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Fabrication and Characterization of Polyaniline and Polyaniline/Nanostructured-ZnO FET Hydrogen Gas Sensors

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Abstract: In this study, micron-sized Field Effect Transistor (FET) based sensors were produced using Polyaniline (PANI) channels. Pristine and nanostructured-ZnO added PANI was synthesized by free radical chemical oxidative polymerization method. FET production was carried out by producing PANI and PANI/nanostructured-ZnO composite channels on Si/SiO_2 (285 nm) substrate by the optical lithography method. The electrical responses of the produced sensors against hydrogen (H_2) gas were determined by measuring the source-drain current at 25 ˚C, 50 ˚C and 80 ˚C while applying the +20 V gate voltage to the transistors. It has been observed that PANI channel FET sensor detects H_2 gas but adding nanostructured-ZnO into PANI improves the detection performance. Besides, unlike the PANI channel FET sensor, it has been determined that PANI/nanostructured-ZnO composite channel FET sensors operate with an excellent performance at room temperature.

Polianilin ve Polianilin/ ZnO Nanoyapılı FET Hidrojen Gazı Sensörlerinin Üretimi ve Karakterizasyonu

Anahtar Kelimeler
Gaz Dedektörleri,
FET Sensör Sistemleri,
İnce Film H_2 Sensörleri

Öz: Bu çalışmada, mikron-boyutlu alan etkili transistör (FET) sensörler polianilin kanallar kullanılarak üretilmiştir. Katkısız ve ZnO nanoparçacık katkılı PANI, serbest radikal kimyasal oksidatif polimerizasyon yöntemi ile sentezlenmiştir. Sentezlenen her iki PANI kullanılarak gaz algılama uygulaması için mikrofabrikasyon yöntemiyle mikron boyutlu, alan etkili transistör (FET) yapıda sensörler üretilmiştir. FET üretimi optik litografi yöntemiyle Si/SiO_2 (285 nm) alttaş üzerine PANI ve PANI/nanoyapılı ZnO kanalların üretilmesiyle gerçekleştirilmiştir. Üretilen sensörlerin hidrojen (H_2) gazına karşı gösterdiği elektriksel tepkiler, 25 ˚C, 50 ˚C ve 80 ˚C sıcaklıkta transistöre +20 V kapı gerilimi uygulanırken, kaynak-akaç akımı değişimleri ölçülerek belirlenmiştir. PANI kanal ile üretilen sensörlerin H_2 gazını algıladığı ancak PANI içerisine nanoyapılı ZnO katkılamanın algılama performansını iyileştirdiği gözlemlenmiştir. Ayrıca PANI kanallı FET sensörün aksine PANI/nanoyapılı ZnO kompozit kanallı FET sensörlerin oda sıcaklığında oldukça iyi bir performansla çalıştığı tespit edilmiştir.

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1. Introduction

Today, the importance of chemical sensors used in the industrial field is undisputed. Gases are used both as precursors in industrial processes and as a by-product due to the combustion of any fuel. Most of these types of gases are harmful to humans, animals and plants. While some of them do not directly affect living organisms, they indirectly damage the environment. The allowable limit of most gases is set by environmental and safety standards [1, 2]. Although hydrogen (H_2) is not toxic, it is a flammable and suffocating gas. Compared to other gases, H_2 is a reducing gas with low minimum ignition energy (0.017 mJ) and a wide range of flammability with air from 4.6% to 75%. H_2 has attracted great attention as a green, clean, efficient and sustainable energy source [3]. However, it is very important to prevent accidents during the use of this gas, which can leak easily due to its small molecules. For this reason, it has become a necessity to be able to monitor it at room temperature (25-27 °C) and standard air pressure (1 atm) in order to develop a safe hydrogen technology. Accordingly, the production of low-cost sensors that can be sensitive to hydrogen in standard room conditions, have fast recovery time and long-term operation capability, has come to the fore.

Nowadays a popular class of sensing material is conductive polymers. In the last thirty years, conductive polymers have emerged as a new material in developing new generation electronic devices with advanced technology due to their excellent electrical properties [4-10]. Essential members of conductive polymers used in sensors are polyaniline (PANI) [11], polythiophene, and polypyrrole [12]. PANI is unique among conductive polymers due to its excellent electrical properties, stability, low monomer price, simplicity of polymerization reaction, easy deposition procedure, and chemical structure suitable for structural modification [8-10, 13-18]. This unique properties enable it to be sensitive to many factors, such as various gases in ambient conditions [10, 13-14].

