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Synthesis of copper–ferrous (CuFe) nanowires via electrochemical method and its investigations as a fluid sensor

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Abstract. The special behaviour of nanowires with respect to electrical conductivity makes them suitable for sensing application. In this paper, we present a copper–ferrous (CuFe) nanowires based sensor for detection of chemicals. CuFe nanowires were synthesized by template-assisted electrochemical method. By optimizing the deposition parameters, continuous nanowires on a copper substrate were synthesized. The morphological and structural studies of the synthesized CuFe nanowires were carried out using scanning electron microscope (SEM) and X-ray diffraction (XRD). Substrates containing CuFe nanowires were moulded to form a capacitor. Different chemicals were used as dielectric in the capacitor which showed that the capacitance was a nonlinear function of the dielectric constant of fluid unlike the linear relation shown by conventional capacitors. This unique property of the nanowires based capacitors may be utilized for developing fluid sensors with improved sensitivity.

Keywords. Electrochemical deposition; nanowires; nanosensor; dielectric.

1. Introduction

A better understanding of the fundamental properties of matter in reduced dimensions has been contributed by the development of nanotechnology (Sordan *et al* 2001). Studies of nanomaterials are of great interest due to their potential applications in many fields of science and technology (Wilson and Gifford 2005). Depending upon the dimensions, nanomaterials are divided into four categories; 0D, 1D, 2D and 3D nanostructured materials. Out of these four nanostructured materials, 1D nanostructures, commonly exist in the form of nanowires and nanotubes and are extensively explored because of their wide range of applications in microelectronics, medicine, biology, catalysis and sensing technology. The scope of this paper is limited to only nanosensors.

Sensors are composed of an active sensing material with a signal transducer. These components in sensors transmit the signal without any amplification from a selective compound or from a change in a reaction. Sensors produce signals in the form of electrical, thermal or optical variations. These signals may be converted to digital signals for further processing (Konishi *et al* 2003; Wilson and Gifford 2005; Yogeswaran and Chen 2008). Both nanowires and nanotubes can function as sensing element and the electrical contact that accesses them. These are the primary building blocks of the nanosensors (Myung *et al* 2004). High surface-to-volume ratio makes nanowires and nanotubes excellent candidates for sensing applications. High surface-to-volume ratio improves detection sensitivity and response time due to more reaction area per volume and reduced diffusion time (Grujicic and Pesic 2002; Xie 2002; Huang *et al* 2004).

Nanowires can be fabricated by various techniques that include lithographic patterning (Rahman *et al* 2009; Bandaru and Pichanusakorn 2010), vapour transport techniques (Bae *et al* 2004; Malandrino *et al* 2004), template-based synthesis methods (Martin 1996; Kline *et al* 2006), and other synthesis methods (Xu *et al* 2002; Zheng *et al* 2005). The template-based synthesis involving electrochemical deposition is more promising owing to its specific advantages of low cost and control over the nanowire properties by changing the electrolyte composition, pH, temperature and applied potential or the current (Chakarvarti 2006). Today, various techniques are being used for the fabrication of 1D nanostructures, but the template synthesis is a versatile and economic one for synthesizing a variety of 1D nanomaterials including metals, semiconductors, heterojunctions, conducting polymers, CNTs and much more (Singh *et al* 2006). Metallic nanowires synthesized by template-assisted electrodeposition method have been proved to be a cheap and high yield technique (Hamrakulov *et al* 2009). Nuclear array glasses, mesoporous channel hosts, polycarbonate membrane and self-ordered anodized aluminum oxide (AAO) films are used as templates in electrodeposition process for synthesizing nanowires. Track-etch polycarbonate nanopore membrane

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(Whatman) was used as template in this to synthesize 1D nanostructures of copper–ferrous. The size and spacing of nanofeatures can be controlled using templates with different characteristics (Huang *et al* 2006; Chen *et al* 2008; Arya *et al* 2013). Nanowires are mechanically stable within the templates and easy to handle. In conclusion, the template based electrodeposition method for the fabrication of nanowires has proved to be a reliable and effective technique.

The objective of this paper is to investigate the applications of electrochemically-deposited CuFe nanowires as fluid sensors. The investigations carried out included various fluids such as water (H_2O), acetone (C_3H_6O), ethanol (C_2H_5O), dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$). The methodology of the investigations was carried out and is presented in the next section. Results and conclusions are presented, thereafter.

