Structural, field emission and ammonia gas sensing properties of multiwalled carbon nanotube-graphene like hybrid films deposited by microwave plasma enhanced chemical vapor deposition technique

Atul Bish6,1, S. Chockalingam3, O. S. Panwar7,1, A. K. Keswani2, Ishpal Rawal1, B. P. Singh2, V. N. Singh1, 1Polymorphic Carbon Thin Films Group, Physics of Energy Harvesting Division, 2Physics and Engineering of Carbon, Materials Physics and Engineering Division, 3Electron and Ion microscopy, Sophisticated and Analytical Instruments, CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi-110012 (India).

Abstract
This paper reports the direct deposition of multiwalled carbon nanotube (MWCNT)-graphene like hybrid films on nickel substrate using 2.45 GHz microwave plasma enhanced chemical vapor deposition (MW-PECVD) technique in the temperature range of ~500-700 °C at 20 torr pressure. The films have been characterized by Raman spectra, high resolution transmission electron microscope (HRTEM), scanning electron microscope, high resolution X-ray diffraction and contact angle measurement. Raman spectroscopy and HRTEM reveal the formation of MWCNT and graphene like hybrid carbon sheet structures. The effect of processing temperature on the field emission properties of MWCNT-graphene hybrid films has been investigated. Field emission measurement reveals that the turn-on field decrease and the emission current density increase with increase of deposition temperature. The rambutan structure of MWCNT formed at 700 °C is responsible for the improvement in the field emission properties. The film deposited at 700 °C shows fast response and recovery time of ~40 and 96 s, respectively, for ammonia gas sensing due to the high surface area of the film. It has also been found that the hydrophobic surface of the film helps to perform the gas sensing in the humid environment.

Key words: MWCNT, Graphene, Hybrid film, MW-PECVD, Field Emission, Raman spectroscopy, Ammonia gas sensing.
Corresponding author E-mail address: ospanwar@mail.nplindia.ernet.in (O. S. Panwar)
Tel.: 011 4560 9175, Fax: 011 45609310

1. Introduction
Recently, sp2 hybridized carbon based nanostructures such as carbon nanotube (CNT) and graphene have emerged as a subject of intense research due to their unique chemical, electrical, mechanical and thermal properties [1-6]. Graphene is a two dimensional sheet composed of sp2 bonded carbon atoms arranged in a honeycomb structure, whereas, CNT is one dimensional rolled graphene sheets. Due to the high surface to volume ratio, capability to be grown on the flexible substrates and unique geometry, both these carbon allotropes are seemed to be promising candidates for the gas and chemical sensing applications. Recently, carbon based hybrid materials composed of graphene and CNT attracted much attention [7-9]. The hybrid material contains extraordinary properties of both the graphene as well as CNT. CNTs are generally grown by pre-seeding the grown substrate by catalyst metal nanoparticles [10, 11]. These metallic nanoparticles remain on the top of the CNT as residues, which are not desirable for their applications in many areas like field emitter, supercapacitor, electrode for lithium ion battery, etc., where there is a need of proper adhesion between the CNT and the substrate. In addition, CNT growth involves a two-step deposition process viz. deposition of catalytic nanoparticles on the desired substrate and then growth of CNT with suitable precursor on this substrate. The two step process can be reduced to a single step by directly synthesizing multiwalled carbon nanotube (MWCNT) on the bulk substrate. Many reports suggest that the CNT, graphene and CNT-graphene based hybrid materials are promising for field emission application due to their high aspect ratio, sharp edges and high conductive nature with sp2 bonded carbon channels, etc. [12, 13]. Such hybrid materials can be grown by different techniques such as chemical vapor deposition (CVD) [7, 8], microwave plasma enhanced CVD (MW-PECVD) [11], radio frequency plasma enhanced CVD (RF-PECVD) [12], sputtering [13] and chemical based methods [14]. CNT and graphene sensors for gas sensing applications are of significant interest due to their tunable electrical and chemical properties [15-17]. Generally, sensors based on CNT and graphene are fabricated by using patterning and post electrode deposition with the help of lithography which increase the production cost. The process described in present work involves the easy and cost effective deposition of electrodes without any lithography process. Ammonia is widely used for different industrial applications such as fertilizer, cleaner, fermentation, precursor for nitrogenous compound, as antimicrobial, etc., but it is a highly toxic, corrosive and hazardous gas [15-17]. Even a very low concentration of it can kill the aquatic animals and affect the human respiratory system, skin, etc. Thus, the detection and quantification this gas is an important issue for the environmental conditions. Although, metal oxides based gas sensors are commercially used for ammonia detection, but they require high operating temperature (200-400 °C) [18], which may limit their life time and performance. Besides the high operating temperatures of the conventional sensors, humidity is another crucial factor which affects the performance of the sensing device. The remedy of these two problems is the main center of attention for the present study, to grow a hydrophobic material with room temperature sensing response. The hydrophobic nature of the sensing material may help to maintain its sensitivity in the high humidity conditions. Some et al. [19] have studied the hydrophilic and hydrophobic graphene for the high sensitive and selective gas sensing. Hydrophobic membrane is also used to protect the sensor from the fluid and allow sensing material to pass. Though, a simple drop cast method is the easiest method, but it is difficult to control the layout of nanomaterial. CNT based film may be a solution for uniform layout and base resistance [16]. One advantage of CNT based sensors is that it can absorb ammonia gas from the water [20].

