Section A-Research paper

Room Temperature Measurement of NO and NO_2 using Chemi-resistive Chalcogenide based Sensor

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Abstract

The advancement in chemi-resistive gas sensing at room temperature employ chalcogenides as an active layer owing to their excellent physicochemical characteristics such as lacking of the oxygen in the crystal lattice and low bandgap energy. Herein, we report the preparation of chalcogenide ($Sn_{20}Te_{80}$) using heat treatment and their usage as active layer in the chemi-resistive sensor for the detection of most prominent toxic gas analytes such as NO_2 and NO under room temperature (~25 ^{0}C) measurement. The electron interaction after the exposure of analytes and determination of their trapping at charged centres affirms the sensing characteristics with excellent recovery and response time. The higher order of concentrations (NO_2 and NO) resulted in increased sensitivity with maximum exposure limit of 5ppm (NO_x) as per OSHA standards. The mechanism of chalcogenide ($Sn_{20}Te_{80}$) based sensor device deposited over IDE is tested to the exposure of NO_2 and NO gas and the sensor response with sensitivity and selectivity is discussed.

Keywords: *Chalcogenides, Chemi-resistive gas sensor, toxic gas, Nitrogen dioxide (NO_x)*

1. Introduction

Gas sensors are considered as one among the paramount sensors in the field of electronics. The gas sensors are noted for monitoring and detecting toxic gases, preserving the environment's quality and safety, and supporting human society [1-6]. Metal Oxide Semiconductors (MOS) are the most frequently used materials for gas sensing applications from past several decades [7-9]. MOS based gas sensors are leading innovations in the field of sensors owing to the fact that they require higher operating temperature to achieve desired sensing concentrations of gas analytes (ranging ppm/ppb). Sensitivity, selectivity, stability, detection limit, life cycle, response time and recovery time are a gas sensor's most important performance parameters. Sensitivity typically measures the ratio of the targeted gases resistance to that of the reference gas. Detection of the target gas in the presence of other gas analytes determines the selectivity of the device. The response and recovery time of a gas sensor determines the suitability for various applications. Modifying the size, morphology,

porosity, thickness, doping level and doping element, noble metal decoration, hetero-structure, and hybrid structures made of 1D or 2D materials are just a few techniques for improving sensor performance [10-12]. The possibility of using chalcogenides semiconductors as the sensitive layer in chemical sensors for the analysis of industrial solutions and pollutant gases has received a lot of attention in recent years [13-15].

At room temperature, chalcogenides exhibits photoconductivity, thermoelectric effect, and catalytic activity, and it has been utilized in a variety of devices such as gas sensors, thin-film transistors, and infrared detectors owing to its unique crystal lattice structure formation [16-19]. One of the contaminations, nitrogen dioxide (NO_2) gases produced from burning of petroleum derivatives, i.e., car fumes and modern releases are environmental hazardous. The base identification and centralization of NO_2 sensors ought to be under 0.2 ppm for environmental safety. People can experience pharyngeal discomfort, chest tightness, respiratory distress, cough, and other symptoms after prolonged exposure to NO_2 at a concentration greater than 1 ppm. Humans should not be exposed to more than 3 ppm NO_2 for more than 8 hours, according to safety and health guidelines. Subsequently, it is important to foster a NO_2 gas sensor to screen climate constantly. The Proposed material finds application in the detection of NO_2 and NO at much lower concentrations (<5ppm) under room temperature. The MOS devices can further be utilized to detect NO and NO_2 gas analytes at much higher concentrations ranging from 10ppm to 100ppm with elevated temperature ranging from 30^0C, 50^0C, 60^0C, 90^0C, 120^0C, 150^0C, 180C and so on [20-22].

2. Materials and Methods

2.1 Chemicals:

Chemicals such as Stannous (Sn) and Telluride (Te) were procured from Sigma Aldrich, Acetone and Iso-Propyl-Alcohol were purchased from Merck and Inter-Digitized Electrode (IDE) from Micrux Technologies. Sample preparation and deposition were carried out in normal laboratory conditions.

