https://doi.org/10.48048/tis.2022.5617

Study of Structural, Morphological and Electrochemical Properties of Multilayer Nanowires

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Received: 1 May 2021, Revised: 5 July 2021, Accepted: 15 July 2021

Abstract

Ni/Cu nanowires were fabricated by electrodeposition in potentiostatic mode, into the pores of polycarbonate membrane. In present work metallic multilayer nanowires were deposited in polycarbonate membrane having pore size of 400 nm. It is found that the growth of nanowires is not constant, it varies with the pH values of electrolyte used for the deposition. Scanning electron microscopy (SEM) confirmed formed nanowires are cylindrical in shapes, dense and homogeneous for low pH depostion. X-ray diffraction technique is used to study the morphology and structure of fabricated Ni/Cu nanowires and found nanowires have FCC structure. An energy dispersive X-ray spectroscopy (EDS) is used to study the composition of multilayer nanowires. The electrochemical impedance spectroscopy has been carried out to study the in-situ growth process of multilayer nanowires.

Keywords: Multilayer nanowires, Cu/Ni, pH, Polycarbonate membrane, Electrochemical deposition

Introduction

Nanostructures have attracted much attention because of their properties like small diameter, high density of electronic states, and high surface to volume ratio, increased surface scattering to electrons and phonons and increased excitation energy has excessive potential applications in different fields as compared to bulk materials [1,2]. Nanowires exhibits different electrical, magnetic, optical and thermo electric properties as compared to bulk materials [3-9]. Nanostructures have been studied not only due to their physical, chemical, electronic and magnetic properties but also due to their practical applications as nano devices [10]. Properties and applications depends on composition (metallic, nonmetallic, semi-conductor, alloy etc.), size and structure of the fabricated nanowires. Due to these reasons research has been carried for the preparation of suitable composition and size of nanowires for suitable applications. Different techniques were used to fabricate nanowires like lithography [11], chemical vapor deposition [12], sol-gel method [13], electrodeposition [14,15] and displacement deposition [16]. For conducting (metallic) materials, electrodeposition method is more useful and simpler than other methods, because it is a template-based method and diameter of nanowires will be confined according to size of template. Also, template-based method is cost effective, simple and nanowires formed are parallel. In previous study of only Cu nanowires deposition, it revealed that pH effect on composition of material i.e. higher values, Cu/Cu_2O deposit [17]. In present paper instead of single metal (Cu), nickel-copper (Ni/Cu) multilayer nanowires fabricated with variation of electrolyte pH. Nickel and copper both have FCC structure and have almost similar lattice parameters [18]. These materials have great advantages due to their unique properties like ferromagnetism and high corrosion resistance [19]. Electrodeposition process is quite useful for the fabrication of Ni/Cu multilayer nanowires due to great difference in their standard electrode potentials. In current work Ni/Cu multilayer nanowires were prepared by using potentiostat electrodeposition technique. In situ Electrochemical impedance spectroscopy technique is used to study deposition process [20]. Electrochemical impedance spectroscopy (EIS) has used to investigate porous interface of electrode and electrolyte. The results obtained were fitted with equivalent circuit and obtained corresponding electrical parameters. Scanning electron microscopy (SEM) has been used to study the morphology of fabricated nanowires and energy dispersive X-ray spectroscopy (EDS) for composition of multilayer nanowires.

Materials and method

Materials $NiSO_4.6H_2O$, $CuSO_4.5H_2O$, H_3BO_3, and H_2SO_4 (Sigma Aldrich), commercial poly carbonate membrane (pore density 108 cm^{-2}, thickness of 10 μm and pore size is 400 nm) as a template were used for nanowires synthesis.

