Sensors and Actuators B 233 (2016) 582–590

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Graphene quantum dot soil moisture sensor

Hemen Kalita [a,1], Vinay S. Palaparthy [b,1], Maryam Shojaei Baghini [c,*], M. Aslam [a,*]

[a] Department of Physics, Indian Institute of Technology Bombay, India
[b] Centre for Research in Nanotechnology and Science, Indian Institute of Technology Bombay, India
[c] Department of Electrical Engineering, Indian Institute of Technology Bombay, India

ARTICLE INFO

Article history:
Received 17 August 2015
Received in revised form 18 April 2016
Accepted 23 April 2016
Available online 25 April 2016

Keywords:
Graphene
Graphene quantum dots
MEMS
Humidity sensor
Soil moisture sensor
Agriculture application

ABSTRACT

A soil sensor to measure moisture content in soil is fabricated and described. The sensor is based on graphene quantum dots (GQDs) and is highly sensitive. The simplicity of the process and use of an inexpensive material GQDs make it an affordable low cost sensing unit in comparison to existing soil moisture sensing units. It is a resistive micro-sensor with interdigitated electrodes (IDE) where MEMS fabrication process is used and GQDs serve as the channel material between IDEs. The sensor is tested in two different soil environments viz. white clay (passive soil) and bentonite clay (an active soil). The conductance of IDE structure with GQDs changes from 0.06×10^{-6} 1/Ω to 0.68×10^{-6} 1/Ω in white clay as the gravimetric moisture content changes from 4 to 45%. For bentonite soil, the conductance of the sensor changes from 0.06×10^{-6} 1/Ω to 0.48×10^{-6} 1/Ω across the gravimetric moisture range of 11 to 90%. The sensor shows higher sensitivity at higher moisture content which can be attributed to Grotthuss chain reaction and ionic conductivity. Response time of the fabricated micro-sensor is found to be 2–3 min which is the lowest response time reported for a resistive based soil moisture sensor. The sensitivity of sensor towards gravimetric moisture contents is 0.014×10^{-6} 1/Ω per percent increase in moisture content (1/Ω/1%) for the white clay and 0.005×10^{-6} 1/Ω/1% for the bentonite soil.

1. Introduction

In the field of agriculture, continuous monitoring of soil moisture is extremely essential for a proper yield of crops, as soil moisture determines the amount of water present in the soil matrix. Various soil moisture sensors have been reported by the researchers [1–6]. Soil moisture content is measured in two ways viz. gravimetric moisture content (w) and volumetric moisture content (θ). Volumetric soil moisture measurement holds an edge over gravimetric moisture measurements since gravimetric measurements are limited to the lab and cannot be used for in-situ measurements. Time domain reflectometry (TDR), frequency domain reflectometry (FDR) and capacitance probe are some of the techniques used for accurate volumetric moisture measurements [1,3]. However the main drawback of these sensors is that they are expensive and cannot be afforded by many farmers [1,3]. Another reliable and low cost solution is dual probe heat pulse sensor but high power consumption is a major flaw in such system [1,3,7,8]. Researchers have also focused on polymer based soil moisture sensor using MEMS devices, where the resistance changes with increase in the soil moisture content [9,10]. Besides that, cantilever based soil moisture sensor was also reported recently, where, polyaniline a moisture sensitive material is used on top of the cantilever [11]. Polyaniline is a piezoresistive polymer which reacts with water molecules present in the soil thereby creating stress on the cantilever beam which causes the cantilever beam to deflect [11]. Similarly, cantilever based soil moisture sensor having water sensitive nano-polymer film on top of the cantilever beam has also been reported [12]. The drawback of the cantilever based sensor is the instability apart from the fact that fabricating cantilevers is an expensive process as well. Single step lithography for fabricating the IDE structure is a cost effective alternative as compared to the cantilever based sensors. In comparison to simple two-probe electrode, IDE will increase the effective contact area of the channel material and thus increase the sensitivity as well. Researchers have also reported electrode based micro-sensor which uses PEDOT:PSS conducting polymer [13]. When exposed to the moisture, conductivity of PEDOT:PSS changes due to the change in the resistance [13]. The disadvantage of resistive based technique is its high response time (2–3 h) and short life span [1,3]. The electrodes used in these sensors get oxidized, hence lifespan of these sensors is short [1]. Therefore, use of gold (Au) as the electrode

