SHORT TERM SCIENTIFIC MISSION (STSM)
SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: Context COST Action (CA17107)
STSM title: Gas sensors on flexible Polyimide, rigid Alumina and Silicon substrate for the Nitrogen dioxide (NO_2) and Ammonia (NH_3) gas detection at room temperature.
STSM start and end date: 21/06/2021 to 21/07/2021
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PURPOSE OF THE STSM

This STSM is relevant to CA17107 Context WG 2 and 5 objectives WG2: Smart textiles for automotive and aeronautic applications and WG5: Smart textiles for sports and wearable applications.

Gas related accidents such as toxic gas leakage in Industries, carbon monoxide leakage of boilers, or toxic gas suffocation during manhole cleaning continue to claim lives and cause injuries, gas sensors are life. Developing a sensor that can quickly detect toxic gases or biochemical is still an important issue in public health, environmental monitoring, and military sectors. However, conventional gas sensing devices are not widely used due to their high cost of being made with complex machines and electronic devices. In addition, commercial gas sensors have limitations in that they are difficult to use, and have poor portability and reaction speed[1].
Wearable electronics is expected to be one of the most active research areas in the next decade. Today, flexible and stretchable sensing devices are in great demand due to their promising applications in wearable electronics, especially for healthcare industries. People like to use nanomaterials for sensing because their large surface-to-volume ratio makes them highly sensitive. Graphene has major role in fabricating flexible gas sensors for the detection of various hazardous gases, including nitrogen dioxide (NO2), ammonia (NH3), hydrogen (H2), carbon dioxide (CO2), sulfur dioxide (SO2), and humidity in wearable technology[2]. SWCNT and Graphene monolayer and multilayers can be transferred to different flexible substrates without any cracks or defects for fabricating flexible, stretchable, and foldable and cheap electronic devices. The performance of a chemical gas sensor is assessed based on parameters such as sensitivity, selectivity, time response, stability, durability, reproducibility, and reversibility, which depend on the properties of the sensing material. In this work. The three sensor substrates configuration are used, the polyimide foil as a substrate for Graphene/PANI sensors, rigid substrates consist of an alumina substrate (25.4 mm x 3.8 mm) with platinum interdigitated electrodes (IDE) and heater and PCB wire-bonded ZnO sensor using Silicon as substrates[3].

DESCRIPTION OF WORK CARRIED OUT DURING THE STSM

Within this STSM, we have focused on fabrication and electrical testing of three different gas sensors configuration.

1. **Graphene–polyaniline composite film for flexible NO_2 room temperature Sensor**

In this work, a nanostructured graphene–polyaniline composite film is developed and assembled for a flexible, electronic gas sensor to be integrated into wearable and foldable electronic devices. The Graphene/PANI solution deposition on flexible Polyimide substrate was investigated. The sensor response of modified Graphene/Pani to Nitrogen dioxide gas has been studied. Prior to the deposition the polyimide substrates were cleaned. The substrate was immersed in acetone (Scharlau, 99.5%) for 5 minutes, then in ethanol (Sigma-Aldrich, 96%) for another 5 minutes. Finally, they were rinsed with deionized water and dried in an oven at 110 °C for 10 min. After cleaning, the substrate was subjected to a surface treatment of oxygen plasma for 5 min. The main purpose of oxygen plasma treatment was to improve the hydrophilicity of the substrate. A graphene solution was prepared using 1 mg of graphene nanoplatelets from Strem Chemicals, Inc. (USA) dispersed in 1 mL of toluene. Then, graphene nanoplatelets were sonicated employing a Sonic Tip (FisherbrandTM Model 705) at 40% of 700W for 1 h and 30 min using a 1s on -2s off pulsed sonication. The PANI solution was prepared using 1mg of Commercially available PANI powder from Merck KGaA, Darmstadt, and dispersed in 1mL of methanol, then solution was sonicated for 30mins. Then Graphene/Pani Solution was added and sonicated for 1h. The flexible substrates were dip-coated into the solution and withdrawal 3 times after every 10s. The carrier gas was nitrogen dioxide for testing flexible sensors.