2. Experimental

The experimental set up used for investigating the applications of electrochemically deposited nanowires is divided into two phases. In the first phase, the nanowires are synthesized using a two-electrode system. The cell consists of a cylindrical container mounted over one side of a disc-shaped acrylic sheet with a strong adhesive. An orifice of precise diameter is made in the disc along the axis of the cylinder and a ring-shaped rubber cork is attached to it. This arrangement is placed over a metallic plate which completes the cell system. Two electrodes are used in the experiment; a platinum electrode acting as anode and self-adhesive copper tape on metallic circular sheet as cathode. The mechanism of deposition process for nanowires is shown in figure 1. A 100 nm pore sized polycarbonate membrane is placed over copper tape substrate which acts as a sacrificial layer.

The copper substrate along with the membrane is placed in contact with metallic plate, which serves as the cathode. The growth of nanowires by electrochemical process was achieved by applying a d.c. voltage of 0·8 V across the plating bath, which is filled with the electrolytic solution of 0·2 M of $CuSO_4{\cdot}6H_2O$, 0·2 M of $FeSO_4{\cdot}7H_2O$ and 0·1 M of H_3BO_3 prepared in 50 ml of double-distilled water. pH of the electrolyte was 2·9 in this experiment. The electrodeposition was carried out at room temperature for 12 min duration. The length of the nanowires was controlled by the duration of the electrodeposition.

The polycarbonate membrane was dissolved in dichloromethane to release the nanowires. Change in current density during deposition was monitored and it was observed that at initial stage of the electrodeposition process, current density had high value and started decreasing, reaching a constant region, where deposition of nanowires occurred and after that over-deposition process took place. The structural properties were studied by X'PERT-PRO Phillips X-ray diffractometer using CuKα radiation at 45 mA and 45 keV. The morphologies of CuFe nanowires were investigated by JEOL JSM-6100 analytical scanning electron microscope (SEM).

3. Results and discussion

3.1 *SEM characterization*

The surface morphology of CuFe nanowires have been studied by scanning electron microscopy. The dried sample were mounted on aluminum stub with the help of adhesive carbon tape and coated with a layer of gold in JEOL JFM 1100 Sputter Coater and then viewed under scanning electron microscope. Figures 2 and 3 show surface morphology (top view) of grown CuFe nanowires of

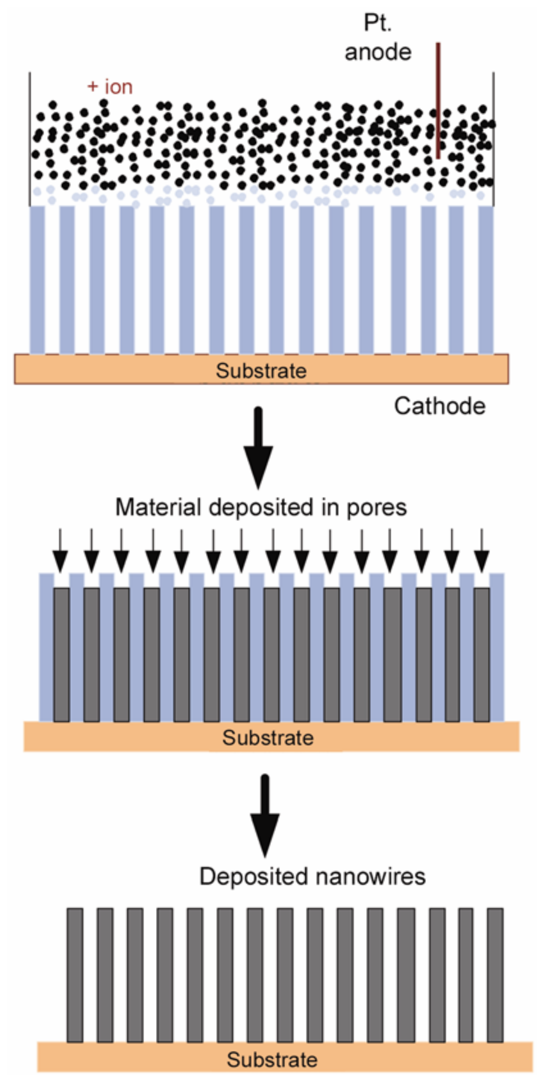

Figure 1. Schematic diagram showing mechanism of nanowires synthesis via electrochemical method.

diameters 100 nm with zooming X = 6500 and X = 9000, respectively.