* Corresponding authors.
E-mail addresses: mshojaei@ee.iitb.ac.in (M.S. Baghini), m.aslam@iitb.ac.in (M. Aslam).
[1] First two authors have equal contribution.

http://dx.doi.org/10.1016/j.snb.2016.04.131

enables us to achieve good stability and higher life time due to its low oxidation (corrosion resistant) nature. Thus, soil moisture sensor with a wider range of moisture detection, high sensitivity, long life, quicker response time and shorter recovery time are essential to design a state of the art sensor. In order to meet these basic requirements with greater efficiency, researchers are focusing on development of new moisture sensitive materials. Nanomaterials such as 1-D carbon nanotubes, and graphene offer an attractive option as material of choice for soil moisture sensing due to their high surface to volume ratio in comparison to the polymers and metal oxides [14,15].

Out of these many new materials, graphene has been at the centre stage of material research since its discovery [16–19]. Graphene is 2-dimensional single layer of carbon atoms arranged in a honeycomb lattice structure and has shown tremendous potential for various sensing applications, mainly due to its unique electrical properties such as low noise level and high carrier mobility and large specific surface area for molecular adsorption [16–19]. Recently, researchers have been exploring sensors and devices based on different forms of graphene for humidity measurements. However, because of its zero band gap semi-metallic nature, graphene has limited use in the field of electronics [18]. Graphene quantum dots (GQDs) as the zero-dimensional (0D) version of graphene are being explored as a solution to this shortcoming since GQDs have a finite band gap due to quantum confinement and edge effects [18,20]. GQDs have already been investigated for FETs [21], photovoltaics [22,23], light emitting diodes [24,25], electrochemiluminescence [26], bioimaging [27,28], and biolabelling [29,30]. GQDs can be synthesized by various top-down [31–36] and bottom-up approaches [37–39]. In addition, our research group has recently shown that electrochemically synthesized GQDs are highly sensitive to humidity [40]. Taking the advantage of the quantum size of the GQDs, smaller size devices (channel width few nm) would be feasible in future leading to a NEMS device formulation which could be more suitable option for the future IC technology and sensors. Thus, IDE based micro-sensor with GQDs as sensing material and Au as electrodes can be a suitable candidate for soil moisture sensing.

In this work, resistive-type soil moisture sensor is fabricated with electrochemically synthesized graphene quantum dots as the sensing material. Cr/Au inter-digitated electrode (IDE) deposited on Si/SiO_2 substrate is used to fabricate the micro-sensor. The sensor has a short response time of 2–3 min for a wide range of soil moisture. The sensor is stable for about 4 months with negligible change in resistance. The sensitivity of the sensor towards gravimetric moisture contents is $0.014 \times 10^{-6}\,1/\Omega$ per percentage increase in moisture ($1/\Omega/1\%$) for the white clay and $0.005 \times 10^{-6}\,1/\Omega$ per percentage increase in moisture ($1/\Omega/1\%$) for the bentonite soil. The soil sensing mechanism is explained using Grotthuss chain reaction and ionic conductivity.

