The response times at 32, 58, 76, and 97% RH with respect to 11% RH were 8, 9, 10, and 10 s, respectively. Similarly, the recovery times at 32, 58, 76, and 97% RH with respect to 11% RH were 15, 15, 15, and 15 s, respectively. So, the response time increases with increase in RH up to 76% RH and remains constant above 76% RH. But constant recovery time (15 s) was observed for all RH levels. These results for Bi<sub>2</sub>S<sub>3</sub> nanobelts sensor are compared to other metal sulfide nanostructure RH sensors, as given in Table 2. From Table 2, it can be seen that response/recovery time for Bi<sub>2</sub>S<sub>3</sub> nanobelts RH sensor is faster than previously reported metal sulfide nanostructure RH sensors. The reproducibility for RH sensor is another important parameter to investigate its performance. Figure 4f shows that the Bi<sub>2</sub>S<sub>3</sub> nanobelts RH sensor has reproducibility over three consecutive cycles with <5% deviation when RH is varied from 11 to 90 to 11%.

RH sensors have been extensively investigated by complex impedance ($Z^* = Z' + Z''$) analysis, where $Z'$ is the real part and $Z''$ is the imaginary part of $Z^*$. For Bi<sub>2</sub>S<sub>3</sub> RH sensor, $Z'$ vs $Z''$ plots are shown in Figure 5a. These measurements are performed at 0.1 V alternating current (AC) signal with 20 Hz to 2 MHz frequency at ambient conditions. Along $Z'$ from right to left, the frequency increases. From Figure 5a, a complete semicircle and a little straight line after the semicircle in the low-frequency region are seen at all RH levels. But this straight line is more visible at higher RH than at lower RH, which means that at higher level of RH, ionic conductivity is more dominant than the electronic conductivity. Overall conductivity of the Bi<sub>2</sub>S<sub>3</sub> nanobelts increases with increase in RH. Semicircles at different RH levels give the bulk resistance of the Bi<sub>2</sub>S<sub>3</sub> nanobelts. Bulk resistance decreases with increase in RH. The AC measurements compliment the direct current (DC) measurements that as RH increases, the resistance of Bi<sub>2</sub>S<sub>3</sub> nanobelts decreases. So, at 100 Hz, impedance decreases from $4.9 \times 10^5$ Ω (11% RH) to $1.9 \times 10^4$ Ω (97% RH), at 10 kHz, impedance decreases from $3.1 \times 10^5$ Ω (11% RH) to $1.4 \times 10^4$ Ω (97% RH), and at 2 MHz, impedance decreases from $1.7 \times 10^4$ Ω (11% RH) to $4.7 \times 10^3$ Ω (97% RH). The impedance change for Bi<sub>2</sub>S<sub>3</sub> sensor is strongly dependent on RH at lower frequencies compared to the impedance change at higher frequencies.
Figure 5b shows the humidity hysteresis loop for Bi$_2$S$_3$ RH sensor. This humidity hysteresis is the maximum difference in the adsorption–desorption curve and is the most important parameter for RH sensors. The observed maximum hysteresis in Bi$_2$S$_3$ RH sensor is $\sim$5%, which shows its good reliability.

Table 2. Comparison of Sensing Performance with Other Metal Sulfide Nanostructures

| Transducer | Metal sulfide         | Year | Response time (s) | Recovery time (s) | Res/sen (%) | References |
|------------|-----------------------|------|-------------------|-------------------|-------------|------------|
| Resistor   | VS$_2$ nanosheets     | 2012 | 40                | 50                | 70          | 28         |
| Resistor   | MoS$_2$ nanosheets    | 2013 | 9                 | 17                | 30          | 29         |
| Resistor   | MoS$_2$ nanospheres   | 2014 | 90                | 110               | 35          | 30         |
| Resistor   | Bi$_2$S$_3$ nanowires | 2015 | 50                | 60                | 16          | 18         |
| FET        | WS$_2$ nanoparticles  | 2016 | 12                | 13                | 100         | 31         |
| Resistor   | WS$_2$ nanosheets     | 2016 | 13                | 15                | 40          | 32         |
| Resistor   | Bi$_2$S$_3$ nanobelts | 2018 | 10                | 15                | 81          | this work  |

Figure 5b shows the humidity hysteresis loop for Bi$_2$S$_3$ RH sensor. This humidity hysteresis is the maximum difference in the adsorption–desorption curve and is the most important parameter for RH sensors. The observed maximum hysteresis in Bi$_2$S$_3$ RH sensor is $\sim$5%, which shows its good reliability.

