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Synthesis of copper telluride nanowires using template-based electrodeposition method as chemical sensor

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Abstract. **Copper telluride (CuTe) nanowires were synthesized electrochemically from aqueous acidic solution of copper (II) sulphate ($CuSO_4{\cdot}5H_2O$) and tellurium oxide (TeO_2) on a copper substrate by template-assisted electrodeposition method. The electrodeposition was conducted at 30 °C and the length of nanowires was controlled by adjusting deposition time. Structural characteristics were examined using X-ray diffraction and scanning electron microscope which confirm the formation of CuTe nanowires. Investigation for chemical sensing was carried out using air and chloroform, acetone, ethanol, glycerol, distilled water as liquids having dielectric constants 1, 4·81, 8·93, 21, 24·55, 42·5 and 80·1, respectively. The results unequivocally prove that copper telluride nanowires can be fabricated as chemical sensors with enhanced sensitivity and reliability.**

Keywords. **CuTe; nanowires; electrodeposition; characterization; nanosensors.**

1. Introduction

Nanosensors possess implausible potential in computing systems; and in near future, nanosensors may act as a bridge between various nano and macroscopic devices to exploit several advantages due to their unique physical properties (Lee *et al* 2005). The benefits of nano-based devices are their sensitivity which is better than conventional devices, fast response time, wide range of operations and portability. The fundamental core for intelligent nanosensors can be characterized for analysing power (Devreese and Eindhoven 2007). Depending on the field of application, nanosensors can be used for generating electrical, optical or thermal output signals that can be transformed into digital form for further processing. Accordingly, nanosensors can be classified as biosensors, chemical sensors and physical sensors, depending upon the area of application (Turner 2000; Lee and Kotov 2007; Pan *et al* 2008; Zhang and Johnson 2009). Several methods are reported to have been used for the fabrication of nanosensors (Suzuoki *et al* 1987; Caillaud *et al* 1993; Jin and Ying 1994; Inukai *et al* 1995; Mahmood *et al* 1995; Peulon and Lincot 1996; Hussain *et al* 2010). However, capacitive (chemical) sensors can be synthesized easily by using non-conductive material and are very much associated with the capacitor as its dielectric. Nanopore-based chemical sensors can detect the capacitance change with a very high sensitivity due to water adsorption (capillary condensation) inside the nanopores because of its very high surface area-to-volume ratio (An and Mai 2002). The value of the capacitance depends on dielectric constant of the material used and is in proportion to the frequency (Golonka *et al* 1997; Kim *et al* 2000; Steele *et al* 2004).

In this paper, template-based electrodeposition method was used to prepare CuTe nanowire sensors. Anodized aluminum oxide foil (AAO) acts as template and electrodeposition is conducted in a typical two-electrode cell with a platinum electrode in 50 ml solution of electrolyte with copper foil acting as substrate for fabricating nanowires. After deposition, the as-prepared CuTe nanowires were extracted from the template by removing the AAO with an alkali solution. X-ray diffraction (XRD) and scanning electron microscopic (SEM) techniques have been used to characterize the nanowires. A careful analysis of the results shows the formation of defect-free CuTe nanowires in the form of parallel fibres. The nanowires obtained were characterized as sensors by using a simple application of a 555 IC timer as an astable multivibrator.

2. Synthesis of nanowires

A deep insight into the literature suggests the existence of two key methods for the synthesis of nanowires, viz. dry and wet processes. Dry processes include methods such as chemical vapour deposition (CVD), physical vapour deposition (PVD), pulse laser deposition (PLD), metal organic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE) (Suzuoki *et al* 1987; Caillaud *et al* 1993;

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Jin and Ying 1994; Inukai *et al* 1995; Mahmood *et al* 1995; Peulon and Lincot 1996; Hussain *et al* 2010). Wet processes comprise sol–gel, hydrothermal, chemical bath deposition (CBD) and electrodeposition methods. Among these methods, electrodeposition has several advantages such as low cost, environment-friendly, high growth rate at relatively low temperatures and easy control of shape and size (She *et al* 2009). This template method is quite efficient in achieving controlled growth of nanowires; the physical shape, magnitude and orientation of the produced structures are precisely defined by the template. It allows the synthesis of simple and complex multi-segmented nanowire and coaxial nanowire structures. Electrodeposition depends on small but valuable factors such as surface characteristics of template, electrode substrate, pH value, mechanical agitation, temperature, etc. Morphology of the fabricated material depends on the pore morphology and dimensions (Chakarvarti and Vetter 1991).