2.2 Sample Preparation:

Initially, the sample preparation was done by considering the required proportion of Sn and Te which were weighed according to the stoichiometric calculations and was transferred to clean quartz ampoules. The quartz ampoule was then sealed and heated at 750 ^{0}C under vacuum (10^{-5} Torr) in a horizontal rotary tubular furnace which was programmed to soak the molten mixture for 12hrs under constant rotation to ensure homogeneity of the particles. The so obtained homogenous mixture was cooled naturally and further the resultant powder was

crushed using agate mortar to ensure fine grinded material is kept ready for the deposition. The as-prepared bulk samples of $Sn_{20}Te_{80}$ were deposited on the Inter-Digitized Electrode (IDE) device using thermal evaporation technique at 10^{-5} Torr pressure. The IDE device was cleaned using acetone wash followed by IPA (Iso-Propyl-Alcohol) for 3-4 times to remove any sort of contaminations and immediately after the cleaning process the device was exposed to thin film deposition as mentioned earlier. The as-deposited IDE device was exposed to NO and NO_2 analytes in the gas measurement chamber and all the measurements were performed at room temperature. The complete process of sample preparation and deposition techniques along with exposure of gas analytes is depicted in figure 1.

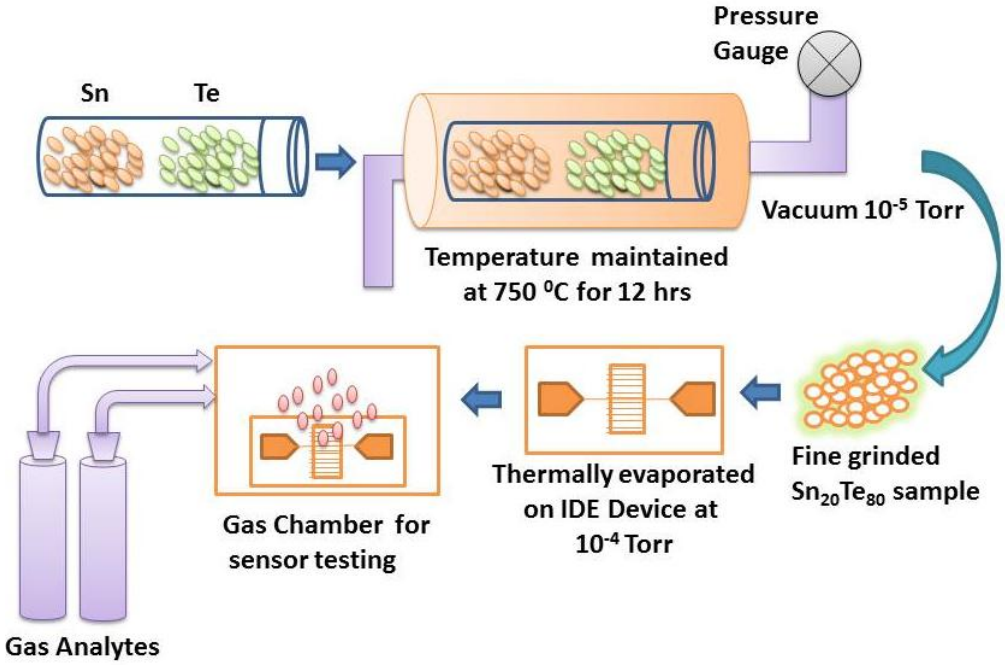


Figure 1: The schematic illustration of sample preparation and deposition over IDE device for sensing the gas analytes.

3. Results and Discussions

The as-prepared sample was characterized using various analytical and spectra/microscopic tools such as XRD, UV-Vis, SEM and EDAX to study the material characteristics; furthermore, the as-deposited IDE device was tested for various gas analytes and the device performance were studied by extracting the electrical parameters as detailed in further sections.