Long-term stability of the Bi$_2$S$_3$ nanobelts RH sensor was checked over 30 days in air at 25 °C. For this purpose, impedance of the sensor was measured at different RH levels after every 5 days at constant AC voltage (0.1 V) and frequency (100 Hz). Figure 5c shows the impedance of sensor...
Figure 5. Bi$_2$S$_3$ nanobelts: (a) $Z'$ vs $Z''$ characteristics; (b) hysteresis loop; (c) stability during 30 days measurement at 100 Hz and 0.1 V; and (d) capacitance vs log $f$.

Figure 6. Bi$_2$S$_3$ nanobelts: (a) AC conductivity vs log $f$; (b) $M'$ vs log $f$; (c) $M''$ vs log $f$; and (d) $M'$ vs $M''$. 
The effect of RH on capacitance, AC conductivity, and modulus ($M^*$) of Bi$_2$S$_3$ nanobelts RH sensors is also studied. The AC measurements were carried out at 0.1 V AC voltage and at different RH levels (11–97%) from 20 Hz to 2 MHz. Figure 5d shows the capacitance vs log$f$ plot for the Bi$_2$S$_3$ nanobelts RH sensor. It is obvious from the graph that at higher frequencies ($\geq 10^3$ Hz), the capacitance is almost constant and at lower frequencies ($\leq 10^3$ Hz), capacitance increases as frequency decreases. At lower frequencies ($\leq 10^3$ Hz), capacitance increases with increase in RH. The hydrophilic nature of Bi$_2$S$_3$ nanobelts facilitates humidification of water molecules on its surface.41 According to dielectric theory of physics, capacitance is almost independent of frequency for an ideal capacitor. At low RH environment, only a small quantity of water vapors adsorb on the surface of nanobelts, which can be considered as ideal. At higher RH, the amount of water adsorbed increases and the leak conductance appears. The effective expression for the capacitance is $C = \epsilon^* \times C_0$, where $C_0$ is ideal capacitor’s capacitance and $\epsilon^* = (\epsilon_r - i\gamma/\omega\epsilon_0)$ is the complex dielectric constant. The $\epsilon_r$, $\gamma$, $\omega$, and $\epsilon_0$ are known as relative dielectric constant for ideal capacitor, leak conductance, angular frequency, and vacuum capacitance constant, respectively. With increase in RH, $\gamma$ increases.42 From the above equations, it is obvious that $C$ is directly proportional to $\gamma$ and inversely proportional to $\omega$, which means that $C$ increases with increase in RH, and this increase is higher at lower frequencies. $C$ is hardly affected in the higher-frequency region. This is because in the lower-frequency region, carriers have enough time to respond, while in the higher-frequency region, carriers do not have enough time to respond due to quick change in the electric field.43 This explains the observed dependence of capacitance of Bi$_2$S$_3$ nanobelts on frequency.

AC conductivity ($\sigma_{ac}$) of Bi$_2$S$_3$ nanobelts is given by

$$\sigma_{ac} = \left( \frac{Z'}{(Z')^2 + (Z')^2} \right) \frac{d}{A}$$  \hspace{1cm} (3)

where $A$ is the cross-sectional area and $d$ is the thickness of the sensor. The $\sigma_{ac}$ of the Bi$_2$S$_3$ nanobelts at different RH levels is shown in Figure 6a, which shows that $\sigma_{ac}$ increases with increase in RH. For each RH level, $\sigma_{ac}$ is independent of frequency at lower frequencies and increases with increase in frequency at higher frequencies. Therefore, change in $\sigma_{ac}$ with RH is in accordance with eq 3. At 100 Hz, $\sigma_{ac} = 3.15 \times 10^{-3}$ S/m for 11% RH and $\sigma_{ac} = 69.15 \times 10^{-5}$ S/m for 97% RH, which is 23 times greater than that at 11% RH. At 10 kHz, $\sigma_{ac} = 6.01 \times 10^{-4}$ S/m for 11% RH and $\sigma_{ac} = 84.14 \times 10^{-5}$ S/m for 97% RH which is 14 times greater than that at 11% RH. At 2 MHz, $\sigma_{ac} = 4.03 \times 10^{-4}$ S/m for 11% RH and $\sigma_{ac} = 24.18 \times 10^{-3}$ S/m for 97% RH, which is 6 times greater than that at 11% RH. So, the effect of RH on $\sigma_{ac}$ is high in the lower-frequency region compared to that in the higher-frequency region.