This work reports the structural, field emission and ammonia gas sensing properties of MWCNT-graphene like hybrid films deposited directly on nickel substrate using the MW-PECVD technique at different temperatures and fixed 20 Torr pressure. The effect of process temperature (500, 600 and 700 °C) on the surface morphology and field emission properties of hybrid films has been studied. Further, the hydrophobic nature of the film for water repelling properties of sensor has been investigated. The sensor shows a better response and recovery time measured at room temperature which is correlated with their field emission behavior. The field emission and ammonia gas sensing property have been dominantly contributed by the MWCNT-graphene like hybrid films.

2. Experimental details
2.1. Sample preparation
MWCNTs-graphene like hybrid films were synthesized on cleaned nickel foil in a custom designed and indigenously built MW-PECVD technique as shown in Fig. 1. It consists of 1.2 KW microwave power supply, magnetron, circulator and three stub tuners. Microwave is coupled to the deposition chamber with a waveguide and a quartz window. Impedance matching is carried out using three stub tuners. The deposition chamber is equipped with a turbomolecular-rotary pump combination and a base pressure of ~3x10−7 Torr is achieved in the system. The temperature of heating stage was raised with the heating rate of 30 °C / min. When the desired temperature was obtained, the sample was further cleaned by flowing H2 gas in the chamber to further remove the surface oxide from the nickel substrate. After 10 min of cleaning, the chamber was processed with Ar gas and the pressure was increased to 1 Torr. Argon plasma was first generated using low power. Subsequently, the pressure was increased up to the desired deposition pressure using H2 and CH4 gas which was kept at 20 Torr in the present study using a throttle valve. Samples were deposited at different temperatures of 500, 600 and 700 °C. The deposition conditions have been summarized in Table 1. After the deposition, the sample was cooled down to room temperature with the natural cooling.
parallel electrode arrangement with a separation of about 1 mm by using the shadow mask. The sensing response of the prepared structure has been recorded both in the inert environment as well as in the atmosphere naturally, sensor was exposed to nitrogen gas for 10 min to make the sensor resistance of the stable and then the exposed to ammonia gas diluted with nitrogen for 200 s to measure the sensing signal. The recovery of the sample was tested by flushing the chamber by the nitrogen for 300 s. Similar gas sensing measurements have also been performed in air ambient at different ppms of ammonia. These gas sensing measurements were performed in a small cell of volume about 100 ml, where the flows of both the analyte (ammonia) as well as diluents (nitrogen/air) gases were controlled by the Alborg mass flow controllers (MFCs). A pre-diluted ammonia gas with dry nitrogen procured from the scientific company (Sigma gases, Pvt. Ltd) was further diluted as per the requirement of ppm levels. To make the 50,100, 150, 200, 250 and 300 ppm levels of ammonia, a flow of 2, 4, 6, 8, 10 and 12 ml/min of ammonia at 10000 ppm, respectively, was injected by one MFC and 400 ml/min of diluent by another MFC, here, 50 ppm = (2 ml/min x 10000 ppm)/400 ml/min. All the measurements were carried out at room temperature and the change in electrical resistance of the sample was recorded at Keithley’s 2410 source measure unit.