3.1 X-Ray Diffraction Studies

The XRD technique was employed initially to ascertain the crystallite structure and crystallite particle size from the broadening width of the peaks recorded using Rigaku Ultima IV X-Ray

diffractometer in the 2theta range (10-90^0) under the room temperature as can be seen in figure 2. The analysis confirmed the crystallite structure of cubic having lattice parameters of a = b = c = 6.31 Å and α = β = γ = 90º with *Fm*-3*m* space group and the lattice parameters are in good agreement with the reported data of standard JCPDS Card No. 46-1210 [23]. The evidence of extra peaks alongside with deviation in the phase depicts the extrinsic impurity of the characteristic peak so obtained.

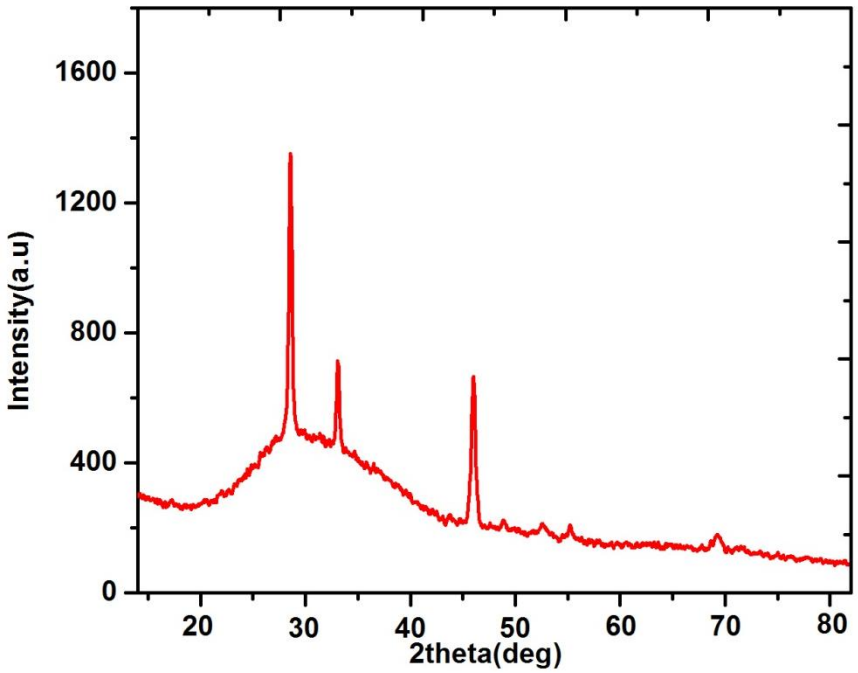
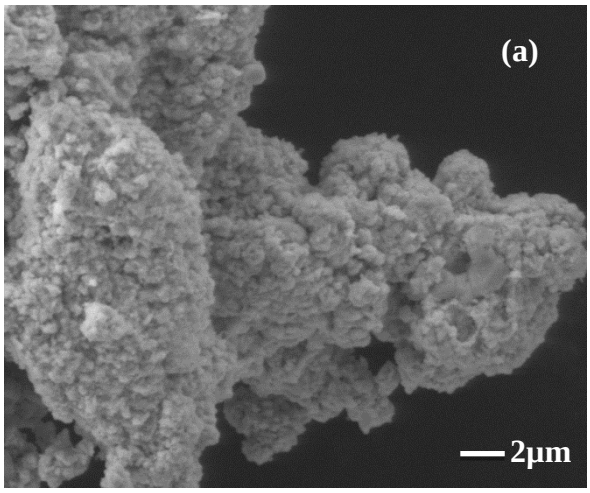
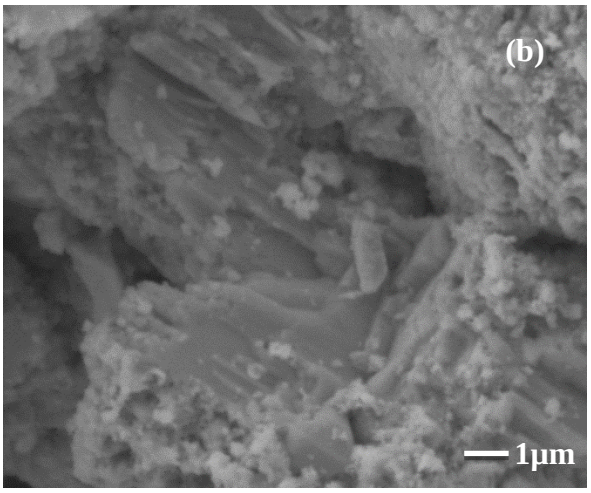