Relaxation process due to the existence of substantial conductivity cannot be described with the support of $C$ or $\epsilon$ illustrations. So, the illustration of modulus is useful to describe the relaxation processes for $C$ or $\epsilon$ with nonzero conductivity.44,45 The modulus $M^* = \omega C_0 Z^*$. The notations used in this equation are already explained in this paper. Figure 6b shows variation of the real part of modulus ($M'$) with frequency. At all RH levels and frequencies $\leq 10^3$ Hz, $M'$ approaches 0. At frequencies $\geq 10^3$ Hz, there is continuous dispersion with increasing frequency, which may be due to the conduction of short-range charge carriers. This may be due to the deficiency of restoring force for the movement of electric charge under the impact of steady electric field. So, the electrode effect is eliminated in the material.46,47 With an increase in RH, $M'$ curves shift toward higher frequencies, indicating the increase in DC conductivity.47 Figure 6c shows the imaginary part of modulus ($M''$) vs log$f$. It can be seen that there is one dominant relaxation due to interface effect. This is because the hydrophilic nature of Bi$_2$S$_3$ nanobelts facilitates the adsorption of water molecules on the surface of nanobelts, which show the relaxation. Peak position of $M''$ can be used to calculate the relaxation time ($\tau = 1/2\pi f_{max}$) by using the peak frequency ($f_{max}$). Therefore, relaxation time decreases with increase in RH.48 Figure 6d shows the complex modulus plane plot at different RH levels as $M'$ vs $M''$. Again, one dominant

Figure 7. Schematic diagram of the relative humidity sensing mechanism.
relaxation due to interface affect can be seen. All incomplete semicircles give another evidence for ion relaxation process. It is important that at the frequency edge, the curves show a common origin similar to the origin of graphs. This common origin at the beginning of the incomplete semicircles at different RH levels is a strong suggestion that at those frequencies, no other relaxation process exists. Figure 6d also shows that the diameter of the semicircle increases with increase in RH, which is due to the movement of ions from adsorbed water layer to sensor’s electrodes, which leads to the development of space charge region at sensor’s electrodes. As relaxation time for ion migration is longer than for the charge-transfer process in this frequency region, resistivity decreases with increase in RH.

Finally, we can propose humidity sensing mechanism for Bi$_2$S$_3$ nanobelts RH sensor from the material (ceramic, semiconducting, or nanomaterial) point of view. For modulation of conductivity with RH, nanometric size and semiconducting properties play a key role. The Bi$_2$S$_3$ nanobelts conductivity increases with increase in RH. This behavior can be comprehended with the Grotthuss mechanism, which explains the tunneling of proton between adjacent water molecules. Water molecules at the triggered sites on the surface of Bi$_2$S$_3$ nanobelts are chemically adsorbed at lower humidity. In general, the interaction of water molecules on the surface of sulfide may result in the development of the SH–groups. However, this impact has not been perceived experimentally as a typical pattern. Therefore, two hydroxyls per water molecule are formed by dissociative mechanism at this stage. After that, physical adsorption occurs with increase in humidity further. Physisorption belongs to a multilayer phenomenon. The initial immovable layer of physically adsorbed water is because of double hydrogen bonding of a solo molecule. The humidity molecules form single bond in succeeding physisorbed layers, and consequently protons may be accessible for conduction. Physisorbed layers increase with increase in further RH, resulting in proton hoping through water layers. Now, protons through water layers can easily move and this conduction process is similar to that in pure water. A schematic diagram of the sensing mechanism is shown in Figure 7.

We have carried out our experiment under normal ambient conditions, andionic conduction at this temperature is prevailing due to humidity content in the pores of the specified sensing material. However, it is published that humidity content reduces with increase in temperature, so the electronic conduction is prevailing instead of ionic conduction during the conduction process.