Multi-layered Ni/Cu nanowires were fabricated by electro-deposition technique using polycarbonate membrane. Electro-deposition process has been carried out in homemade 3-electrode cell using potentiostat (Gamry Reference 600). Ni/Cu nanowires were grown in an electrolyte having following composition - 2.628 g $NiSO_4.6H_2O$ and 2.496 g $CuSO_4.5H_2O$. Samples were prepared at different pH values of the electrolyte which was adjusted by adding few drops of H_2SO_4 and 0.370 g H_3BO_3. Ni/Cu reduction potential –1.1 and –0.6 V was obtained with the help of cyclic voltammetry. This experiment is repeated for 3 different pH values 2.8, 3.2 and 4.1 for Ni- electrolyte and 3.1, 3.5 and 3.7 for Cu-electrolyte because there is a higher possibility of hydrogen gas evolution at the cathode due to presence of H^+ ion. It effects the efficiency of the deposition so efficiency depends upon pH. After setting reduction potential, chronoamperometry (I vs t) was performed by setting the step, maximum current to 300 mA for 600 sec. At the end of the process multilayer nanowires embedded in polycarbonate membrane were obtained at different pH values. Etching of the template was done by using dichloromethane. After dissolution of nanowires were obtained on copper substrate. Structural characterization of fabricated Ni/Cu multilayer nanowires were done by Xrd (model: X-PANalytical X'Pert PRO) using CuKα (λ = 1.54060) Å and operating voltage of 45 kV and current of 40 mA. The sample was scan for 2θ values and 3 peaks were observed in the span ranging from 40° to 80°. Further dimension of deposited nanowires is analyzed through the Scanning electron microscopy up to resolution ×5000 and the composition of Ni and Cu nanowires analyzed using energy dispersive X-ray spectroscopy up to energy range 11 kev. The morphological study of Ni/Cu multilayer nanowires embedded in copper substrate was performed under (HITACHI SU8010) scanning electron microscope.

Results and discussion

The equivalent circuit shown in **Figure 1** was used for modeling the nanowires in nanopores of polycarbonate membranes which has been satisfactorily used for fitting the electrochemical impedance spectra obtained at different pH values as shown in **Figures 2 - 5**. The total cell impedance can be accurately modeled as the serial combination of 2 circuit components one is R1 which is denoting the electrolyte solution resistance and another one in parallel combination where one of the parallel branches is the capacitance of the electrical double layer capacitance C2, while the other one is constituted by a serial- parallel combination of R3 and R5 and surface capacitance of electrode (C4). R3 and R5 represents the charge transfer process [18]. The mechanism can be represented as (1) and (2):

$$Cu^{2+} + e^- \rightarrow Cu^+, Cu^+ + e^- \rightarrow Cu \quad (1)$$

$$Ni^{2+} + e^- \rightarrow Ni^+, Ni^+ + e^- \rightarrow Ni \quad (2)$$

From the study and analysis of the data obtained from the fitting of the experimental data with equivalent circuit model (goodness of fit in order ~10^{-4}), the values shown by R3 various with the pH values. At different pH values for Ni and Cu different impedance parameter is calculated. At pH values 2.8 and 3.1 for Ni and Cu respectively, the value of R3 decreases after the deposition as shown in **Table 1**. It must be noticed that low value of R3 shows fast process, with negligible resistance, this is due to presence of Cu^{2+} ion. It means at low pH values proper filling of the material occur in the pores of the membrane because of free Cu^{2+} ion. But in case of high pH values 4.1 and 3.7 for Ni and Cu, respectively, the value of R3 increases after the deposition showed in **Table 1**. Which means free Cu ion decreases and no proper deposition is seen at high pH value and also shows that value of R5 (Cu^+/Cu) is higher than R3. This performance can be due to necessities of ion formation and accumulation in the electrochemical interfaces in order for the reaction to take place. Similarly, at low pH value, R5 decreases after the deposition which means pores are filled with material. The decrease in R5 value can be related to pores filling when the nanowires reach at the top of the pores. This process is related to resistance and diffusion process with in the pores of the membrane. Actually, lower the deposition rate contributes more to deposited material ion which can be reflecting in a greater and pounced texture. This process is associated with resistance and diffusion process with in the pores of the membrane. At different pH values the value of R3 and R5 varies and shows increase and decrease of geometrical area of the

nanowires during electrodeposition process. Overall, in-situ study reveals that there is variation in impedance. Which gave hints that required materials successfully deposited. Because if there is no change takes place in impedance parameter before and after the deposition, it means deposition does not take place. Hence EIS revealed successfully take in present work and deposition parameters are suitable for nanowires fabrication.