SEM studies show that the growth nanowires are uniform and have diameter equal to the diameter of the pores of polycarbonate template used. The electrochemically synthesized CuFe nanowires are found to be highly ordered, vertically aligned and of high aspect ratio. SEM image of a copper–ferrous mixed metal nanowire is fabricated using a polycarbonate membrane. It may be observed from SEM that mixed metal nanowires of copper and ferrous have been successfully fabricated. The diameter of the nanowires was fixed by the actual pore size of the polycarbonate membrane, while the length of the nanowires was varied based on time duration of the applied voltage.

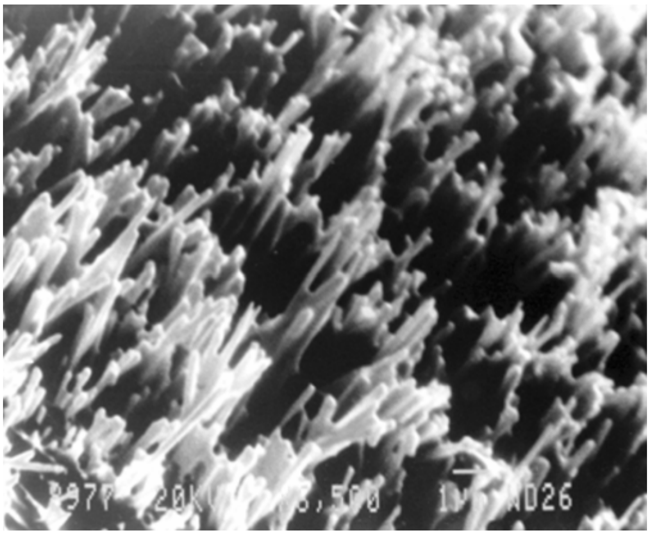

Figure 2. SEM of CuFe nanowires (100 nm) deposited on copper substrate with X = 6500.

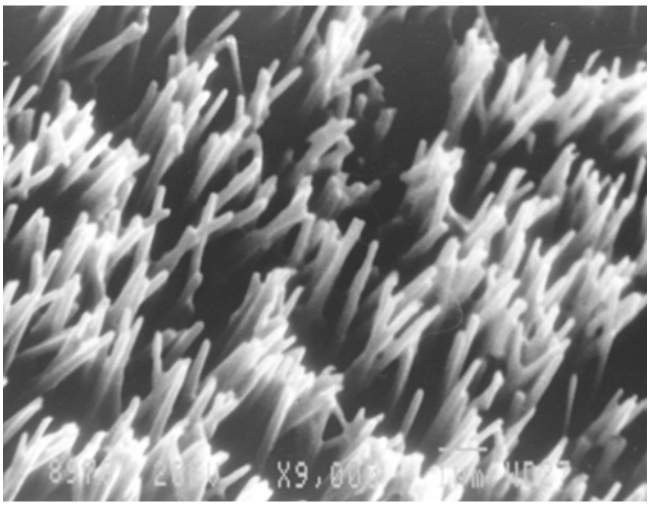

Figure 3. SEM of CuFe nanowires (100 nm) deposited on copper substrate with X = 9000.

3.2 *XRD characterization*

Figure 4 shows XRD pattern of electrochemically synthesized CuFe nanowire arrays of diameter 100 nm on copper substrate. XRD patterns were recorded in the range of scanning angle, 10–70° with a step size of 0·0170° using wavelength ($K\alpha$), 1·5406 Å. From the XRD studies, it is found that the CuFe nanowires are determined to have cubic structure since the characteristic diffraction peaks in the diffraction spectrum of CuFe nanowires match with the standard ICDD copper ferrous (Cu_xFe_{1-x}) data file (JCPDS number: 49-1399). XRD studies confirm the formation of CuFe nanowires.