2. Chemical vapor deposition (CVD) grown ZnO NWs for PCB Sensor

The PCB based sensor fabrication steps, first we welded the male pins to the PCB using tin welding wire. than connected platinum wires to both extremes of the heater by using silver paste than applying silver paste at the backside of the alumina heater for attaching both substrates. Next Welding two platinum wires using the tin copper for the electrode's connection. In the final step bend and shape the platinum wires to touch the sensitive layer by using silver paste to do the electrode's contacts and place the sensor in the oven for 30 minutes at 100 °C.
For the active layer the Chemical vapor deposition used to grow ZnO nanostructure, the pure Zinc powder was placed in a glass boat inserted into a quartz tube and placed close to the right of the furnace. A heating system was used to increase the temperature inside the furnace, then temperature was raised from RT to the desired growth temperature of 800 °C in four different cycle. when the temperature reached at 600°C Ar/O2 flow rate of 60/0.2sccm was introduced to inside the vacuum chamber furnace tube. As the temperature is reached up to 800°C both the gases was turned off and the sample was taken out from the furnace after it cool down over night. Prior to CVD deposition the on Silicon substrates a silver layer was deposited on the substrates by sputtering method. The carrier gas was Ammonia for testing PCB based sensor.

3. Aerosol assisted chemical vapour deposition (AA-CVD) grown ZnO thin films Sensor

A zinc oxide thin film deposited on top of commercial alumina substrates with screen printed interdigitated platinum electrodes, was synthetized through Aerosol Assisted Chemical Vapor Deposition methodology, AACVD. The AACVD consisted in 3 different steps and a final annealing step.

1) **Substrate preparation**: Two alumina substrates were placed inside the AACVD hot-wall reactor and preheated at 400 ºC.
2) **Solution preparation**: 25 mg of zinc acetylacetonate, Zn(acac), were dissolved in a mixture of 15 ml acetone and 5 ml methanol in a volumetric flask.
3) **Thin film growth:** The volumetric flask was placed inside a high frequency wave generator and the solution was brought into an aerosol, the aerosol then was carried towards the hot-wall reactor through a N_2 stream at 1 L/min. The total synthesis time was set at 20 min. The reactor was cooled down naturally.
4) **Annealing:** In order to remove the remnant carbon impurities and to further increase the oxidation and crystallinity of the film, the sensors were placed into a muffle and annealed at 500 ºC during 2 hours under synthetic air. The thin film resulting in a transparent film covering homogenously the interdigitated area of the electrodes.
5)

4. Setup for Gas Sensing

The gas detection of all three sensors was investigated by placing the sensors separately inside a Teflon chamber. During gas measurements, the sensors were 1 h under a flow of synthetic dry air (Air Premier Purity: 99.995%) to clean the surface of the active layer. Also, this period allowed the stabilization of the resistance of the sensor. Subsequently, sensors were continuously exposed to one gas concentration for 30 min, and synthetic air for 30 min. The target gases were nitrogen dioxide (NO_2), and Ammonia (NH_3). The concentrations tested were obtained by diluting the gases on synthetic air. The NO_2 and NH_3 gas exposure has 10 min pulses of 10,20,30,40,50 PPM.

The gas detection was measured as changes in the electrical resistance of the active layer. The resistance was measured using a Keithley Electrometer 6517A (Keithley Instruments, Inc., Cleveland, Ohio, U.S.A.) and data was acquired through a custom-made application. A generic power supply was used to apply power to the heaters.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

1. **Flexible NO_2 RT Gas Sensor: -**

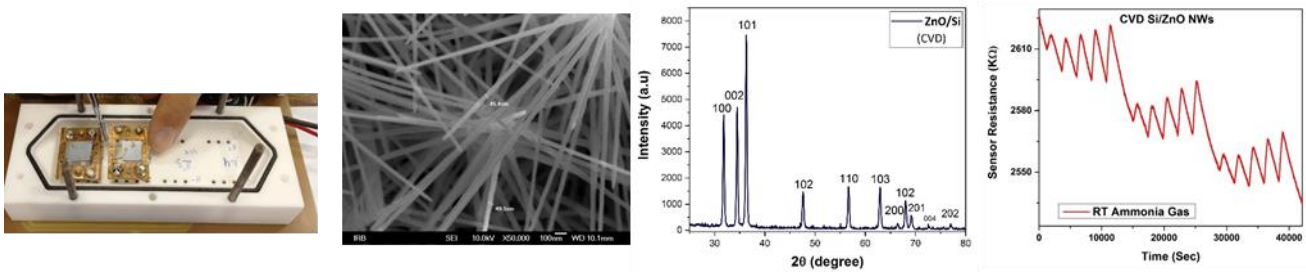
The flexible sensors fabricated include a flexible polyimide substrate 25.4 µm thick. An electrode made of conductive silver ink, an active layer Graphene/ Pani film were prepared shows in figure 1. We used two different gases, nitrogen dioxide (NO_2) and ammonia (NH_3) due to the danger human health derived from their exposure at certain levels were measured. Unfortunately, bare graphene sensors show no responses, probably because of its inertness and low specificity. Conversely, the dip-coated Graphene/Pani sensor shows clear resistance towards for nitrogen dioxide detection by applying repeated exposure and recovery cycles to increasing concentrations of the analyte considered. Figure 4d. shows the response to 10, 20, 30, 40 and 50 ppm, in which graphene with PANI obtained responses at room temperature. A baseline drift appears, given the difficulty to completely clean the surface from adsorbed gas molecules due to the room temperature working conditions. Several strategies can be developed in the future for improving the sensor recovery (i.e. desorption of gas molecules), as increasing the operating temperature or applying UV light to break the bonds between the sensitive layer and the gas species[4]. The flexible sensors do not detect Ammonia gas, could be NH_3 is a molecule with poor charge transfer compare to nitrogen dioxide gas leads to greater charge transfer and more energy binding.