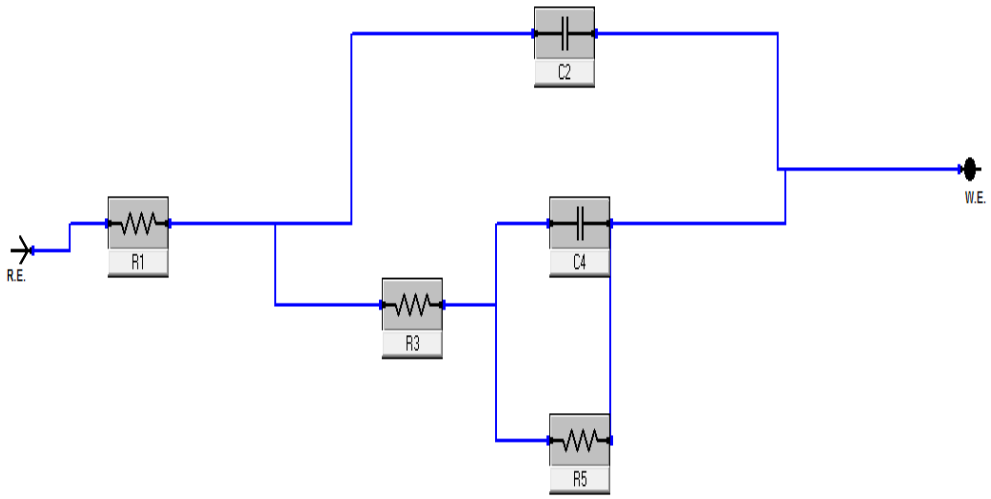


Figure 1 Equivalent circuit model to study the in-situ growth of Ni/Cu multi-layered nanowires [18].

Table 1 Summarizes the numerical data derived from the different samples by fitting the experimental curve with equivalent circuit.

pH value	Sample name	R1 (Ω)	C2 (µF)	R3 (Ω)	C4 (µF)	R5 (Ω)
3.1	Cu (before)	72.44	3.056	20.37	21.83	24.81
3.1	Cu (After)	76.49	2.75	23.81	25.42	23.92
3.7	Cu (before)	88.14	17.94	7.087	96.37	7.959
3.7	Cu (after)	87.79	8.42	10.86	84.84	12.03
2.8	Ni (before)	157.5	2.509	169.6	27.25	860.3
2.8	Ni (after)	163.3	6.350	167.0	56.23	666.2
4.1	Ni (before)	156.3	1.613	141.8	16.07	381.2
4.1	Ni (after)	151.9	172.4	30.55	171.1	134.9

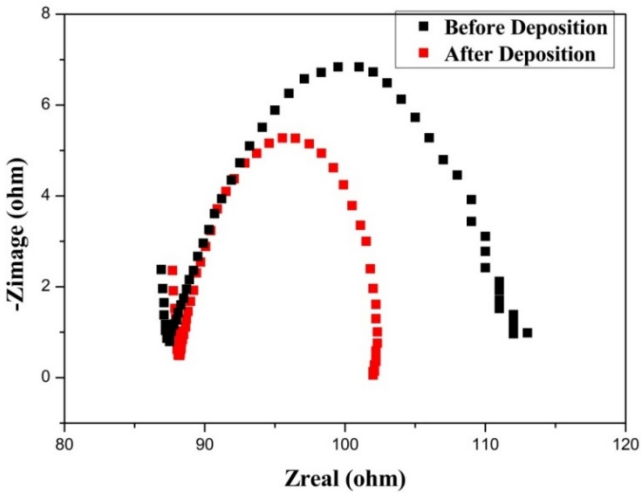


Figure 2 Nyquist plot before and after Cu deposition at pH 3.1.

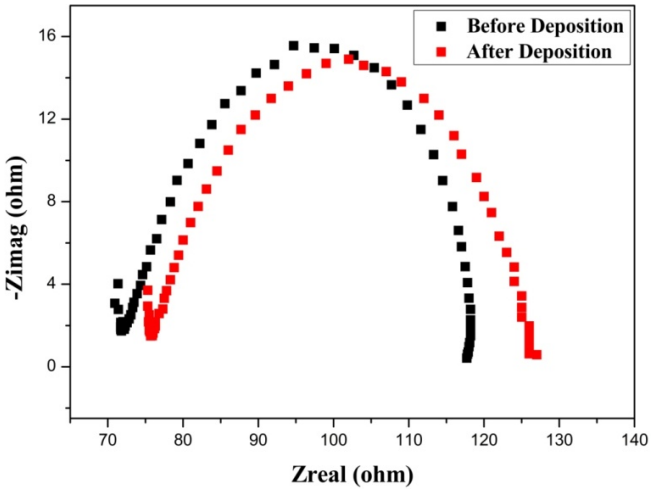


Figure 3 Nyquist plot before and after Cu deposition at pH 3.7.