The first gas detection materials developed for use in sensors were inorganic materials [19]. The prominent metal oxide sensors among inorganic sensors have been used to determine the type and amount of gases in the atmosphere. For example, different crystal forms of zinc oxide (ZnO) were used as sensors [11, 20-22]. It has been reported that nanocrystal ZnO is used to detect H_2 [20], nitrogen (N_2) [23], and liquid petroleum gas [24] from various gases. However, it has also been reported that metal oxides such as ZnO, SnO_2, WO_3, and TiO_2 are used to detect ammonia (NH_3) [23, 25-26] gas. The biggest problem with most inorganic sensors has been the high operating temperatures, mainly cause stability and durability problems during long-term use [20]. Inorganic semiconductor metal oxides such as TiO_2 and SnO_2 have been the subject of intensive studies to detect H_2 gas due to their favorable physical and chemical properties, good responses, low costs, and simple detection methods. However, the problems such as high operating temperature (200-500 °C) and high energy consumption limit the production of portable detectors [27-28] and require the development of H_2 gas sensors with new materials that can operate at low operating temperatures and require low energy consumption.

The properties of conductive polymers can be modified by combining them with inorganic materials [29]. Therefore, conductive polymer/inorganic nanocomposite structures have recently been shown as promising materials in sensor applications with higher sensitivity at room temperature [30]. In studies published in this area, it has been reported that the electrical resistance of the PANI/TiO_2 nanocomposite for the NH_3 and CO sensors varies in direct proportion with the concentration of the analyte gases [31]. Similarly, the PANI/SnO_2 hybrid material served as the sensor material for acetone and ethanol [32], while the PANI/WO_3 composite was used in the moisture sensor application [33]. Another example of such composite sensors is the PANI/nanostructured-ZnO composite structure used to detect toxic gases [34-35], including NH_3 [30, 36] and some volatile organics such as acetone, ethanol, and methanol [37]. PANI has received significant interest as a useful conductive polymer with important H_2 gas detection properties at room temperature [4, 10, 38-40]. However, PANI also has disadvantages such as low thermal stability and insufficient detection of H_2 gas in standard room conditions. It has become a common belief that this may hinder potential applications in the future [4, 14, 38]. Combining the PANI matrix with nanoscale semiconductor metal oxides suggests forming an n/p heterojunction between p-type Polyaniline-Emeraldin salt (ES) and n-type semiconductor metal oxide. It would be a viable strategy for improving H_2 gas sensor efficiency at room temperature [39-42]. Moreover, it is argued that semiconductor metal oxide nanoparticles not only generate better oxidation of PANI during polymerization but can also be used as a switch to control the electrical resistance and flow of the electric current of the PANI/semiconductor metal oxide nanocomposite structure in practical applications such as the H_2 gas sensor [14, 39, 42-44].

Semi-oxidized Polyaniline-Emeraldin, which contains amine (—NH—) and imine (=N—) groups in equal proportions, is one of the forms of PANI. Emeraldin base (EB) is the electrically insulating form of PANI and can become the conductive Polyaniline-Emeraldin salt (ES) by non-redox acid doping (deprotonation) method. Conversely, ES can be converted back to EB by treatment with base [14, 15]. This situation occurs as a result of the formation of a polaron lattice in the PANI backbone by protonating the imine nitrogen sites in ES by using a suitable

substance. Polaron lattice induces charge carriers in the PANI network that can provide more conductivity than EB. The higher conductivity of the ES is due to the charge carriers' ability to jump between the polaron cage and the polymer chains. Also, it is accepted that the oxygen molecules on the surface of different n-type semiconductor metal oxide particles are in the form of O_2^-, O^- and O_2^- ions that create a positive charge by removing electrons from conductivity bands [45, 46].
During the synthesis of PANI with nanoparticles, metal oxide particles are suspended in aniline solution with Ammonium Peroxydisulphate (APS). Aniline monomers are transformed into anilinium cations, and adsorbed anions can be formed on the particles' surface by electrostatic interaction [14, 41]. After the reaction, electrons captured by the oxygen on the particle surface are released [41, 47]. The gas detection mechanism of the PANI/semiconductor metal oxide nanocomposite sensor is governed by the reaction between the surface layers of the sensor and H_2 gas molecules. MacDiarmid [48] provided a possible mechanism for H_2 to interact with PANI. According to the mechanism, the nitrogen regions in the structure of charged amines in the protonated PANI-ES molecules on the sensor surface can react with H_2 due to contact with H_2 gas. It has been suggested that H_2 molecules can form a bridge between the nitrogen atoms of two adjacent chains. The cleavage of H_2 bonds possibly leads to the formation of new N-H bonds to the amine nitrogen of PANI chains. Due to charge transfer in PANI chains, the structure reverts to the polaron lattice state [13]. The increase in the number of carriers and the speed of charge transfer in the presence of H_2 molecules is explained in this way. It is also suggested that this may result in a completely reversible carrier transfer [49].