(a) (b) (c) (d)

Figure 1a: shows the acutal polimide flexible gas sensor (b) installation of sensor inside a Teflon chamber (c) FESEM images of Graphene surface adopted from [5] (d) resistance resposne detecting NO_2 at room temperature.

2. **Printed Circuit Board (PCB) based RT NH_3 Gas Sensor**

Figure 2a: display the autal PCB wire-bonded gas senor installed in the chamber. The SEM images of CVD grown ZnO nano-rods active layer on silicon substrate shown in figure 2b. The sensor detected ammonia gas at room temperature for several concentrations (10, 20, 30, 40 and 50 ppm) in which ZnO NRs are randomly oriented on the substrates surface show in the x-ray diffracton pattern in figure 2d. It is observed that it has polycrystalline hexagonal wurtzite crystal structure with Eight well defined peaks as follows; (100), (002), (101), (102), (110), (103), (200), (112) and (201). In figure 2d. the sensor shows a low electrcial resistance (during 3 cycles) baseline level due to silicon substrate. If there is not an electrical layer insulator, the electron conduction is mainly located through the pathway with minimum resistance. This can explain the low resistance level for a metal oxide based gas sensor[6]. Therefore, underestimating the sensing responses of the ZnONRs.

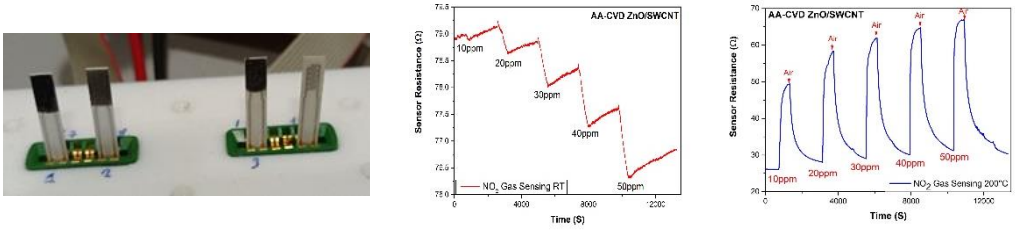


(a) (b) (c) (d)

Figure 2: (a) Actual ZnO PCB based sensor (b) SEM images of ZnO nano-rods grown on Ag Coated Si (100) substrates by CVD (c) X-ray diffraction (XRD) patterns of ZnO nanostructure (d) The electrical responses to 10, 20, 30 40 and 50 ppm of Ammonia gas at RT during 3 cycles**.**

3. Commercial Alumina substrate based Nitrogen dioxide (NO_2) Sensor

Figure: 3a. shows the AA-CVD ZnO coated with SWCNT installed in Teflon chamber. Specifically, commercial alumina substrates were used to deposit the nanomaterials on platinum screen-printed interdigitated electrodes (IDE). It is worth noting that a heating element was placed at the backside of the IDE for increasing the operating temperature of the sensors. Figure 3b shows the gas sensing performance at room temperature, revealing responses to NO_2 ranged from 0.34% and 1.2% for 10 and 50 ppm, respectively. However, after every gas exposure, the initial resistance cannot be restored, resulting in a significant baseline drift. The reason is the slow rate of desorption under RT conditions. Conversely, by increasing the operating temperature up to 200 °C, the initial resistance level is almost recovered (figure 3c), revealing suitable gas desorption. In addition, the responses at 200 °C are 5 times higher than those obtained in RT conditions, due to the activation of the catalytic properties of the nanomaterials.



(a) (b) (c)

Figure. 3a: Actual Alumina ZnO/SWCNT senor placed in Teflon chamber (b) NO_2 senor resistance at RT (C) NO_2 sensor resistance annealing treatment at 200 °C

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Future collaborations

Development of flexible gas sensors and flexible Organic field effect transistor (OFETs) on plastic and flexible foils. Our main focus is on the integration of temperature, humidity, and gas sensors on plastic substrates targeting low-power operation for wearable electronics application.

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