Table-1: Various parameters of MWCNT-graphene like hybrid films evaluated from the Raman spectra

<table>
<thead>
<tr>
<th>No.</th>
<th>S. Properties/Parameter</th>
<th>500 °C</th>
<th>600 °C</th>
<th>700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D (cm⁻¹)</td>
<td>1350.3</td>
<td>1340.7</td>
<td>1368.3</td>
</tr>
<tr>
<td>2</td>
<td>G (cm⁻¹)</td>
<td>1587.5</td>
<td>1597.5</td>
<td>1592.5</td>
</tr>
<tr>
<td>3</td>
<td>2D (cm⁻¹)</td>
<td>2694.5</td>
<td>2641.2</td>
<td>2728.9</td>
</tr>
<tr>
<td>4</td>
<td>D+G (cm⁻¹)</td>
<td>2939.0</td>
<td>2933.2</td>
<td>2954.9</td>
</tr>
<tr>
<td>5</td>
<td>I_D/I_G</td>
<td>0.73</td>
<td>0.88</td>
<td>0.73</td>
</tr>
<tr>
<td>6</td>
<td>I_D/I_G</td>
<td>0.19</td>
<td>0.28</td>
<td>0.26</td>
</tr>
<tr>
<td>7</td>
<td>FWHM_2D (cm⁻¹)</td>
<td>201.3</td>
<td>116.2</td>
<td>147.8</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Raman spectroscopy

Raman spectroscopy is widely used to study the electronic and molecular structure of carbon and thereby differentiate various forms of carbon based allotropes. Fig. 3 shows the Raman spectra of the MWCNT-graphene like hybrid films deposited at different temperatures of (a) 500, (b) 600 and (c) 700 °C. All the samples show the characteristic peaks identified as D, G, 2D and D+G peak. The G peak originates due to the E₁g bond stretching of pair of sp² bonded carbon atoms either in the ring or chain arrangement and D band is the disorder induced peak, which originates due to sp³ breathing mode of sp² carbon atoms in aromatic ring [21,22]. The disorderliness may originate due to the presence of edges, sp³ bonded carbon atoms, impurities, vacancies, etc. [23]. Peak around 2500-2600 cm⁻¹ mainly exists in the sp³ hybridized carbon allotropes e.g. graphite, CNT, graphene, etc., which originates due to the double phonon resonance process [24]. The intensity ratio of I_D/I_G and I_G/I_D give the crucial information about the presence of defects and the number of layers in graphene sheets, respectively. Table 1 summarizes the different parameters of I_D/I_G, I_G/I_D and full width at half maximum of 2D peak (FWHM_2D) along with G, D, 2D and D+G peak positions calculated from the Raman spectra by Lorentzian fitting as shown in Fig. 3(d). CNT generally shows the G peak at 1580 cm⁻¹ and shifting of G peak towards the higher wavenumber of the film deposited at higher temperatures (600 and 700 °C) indicates the presence of graphic sheets in the samples. It is clear from the Table 1 that the I_D/I_G ratio decreases with the increase of deposition temperature, which suggests the decrease in disorderliness with rise in deposition temperatures from 500 to 700 °C. The value of I_G/I_D ratio is found to be 0.19, 0.28 and 0.26 for the films deposited at different temperatures of 500, 600 and 700 °C, respectively, which shows a maximum value of I_G/I_D at 600 °C deposition temperature. The value of FWHM_2D is found to be in the range 116.2-201.3 cm⁻¹. The film deposited at 600 °C has the lowest value of FWHM_2D is 116.2 cm⁻¹ and highest value of I_G/I_D (0.28). Thus, it can be stated that the formation of MWCNT-graphene like hybrid nature is more at the deposition temperature of 600 °C compared to other deposition temperatures of 500 and 700 °C.