3. CONCLUSIONS

Bi$_2$S$_3$ nanobelts were prepared via liquid–solid phase reaction technique with different thicknesses, widths, and lengths. Different characterization techniques were applied to explore their structure, morphology, chemical composition, band gap, surface area, pore size, etc. Bi$_2$S$_3$ nanobelts showed excellent features for humidity sensing, including large response, low hysteresis (<5%), good repeatability, fast response time (10 s), fast recovery time (15 s), and very good stability compared to other metal sulfide nanostructure sensors. During the direct current (DC) measurements, the resistance of the sensor at 97% RH was 14 times less than that at 11% RH. The response of the sensor increases linearly with increase in RH with percentage values ~0.15, 34, 49, 65, and 81 at 11, 32, 58, 76, and 97%, respectively. Fast response time (8–10 s) and recovery time (15 s) were observed. Reproducible and large response was also observed between 11 and 97% RH. A 24 times decrease in impedance was observed when RH increase from 11 to 97%. These good features are attributed to smaller thickness and porous nature of nanobelts. We believe that such an extremely sensitive RH sensor will support the improvement of upcoming generations of RH sensors. Both the capacitance and AC conductivity are greatly affected by RH in the lower-frequency region and hardly affected in the higher-frequency region. Linearity in $I$–$V$ curves proves the Ohmic contact, and electrical modulus study eliminates the electrode effect in our sensor and also proves one relaxation process. The exceptional characteristics of RH sensing for Bi$_2$S$_3$ nanobelts proved them to be a potential candidate for high-performance RH sensors.

4. EXPERIMENTAL SECTION

In this experiment, liquid–solid phase reaction method was used to prepare Bi$_2$S$_3$ nanobelts. Precursurs in the preparation of Bi$_2$S$_3$ nanobelts were bismuth acetate and thiourea. As thiourea decomposes at a low rate, it was taken as a source of sulfur. These precursors were of analytical grade and were used without further purification. Stoichiometric quantities of bismuth acetate and thiourea were taken and ground in an agate mortar separately. Fine powders of both the precursors were mixed in a corundum crucible and then heated at 190 °C for 3 h in air. The heating and cooling rates during heat treatment were 10 °C per min. Blackish Bi$_2$S$_3$ powder was the final product. This powder was again finely ground. This fine powder was used for structural characteristics and device fabrication for RH sensor.

The resulting powder was characterized using XRD "Bruker D8 Advance Powder" with Cu Kα radiation ($\lambda = 1.5418$ Å). The morphology analysis of Bi$_2$S$_3$ and EDS analysis for chemical composition were performed using "JEOL JSM-6340F". Low- and high-resolution TEM images were obtained using "TEM JEOL 2100F". The optical properties were studied using a "Shimadzu UV-1201 UV-visible spectrophotometer". BET specific surface area was evaluated by using "Micromeretics ASAP 2020". The density of the Bi$_2$S$_3$ powder was investigated by the displacement method using gas pycnometer "G PYC-100-A".

For RH sensing measurements, the prepared Bi$_2$S$_3$ powder was pressed into pellets in a uniaxial hydraulic press system using a 10 mm diameter die and a pressure of 3 ton/mm$^2$. The thickness of the prepared pellet was 1 mm. The pellet was sintered at 100 °C for 2 h to remove pores and to obtain physical strength. The pellet was removed from the furnace box and allowed to cool naturally before using it as an RH sensor. Electrical contacts were made with the help of conducting silver paste on both sides of the pellet. After forming the contacts, the pellet was cured at 100 °C for 2 h again for better adhesion of the silver paste with Bi$_2$S$_3$ nanobelts.

Current–voltage ($I$–$V$) and impedance measurements of the RH sensor of resistive type were successively performed by putting it into several RH chambers with different RH levels obtained with saturated salt solutions. Saturated solutions of lithium chloride (LiCl), magnesium chloride (MgCl$_2$), sodium bromide (NaBr), sodium chloride (NaCl), and potassium sulfate (K$_2$SO$_4$) were utilized to obtain 11, 32, 58, 76, and 97% RH, respectively, in sealed glass chambers at room temper-
ature. Each saturated salt solution was kept in a glass chamber for more than 16 h to achieve the required RH and continuously monitor through a digital hygrometer before DC/AC electrical measurements. An Agilent 4156C parameter analyzer was used for I–V and dynamic response–recovery measurements. The measuring instrument for impedance was an Agilent E4980A LCR meter. Utilization of AC signal maintains a strategic distance from the polarization impacts of adsorbed water. In any case, for this situation, the signal-handling circuits are confusing. Consequently, in some cases, DC measurements are additionally used to assess the humidity sensors. In a clean room environment, the complete RH measurements setup was maintained at ambient conditions.