The chemical and physical properties of the sensing material used in sensors change during detection. This situation causes a change in the color, temperature, or electrical conductivity of the material. Manufactured sensors are characterized by observing changes in the material in their structure. Although most of the PANI-based sensor studies in the literature have focused on resistive structures, the device's resistance does not change only with the conductive polymer film's resistance, which is the sensing material. Device resistance is also affected by many environmental factors, and even the contact resistance of the electrodes creates a disruptive effect on the sensor.

For this reason, the investigation of the sensors' response properties that PANI/Field Effect Transistor (PANI channel FET) structure for H_2 gas at different gate voltages and different temperatures adds an advantage to the study. Also, there has been a recent trend towards using environmental sensors in mobile devices. Therefore, sensors are needed that provide low power consumption due to their micron size [50]. Because of these facts, in this experimental study, the microfabrication method was used to produce a micron-sized PANI based FET sensor. This study aims to investigate the contribution of the semiconductor metal oxide used in the PANI/nanostructured-ZnO composite channel FET sensor to the detection performance for the analyte gas H_2. PANI/nanostructured-ZnO composite channel FET produced by using nanostructured-ZnO doped PANI and PANI channel FET produced by using PANI without ZnO additive. In order to explain the contribution of ZnO, which is used as a semiconductor metal oxide nanocomposite additive, to the sensing behavior for H_2 gas, the electrical properties of individual sensors have been examined at different gas concentrations and changing sensor temperatures.

2. Material and Method

PANI-ES, the precipitate was prepared by free radical chemical oxidative polymerization through indirect routes as ref [51]. In this reagent, in 100 mL distilled water, 0.1 mol HCl, and 0.01 mol aniline were mixed. This mixture was magnetically stirred for about 30 min. Afterward, 677450-5G coded nanostructured-ZnO that was purchased from Sigma Aldrich was added up to 1% of the mass of Aniline in the mixture. 0.01 mol APS ($(NH_4)_2S_2O_8$ - ammonium peroxidisulfate) was combined with 10 mL distilled water. Subsequently, this aqueous solution was added to ammonium persulfate. It was joined dropwise to the HCl/aniline solution, and polymerization was started. The mixture was thermally maintained at 0 °C. This mixture was stirred vigorously for 6 h. The polymer produced a dark green precipitate. The precipitate was repeatedly washed in ultrapure water until the filtrate became colorless and its pH became neutral. Polymerization steps were carried out as shown in Figure 1. The final precipitate was dried at room temperature to form nanostructured-ZnO doped PANI-ES dry powder. The same procedures were repeated with the same method and material quantities for nanoparticle additive-free PANI synthesis without adding ZnO nanoparticles to the mixture.

HCl doped conductive PANI-ES is not soluble in any solvent. It has to interact with ammonia to be soluble, and eventually, the powder converted to an undoped Polyaniline-Emeraldine Base (PANI-EB) form. When ammonia interacts with PANI-ES, not only can the polymer be dissolved rapidly insolvent (1-methyl-2-pyrrolidone), but the precipitate also becomes a dark blue color. Conversely, because of deprotonation, the precipitate changes its structure to an insulated form, and then this situation causes an increase in resistance, and equal conductivity disappears.