Fig. 2. Schematic diagram of the sensor fabrication

Fabrication of the sensor is depicted in Fig. 2. The thermally evaporated silver (Ag) electrode with the dimension of 5 mm × 2 mm was deposited on the MWCNT-graphene film supported on glass with a...
combined effect of D and G peak and this originates due to the damaged graphitic sheets [22]. It is evident from Fig. 3 that D+G peak is nearly absent for the deposition temperature of 500 °C.

Fig. 3. Raman spectra of MWCNT-graphene like hybrid films deposited at different temperatures of (a) 500, (b) 600, (c) 700 °C, and (d) Lorentzian fitting of Raman spectrum of MWCNT-graphene like hybrid film deposited at 700 °C.

Fig. 4. Raman mapping of 2D peak in MWCNT-graphene like hybrid film deposited at 600 °C temperature.
3.2. XRD spectra

Fig. 5 shows the typical XRD pattern of the MWCNT-graphene like hybrid film deposited at 600 °C on nickel substrate. A sharp and intense peak at 2θ ~26.6° in the XRD pattern shows the graphitic nature of the hybrid film. Perfect hexagonal graphite shows a peak at 2θ =26.55° corresponding to <002> plane (JCPDF no.98497). Interlayer spacing can be calculated from the Bragg’s equation:

$$d = \frac{\lambda}{2\sin\theta}$$  

where, $d$ is the interlayer spacing between the crystal plane, $\theta$ is the angle of incidence and $\lambda$ is the wavelength of incident X-ray (1.54 Å). The interlayer spacing evaluated from equation 1 is found to be 0.334 nm which is close to the interlayer spacing of bulk graphite (0.335 nm).

![Fig. 5. Typical grazing incidence XRD spectra of MWCNT-graphene like hybrid film deposited at 600 °C temperature.](image)

3.3. Surface microstructural analysis by SEM and HRTEM studies

Fig. 6 shows the SEM micrograph of the MWCNT-graphene like hybrid films deposited at different temperatures of (a) 500, (b) 600 and (c) 700 °C. Generally, the growth of 1D nanomaterials e.g., nanowire, CNT needs catalyst nanoparticle to grow on the basis of the tip or base growth model. In the present study, no catalyst nanoparticle or any substrate pre-treatment has been used to grow nucleation center. Fig. 6(a) shows the MWCNT growth at the deposition temperature of 500 °C, showing low density growth. Fig. 6(b) shows highly dense MWCNT spread all over the substrate at the deposition temperature of 600 °C. Fig. 6(c) shows clustering of MWCNT in the flowered like structure at the deposition temperature of 700 °C. The clustering of MWCNT in such a manner is an interesting phenomenon. Tong et al. [25] have also found such a uniform and typical rambutan (tree bearing spiny red fruit) like nanostructure on octahedral nickel oxide (NiO) in the powder form and proposed that initially carbon atoms absorbed on octahedral NiO particle reduces them into Ni. Carbon atoms diffused through nickel and MWCNT are grown by the tip growth model. The octahedral NiO crystal plays an important role in the growth of such structures. Such rambutan like nanostructure has been grown in the present study without any pre-defined on plane Ni foil. No Ni nanoparticles are seen on the MWCNT tip as revealed by the HRTEM image. Since no pre-treatment of the substrate has been performed, the growth may be considered on the basis of pre-nucleation of graphitic nanocrystals, which acts as seed for the growth of carbon nanotubes. The growth of these nanocrystals is found to be temperature dependent, which affects the growth of MWCNT. At low temperature, the lower nucleation density of seeding nanocrystals reduces the density of MWCNT’s. At high temperature, the density of seeding nanocrystals is high, which results in dense MWCNT’s formation. Besides of MWCNTs, graphene sheets also appear at high temperature. At high temperature, graphene sheets are produced due to the diffusion and segregation of carbon atoms on nickel foil [26]. Generally, amorphous carbon changes into graphite at high temperature (from 2500-3500 °C) in the absence of a catalyst, whereas, in the presence of a catalyst (Ni), it transforms into graphitic at low temperature (from 600-900 °C) [25]. This is a post MWCNT deposition phenomenon, where first MWCNTs are deposited on nickel substrate with some carbon atoms diffused to nickel foil. After MWCNT is deposited, substrate is cooled very fast by shutting off the power to the heater. With this fast cooling, some carbon atoms are segregated to the surface followed by the graphene deposition in some areas. This is also confirmed by the Raman spectra and HRTEM image of the sample. The clustering of MWCNT as flowered structure is also an interesting observation having applications in field emission, gas sensing, etc., due to its unique structure. Notably, MWCNT along with the thick graphene sheets are visible in the HRTEM image of sample deposited at 700 °C as shown in Fig. 7. In SEM micrograph, graphene sheets may not be visible due to the high density of CNTs. As we etch the nickel surface and observe in HRTEM micrograph, graphene like sheets and CNTs are clearly visible. The MWCNT part has been encircled in the image in Fig. 7a. Fig. 7b shows the low magnification HRTEM image of the graphene sheet like structure. The fast Fourier transform (FFT) also confirms the crystalline nature of the film. Fig. 7c depicts the interplaner distance of planes generated using digital micrograph provided by Gatan software. The interplaner distance of about 0.33 nm has been observed, which is slightly less than the interplaner distance for graphite (0.34 nm) corresponding to d spacing of <002> plane evaluated from the XRD spectra in section 3.2.

