



ELSEVIER

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Effect of reaction time on the dielectric behaviour of reduced graphene oxide–layered cobalt hydroxide composite for high-*k* gate dielectrics

N. Ambikeswari, S. Manivannan*

Carbon Nanomaterials Laboratory, Department of Physics, National Institute of Technology, Tiruchirappalli 620015, India



ARTICLE INFO

Keywords:

Reduced graphene oxide
Graphene oxide
Cobalt hydroxide microdisks
Dielectric properties
I-V curve

ABSTRACT

Reduced graphene oxide (RGO)–cobalt hydroxide [Co(OH)₂] composite was synthesized using one-pot hydrothermal method. The frequency-dependent dielectric properties and leakage conduction mechanism were studied for the composite. Samples were made with different reaction times of 2, 4, 6 and 12 h for the same concentration of graphene oxide and cobalt nitrate at constant temperature and pH. A high dielectric constant of 7.19×10^6 with a capacitance of 2.45×10^{-6} F was achieved for a reaction time of 2 h, at 100 Hz frequency and 27 °C temperature. One order decrement in the dielectric constant (10^6) was found with an increase in time starting from 4 to 12 h. The leakage current characteristics revealed Schottky barrier-type conduction mechanism in the composites. Thus, RGO-Co(OH)₂ composite with a high dielectric constant, microcapacitance and large leakage current could be regarded as a potential high-*k* candidate, which has its application as a gate dielectric material in the fabrication of metal oxide semiconductor field effect transistor.

1. Introduction

Graphene, a two-dimensional monolayer of carbon, in a honeycomb lattice, engulfed the research world with its drastic and peculiar properties. Graphene, sp²-hybridized, with its superior characteristics remains to be a potential candidate for a wide range of applications such as supercapacitors, transparent conducting films, electronic devices, lithium-ion batteries, memory devices and gas sensors [1]. It finds itself compatible with any material to form composite, so that its unique properties can be incorporated along with the required properties of the other materials. In recent years, layered double hydroxides (LDHs) have gained attention in the flourishing areas of energy storage and energy harvesting. Among all inorganic metal hydroxides, cobalt hydroxide [Co(OH)₂] stands out the best due to its layered structure and large interlayer spacing [2,3]. The high electrical conductivity and good mechanical strength of carbon materials combined with the high chemical reactivity of LDHs play a vital role in the formation of hierarchical composites. The synergy between the carbonaceous materials and the metal hydroxides results in a great deal of applications such as catalysis, environmental protection and drug delivery [4]. Reduced graphene oxide (RGO), an intermediate between graphene oxide (GO) and graphene, also finds its best part in the aforementioned areas due to its partial removal of functional groups during reduction process [5].

RGO-Co(OH)₂ composite has been reported by Li et al. for producing an enhanced supercapacitance of 474 Fg⁻¹ for a current density of

1 Ag⁻¹ [3]. Liu et al. synthesized the same composite for sensing NO_x gases at room temperature [6]. In this report, the surface enhanced properties of RGO with the accumulation of excess charge carriers and the layered structural properties of Co(OH)₂ has been tethered together for better dielectric properties. Thus, the composite RGO-Co(OH)₂ is expected to produce a high dielectric constant compared to the previously reported values.

Dielectrics are the materials with high permittivity and low loss that are used in fabricating microelectronic components in semiconductor industry for large-scale power appliances. The materials with colossal permittivity were used in capacitors to some extent and achieved a limited success. Nevertheless, from the material point of view, several factors such as morphology, contribution of grain boundaries, internal material layers and interfacial polarization are responsible for the large dielectric constants [7]. Perovskite ferroelectric materials such as barium titanate (BT) with a dielectric constant (ϵ') of 10^3 combined with GO increase its value to 10^4 [8]. Giant ferroelectric materials such as CaCu₃Ti₄O₁₂ and doped Y_{2/3}CaCu₃Ti₄O₁₂ with ϵ' in the order of 10^5 and 10^6 , respectively, at 100 Hz were produced at room temperature [9,10]. These values were comparatively higher than those of the conventional dielectric materials such as Li- and Co-doped NiO with its ϵ' of about 10^4 at 100 Hz [11]. In spite of such high values, these perovskite ferroelectrics find limited applications in energy storage devices due to brittle and inflexible nature. Alternatively, highly flexible and light-weighted polymers were more suitable to replace the

* Corresponding author.