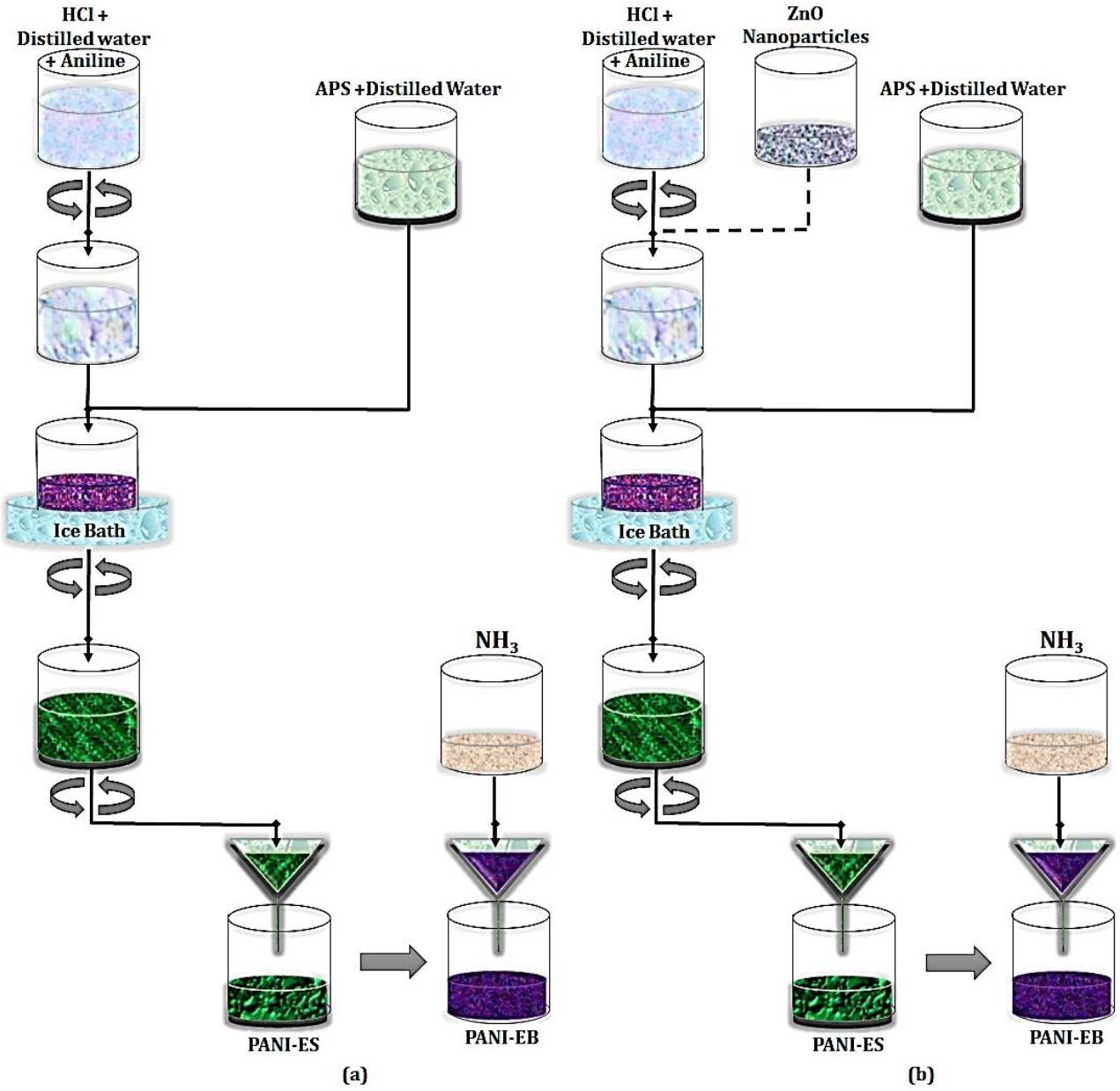

Figure 1. Schematic representation of the polymerization procedures of (a) Polyaniline and (b) Polyaniline/nanostructured-ZnO

The sensor was fabricated on a high p-type doped Si wafer with a 285 nm SiO_2 cap layer. First, the source-drain connections and the channel were formed by using standard photolithography techniques on designed locations. After the lift-off procedure, the thermal evaporation system evaporated Cr/Au (20/30 nm) contacts. Using a very thin bristle, a PANI and a PANI/nanostructured-ZnO composite channels were formed between source-drain contacts under a meteorological microscope. After the devices' fabrication, the channel length and width were determined as L= 2 μm and W= 6 μm, respectively. The thickness of the channel was measured as 65 nm with a profilometer. The schematic diagram of the PANI and PANI/nanostructured-ZnO composite channel FET sensors is shown in Figure 2. After the PANI and PANI/nanostructured-ZnO composite films were simultaneously formed between the electrodes of FETs, to overcome the conductivity problem of PANI, the FET sensors were put in an HCl (1 %) solution for 3 s.