![Fig.6. Typical SEM image of MWCNT-graphene like hybrid films deposited at different temperatures of (a) 500, (b) 600 and (c) 700 °C.](image)
3.4. Field-emission

Fig. 8 shows the variation in field emission current density \( J \) versus electric field \( E \) characteristics of the MWCNT-graphene like hybrid films deposited at different temperatures of (a) 500, (b) 600 and (c) 700 °C. Field-emission is a quantum-mechanical phenomenon in which electrons tunnel out of the electrodes into vacuum when subjected to a very high electric field. It is a non-linear process, in which the \( J-E \) characteristics are usually described by the classical Fowler-Nordheim (FN) equation [27]:

\[
J = \frac{A \beta}{\Phi} E^2 \exp \left( \frac{B \Phi}{E} \right)
\]

where, \( J \) is the current density, \( \Phi \) is the barrier height (taken as the work function), \( E \) is the applied electric field, \( \beta \) is the field enhancement factor. A and \( B \) are constants having the values of \( 1.54 \times 10^6 \) AV\(^{-2}\) and \( 6.83 \times 10^9 \) Vm\(^{-1}\)eV\(^{-3/2}\), respectively. The plots of log \( J/E^2 \) versus 1/E are shown in (Fig. 8d). It is revealed from the figure that log \( J/E^2 \) varies almost linearly with 1/E, which confirms that the \( J-E \) characteristics satisfy the FN relation. The slopes of these plots give the effective emission barriers \( \Phi \), if we assume an ideal plane emitter with a field enhancement factor \( \beta \) of 1. The values of \( \Phi \) calculated for the carbon based films were ≤ 0.1 eV [28-30]. These values are obviously quite low and the true barrier may be quite large [28]. If we consider a work function \( \Phi \) of 5 eV, typical of graphite bonding, then the FN plots correspond to the field enhancement factor \( \beta \) of 1250-3214 for these MWCNT-graphene like hybrid films. The turn-on field \( (E_\text{T}) \) (corresponding to 1 µA/cm\(^2\) emission current density) on MWCNT-graphene like hybrid film has been found to be 4.7, 3.6 and 2.7 V/µm at different temperatures of 500, 600 and 700 °C, respectively. The value of \( J \) at 3.8 V/µm electric field in the hybrid film deposited at different temperatures of 500, 600 and 700 °C, are found to be 3.8×10\(^{-7}\), 1×10\(^{-6}\) and 1×10\(^{-3}\) A/cm\(^2\), respectively. Thus, the value of \( E_\text{T} \) decrease and \( J \) increase with the increase of the deposition temperature of MWCNT-graphene like hybrid films. The corresponding values of \( \beta \) in the samples deposited at different temperatures of 500, 600 and 700 °C were found to be 1250, 3214 and 1600, respectively, which increase with the increase of deposition temperature up to 600 °C. The improved turn-on field at high temperature may be due to the unique rambutan like structure and the presence of graphene like sheets. These types of structures enhance local field in large amount besides the external applied field which improve the field emission. CNT alone has also proved to be a promising field emitter material. Recently, direct deposition of the CNT on a bulk metallic substrate has proven better field emitter due to the low contact resistance to substrate [31, 32]. Lahiri et al. [31] also studied CNT deposition directly on copper and argued that the direct deposition of field emitter on the metal substrate helps to extract any heat generated due to the presence of contact resistance. Neupane et al. [32] synthesized CNT growth on the copper substrate with the help of nanosphere lithography and studied their field emission properties. Chen et al. [33] studied field emission properties of bare CNT and ammonia treated CNT and have found very high turn-on field up to 11.93 V/µm (corresponding to 0.1 µA/cm\(^2\) emission current density) and 8.84 V/µm with the plasma treatment. Pandey et al. [34] have studied the field emission properties of morphological disordered graphene, transferred to the silicon substrate and proposed a two barrier model (first barrier from