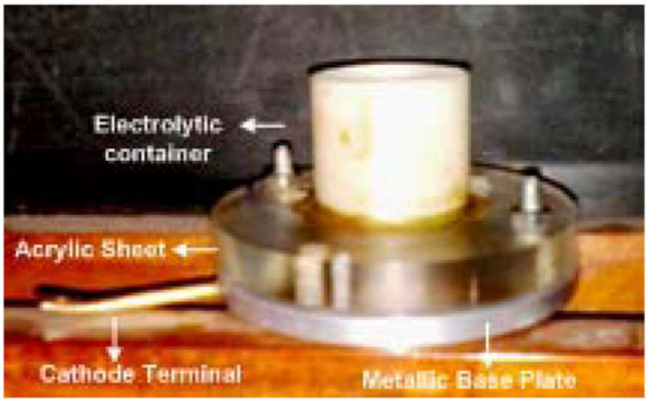

Figure 2. Electrochemical cell used for electrodeposition of CuTe nanowires.

3. Experimental

Copper telluride (CuTe) nanowires were synthesized by using template-based electrodeposition method as shown in figure 1.

It was carried out in a two-electrode electrochemical cell (Chakarvarti and Vetter 1991) as shown in figure 2. The commercially available self-adhesive copper tape (3 M 1181) was used as a substrate. The copper tape was fixed on the metallic base of the self-made electrochemical cell and it acts as cathode. Platinum (Pt) electrode acts as anode.

Commercially available template with a porosity of 0·43 (Whatman Inc. –100 nm diameter) was utilized to deposit CuTe nanowires. It was a precision membrane filter with a closely controlled pore size distribution. It was fixed gently on the copper substrate through a rubber ring fitted in the top portion of the cell. Thus, an area of $\sim$1 cm^2 on the copper substrate was allowed for exposure to the electrolyte through a nanoporous membrane. The system was tightly closed to ensure that no air bubble exists between membrane and substrate. The length of the nanowires was 6 μm as it depended on the thickness of membrane used. Table 1 shows the specifications of commercially available membranes/templates for nanowire fabrication with varying sizes.

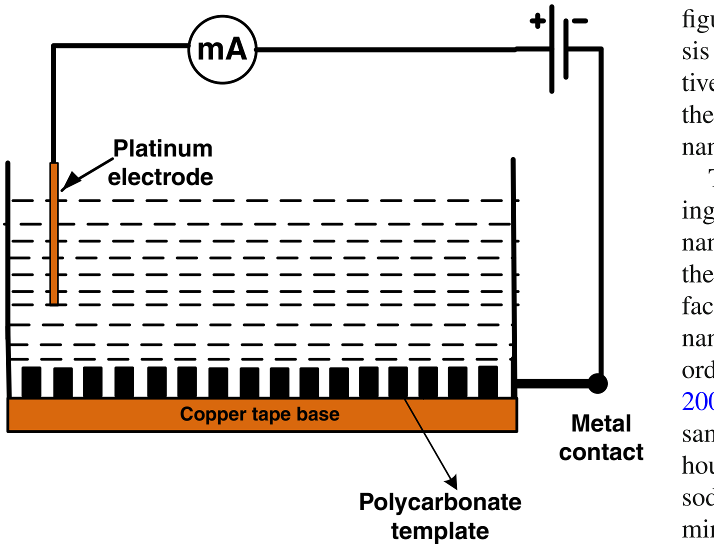

Figure 1. Schematic diagram for electrodeposition of CuTe nanowires.

Electrolytic solution of about 50 ml was used for nanowire synthesis. The electrolytic solution contained 0·2 M of $CuSO_4{\cdot}5H_2O$, 0·2 M TeO_2 and 0·2 M KOH and was prepared in double distilled water at room temperature. pH value of the electrolytic solution was observed between 2·5 and 3·5. The electrolyte was poured in the cell and a voltage of 0·8 V was applied to the electrode through a variable d.c. power supply.