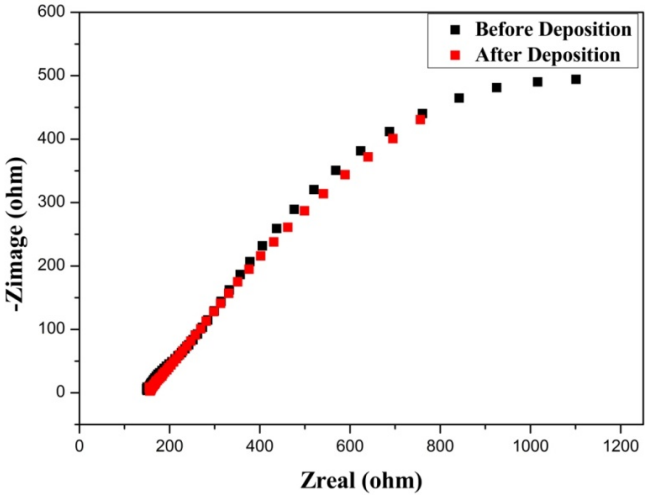


Figure 4 Nyquist plot before and after Ni deposition at pH 2.8.

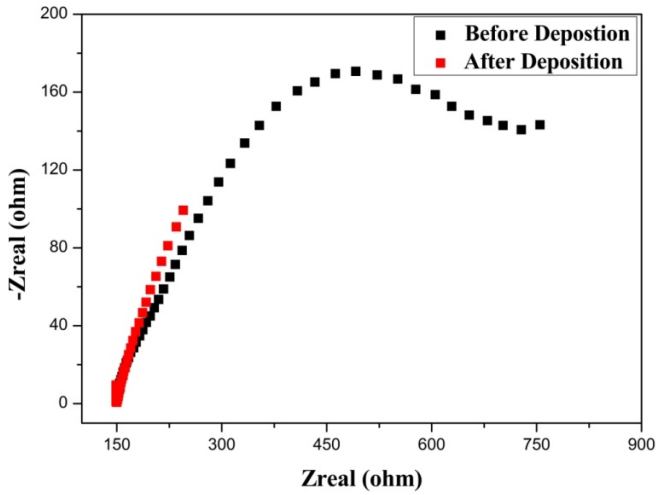


Figure 5 Nyquist plot before and after Ni deposition at pH 4.1.

Structural characterizations

Figure 6 shows XRD patterns of deposited nanowires. Phase identification is performed by comparing the position of the 3 most intense peaks in the diffractrograms with known diffractrograms of pure substances referred in the PCPDF software database [7]. As seen from XRD patterns, the reflection of 3 characteristic crystal planes of Ni/Cu are found to be (111), (200) and (220) having 2θ values of approximately 45°, 53° and 76° for Ni and 44°, 51° and 74° for Cu, respectively. All multi-layered nanowires have FCC structure and no reflection peak corresponding to body-centered crystal exists. In addition, it is noted that the intensity of the peaks increases with increasing pH values. The Cu content promotes the development of (111) peak. The intensity of the Ni peak is found to be very low because conductivity of the Ni is very low which is approximately one 4th of Cu in the electrolytic solution due to which it has less rate of deposition as compared to its counterpart. The preferred orientation of the samples is determined by calculating the texture coefficients using formula given by Eq. 3 [8].

$$TC(h_i k_i l_i) = \frac{I(h_i k_i l_i)/I_o(h_i k_i l_i)}{\frac{1}{n}\sum_{i=1}^{n}[I(h_i k_i l_i)/I_o(h_i k_i l_i)]} \quad (3)$$