Various XRD peaks of CuFe from (111), (220), (311) and (333) planes are observed at 2θ angle of 17·89°, 29·61°, 31·69° and 56·52° for 100 nm nanowires, respectively. Two strong peaks of copper are also observed in

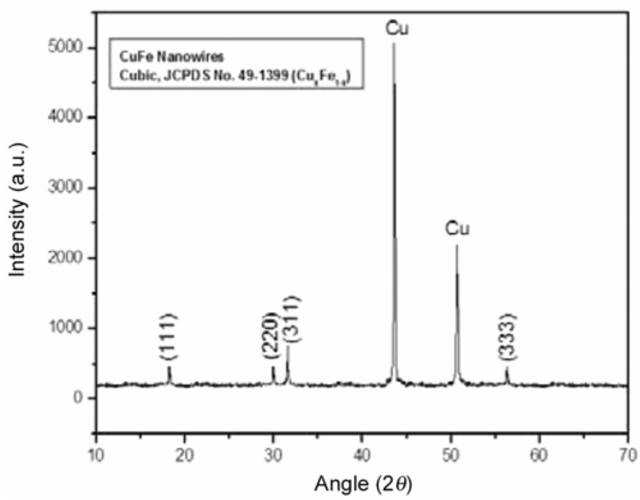

Figure 4. XRD pattern of CuFe nanowires (100 nm) on copper substrate.

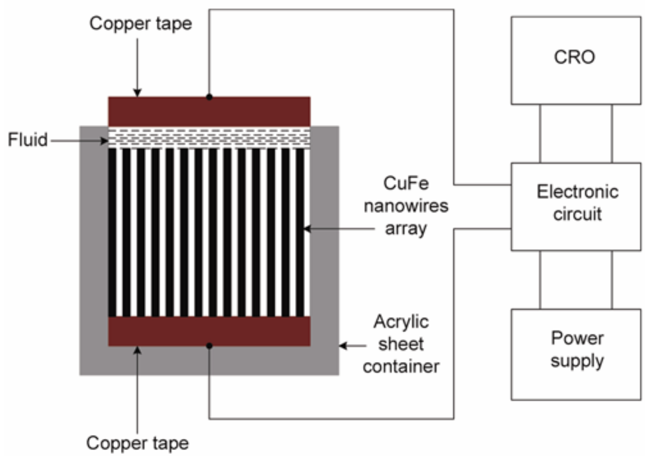

Figure 5. Block diagram implementing CuFe nanowires in electronic circuit.

the XRD pattern which arises from the copper substrate. XRD peaks of CuFe shows crystalline nature of as-grown CuFe nanowires. The diffraction peaks of 100 nm CuFe nanowires were also observed to be broadened as compared to bulk material. This broadening of the diffraction peaks is due to nanometer size of nanowires.

3.3 *CuFe nanowire as fluid sensor*

In order to use CuFe nanowires as sensor in electronic circuitry, a capacitor is made from the substrate containing CuFe nanowires. The schematic of the circuit implementing capacitor made from substrate containing CuFe nanowires is shown in figure 5. The capacitor is used in a stable mode of multi-vibrator electronic circuit (Karris 2008). The capacitor parameters such as charging time, discharging time and oscillation time period were estimated from the CRO. Capacitance values with different dielectric medium were calculated from the following formulae:

$$T_d = 0{\cdot}693 R_B C,$$

$$T_c = 0.693(R_A + 2R_B)C,$$

where $R_A = 10$ kΩ and $R_B = 220$ kΩ. Total time period of oscillations is estimated from CRO by visualizing the output waveform, which is given as

$$T = T_c + T_d.$$

The values of capacitances were calculated for various chemical fluids taking them as a dielectric medium between the plates of CuFe nanowires-based capacitor. The dielectrics were chosen in increasing order of dielectric constant. The fluid chosen for dielectric medium are water (H_2O), acetone (C_3H_6O), ethanol (C_2H_5O), dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) having dielectric values 80, 21·5, 16·2, 8·93 and 4·8, respectively at room temperature.

Table 1 shows estimated values of the total oscillation time period for these fluids. It was observed that on changing the dielectric in between the plates of the capacitor, duration of the 'ON' and 'OFF' states of a stable multivibrator was changed (figure 6). Although, it seems very common, the amount of change is not predictable from the basic formula of the capacitance.

