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Linear humidity sensor fabrication using bi-layered active region of transition metal carbide and polymer thin films

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ABSTRACT

A linear humidity sensor based on bi-layered sensing area using exfoliated chromium carbide (Cr_3C_2) and polyacrylamide (PAM) thin films has been fabricated through all printed methods. Transition metal carbides have unique properties that can be applied in various gas sensing applications. In this work, different combinations of Cr_3C_2 with two polymers have been used to fabricate high performance linear humidity sensors. Cr_3C_2 was processed using wet grinding exfoliation to achieve flakes and small particles of the material. Based on the working principle and sensing results of the single layered sensors, a novel bi-layered structure was proposed and fabricated with stable linear response and good sensitivity. The sensors are capable of measuring percentage relative humidity accurately in range of 0% RH to 90% RH with an absolute change of 660 Ω/%RH and fast response and recovery times of 1 s and 1.9 s respectively. The sensors can also work with simple frequency based read-out circuit with a highly linear and stable response. The fabricated sensors are cheap, easy to fabricate, and are ideal to be used in high end environmental and health monitoring applications.

1. Introduction

Relative humidity is a crucial environmental factor in industry, food, and health care applications. There is a lot of research underway on the development of accurate, cheap, and easy to interface sensors for the applications of monitoring and control of environmental humidity [1–4]. There are various factors including range of detection, sensitivity, response and recovery times, stability, accuracy, and others, which are targeted for improvement while designing the sensors for specific applications. In some cases, wide range is the most crucial factor while in others, fast response and recovery times are focused [5–8]. Researchers develop various sensor structures, materials, and working principles to improve the parameter of interest [2,9–13]. The mainstream research targets to develop capacitive and resistive sensors because of their low cost and wide variety of available sensing mechanisms that can be tuned mostly by developing novel materials with desired properties [14–16]. There is a huge number of material categories that have been developed and tested in resistive and capacitive sensors including ceramics, metal oxides, polymers, bio-materials, 2D materials, transition metal dichalcogenides (TMDs), carbon and its derivatives, composites, supra molecules, block copolymers, and so on [7,12,17–25].

The major focus in most of the research in material based humidity sensors had been on the development of either a single material or a composite to achieve the targeted performance but they have mostly used single layers of the developed material as the sensing layers and have ignored the importance of device structure and configuration [21,23,26]. This no doubt leads to improvement in the targeted parameter but effects the other interlinked ones like curve linearity, user friendly readout signal, response time, etc. Other researchers have tried to change the configuration and structure by using bi-layered sensing films and even successfully improved certain parameters, yet, compromising the response time, detection range, and linearity [13,27–30].

The focus of this research is to keep in view both the material aspect and the importance of device configuration and then employ it to fabricate sensors without compromising any major performance parameter. For this target, we have used Cr_3C_2, a transition metal carbide (TMC), for the first time in humidity sensing application. The high surface area to volume ratio of the thin films of

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TMC and TMD flakes and their semiconductor like electrical characteristics allowing ionic current flow when exposed to electrolyte and solvent molecules like water make them a good candidate to be used in humidity sensing thin films [31–35]. Combinations of Cr_3C_2 with well-established humidity sensing polymers like poly acrylamide (PAM) and polyvinyl alcohol (PVA) have been used in both composite and bi-layered structures to improve the response curve linearity while maintaining the good sensitivity, wide range, and fast response. Another novelty of this research work is the process of mechanical liquid exfoliation that was used to achieve fine flakes and particles of TMCs that exhibit the desired properties for humidity sensing application. Most of the previous methods used to synthesize TMCs include selective etching [36], nano-casting [37], and CVD [38].

2. Experimental

2.1. Materials and methods

Chromium carbide powder (−325 mesh, formula weight 180.01 g/mol) and N-Methyl-2-pyrrolidone (NMP) (C_5H_9NO, formula weight 99.13 g/mol, 99.5% anhydrous) solvent to prepare Cr_3C_2 ink were purchased from Sigma. Conductive ink to fabricate electrodes was Silverjet DGH ink for reverse offset (viscosity: 1.5 cps, surface tension: 24.4 mN/m, dispersion matrix: octane based). Polyacrylamide (PAM) average M_n 150,000 and polyvinyl alcohol (PVA) M_W 89,000–98,000, 99+% hydrolyzed polymer powders were purchased from Sigma.

Cr_3C_2 ink was prepared by exfoliating the bulk powder into smaller flakes and particles using a combination of mechanical wet grinding and liquid exfoliation. Cr_3C_2 powder was first dispersed in the form of a thick paste in NMP and was ground in a mortar for 90 min to physically break and exfoliate the bulky chunks into smaller flakes and particles. The mixture was further diluted in NMP solvent to make a liquid ink. The solvent was probe sonicated for 60 min, then bath sonicated for 30 min, and then again probe sonicated for 30 min for fine exfoliation of Cr_3C_2 particles. The resultant solution was centrifuged at 4000 rpm to separate the heavier chunks and non-exfoliated Cr_3C_2 particles from the ink. This method can produce a large number of 2D flakes of transition metal carbides and has been successfully employed for other 2D materials including TMDs and hBN [39,40].