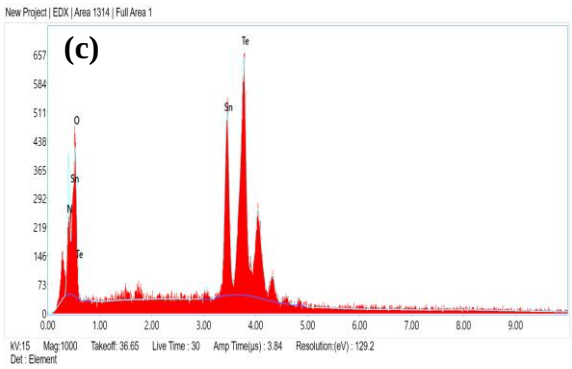
Figure 2: The XRD pattern intensity vs. 2theta recorded for the as-prepared $Sn_{20}Te_{80}$ bulk sample.

3.2 Surface Morphology and EDAX Studies

The surface morphology of $Sn_{20}Te_{80}$ was investigated using Scanning Electron Microscopy (SEM) images depicted in figure 3 (a) and (b). The SEM images reveal that the as-prepared bulk specimen of $Sn_{20}Te_{80}$ shows uniform microstructure with micro-sized grains distributed uniformly over a smooth homogeneous grain boundary. The flower-like pattern was noticed with slight agglomeration of multiple flakes attributed to the variations of reactants concentrations (Sn and Te) or can be attributed to the reaction environment [24]. The EDAX analysis affirms the presence of Sn and Te with their atomic weight percentage of Sn (34.6%) and Te (53.3%) respectively. The atomic weight percentage so obtained was slight deviated with respect to the theoretical stoichiometric ratio indicating the presence of impurity as can be seen in figure 3 (c) and the elemental composition figure 3 (d) affirms that the reactant variations or environment growth is a possible reason of impurity.







(d)

Element	Weight %	Atomic %
N K	5.7	27.0
O K	6.3	26.1
Sn L	34.6	19.3
Te L	53.3	27.6

Figure 2: **(a)** and **(b)** shows SEM images with different magnification; EDAX pattern **(c)** and elemental atomic weight percentage **(d)** recorded for $Sn_{20}Te_{80}$ as-prepared sample.

3.3 UV-Vis Spectroscopic Studies

The UV-Vis reflection spectra for $Sn_{20}Te_{80}$ as-prepared sample is as shown in figure 3. The $Sn_{20}Te_{80}$ possessed to greater exhibition of electron excitation with bandgap of almost 1.8eV and strongly confined with their bulk properties as depicted [25]. The data also affirms the higher tendency of oxidation and air sensitive which exhibits the significant surface oxidation even at room temperature creating the space of room temperature sensors using chalcogenides.

