Electro-Magnetic switching in NiO-Graphene film

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Abstract. Nickel oxide (NiO) thin film is grown via pulse laser deposition (PLD) technique and it is trapped in between conducting graphene films deposited through the same technique. Epitaxial crystalline growth of both NiO and graphene films are confirmed from X-ray diffraction studies. Raman studies propose creation of pure graphene film with acceptable defects. Electrical transport of the NiO film reveal resistance switching properties for an wide range of temperature which is useful for resistive random access memory (RRAM) and electric-switch. Besides electrical switching, the transport properties of the NiO film depict a systematic response in influence of magnetic field. Resistance of the NiO film changed significantly with external magnetic field which makes the system useful as a magnetic-switch.

1. Introduction
Nickel oxide (NiO) is widely studied since decades because of its rich applications in gas sensors, spin valves, supercapacitors besides nonvolatile resistive random access memory (RRAM) in 2D geometry (film) because of its simple structure, low power consumption, high-speed performance etc. NiO thin films formed via chemical/physical vapor deposition, drop/dip casting, pulse laser deposition (PLD) technique etc. occasionally form metal-insulator-metal (MIM) structure and reveal voltage-induced switching useful for potential applications in resistive random access memory (RRAM). In 1964 Gibbons et al [1] observed electrical switching in NiO thin pallet and since then this has been extensively studied by the scientific community. Formation of localized metallic conducting filaments (as observed from transmission electron microscopy (TEM) and atomic force microscopy (AFM)), phonon-associated tunneling mechanism, Schottky barriers with trapped charges in the interface states, space-charge-limited current are proposed to be responsible in different studies for this switching of resistive values between two applied voltages of same polarities [2, 3, 4, 5, 6, 7]. However, the exact reason behind switching mechanism in RRAM is yet to be understood completely. Emphasis has been given to study the nonvolatile performance, tuning the switching voltage and explore applications at/near room temperature after preparing films of NiO on different substrates [8, 9]. In this regards introduction of suitable doping and variation film thickness has been extensively studied whatsoever [3]. Semiconducting metal oxide NiO shows promising resistive switching memories (RSM) characterized via hysteresis in the $I-V$ loop. Because of widespread application on nanostructure RSM, controlling the same by externally applied parameters has been a key issue of research. Controlling RSM by externally applied magnetic field using the strong influence of the same on NiO film, is one important probable solution [10].
Figure 1. Schematic representation of the graphene-NiO-graphene film.

Nowadays, exfoliated Graphite and Graphene films are extensively studied because of its rich electrical and thermal conductivity, mechanical stability, flexibility, transparency and unique physico-chemical properties. Graphene film is also a suitable alternate of indium tin oxide (ITO) for using as conducting electrode [11]. Multilayer films using graphene and metal oxide may explore the combined physical properties and thus may be used as multifunctional smart materials, useful for potential device fabrications. Pulse laser deposition (PLD) is one simplified technique which provides the platform to grow graphene films on metal/glass/Si substrates directly from Graphite [12, 13]. At the same time NiO film deposition is possible via the same technique in next step without hampering the morphology or unwanted air contamination in one advanced PLD system with multiple targets. However, at the same time PLD extends the flexibility of tuning the characteristics of the film by controlling substrate temperature, laser power, wavelength, gas pressure etc. Herein, we have prepared multilayer thin film of graphene-NiO-graphene for exploring resistive switching properties under influence of electrical and magnetic fields [10]. The fabricated film demonstrates a switching from high resistance to low resistance state at a particular threshold voltage. At a small applied voltage, the resistance of NiO film is generally very high (known as OFF state), by increasing the voltage gradually, at a critical threshold, the resistance of the system reduces significantly – which is known as the ON state.

2. Fabrication
Tri-layer graphene-NiO-graphene is deposited on Si(100) substrate using a pulsed laser deposition (PLD) system (Model No: CompexPro 205 F, KrF) [14, 15]. Thick pallets of Graphite and NiO are prepared and calcined well before using as source. Target Si substrate is carefully cleaned several times with acetone and water in ultrasonic bath before being placed into the vacuum chamber as target. At first, for deposition of graphene film, the operating energy of the laser and target-to-substrate distance set to 450 mJ (λ=248 nm) and 10 cm respectively. Substance temperature is maintained at 650°C, number of laser pulse applied 10,000 with frequency 10 Hz and the whole procedure is done in ~ 10⁻⁶ Torr pressure with flow of Ar gas in the deposition chamber. Ar is used to prevent the possibility of oxidation leading to formation of graphene oxide (GO). After completion of deposition, the substrate temperature is brought to room temperature slowly (4 K/min) to allow crystallization and formation of epitaxial film [16, 17].
After the substrate reaching room temperature, second step of the deposition is started with suitable masking, so not expose the whole film. Now, for the deposition of NiO film, 60,000 laser pulse is applied on the NiO source in $\sim 10^{-3}$ Torr oxygen ambient atmosphere and other conditions are kept unaltered. Substrate temperature is maintained at 400$^\circ$C [12, 13]. After the laser exposure is over, the substrate is again brought to room temperature slowly (2 K/min). The final layer of graphene is fabricated on NiO similarly like the initial layer after desired masking.

Characterization of the as-synthesized film is performed by powder X-ray diffractometer (PXRD) (Bruker D8 Advanced Diffractometer) using Cu K$_\alpha$ ($\lambda=1.54184$ Å) radiation source; PXRD pattern of the samples are recorded with a scan speed of 0.02 $^\circ$/2 s. Dc electrical transport measurements are performed via commercial PPMS using a source meter (Keithley, 2400) coupled with a computer by the GPIB network and magnetization measurements are performed in commercial SQUID magnetometer (MPMS-3).