Mechanism for the formation of nanowires is shown in figure 3. As current passes through the solution, electrolysis takes place and Cu and Te atoms dissociate into positive ions and these ions move towards the cathode through the membrane pores and deposit on the Cu substrate in the nanoporous space.

The length of the nanowires was controlled by adjusting the time of deposition. As the nanowires grew, the nanopores of the template, typically AAO, were filled. Since the nanopores were perpendicular to the AAO membrane surface and were uniform in diameter and hexagonally packed, nanowires embedded in the template form were highly ordered and vertically aligned nanowire arrays (Prieto *et al* 2001). After deposition of nanowires on the substrate, the samples were detached from the cell and dried for half an hour. The sample was dipped in the aqueous solution of sodium hydroxide (NaOH) for the removal of anodized alumina from the nanowires. Finally, the sample was dried at room temperature for further characterization.

During deposition process, high current was observed in the beginning that corresponds to the phenomenon of polarization. Thereafter, the current was found relatively steady and it served as an indication of the actual filling of the pores within the cell. This process required periodic monitoring to avoid overdeposition on the membrane surface. This led to successful fabrication of nanowires.

Morphology of the nanowires deposited on the Cu substrate was studied using SEM and XRD. Figure 4 shows SEM of CuTe nanowires which reveals that there is an optimum deposition of nanowires on the copper substrate with uniform growth and that the nanowires are vertically aligned with high aspect ratio.

The structural properties were studied using Panalytical X'PERT PRO Diffractometer using Cu-Kα radiation at 45 mA, 45 keV. The XRD pattern was recorded in the range of 20 to 70 degree (2θ angle) with a step size of 0·01700 per second using Cu-Kα radiation (wavelength), 1·5406 Å. Figure 5 shows the XRD pattern of 100 nm copper telluride nanowires on copper substrate.

The copper telluride (Cu1·75Te) nanowires are found to have hexagonal structure since the diffraction peaks in the patterns match with the standard ICDD copper telluride (Cu1·75Te) data file (JCPDS Number: 45-1287). A number of XRD peaks are obtained that are reflected from various planes (103), (108), (200) and (209) which confirm the formation of crystalline growth of copper telluride nanowires. A high intensity peak of copper is also observed in the XRD pattern indexed as (111) that appears due to copper substrate used.

The experimental set up for the characterization of sensing properties of CuTe nanowires is presented in figure 6. CuTe nanowires are assumed to be one plate of the capacitor while a simple copper substrate acts as another plate. Dielectrics used for the experiment are air, chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), acetone (CH_3COCH_3), ethanol (C_2H_5OH), glycerol ($C_3H_8O_3$) and distilled water (H_2O), respectively.

Table 1. Standard specifications of different membranes/templates.

Material	Pore size (μm)	Diameter (mm)	Thickness (μm)	Pore density (pores/cm^2)
Polyester	0·1–5·0	13, 25, 47	9–23	10^5 – 6×10^8
Polycarbonate	0·01–12·0	13, 19, 25, 37, 47, 50, 76, 90, 142, 293	7–20	10^5 – 6×10^8
Aluminium oxide	0·02–0·2	13, 21, 47	60	10^5 – 6×10^8