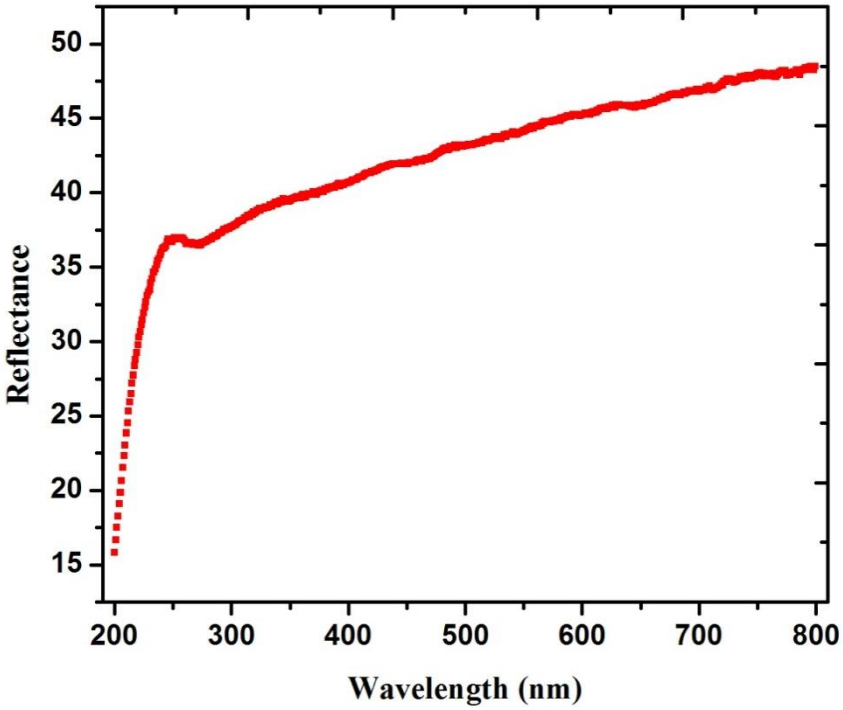


Figure 3: The UV-Vis reflection spectra for chalcogenide ($Sn_{20}Te_{80}$) as-prepared sample.

3.4 Sensor Device Characterization

The Preparation of $Sn_{20}Te_{80}$ IDE devices are as detailed in the earlier sections. Further, this device was exposed to gas analytes in a customized gas sensing measurement setup and all the measurements were carried out at room temperature. The first device was initially exposed with NO_2 at different concentrations (0.5 ppm, 1 ppm, 3 ppm and 4.8 ppm) as depicted in figure 4 (a) which was in well agreement with OSHA standards for limit of detection. The sensing current vs time was plotted to understand the sensor behaviour (transient characteristics) for the set time period and the graph revealed that the sensing properties of $Sn_{20}Te_{80}$ chalcogenides was well defined with previous sensors design using chalcogenides. The process was repeated for second device with NO concentrations (1 ppm and 3 ppm) and transient characteristics are in figure 4 (b). The device showed excellent reversibility for aforementioned concentrations of both analytes NO_2 and NO respectively by flushing through the device with synthetic air after every exposure. The sensitivity graph (figure 4 (c)) shows better response to NO_2 as in comparison to NO gas analyte under room temperature (~25 ^{0}C) and curve (figure 4 (d)) depicts the sensitivity percentage vs concentration ppm levels. The study on sensitivity and selectivity of the device fabricated to test the gas analytes plays major role in the field of sensing applications [26-28], but the chalcogenide designed sensor performance improvement will be considered as key focus for the future aspects.