E-mail address: ksmani@nitt.edu (S. Manivannan).

ferroelectrics. Polymers such as polypropylene combined with RGO exhibiting a very low percolation threshold and poly(vinylidene fluoride) with poly(vinyl alcohol)-functionalized graphene composite produced a dielectric constant in the order of 10^3 and 10^2 , respectively, at room temperature for a frequency of 10^2 to 10^3 Hz [12,13]. However, these polymers resulted in comparatively low permittivity, which could not bridge the technological demand of high- k materials in semiconductor industry.

Here, we have considered a low dielectric and pseudocapacitive material $\text{Co}(\text{OH})_2$ to form composite with RGO. The pseudocapacitive property arises in the presence of OH^- ions in the material leading to high capacitance delivered from it [3]. Furthermore, GO with its semimetallic character and with prominent functional groups of $-\text{OH}$ and $-\text{COOH}$ has a potential to drive the dipole formation along a particular direction, which could account for the polarization to take place at low frequency [7]. Besides, the reduction of GO into RGO, the presence of stress due to imperfections in the crystal system reduce the potential barrier height, which causes a large leakage current to produce from them [14]. Thus, the hierarchical combination of RGO- $\text{Co}(\text{OH})_2$ could be regarded as a heterogeneous entity with its dielectric behaviour leading to high dielectric constant and conducting behaviour leading to more leakage current and leakage current density. This dual behaviour enables them to be used in the fabrication of microelectronic components in semiconductor industry, replacing silicon-based materials. Thus, we made an attempt to produce a high- k material that could fit in as a gate dielectric material. A gate dielectric material should possess an appreciable dielectric constant and leakage current with a high capacitance in order to increase the transconductance of field effect transistors (FET) [15]. Therefore, the aim of this work was to produce a composite to fulfill the basic criteria for the gate dielectric material.

In this study, we successfully synthesized a heterogeneous mixture of RGO- $\text{Co}(\text{OH})_2$ composite by wet chemical synthesis. The tremendous change in their dielectric properties and leakage current mechanism was also achieved and so we focus on high- k gate dielectrics, which is a major component in the metal oxide semiconductor field effect transistor (MOSFET) fabrication. The limitations of silicon- and hafnium-based materials such as poor stability, low activity, less durability and cost effectiveness could be overcome by the use of this composite.

2. Experimental details

GO was prepared from commercial graphite powder (Alfa Aesar 250 mesh) using the modified Hummer's method due to its cost effectiveness, ease in preparation and bulk production [16]. The *in situ* growth of RGO- $\text{Co}(\text{OH})_2$ composite was obtained by rapid one-pot method as reported earlier [3]. The resultant product was washed several times with double distilled water (DDW) and ethanol using the vacuum filtration technique. The filtration was done with the aid of isopore polycarbonate filter membranes with the pore size of $3\ \mu\text{m}$. Then, the filtered colloids were dried at $50\ ^\circ\text{C}$ and ground. The pristine $\text{Co}(\text{OH})_2$ was also prepared in the similar manner for 2 h, except with the addition of GO. Below 2 h, no noticeable change in the formation of $\text{Co}(\text{OH})_2$ discs was observed. The reaction times varied for 2, 4, 6 and 12 h and the composites were named as RC2, RC4, RC6 and RC12, respectively. Likewise, we carried out the same reaction for the reaction times of 1, 18 and 24 h. A schematic representation of the formation of $\text{Co}(\text{OH})_2$ on RGO sheets is shown in Scheme 1.

3. Characterization

Powder X-ray diffraction (XRD) was carried out using Rigaku Ultima III, $\text{CuK}\alpha$ radiation ($1.5406\ \text{\AA}$) at a scanning rate of $2^\circ\ \text{min}^{-1}$, in the range of $5\text{--}80^\circ$. Molecular vibrations of the as-synthesized powder samples were obtained using LabRAM HR Evolution Raman spectrometer with an excitation wavelength of $532\ \text{nm}$. The presence of oxygen

functional groups and their interactions in the composite were studied using Perkin Elmer Frontier Fourier transform infrared spectrometer (FT-IR) in the range of 4000 and $400\ \text{cm}^{-1}$. The morphological and microstructural analyses were done using a field emission scanning electron microscope (FE-SEM) (quanta 250 FEG, FEI), and the existence of elements in the composites was determined by energy-dispersive X-ray spectroscopy (EDS) (Oxford INCA 350 energy). Frequency-dependent dielectric measurements at $27\ ^\circ\text{C}$ were taken using a Hioki 3532-50 LCR Hi-Tester, in which the synthesized powders were made into pellets with a pelletizer, with a diameter of $8\ \text{mm}$ and a thickness of $1.3\ \text{mm}$. The ohmic contacts for the as-prepared pellets were made with the aid of a conducting silver paste on both the sides and dried for sufficient time, in order to prevent diffusion of silver ions into the pellets. I-V characteristics were determined using Keithley-2450 source measurement unit.