3. Experimental Results

3.1. X-Ray and Raman Studies

X-ray diffraction pattern of the thin film recorded at room temperature is depicted in Figs. 2(a) and (b). Figure 2(a) focuses on the layer of only NiO deposition whereas Fig. 2(b) reveals the diffraction pattern after deposition of both the layers (graphene and NiO). Most intense peaks in both the figures around 70$^\circ$ appears from the contribution of Si(100) substrate. Significantly, simultaneous presence of honeycomb ($P6_3/mmc$) plane (022) for graphene and ($Fm\overline{3}m$) planes (111,200,220,311) for NiO are noted in Fig. 2(b) [18, 19, 20]. All the planes are well indexed which are in accordance with standard JCPDS. Lattice constants may be roughly estimated from the peak positions (for graphene $a=2.45$ Å, for NiO $a=4.18$ Å). Significant mismatch between the lattice constants of the samples and substrate (a=5.43 Å) provides moderate tensile strain at the interface [15, 14].

NiO-graphene film has undergone Raman spectroscopy studies (measured at 514.5 nm excitation) to characterize vibrational, rotational and other low-frequency modes present in the system [21, 22, 23, 24]. As expected for graphitic structure, characteristic $D$ ($\sim 1350$ cm$^{-1}$), $G$ ($\sim 1600$ cm$^{-1}$), $2D$ ($\sim 2700$ cm$^{-1}$) and $S3$ ($\sim 2940$ cm$^{-1}$) peaks are noticed with increase in
Figure 3. (a) Variation of resistance with temperature revealing semiconducting behavior of NiO film. Inset [1] magnifies the semiconducting nature. Inset [2] depicts the fitting of $R - T$ curve with VRH model. (b) $I - V$ curves measured at different temperatures exhibit sharp switching between low and high conducting states above a threshold voltage ($V_{Th}$). The inset [3] depicts $I - V$ curves with no switching effect at higher temperature.

3.2. Electric Transport Properties

Variation of electrical resistance with temperature is measured using two probe technique on the NiO film considering the graphene films as contact electrodes (see Fig. 3(a)). In inset [1] of Fig. 3(a) magnified region of $R - T$ curve is plotted. Thermal variation of resistance exhibits typical manifestation of a semiconductor [18, 19]; although $\rho(T)$ could not be calculated, $R - T$ curve may be fitted according to Mott’s variable-range hopping (VRH) model $\ln(\rho_{dc}/\rho_0) = (T_0/T)^{1/4}$, where, $\rho_0$ and $T_0$ are constants; instead of $\rho_{dc}$ a fitting with $R$ is proposed\cite{20}. With VRH formula, curve is fitted well between 160 K to 300 K (see inset [2] of Fig. 3(a)). Current-Voltage ($I - V$) curves measured in between $\pm 40$ V at different temperatures are shown in Fig. 3(b). $I - V$ curves at 90 K, 100 K, 120 K and 140 K reveal that $I$ increases abruptly after a certain threshold voltage ($V_{Th}$) as a result of certain change in conductance [28, 10]. The low and high conductance states are generally denoted as OFF and ON states and thus this NiO film may be used as an electrical switch. At a fixed temperature and fixed voltage sweep rate, $I - V$ curves are highly reproducible and they repeat exactly same $V_{Th}$. However, lots of reports are there where $V_{Th}$ shows a tunable property with variation of voltage sweep rate [10]. It may be noted that after switching, the current does not follow the same path with decreasing voltage. Rather current follows the identical path during the next cycle with increasing voltage. We further note that the resistive switching has a strong dependence on measurement temperature and amount of
change in resistance is inversely proportional to $T$. Inset [3] of Fig. 3(b) reveals the absence of switching tendency and almost semiconducting $I-V$ characteristics of the film on and above 160 K.

It is observed that the prepared film has a strong dependence on magnetic field. To explore the probability of magnetic switch, where the resistance can be controlled by external influence of magnetic field, a fixed voltage is applied (well above $V_{th}$) to the film and variation of current ($I$) is recorded with change in applied magnetic field ($H$). Figures 4(a)-(c) show that $I$ eventually falls to almost zero value on application of less than 1 T field. This experiment is good example of exploring the probability of using the prepared film as a magnetic switch. To understand the magnetic state of NiO at low temperature, the film undergone a magnetic hysteresis study at 150 K and that reveals antiferromagnetic characteristics primarily, as evident from Fig. 4(d).

4. Conclusion
Switching mechanism in NiO films due to local filamentary conduction accompanied with Joule heating is one common phenomenon. Here we have prepared tri-layer graphene-NiO-graphene film in a single step in PLD with a view to explore the provision of using graphene films as contact electrodes with the NiO film. At the same time, in future we aim to analyze the superiority of this type of films to enhance the magnetoresistance, explore resistance switching near room temperature, magnetic switching possibilities etc. The prepared film is well characterized via XRD and Raman studies, where the purity of the film and crystalline growth is established. However, analysis via cross-sectional electron microscopy may be done after a variation of thickness of different layers. Variation of film thickness may introduce unique characteristics and thus physical properties of the film may show suitable tunable dependence on thickness. Though electrical resistance switching property is observed for an wide range of temperature (90 K- 140 K), the film preparation demands further modification to explore similar properties near room temperature. For any kind of switching properties, order of magnitude of switch in resistance/conductance is important for device fabrication. This is not very high here (one order of magnitude) despite systematic and reproducible change in resistance on application of a threshold voltage. Most importantly, this film demonstrates a resistive switching property which may be controlled via application of external field. On application of magnetic field over a threshold value at a particular temperature it becomes possible to switch the current to almost zero. This film requires further exercise to understand completely and have a control over the observed electro-magnetic switching effect.
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