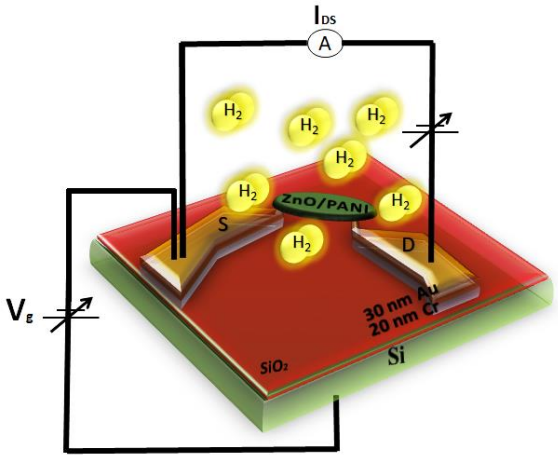

Figure 2. Schematic diagram of the PANI/nanostructured-ZnO composite channel FET sensor

To test the fabricated PANI based FETs, a typical set of drain-source current (I_{ds}) voltage characteristics were measured at various gate voltages (V_g). The results are shown in Figure 3. The polyaniline channel can be understood as p-type doped due to increasing negative V_g causing an increase in the I_{ds}. The effect of an electric field on the channel conductance, which is constituted between the gate and source electrodes, is clearly seen at the I_{ds}. However, there are linear I_{ds} vs. V_{ds} (drain-source voltage) characteristics. For FETs with polyaniline as the semiconductor, Renkuan et al. [52] reported that the I_{ds}-V_{ds} characteristics are approximately linear when the negative bias is applied to the gate implies that the characteristics are different from those of conventional inorganic FETs.

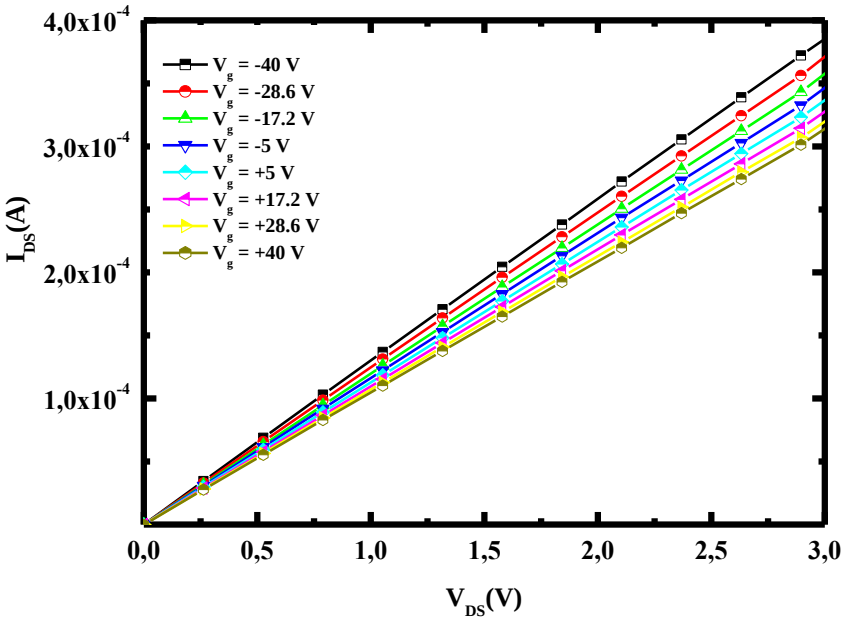

Figure 3. I_{ds}-V_{ds} characteristics of the PANI channel FET at different gate voltages

The PANI channel FET and PANI/nanostructured-ZnO composite channel FET sensor responses were investigated for H_2 gas at different gas concentrations. To test the fabricated FETs and measure the sensor's response, a computer-controlled Keithley 2612 source-meter was used. All measurements were done at atmospheric pressure at 25 °C, 50 °C, and 80 °C sensor temperatures. The sensor temperature was controlled by Lakeshore 332s and a Cernox sensor, which was fixed on sensor substrate. The H_2+N_2 gas mixture was supplied to the sensor surface as schematically shown in Figure 4.