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: afatab@cantab.net. Tel: +92 (51) 1111, +92 (51) 1111 74327. Fax: +92 (51) 924 8600.*

**ORCID**
M. A. Rafiq: 0000-0002-3880-8801

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
The authors acknowledge the Higher Education Commission (HEC) of Pakistan for their support through International Research Initiative Program (IRISIP). This work was financially supported by HEC of Pakistan under National Research Program for Universities (NRPU Project No. 3662).

**REFERENCES**

1. Usman, M.; Rasool, K.; Batool, S.; Imran, Z.; Ahmad, M.; Jamil, H.; Rafiq, M.; Hasan, M. Humidity effect on transport properties of titanium dioxide nanoparticles. J. Mater. Sci. Technol. 2014, 30, 748–752.
2. Stetter, J. R.; Penrose, W. R.; Yao, S. Sensors, chemical sensors, electrochemical sensors, and ECS. J. Electrochem. Soc. 2003, 150, S11–S16.
3. Carr-Brown, K. Moisture Sensors in Process Control; Elsevier Applied Science Publishers; Sole distributor in the USA and Canada Elsevier Science Pub. Co., 1986.
4. Ahmad, Z.; Zafar, Q.; Sulaiman, K.; Akram, R.; Karimov, K. S. A humidity sensing organic-inorganic composite for environmental monitoring. Sensors 2013, 13, 3615–3624.
5. Smetana, W.; Unger, M. Design and characterization of a humidity sensor realized in LTCC-technology. Microsyst. Technol. 2008, 14, 979–987.
6. Farahani, H.; Wagiran, R.; Hamidon, M. N. Humidity sensors principle, mechanism, and fabrication technologies: a comprehensive review. Sensors 2014, 14, 7881–7939.
7. Shi, Y.; Luo, Y.; Zhao, W.; Shang, C.; Wang, Y.; Chen, Y. A radiosonde using a humidity sensor array with a platinum resistance heater and multi-sensor data fusion. Sensors 2013, 13, 8977–8986.
8. Imran, Z.; Batool, S.; Jamil, H.; Usman, M.; Israr-Qadir, M.; Shah, S.; Jamil-Rana, S.; Rafiq, M.; Hasan, M.; Willander, M. Excellent humidity sensing properties of cadmium titanate nanofibers. Ceram. Int. 2013, 39, 457–462.
9. Jamil, H.; Batool, S. S.; Imran, Z.; Usman, M.; Rafiq, M.; Willander, M.; Hassan, M. Electrospun titanium dioxide nanofiber humidity sensors with high sensitivity. Ceram. Int. 2012, 38, 2437–2441.
10. Mehrabani, S.; Kwong, P.; Gupta, M.; Armani, A. M. Hybrid microvapour humidity sensor. Appl. Phys. Lett. 2013, 102, No. 241101.
11. Mohd Syafuddin, A.; Mukhopadhyay, S.; Yu, P. Modelling and fabrication of optimum structure of novel interdigital sensors for food inspection. Int. J. Numer. Modell. Electron. Networks, Devices Fields 2012, 25, 64–81.
12. Trankle, H.-R.; Kanoun, O. In Recent Advances in Sensor Technology, Instrumentation and Measurement Technology Conference, 2001 (IMTC 2001), Proceedings of the 18th IEEE, IEEE, 2001; pp 309–316.
13. Connolly, E.; O’Halloran, G.; Pham, H.; Sarro, P.; French, P. Comparison of porous silicon, porous polysilicon and porous silicon carbide as materials for humidity sensing applications. Sens. Actuators, A 2002, 99, 25–30.
14. Lee, C.-Y.; Lee, G.-B. Micromachined humidity sensors with integrated temperature sensors for signal drift compensation. J. Micromech. Microeng. 2003, 13, 620.
15. Yang, B.; Aksak, B.; Lin, Q.; Sitti, M. Compliant and low-cost humidity nanosensors using nanoporous polymer membranes. Sens. Actuators, B 2006, 114, 254–262.