Si to graphene and the second barrier from graphene to vacuum). The two barrier model does not affect the present case as the films are directly deposited on the nickel substrate. Koh et al. [14], while studying the field emission properties of CNT-graphene hybrid synthesized by electrophoretic deposition (EPD) technique, proposed that graphene improved the conductivity of CNT matrix acting as the connector particle between the CNTs as well as additional local field enhancer in the surface region. The reason of better field emission of the sample deposited at 700 °C in the present study may be due to the improved conductivity of CNT due to presence of graphene sheets and lower contact resistance between the substrate and CNTs, which also play an important role in the field emission. Nguyen et al. [35] found the applicability of CNT-graphene hybrid in the flexible transparent conductor and field emission and reported the improved sheet resistance of 420 ohm/sq with turn-on field up to 2.9 V/µm (corresponding to 10 μA/cm² emission current density), which is due to the low contact resistance caused by the π-π interaction between graphene and CNT. Nguyen et al. [36], while studying the field emission on CNT-graphene hybrid material, have reported the improvement in turn-on field from bare CNT (2.68 V/µm) to their hybrid counterpart (2.12 V/µm) as graphene facilitate electron transport from nickel substrate to carbon nanotubes. On the basis of the reported literature [14,27-36], it can be concluded that the field emission properties of the carbon based materials are strongly dependent on the deposition parameters and film quality (adhesion with substrate and contract resistance, etc.) For a material to be good field emitter, it should be highly conductive to provide the proper channel to the electron flow and should have sharp edges, vertical structure to provide high local field enhancement. Another factor directing the field assisted cold electron emission is the field enhancement factor (β) which depends totally on the sharp edges, miniaturizing the structure to nanoscale, vertical structures, large aspect ratio etc. The values of β may be related to the SEM microstructure as shown in Fig. 6. For the 500 °C hybrid film, SEM micrograph shows dispersed MWCNTs with lateral orientation, whereas the microstructure for 600 °C deposited film shows the dense MWCNTs and for 700 °C deposited film, the microstructure shows highly dense, rambutan like clustering.

![Fig. 8. Variation of emission current density (J) versus electric field (E) of MWCNT-graphene like hybrid films deposited at different temperatures of (a) 500, (b) 600, (c) 700 °C, and (d) their FN plots at different temperatures.](image)

Field emission not only depends on the field enhancement factor (which depends on the shape and aspect ratio of emitter) but also depends on the work function of emitter and contact resistance of substrate to the film. In case of CNT, local field screening of individual CNT due to the surrounding CNTs also play an important role. Further, moderate density of CNTs is preferred for the field emission. Highly dense and randomly oriented CNTs yield decreased local field due to quantum electric field screening effect in which nearby CNTs affect the field emission. Further, the electrons are emitted from the tips of CNTs, vertically aligned CNTs are better field emitter than the randomly oriented CNTs. The sample deposited at 600 °C show randomly oriented CNTs compared to the sample deposited at 700 °C which shows clustered rambutan like structure but oriented vertically. These factors do not come in the formulation of field enhancement factor. These may be reasons for high current density and low turn-on field of sample deposited at 700 °C compared to the sample deposited at 600 °C besides of having high field enhancement factor.