These results are further emphasized in figure 7. It shows that the change in capacitance of CuFe nanowires based capacitor as sensor is not directly proportional to the dielectric constant of the fluid; hence the behaviour is not similar to a conventional capacitor.

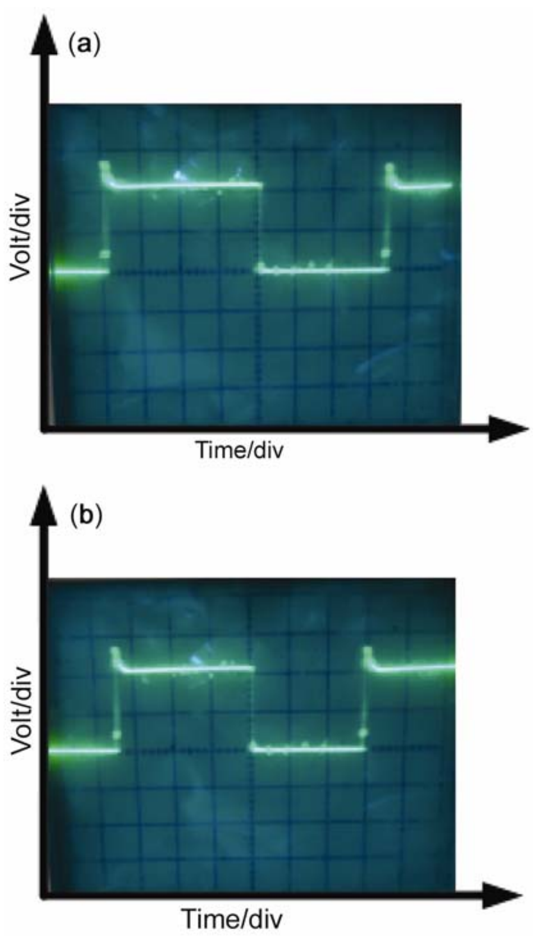

Figure 6. Depending upon dielectric, change induced in time period of a stable multivibrator: (**a**) H_2O and (**b**) air, dielectric recorded on CRO.

Table 1. Calculated capacitor parameters.

Fluid	Dielectric value	Oscillation time (μs)	Capacitance (pF)
H_2O	80	3·7	11·865
C_3H_6O	21·5	2·1	6·73
C_2H_5O	16·2	2·7	8·65
CH_2Cl_2	8·93	1·4	4·48
$CHCl_3$	4·8	1·7	5·45

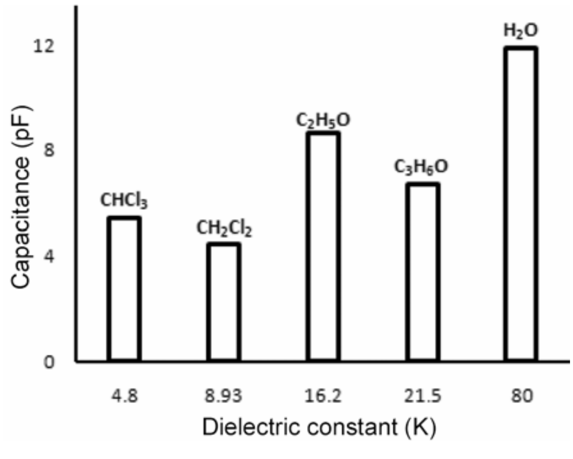

Figure 7. Calculated values of capacitance of CuFe nanowires capacitive sensor with increasing order of dielectric value.

CuFe noanowires show different capacitive behaviours toward the dielectric material used in the moulded capacitor. This property of CuFe nanowires may be used for fabrication of fluid sensors which can be further investigated to characterize different fluids in the environment.

4. Conclusions

The dielectric-dependent capacitive properties of CuFe nanowires of diameter 100 nm, synthesized electrochemically via template synthesis using polycarbonate track-etch membrane have been studied and reported. SEM studies have confirmed that the CuFe nanowires are ordered, vertically aligned and of high aspect ratio. Capacitance measurements of CuFe nanowires embedded in polycarbonate membrane have shown nonlinear characteristics. The analysis of the results of using copper substrate along with the deposited CuFe nanowires as one plate of a parallel plate capacitor showed that the change in the capacitance is different from the predicted value using simple classical formula. These results may be very useful for developing a fluid sensor.

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