16. Wang, L.; He, Y.; Hu, J.; Qi, Q.; Zhang, T. DC humidity sensing properties of BaTiO3 3 nanofiber sensors with different electrode materials. Sens. Actuators, B 2011, 153, 460–464.
17. Qi, Q.; Zhang, T.; Yu, Q.; Wang, R.; Zeng, Y.; Liu, L.; Yang, H. Properties of humidity sensing ZnO nanorods-base sensor fabricated by screen-printing. Sens. Actuators, B 2008, 133, 638–643.
18. Kunakova, G.; Meija, R.; Bite, L.; Prikulis, J.; Kosmaca, J.; Varghese, J.; Holmes, J. E.rtis. S. Sensing properties of assembled Bi2S3 nanowire arrays. Phys. Scr. 2015, 90, No. 094017.
19. Yao, K.; Zhang, Z.; Liang, X.; Chen, Q.; Peng, L.-M.; Yu, Y. Effect of H2 on the electrical transport properties of single Bi2S3 nanowires. J. Phys. Chem. B 2006, 110, 21408–21411.
20. Yu, Y.; Sun, W.-T. Uniform Bi2S3 nanowires: Structure, growth, and field-effect transistors. Mater. Lett. 2009, 63, 1917–1920.
21. Yu, Y.; Sun, W.-T. Uniform Bi2 S3 nanowires: structure, growth, and field-effect transistors. Mater. Lett. 2009, 63, 1917–1920.
22. Liu, Z.; Peng, S.; Sie, Q.; Hu, Z.; Yang, Y.; Zhang, S.; Qian, Y. Large-Scale Synthesis of Ultragong Bi2S3 Nanoribbons via a Solvothermal Process. Adv. Mater. 2003, 15, 936–940.
23. Lu, J.; Han, Q.; Yang, X.; Lu, L.; Wang, X. Microwave-assisted synthesis and characterization of 3D flower-like Bi 2 S 3 superstructures. Mater. Lett. 2007, 61, 2883–2886.
24. Yu, X.; Cao, C. Photoresponse and field-emission properties of bismuth sulphide nanoflowers. Cryst. Growth Des. 2008, 8, 3951–3955.
25. Afsar, M.; Rafiq, M.; Tok, A. Two-dimensional Sn5N nanoflakes: synthesis and application to acetone and alcohol sensors. RSC Adv. 2017, 7, 21556–21566.
26. Afsar, M. F.; Jamil, A.; Rafiq, M. A. Ferroelectric, dielectric and electrical behavior of two-dimensional lead sulphide nanosheets. Adv. Nat. Sci.: Nanosci. Nanotechnol. 2017, 8, No. 045010.
27. Afsar, M.; Rafiq, M.; Siddique, F.; Saira, F.; Chaudhary, M.; Hasan, M.; Tok, A. Two-dimensional molybdenum disulphide nanoflakes synthesized by liquid-solid phase reaction method: regenerative photocatalytic performance under UV-visible light irradiation by advance oxidation process. Mater. Res. Express 2018, 5, No. 056206.
28. Feng, J.; Peng, L.; Wu, C.; Sun, X.; Hu, S.; Lin, C.; Dai, J.; Yang, J.; Xie, Y. Giant moisture responsiveness of VS2 ultrathin nanosheets for novel touchless positioning interface. Adv. Mater. 2012, 24, 1969–1974.
29. Zhang, S.-L.; Choi, H.-H.; Yue, H.-Y.; Yang, W.-C. Controlled exfoliation of molybdenum disulfide for developing thin film humidity sensor. Curr. Appl. Phys. 2014, 14, 264–268.
30. Tan, Y.; Yu, K.; Yang, T.; Zhang, Q.; Cong, W.; Yin, H.; Zhang, Z.; Chen, Y.; Zhu, Z. The combinations of hollow MoS2 micro-nano-spheres: one-step synthesis, excellent photocatalytic and humidity sensing properties. J. Mater. Chem. C 2014, 2, 5422–5430.
31. Pawbake, A. S.; Waykar, R. G.; Late, D. J.; Jadkar, S. R. Highly transparent wafer-scale synthesis of crystalline WS2 nanoparticle thin film for photodetector and humidity-sensing applications. ACS Appl. Mater. Interfaces 2016, 8, 3359–3365.
(32) Jha, R. K.; Guha, P. K. Liquid exfoliated pristine WS2 nanosheets for ultrasensitive and highly stable chemiresistive humidity sensors. Nanotechnology 2016, 27, No. 475503.