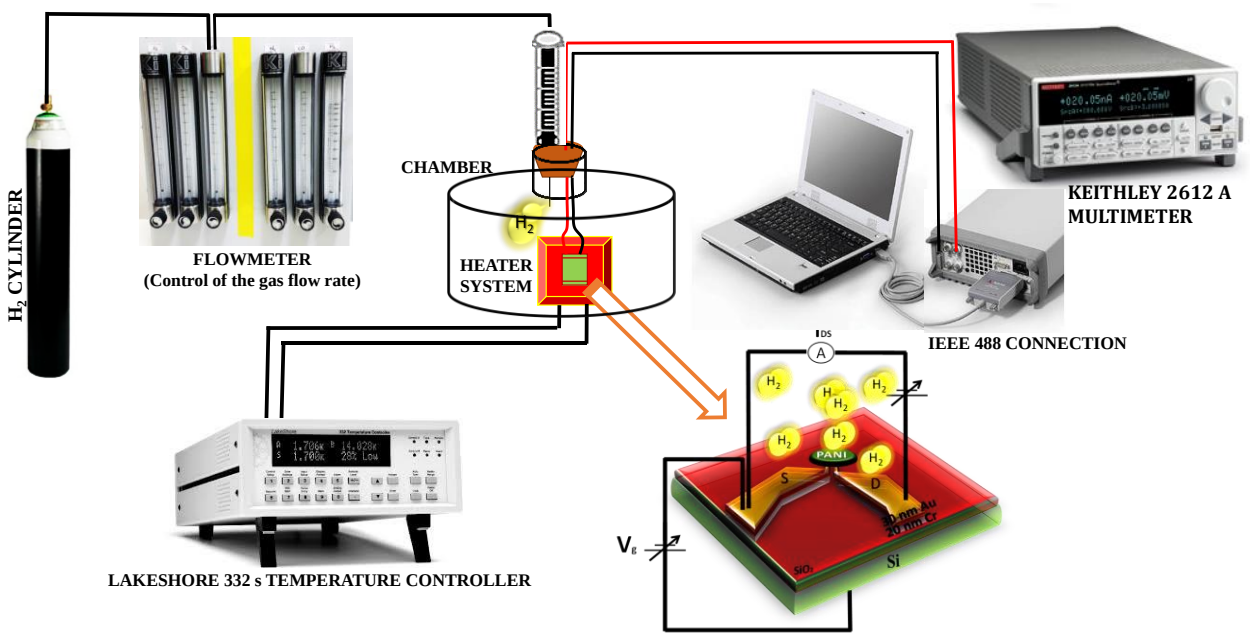

Figure 4. H_2 gas response measurement system of the FET sensors

H_2 gas concentration and flow rates were controlled with 150 mm flow meters, fabricated by Key Instruments with a ±3 % accuracy. For the gas flow system, all fittings and 316 Stainless Steel Seamless Tubing were supplied from Swagelok. H_2 and N_2 gas had 99.50% and 99.99% purities, respectively. The sensor sensitivities were calculated from Eq.1 [53] where I and I_0 are the current values before and after exposure to H_2, respectively:

$$Sensitivity\ (\%) = \left[\frac{I - I_0}{I_0}\right] x100 \quad (1)$$

3. Experimental Results

To compare the H_2 gas detection performance for PANI channel FET and PANI/nanostructured-ZnO composite channel FET sensors, sensor responses at different temperatures and varying gas concentrations were studied. Firstly, as can be seen in Figure 5, XRD analysis of the samples were performed. Figure 5 depicts the XRD patterns of PANI and PANI/nanostructured-ZnO composite, which contains ZnO nanoparticles. It was obtained 4 characteristic peaks at 9.21°, 20.08°, 24.39°, and 43.39° for the prepared PANI. Those are in agreement with the literature [54]. Although ZnO was added to the monomer before the polymerization, no peaks were observed for ZnO. When low concentration nanoparticles were added to the polymer matrix, enough X-ray reflection may not be supplied. Thus, ZnO peaks didn't appear in the XRD graph. Similar observation can be found in the literature for PANI/nanostructured-ZnO [55].