$I(h_i k_i l_i)$ and $I_0(h_i k_i l_i)$ is the diffraction intensities of the $(h_i k_i l_i)$ lattice plane of the sample under investigation and the standard diffraction pattern, respectively. If $TC(h_i k_i l_i)$ >1 it indicates that there is preferred orientation of the samples. According to Eq. (1) the *TC* values of Ni/Cu (111), Ni/Cu (200) and Ni/Cu (220) are shown in **Table 2** which shows that at low pH values Ni/Cu orientation is along the (200) planes and indicating that Ni/Cu preferentially grows along this plane. But at higher pH values they show different behaviour. In this case, orientation is along the (111) directions. In addition, it should be noted that texture coefficient for the (200) plane decrease while that for (111) peak increases.

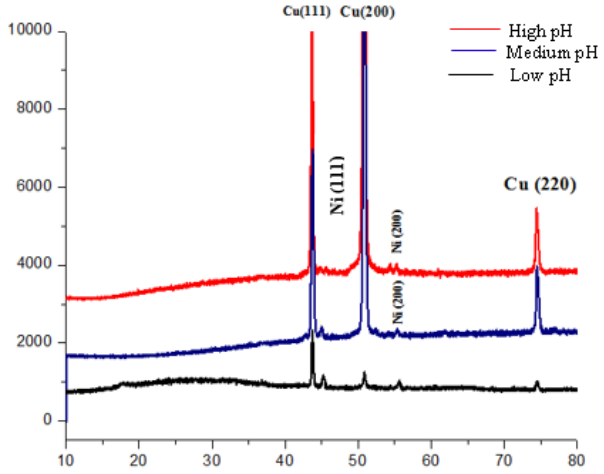


Figure 6 XRD patterns of Ni/Cu multilayer nanowires deposited at different pH values.

Table 2 The value of TC calculated from different diffractions peaks.

pH Values→	**Low pH (Ni/Cu 2.8 and 3.1)**	**Medium pH (Ni/Cu 3.2 and 3.5)**	**High pH (Ni/Cu 4.1 and 3.7)**
(hkl) Planes ↓	**Texture coefficients (TC)**		
M111	0.2942	0.6889	2.27
M200	2.5992	2.0765	0.5013
M220	0.1065	0.2347	0.2279

Morphological characterization

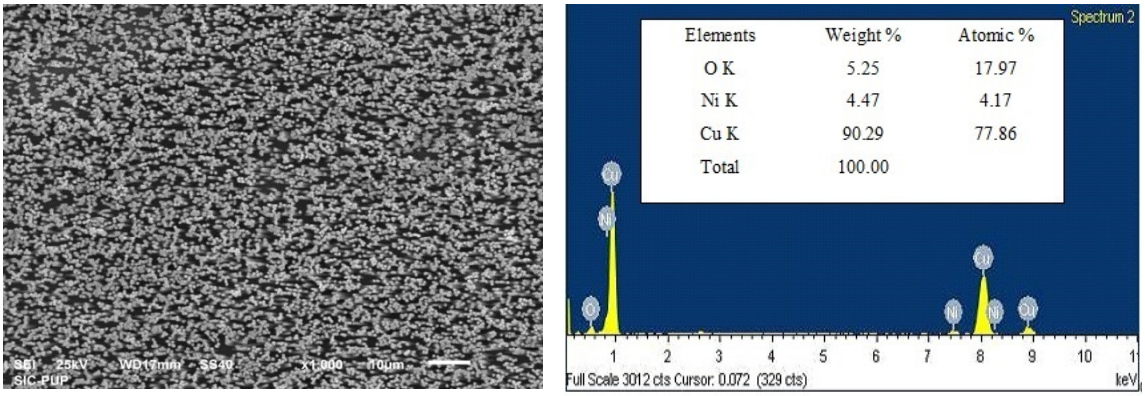
SEM images shows different morphology of multilayer nanowires fabricated at different pH values. At low pH values 2.8 and 3.1 for Ni/Cu multilayer nanowires formed are cylindrical in shapes, dense, homogeneous and continuous throughout the whole length as shown in **Figure 7(a)** and its EDS **Figure 7(b)** and inserted Table confirms the presence of both nickel and copper metal as composition. **Figures 8(a)** and **8(b)**, respectively shows morphology and composition of multilayer nano wires fabricated at pH values of 3.2 and 3.5 for Ni/Cu. Growth of nanowires is dense but less homogeneous and some of the pores remains unfilled, which is due to hydrogen bubbles, whose production can be easily seen during deposition process, as it get stuck in the pores of membranes thereby preventing further deposition. SEM image of multilayer nanowires fabricated at pH values 4.1 and 3.7 for Ni/Cu shows that the growth of nanowires are dense but not perpendicular to the membrane and hemispherical cap formation is being started as shown in **Figure 9(a)** by circle and EDS in **Figure 9(b)**. The hemispherical caps on the top of the wires develop just after the pores are completely filled because the deposition process is carried out even after complete filling of the pores in the membrane.