3.5. Wettability properties

Humidity has a speculative effect on the properties like gas sensing of the deposited films and deteriorates the properties with passage of time. For a sensor, it must be resistive to different environmental conditions in which humidity is the most effective. One important reason of the oxide based sensor to work at high temperature is that below 100 °C, the water molecules are adsorbed at the surface of sensing material which prevents the gas molecule to come in contact with the sensing material. Hsu et al. [37]
have shown that the commercial metal oxide based sensor need high operating temperature (100 °C) to remove the humidity effect. Once water molecules are absorbed, heating or UV exposure is the only treatment to remove the water molecule which may deteriorate the sensor performance. Self-cleaning of the film has an important relation with the contact angle of water with the film [38]. Cantalini et al. [39] have shown the negligible effect on CNT in a humid (80 %) environment and performed the experiment at an elevated temperature of 165 °C. To check the humid resistive nature of the film, the wettability properties of the sample deposited at 700 °C have been measured by the contact angle measurement. Hydrophobicity is the property of material to remove water. Fig. 9 shows the wettable properties of the bare nickel and MWCNT-graphene like hybrid film on nickel with the shape of a water droplet. It is evident from the figure that bare nickel has a contact angle of 77.8°, whereas, the contact angle increases up to 128.4° in MWCNT-graphene like hybrid film coated on nickel showing the hydrophobic nature of the film. The contact angle can be further enhanced by the surface treatment of the film. Some et al. [19] have studied the hydrophobic and hydrophilic nature of graphene oxide (GO) and reduced graphene oxide (rGO) and reported the contact angle as 48.8° and 79.3°, respectively.

Fig.9. Wettability of (a) bare Ni substrate and (b) MWCNT-graphene like hybrid film deposited at 700 °C.

3.6. Ammonia sensing

The ammonia gas sensing measurement has been performed on the film deposited at 700 °C and transferred on glass substrate, at different ppm levels of ammonia in nitrogen as well as air environments (Fig. 10). Fig. 10(a) shows the ammonia gas sensing response of MWCNT-graphene like sensor deposited at 700 °C with the increase of ppm level of ammonia in nitrogen environment. It is evident from the figure that there is a repeatable response and recovery for ammonia gas. CNT and graphene shows p-type behavior in the ambient condition with the hole as majority of charge carriers [16]. Ammonia behaves as a strong reducing agent or electron donating gas evacuating/neutralized the majority charge carrier (holes), which result in an increase in the electrical resistance of the film (Fig. 11(a)). Zhao et al. [41] showed that there is no significant change in the density of states in the bare CNT and ammonia doped CNT, which indicates that the charge transfer is not substantial. It is evident from the Fig. 10(a) that the sensor recovers more than 90 % of the original baseline in a very short time when purged with nitrogen without having any extra treatment e.g., heating or exposed to infrared radiation, etc. The sensor shows recoverable nature with the consequent absorption/desorption cycle as shown in Fig. 10(a). The gas sensing response of the film deposited at 700 °C also measured in air ambient (Fig. 10(b)). It has been observed that the electrical resistance of the sample is not much affected by the ambient air environment or presence of humidity in air. The change in electrical resistance in both the dry nitrogen as well as air environment remains almost same. This could be due to the hydrophobic nature of the samples as observed from the wettability test. It is reported in literature that humidity and ammonia acts in the opposite manner on the conductivity of a sensing material [40]. Humidity acts as an acceptor and ammonia acts as a donor. Thus, the humidity may cancel out the effect of ammonia. Humidity can also be added up to the ammonia effect if it produces swelling type of effect, which may causes the bond angle and bond length alteration and hence, increase in electrical resistance. But, we have not observed much effect of testing environment on the sensor performance. Since the sample is hydrophobic, thus, humidity effect can be ignored. Fig. 10(c) also shows the exponential fitting of the conductance curve for the response and recovery of the MWCNT-graphene like hybrid sensor at fixed 50 ppm ammonia at room temperature with the help of equation (2) and (3).