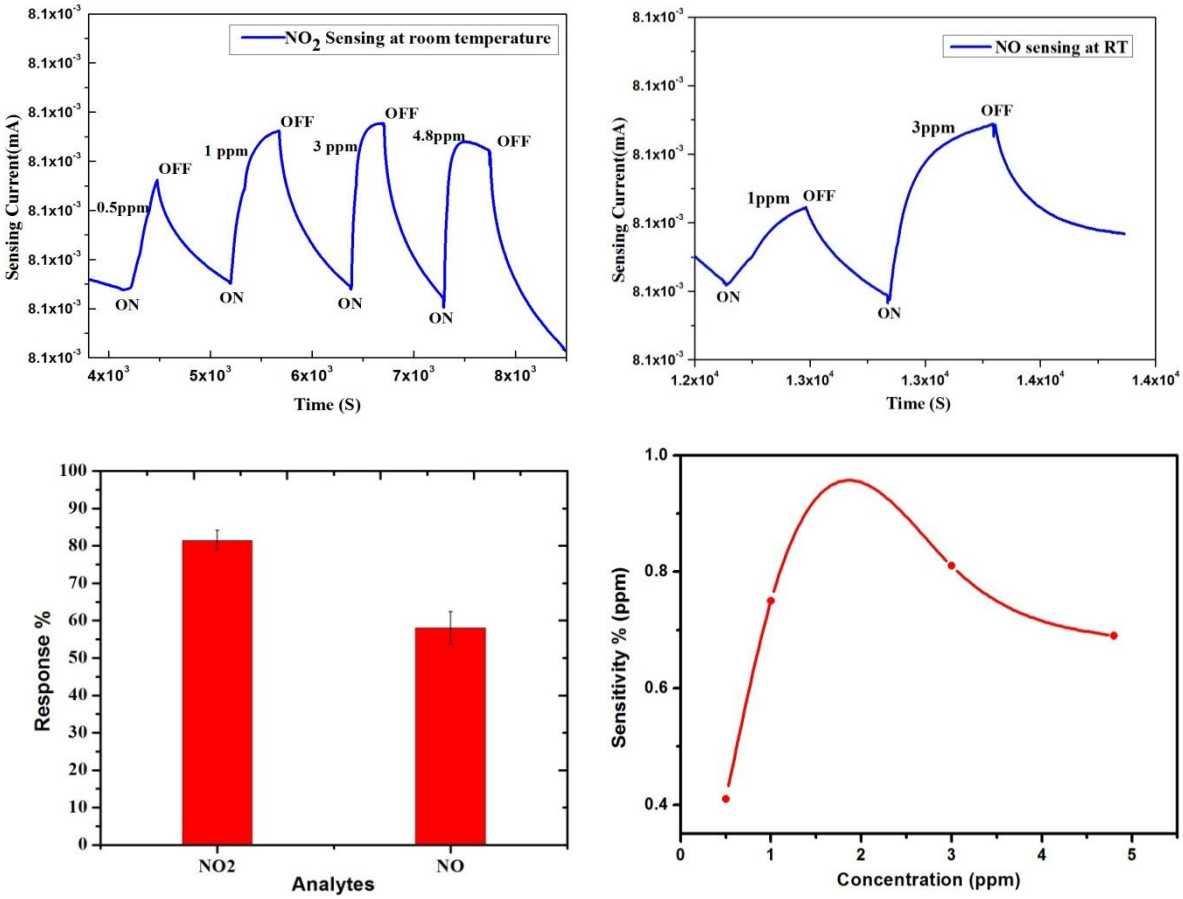


Figure 4: (a) Sensing Characteristic curve of $Sn_{20}Te_{80}$ for the exposure of NO_2 and **(b)** NO gas analytes respectively; the response graph **(c)** and **(d)** sensitivity percentage vs concentration curve for both analytes

4. Conclusion

The as-prepared chalcogenide ($Sn_{20}Te_{80}$) bulk specimen in powder form was thermally evaporated over IDE substrates to obtain sensor devices. These were tested for NO_2 and NO detection at room temperature in gas chamber setup as detailed. The as-prepared material was initially characterized using spectroscopic tools to understand the material characteristics prior to the thermal deposition over IDE devices. The chalcogenide ($Sn_{20}Te_{80}$) exhibited good physicochemical characteristics and a bandgap energy of 1.8eV. The atomic weight percentage was determined by EDAX affirming the presence of Sn (34.6%) and Te (53.3%) respectively. Furthermore, the sensing studies ascertain that the devices show better characteristics to NO_2 detection as compared to NO detection and the devices showed better sensitivity at lower concentration levels(<5ppm). The chalcogenides can be future promising materials for researchers to investigate on to realize chemical sensors for real-time applications to sense low levels of gas analytes at room temperature.

Conflicts of Interest

There is no conflict of interest.

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