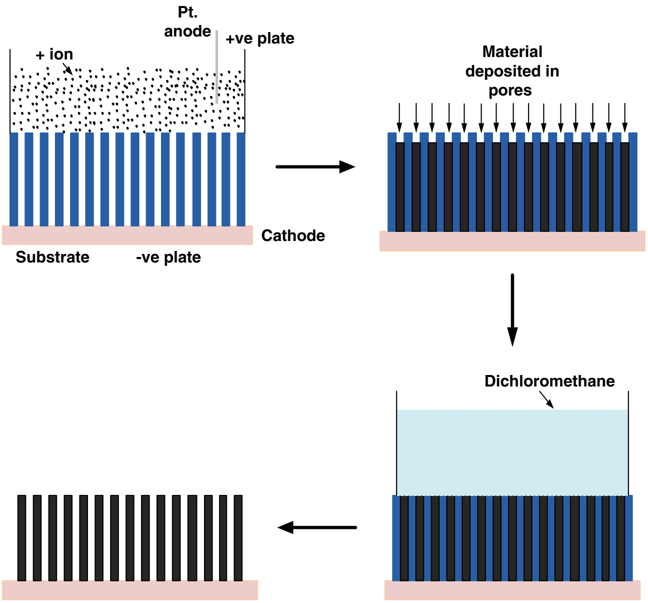

Figure 3. Schematic showing formation of CuTe nanowires by electrodeposition method.

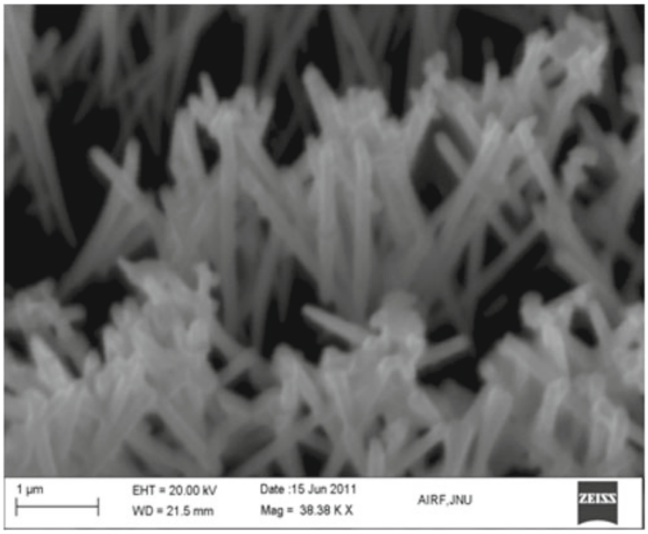

Figure 4. SEM of 100 nm CuTe nanowires deposited on Cu substrate.

The connections were made as per the circuit diagram using the application of a 555 timer as an astable multivibrator. The foils were separated by some specific distance (μm) between them to be filled by different dielectric chemical liquids. The output was observed on a cathode ray oscilloscope (CRO). Mathematically, using a 555 timer as an astable multivibrator, the overall period of oscillations is given by

$$T = 0{\cdot}693\,(R_{\mathrm{A}} + 2R_{\mathrm{B}}) * C,$$

where $R_{\mathrm{A}} = 10\ \mathrm{k\Omega}$ and $R_{\mathrm{B}} = 220\ \mathrm{k\Omega}$.

The frequency of oscillation being the reciprocal of overall period of oscillation, T and is given by

$$f = \frac{1}{T} = \frac{1{\cdot}44}{(R_{\mathrm{A}} + 2R_{\mathrm{B}}) * C}.$$

The capacitance can be calculated as

$$C = \frac{T}{0{\cdot}693(R_{\mathrm{A}} + 2R_{\mathrm{B}})}.$$

This method is used for calculating the capacitance after using CuTe nanowires as one of the capacitor plates.

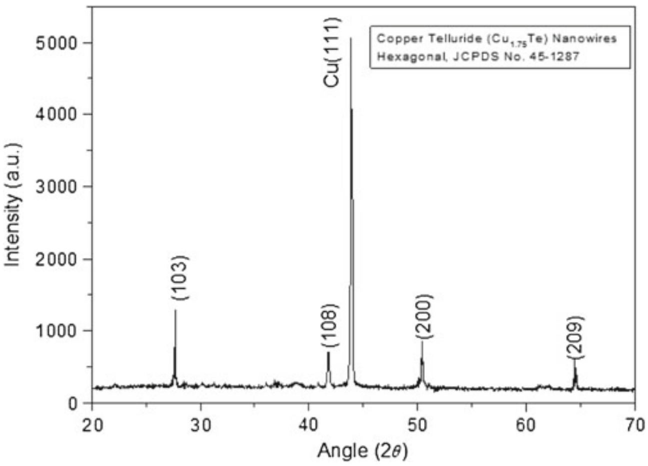

Figure 5. XRD pattern of copper telluride nanowires (100 nm) on Cu substrate.