(33) Salavati-Niasari, M.; Ghanbari, D.; Davar, F. Synthesis of different morphologies of bismuth sulfide nanostructures via hydrothermal process in the presence of thioglycolic acid. J. Alloys Compd. 2009, 488, 442–447.

(34) Killedar, V.; Katore, S.; Bhosale, C. Preparation and characterization of electrodeposited Bi 2 S 3 thin films prepared from non-aqueous media. Mater. Lett. 2000, 64, 166–169.

(35) Li, W.-h. Synthesis and characterization of bismuth sulfide nanowires through microwave solvothermal technique. Mater. Lett. 2008, 62, 243–245.

(36) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yang, J.-S. One-dimensional nanostructures: synthesis, characterization, and applications. Adv. Mater. 2005, 17, 353–389.

(37) Xu, C.; Tamaki, J.; Miura, N.; Yamazoe, N. Grain size effects on gas sensitivity of porous SnO2-based elements. Sens. Actuators, B 1991, 3, 147–155.

(38) Li, J.; Fan, H.; Jia, X. Multilayered ZnO nanosheets with 3D porous architectures: synthesis and gas sensing application. J. Phys. Chem. C 2010, 114, 14684–14691.

(39) Dubourg, G.; Segkos, A.; Katona, J.; Radović, M.; Savić, S.; Niarchos, G.; Tsamis, C.; Crnojević-Bengin, V. Fabrication and characterization of flexible and miniaturized humidity sensors using screen-printed TiO2 nanoparticles as sensitive layer. Sensors 2017, 17, 1854.

(40) Zhang, T.; He, Y.; Wang, B.; Geng, W.; Wang, L.; Niu, L.; Li, X. Analysis of dc and ac properties of humidity sensor based on polythiophene materials. Sens. Actuators, B 2008, 131, 687–691.

(41) Xiao, Z.; Xu, C.; Jiang, X.; Zhang, W.; Peng, Y.; Zou, R.; Huang, X.; Liu, Q.; Qin, Z.; Hu, J. Hydrophilic bismuth sulfide nanoflower superstructures with an improved photothermal efficiency for ablation of cancer cells. Nano Res. 2016, 9, 1934–1947.

(42) Wang, J.; Wang, X.-h.; Wang, X.-d. Study on dielectric properties of humidity sensing nanometer materials. Sens. Actuators, B 2005, 108, 445–449.

(43) Batool, S.; Imran, Z.; Israr-Qadir, M.; Jamil-Rana, S.; Usman, M.; Jamil, H.; Rafiq, M.; Hasan, M.; Nur, O.; Willander, M. Silica nanofibers based impedance type humidity detector prepared on glass substrate. Vacuum 2013, 87, 1–6.

(44) Tian, F.; Ohki, Y. Charge transport and electrode polarization in epoxy resin at high temperatures. J. Phys. D: Appl. Phys. 2014, 47, No. 045311.

(45) Fan, P.; Wang, L.; Yang, J.; Chen, F.; Zhong, M. Graphene/poly (vinylidene fluoride) composites with high dielectric constant and low percolation threshold. Nanotechnology 2012, 23, No. 365702.

(46) Hossen, M. B.; Hossain, A. A. Complex impedance and electric modulus studies of magnetic ceramic Ni 0.27 Cu 0.10 Zn 0.63 Fe 2 O 4. J. Adv. Ceram. 2015, 4, 217–225.

(47) Yamamoto, K.; Namikawa, H. Conduction current relaxation of inhomogeneous conductor I. Jpn. J. Appl. Phys. 1988, 27, 1845.

(48) Imran, Z.; Rasool, K.; Batool, S.; Ahmad, M.; Rafiq, M. Effect of different electrodes on the transport properties of ZnO nanofibers under humid environment. AIP Adv. 2015, 5, No. 117214.

(49) Chen, Z.; Lu, C. Humidity sensors: a review of materials and mechanisms. Sens. Lett. 2005, 3, 274–295.

(50) Ratnasamy, P.; Fripiat, J. J. Surface chemistry of sulphides. Part 1.—Infra-red study of molybdenum and germanium sulphides and of their reaction with H 2, H 2 O, thiophene and ethanethiol. Trans. Faraday Soc. 1970, 66, 2897–2910.

(51) Nahar, R. Study of the performance degradation of thin film aluminum oxide sensor at high humidity. Sens. Actuators, B 2000, 63, 49–54.