$$G(t)_{\text{response}} = G_0 + G_1 \left\{ \exp \left(-t/\tau_{\text{response}} \right) \right\}$$

$$G(t)_{\text{recovery}} = G_0 + G_1 \left\{ \exp \left( t/\tau_{\text{recovery}} \right) \right\}$$

where $G_0$ and $G_1$ are the fitting parameters and $\tau_{\text{response}}$ and $\tau_{\text{recovery}}$ are the response and the recovery time of the sensor. For a good sensing property, both the response and recovery time must be low. From the fitting curve, the response and recovery time were found to be 40 and 96 s, respectively, showing very low values. No saturation of the time response was observed in the present study as we have limited the inserting and flushing time of 200 and 300 s, respectively. However, when we have increase the ammonia exposure time upto 400 s, the sensor almost attain the saturation in the electrical resistance of the sensor (Fig. 10(d)). Moreover, it has been observed that the sensor does not recover the base line as in the case of flushing with nitrogen, which may be due to some stronger interaction of ammonia with film in air ambient

The activation energy required for the molecular desorption of gas is higher than the thermal energy of molecule at room temperature, so higher temperature is needed for the complete desorption of gas molecules, which makes the sensor more complex and costly [42]. However, the recovery time of the ammonia gas sensor in the present study is very low. The low value of response and recovery time may be related to the physisorption by Vander wall force of ammonia on the surface. Due to the π electron system in sp² based carbon nanostructure, the electrical properties are very sensitive to the charge transfer by adsorbed molecules. Generally, CNT and graphene behave as p-type materials at room temperature with the hole as majority of charge carriers. Ammonia being a reducing gas donates electron to the CNT and lowers the majority charge carrier and thus increasing the resistance in the presence of gas. One advantage of the CNT-graphene film over the composite film as sensor is that it can be transferred easily to the flexible substrate for the flexible gas sensor. Recently, Pandey et al. [43] developed a very simple and cost effective technique for the room temperature ammonia gas sensing by silver nanoparticle/guar gum based composite. They claimed that the sensor based on guar gum/silver nanoparticle composite was flexible and ultrasonic type sensitive for the ammonia gas. It consisted of ideal properties of the sensor as room temperature operative, working in the ambient environment, no external factor required for the response and recovery e.g. ultraviolet radiation, heating, low detection limit with the high sensitivity and reproducibility, fast response/recovery with low cost. Lee et al. [44] studied the sensing properties of gold nanoparticle decorated CNT as flexible and transparent ammonia gas sensor and found a high recovery time. Nguyen et al. [45] studied ammonia sensing by CNT decorated with cobalt nanoparticle at room temperature and found recovery time 30-50 s with recovery time of 200 s. Tran et al. [46] also studied graphene silver nanowire composite for ammonia sensing and found high recovery time of 200 s and recovery time 60 s with purging of inert gas argon instead of air. Johnson et al. [47] reported ammonia sensing of CNT, graphitic nanoribbons film bare and found recovery time of 90, 115 s respectively. Llobet [17] reviewed the state of the art for electrical gas sensors using carbon nanomaterials, identifies the bottlenecks for their commercialization and some breakthroughs and gave an outlook with challenges and opportunities.
Fig. 10. Ammonia gas sensing response curve of MWCNT-graphene like hybrid film deposited at 700 °C (a) in nitrogen environment (b) in air ambient at different ppm levels (50-300 ppm), (c) exponential fitting for response and recovery time at 50 ppm ammonia gas in nitrogen environment and (d) sensing response recorded for longer at 300 ppm of ammonia gas in air ambient.

4. Conclusion

MWCNT-graphene like hybrid films have been grown at different temperatures (500-700 °C) and at a fixed pressure of 20 Torr by MW-PECVD technique. Higher wavelength shifting of G peak in the Raman spectra confirms the presence of graphene like carbon sheets along with MWCNT. The value of $E_2$ was found to be 4.7, 3.6 and 2.7 V/µm for the MWCNT-graphene like hybrid films deposited at 500, 600 and 700 °C, respectively. The lowest value of $E_2= 2.7$ V/µm accompanied with the highest value of $J = 1$ mA/cm² (at 3.8 V/µm electric field) have been obtained in the hybrid film deposited at 700 °C. The ammonia gas sensor showed the fast response and recovery time of 40 and 96 s, respectively, in the hybrid film deposited at 700 °C. The hydrophobic nature of the film makes the films suitable for gas sensing applications even in humid environment. Thus, the field emission behavior accompanied with the good response and recovery time in ammonia gas sensing at room temperature is demonstrated in the MWCNT-graphene like hybrid films.

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