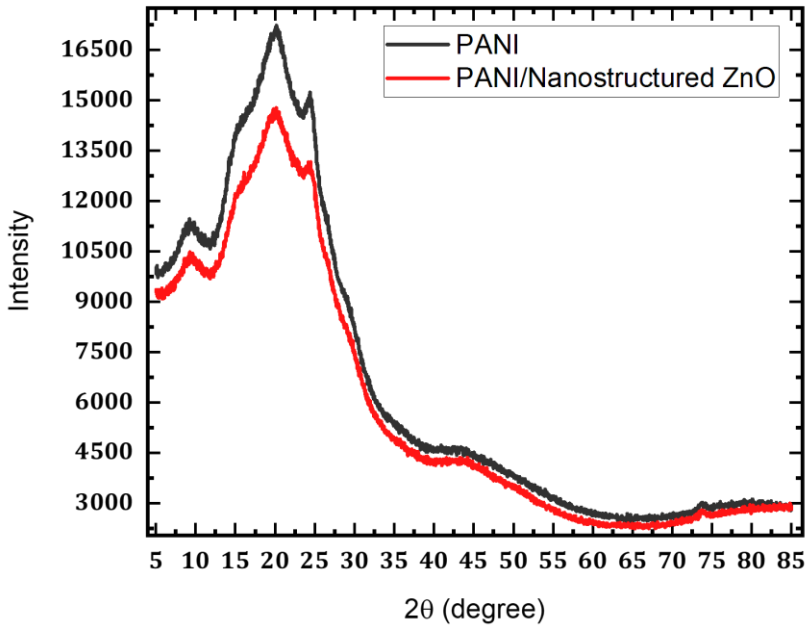

Figure 5. XRD patterns of PANI (black) and PANI/nanostructured-ZnO composite (red)

It is also essential to know the effect of sensor temperature on detection sensitivity. For this reason, the measurements were made at 20, 30, 50 and 80 °C by applying a +20 V gate voltage and decreasing the H_2 gas concentration. The graph of the source-drain currents of the PANI channel FET sensor in Figure 6 and the PANI/nanostructured-ZnO composite channel FET sensor in Figure 7 are given depending on the gas concentration change and sensor temperature. In this case, the PANI channel FET sensor showed a maximum response at 80 °C with a 13% drop in source-drain current at 60 % H_2 gas concentration. The lower sensor temperature caused the reduced gas response. The highest responses to H_2 gas were observed for the PANI channel FET sensor at 50 and 80 °C.

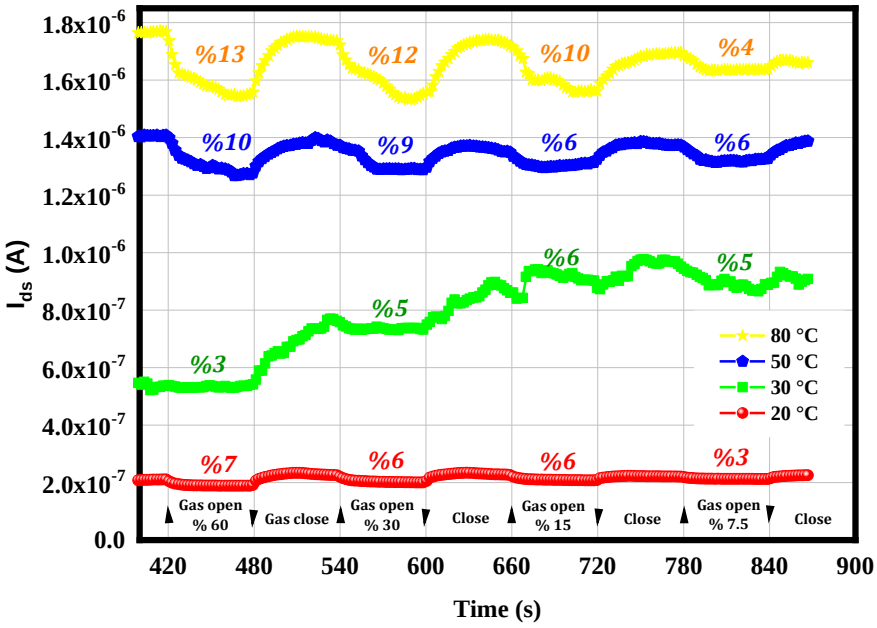

Figure 6. Dynamic response of the PANI channel FET sensor for different concentrations H_2 gas at the different sensor temperatures.

As can be seen in Figure 7, the PANI/nanostructured-ZnO composite channel FET sensor showed the maximum response at temperatures of 20 and 30 °C in contrast to the PANI channel FET sensor. When the H_2 gas at 60 % concentration was applied, there was a 20 % decrease in the I_{ds} at 20 and 30 °C temperatures. The response rate increased with the increase in gas concentration. At 20 °C, the lowest response is 11 % for 7.5 % gas concentration, while this value is very close to the highest response of the PANI channel FET sensor to the highest gas

concentration (60 %). Also, the PANI/nanostructured-ZnO composite channel FET sensor's responses tended to decrease with increasing temperature, dropping up to 1 % at 80 °C. It is an indication that the sensor is performing better at room temperature. The addition of nanostructured-ZnO to PANI has enabled the sensor to work efficiently at low temperatures.