The polymer inks of both PVA and PAM were prepared by dissolving the powders in 5% wt/vol (0.5 g powder in 10 ml) in de-ionized (DI) water as the solvent. The solutions were magnetically stirred at room temperature until homogenous solutions were formed. Two composite inks of the polymers with Cr_3C_2 were prepared by mixing the as prepared solutions in 1:1 vol/vol and stirred until a homogenous solution was achieved. A total of seven different types of sensors were fabricated with active layers composed of Cr_3C_2, PVA, PAM, Cr_3C_2 + PVA, Cr_3C_2 + PAM, Cr_3C_2/PVA, and Cr_3C_2/PAM. Here, the symbol "**+**" is used for the composite based film and the symbol "**/**" is used for a bi-layered structure. This convention will be followed throughout the manuscript to mention composite and bi-layer active films.

2.2. Sensor fabrication

The design of the humidity sensors was based on interdigitated transducer (IDT) electrodes at the bottom and the sensing films deposited on top. Reverse offset printing was used to fabricate silver electrodes on 128° Y-cut $LiNbO_3$ piezo substrate wafers. The electrodes were sintered at 400 °C for 6 h. The step by step fabrication process is show in Fig. 1. After the printing of electrodes (40 finger pairs with 50 μm finger width), the devices were treated with UV Ozone plasma to make their surface hydrophilic and improve their surface affinity towards the active layer ink. The first layer of exfoliated Cr_3C_2 was then deposited using Electrohydrodynamic Atomization (EHDA) technique [40]. The devices were cured at 120 °C for 90 min after the first layer was deposited. The second layer of polymer was deposited using spin coating at 2700 rpm and the samples were again cured at 100 °C for 90 min. For single layered sensors, the polymer and the composite films were deposited using spin coating at 900 rpm while the Cr_3C_2 layer was deposited using EHDA. Four different bi-layered sensors were fabricated with different film thicknesses of PAM and Cr_3C_2 layers and their results were compared. The curing time and temperature for both materials were same.

2.3. Sensor characterization

The sensors and thin films were characterized to find their morphological, structural, and electrical characteristics and determine the sensing mechanism and properties efficiently. The surface morphology of the thin films was investigated using field emission scanning electron microscope (FE-SEM) by Carl Zeiss Supra 55VP. The crystal structure of Cr_3C_2 was determined using X-ray diffraction spectroscopy (XRD) with Cu K-α source while the exfoliated flakes and particles in the TMC thin film were observed using atomic force microscopy (AFM). The impedance response of the sensors towards relative humidity change was recorded through an environmental chamber specially designed to control the temperature and humidity of the device surroundings. HTU-21D was used as the reference sensors to measure the actual level of relative humidity inside the chamber and give a feedback to maintain the level at the desired value. Applent AT-825 digital LCR meter with 0.6 V_{rms} AC output was used to measure the impedance response at 1 kHz test frequency. The humidity level inside the sealed chamber was decreased from atmospheric conditions to 0% RH using controlled flow of dry N_2 as purging gas for the chamber. The humidity level was increased by introducing atomized water vapors from a desktop humidifier. The temperature of the whole system was maintained at 25 °C. To convert the sensor's output to a more user friendly electrical signal, an oscillator circuit was designed to give the response of the sensors in terms of frequency versus relative humidity. Further details of the setup are presented in our previous works [41,42].

3. Results and discussion

3.1. Morphology and crystal structure

Surface SEM images of the bulk and exfoliated Cr_3C_2 were taken to compare their physical morphology. The results are presented in Fig. 2. The image of the bulk Cr_3C_2 powder presented in Fig. 2(a) shows big bulky chunks of the material spread on the surface. The thickness and size of the chunks is in range of several micrometers. The SEM image of the thin film of exfoliated Cr_3C_2 presented in Fig. 2(b) shows large number of smaller particles and flakes distributed throughout the surface. There are also some large area flakes on the surface but their physical structure is like 2D as shown in Fig. 2(c). The surface morphology of the composite films of Cr_3C_2 with polymers show highly porous surface of the PAM based composite Fig. 2(d), and embedded Cr_3C_2 particles in the PVA matrix Fig. 2(e). The cross sectional SEM image of the Cr_3C_2 thin film presented in Fig. 2(f) shows highly porous nature of the film with thickness in range of ~200 nm. The image also shows small flakes and particles of Cr_3C_2 stacked over one another that is ideal for resistive based humidity sensing film. The thicknesses of the multiple thin films were investigated using cross-sectional