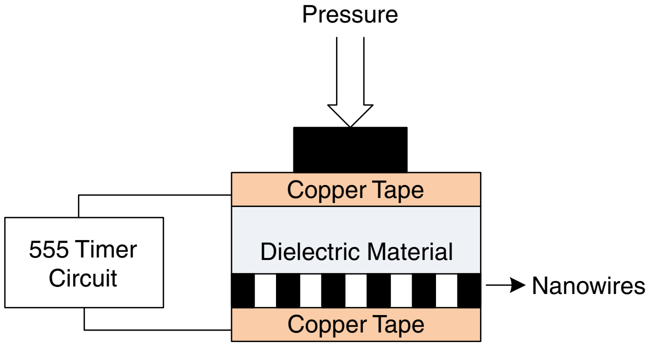

Figure 6. Experimental set up of CuTe nanowires as chemical sensor.

4. Results and discussion

Different capacitance values have been observed for CuTe nanowires fabricated on the copper substrate. A considerable change in the capacitance of CuTe-based nanowires as capacitor illustrates its chemical sensing property for different dielectric materials (chemical liquids). Capacitance values estimated for different liquids are shown in table 2.

A plot of these values is shown in figure 7. It has been observed that capacitance changes with change of dielectric materials. As the dielectric constant of different (dielectric materials) liquids varies, so do the capacitances of CuTe nanowires. From figure 7, it is observed that capacitance of the CuTe nanowires on Cu substrate can sense different liquids effectively and it is further substantiated by the fact that capacitance changes with respect to the dielectric constant. The maximum and minimum values of capacitance were observed for water and chloroform, respectively. The capacitive effect in the CuTe nanowires may be due to the increase in surface area of nanowire-based capacitor.

A detailed analysis of the change in capacitance in different dielectric materials (chemicals) indicates that the change in capacitance is directly proportional to the dielectric constant. The value of the capacitance is observed as a function

Table 2. Variation in capacitance for different dielectric materials.

Dielectric material	Dielectric constant	Capacitance (pF)
Air	1·00	16·00
Chloroform	4·81	25·60
Dichloromethane	8·93	27·82
Acetone	21·00	32·00
Ethanol	24·55	35·16
Glycerol	42·50	41·56
Water	80·10	48·00

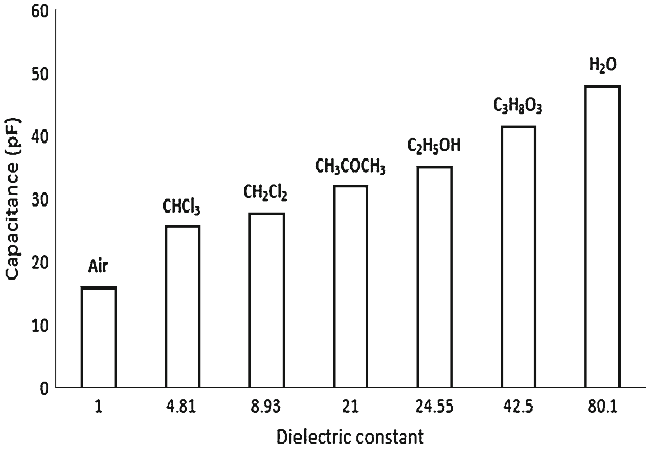

Figure 7. Variation in capacitance (pF) for different chemical liquids used as dielectric.

of its surface area, distance between the two plates of capacitor and the dielectric medium. It means that the nanowire-based capacitor can be used as a chemical sensor for sensing different fluids or liquids.

5. Conclusions

It is a simple and an economical method for fabricating highly ordered single crystalline CuTe nanowires of 100 nm diameter. The nanowires have been successfully characterized as sensors at room temperature. Investigations show that CuTe nanowire-based liquid sensors can be easily fabricated with enhanced properties such as sensitivity and reliability. The sensing property of CuTe nanowires as a capacitor shows change in the capacitance in accordance with the dielectric constant of the liquid used. Future studies will incorporate facilities of smart sensors in nanowire-based structures.

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