It is thought that the decrease in sensor sensitivity at 50 and 80 °C may be due to the decreased adsorption and increased desorption [56]. It is also observed that the source-drain current decreases with increasing temperature. PANI/nanostructured-ZnO composite, which is the FET sensor's active material, exhibits metallic behavior and has the maximum conductivity value at room temperature. The increase in temperature caused a decrease in conductivity [57]. The rising of temperature caused a weakening in conductivity and a deterioration of sensor sensitivity at all H_2 gas concentrations at 50 and 80 °C. It is because gas adsorption of the PANI/nanostructured-ZnO composite channel decreases with the effect of temperature.

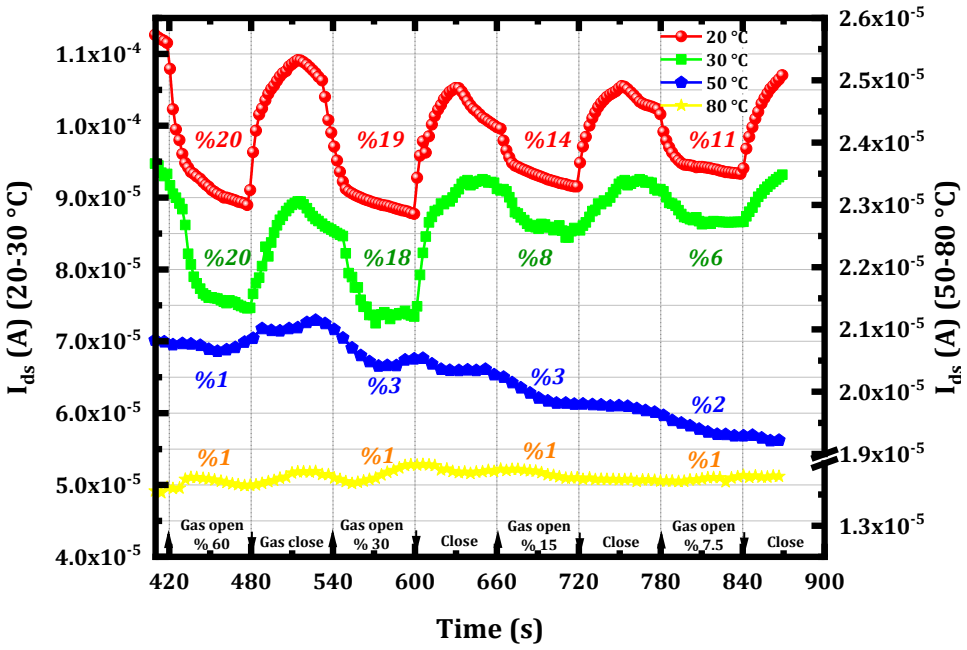

Figure 7. Dynamic response of the PANI/nanostructured-ZnO composite channel FET sensor for different concentrations H_2 gas at the different sensor temperatures.

4. Discussion and Conclusion

In this study, two types of H_2 gas sensors in the micro FET structure with PANI and PANI/nanostructured-ZnO composite channels were produced. Their detection performance at room temperature was tested and compared. For this purpose, H_2 gas detection performances were examined at various sensor temperatures. It has been observed that the PANI/nanostructured-ZnO composite channel FET sensor operates successfully at room temperature in contrast to the PANI channel FET sensor. The sensitivity of the PANI/nanostructured-ZnO composite channel FET sensor has deteriorated as the sensor temperature increases. Thus, it was determined that nanostructured-ZnO presence in the polymer structure caused a significant improvement in sensor response and lowered the operating temperature.

When the sensor responses are compared, it is seen that there is about 100 fold difference between the PANI/nanostructured-ZnO composite channel FET sensor and the PANI channel FET sensor. The PANI channel FET sensor responses are of the order of 10^{-6} A on the current scale and the responses of the PANI/nanostructured-ZnO composite channel FET sensor are of the order of 10^{-4} A. Being able to measure relatively lower current levels means more sensitive equipment is required. This situation means that the equipment's cost to be used in detection increases if the additive-free PANI is used in the sensor structure. In this context, it is clear that the use of PANI/nanostructured-ZnO composite channel FET sensor, which produces response at relatively higher current levels, will provide an advantage in both gas sensitivity and measurement system cost. Besides, PANI/nanostructured-ZnO composite channel FET sensor can measure at room temperature.

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