4. Results and discussion

As shown in Fig. 1, the powder XRD pattern reveals the formation of RGO- $\text{Co}(\text{OH})_2$ for all the reaction times of 2, 4, 6 and 12 h. The composite RC2 consists of partially reduced graphene oxide, an intermediate state between GO and RGO. For the reaction times of 4 to 12 h in the respective samples of RC4 to RC12, the intermediate state will attain a stage of complete reduction. It was clearly understood with the disappearance of 11.31° pattern in all the composites that the GO got reduced into RGO with the efficient removal of functional groups. Thus, the composite RC2 contains the intermediate state of GO/RGO and RC4 to RC12 contain RGO. Moreover, the intensity of the $\text{Co}(\text{OH})_2$ in these composites was much pronounced than that of the RGO formed in the composites. The major XRD patterns at 19.13° , 32.54° , 37.91° , 51.56° , 58.17° and 61.93° correspond to (001), (100), (101), (102), (110) and (111) of the brucite-type $\beta\text{-Co}(\text{OH})_2$, respectively [2]. These results were consistent with the JCPDS data (JCPDS Card No. 30-0443).

The Raman spectra for as-prepared GO, $\text{Co}(\text{OH})_2$ and the composites are shown in Fig. 2(a). GO shows two major bands at 1337 and $1593\ \text{cm}^{-1}$, which correspond to D and G bands, respectively [5]. The band formations around 187 , 470 and $509\ \text{cm}^{-1}$ for RC6 and RC12 correspond to F_{2g} , E_g bending and F_{2g} symmetric stretching modes, respectively, which were not found for RC2 and RC4 [3] reveals the crystalline nature of $\text{Co}(\text{OH})_2$ with time. The band around $674\ \text{cm}^{-1}$ corresponds to A_{1g} mode of $\text{Co}(\text{OH})_2$ and was found to be more intense in $\text{Co}(\text{OH})_2$ than in all the composites. The I_D/I_G ratios for all the composites ranged between 1.05 and 1.09. This was comparatively higher than that of synthesized GO ($I_D/I_G = 0.93$) and clearly indicates that the defects increased, after the reduction of GO into RGO [5]. This was due to the presence of more sp^2 - than sp^3 - bonded carbon atoms in the composite system [3,7].

The FT-IR spectra of GO, $\text{Co}(\text{OH})_2$ and the composites with their functional groups are shown in Fig. 2(b). All the composites showed a strong and sharp absorption peak around $3614\ \text{cm}^{-1}$, attributed to O-H stretching vibrations of pristine $\text{Co}(\text{OH})_2$. It was clearly observed that all the composites consist of absorption peaks at 3629 , 1664 , 1287 and $1023\ \text{cm}^{-1}$, which could be assigned to O-H, C=O, C-OH and C-O functional groups, respectively [5,8]. These major functional groups become reduced as time increases, which confirms the presence of GO and its reduction into RGO in the composites. The metallic region of the spectra projected a peak around $654\ \text{cm}^{-1}$ and was attributed to the bending vibration of $\text{Co}(\text{OH})_2$. Noticeably, the prominent and broad peak around $494\ \text{cm}^{-1}$ was assigned to Co-O stretching vibrations and finally shifted towards $505\ \text{cm}^{-1}$ as time increases, suggesting strong interactional vibrations within the composite materials with an increase in time [3].

The FE-SEM images (Fig. 3) show the morphological changes with the introduction of GO in the composites for all the reaction times. Fig. 3(a) shows the well-exfoliated sheets of GO. Aggregated disc-like elongated $\text{Co}(\text{OH})_2$ structures were formed, and it was evidenced from

Download English Version:

<https://daneshyari.com/en/article/7904761>

Download Persian Version:

<https://daneshyari.com/article/7904761>

[Daneshyari.com](https://daneshyari.com)