2. Experimental methodology

Micro-sensor was fabricated on Si wafer having interdigitated electrodes (IDE) structure using MEMS fabrication process. IDE structure offers a high sensitivity and increases the volume for sample deposit as compared to the electrodes [13]. We have used gold (Au) as electrodes, which results in good stability and higher life span due to its low oxidation nature. On top of the IDE, 20 μL of electrochemically synthesized graphene quantum dots dispersed in water (0.1 mg/mL) were dropcasted and air dried for 3–4 h. In order to protect the micro-sensors from damage, packaging is a crucial parameter for agricultural applications [11,13]. We have used a sensiron (SHT1X) filter cap on the top of IDE electrodes which allows only soil moisture to diffuse inside the chamber and interact with IDE micro-sensor. Such packaging does not allow the soil particles to penetrate inside the chamber and protect the micro sensor from damage [41]. Fabricated micro-sensor is tested in two different soil types' viz. white clay soil and bentonite clay soil. Soil sample is prepared with different moisture contents and its moisture is measured by infrared balance moisture which determines the gravimetric moisture content (Eq. (1)). Detailed synthesis of GQDs, fabrication of IDE structured micro-sensor and packaging is explained in the following subsections.

$$Gravimetric moisture content\,(w) = \frac{Wet weight of soil - Dry weight of soil}{Dry weight of soil} \quad (1)$$

2.1. Electrochemical synthesis of graphene quantum dots (GQDs)

GQDs used for our study are electrochemically synthesized using the method which has been discussed in our previous work [40]. In a typical synthesis about 5 μL of multiwalled carbon nanotube (MWCNT) (0.5 mg/mL) dispersed in ethanol was deposited onto a glassy carbon electrode (GCE) using a micro tip. Prior to deposition of MWCNT, GCE is polished in alumina powder and rinsed/washed thoroughly with acetone and water, and then dried subsequently. The MWCNT coated GCE is kept under an IR lamp for about 30 min to remove the water content and MWCNT forms a thin uniform layer over it. The MWCNT is electrochemically oxidized at a fixed potential of 1.1 V in an Autolab system with the three-electrode system (GCE as working electrode, Pt as counter electrode and Pt wire as the reference electrode). Propylene carbonate containing 3 mM $LiClO_4$ is used as the supporting electrolyte.

In the positive potential of 1 V, breaking of sp^2 carbon atoms start due to the applied electric field in the working electrode i.e. GCE. After oxidation, the potential was fixed at −1 V. In the negative potential, the oxidized MWCNTs get exfoliated because of the intercalation of Li+ ion complex. The exfoliations of oxidized MWCNTs results in size-tunable GQDs. Samples are collected by sonicating the GCE electrode in deionized water. Samples are washed and dialyzed before doing any characterization [40].

2.2. Fabrication and packaging of sensor

Fabrication of IDE involves single step lithography and hence low cost sensors can be fabricated as compared to cantilevers which have minimum 2–5 layer lithographic processes [11,42]. The IDE also offers an advantage of having high sensitivity and an increase in the volume of sample deposit. Fabrication steps for IDEs are shown in Fig. 1.

Initially, *p*-type wafer with <100> orientation is cleaned using standard RCA cleaning procedure. After RCA cleaning 1 μm oxide is grown using thermal oxidation as shown in Fig. 1(a). Positive photoresist (PPR) S1813 is spin coated on the wafer at 3000 rpm by using spin coater and pre bake it for 3 min at 90 °C as shown in Fig. 1(b). A mask was prepared for IDE to pattern it on the Si wafer with dimensions (1500 μm × 2400 μm). The PPR is exposed to UV light by using Karl Suss MJB-3 mask aligner, followed by a post bake for 2 min at 90 °C, and development of pattern in MF319 solution for 30 s, and then rinsing with isopropyl alcohol (IPA) and drying using N_2 gas. Accordingly, we get a pattern as shown in Fig. 1(c). Fig. 1(d) shows deposition of Cr/Au (20 nm/200 nm) on SiO_2 by the metal sputter process. 20 nm chrome (Cr) is usually deposited for the purpose of good adhesion between the SiO_2 and gold (Au). PPR is removed along with Cr/Au present on the top of PPR by using the lift off technique shown in Fig. 1(e). In the lift off technique we keep the wafer in acetone followed by an ultrasonic bath for 5–10 min. The wafer is then cleaned by using IPA followed by rinsing with distilled water (DI). As shown in Fig. 1(f) 20 μL of electrochemically synthesized GQDs dispersed in water (0.1 mg/mL) are dropcasted