In present case, proper wetting of the membrane with distilled water is necessary for simultaneous and uniform growth of nanostructures. SEM images shows multilayer nanowires fabricated for deposition time 200 s gives us best results. So, all the samples were fabricated for 200 s with different pH values. Multilayer nanowires fabricated at low pH values gives most favorable result because there is no empty space have seen in samples and nanowires deposited homogeneously to whole template.

From the results of EDS it is revealed that at pH value 2.8 and 3.1 for Ni/Cu multi-layered nanowires formed inside the nano channels of the polycarbonate membrane. The weight percentage of Ni and Cu multilayer nanowires are 4.47 and 90.29 % as shown in Table inserted in **Figure 7(b)** and peaks of Ni and Cu are shown in **Figure 7(b)**. The intensity of the copper peak is high as compared to nickel which is due to the noble metal characteristic of copper and high conductivity of copper as compared to

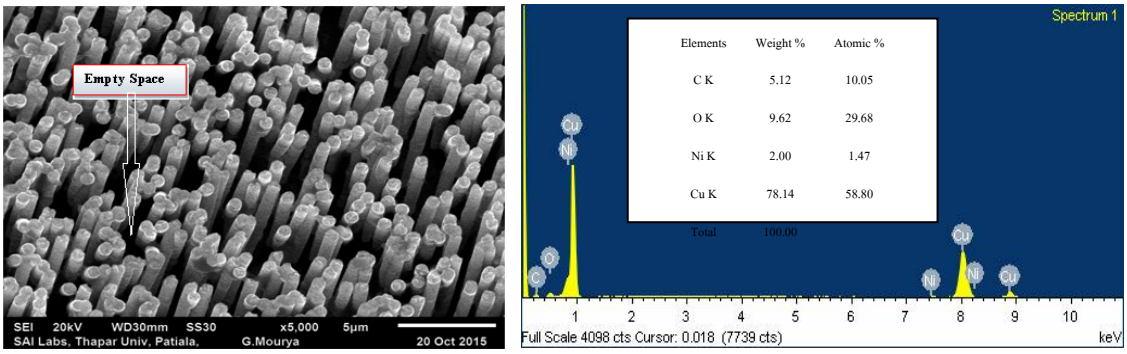
nickel. Here, small oxygen peak is also seen which comes from distilled water used for electrolyte solution or may be from environment or may be due to formation of hydroxide.

With increasing pH values (3.2 for Ni and 3.7 for Cu), weight percentage of Ni and Cu decreases from 4.47 to 2.0 % and 90.29 to 78.14 %, respectively it reveals high pH value not too favorable for deposition. As shown in Table inserted in **Figure 8(b)** and Sharp and high intense peak were observed in the EDS spectrum shown in **Figure 8(b)**. The weight percentage of both Ni and Cu is less as compare to Ni/Cu percentage at low pH values. But still this pH value is suitable for the fabrication of multilayer nanowires. The low percentage of Ni/Cu multilayer nanowires is due to formation of hydrogen on cathode substrate and formed nickel hydroxide by increasing the pH value. The Cu content decreases because of free Cu ion decreases at the cathode substrate. **Figure 9(b)** shows 6 peaks and the intensity of Ni peak is very less at pH 4.1 and 3.7 values. For Ni and Cu, weight percentages of Ni is 1.74 % and Cu is 75.18 % as shown in Table inserted in **Figure 9(b)**, carbon appears due to dichloromethane used for dissolution of membrane and oxygen peak is due to formation of hydroxide at high pH values.



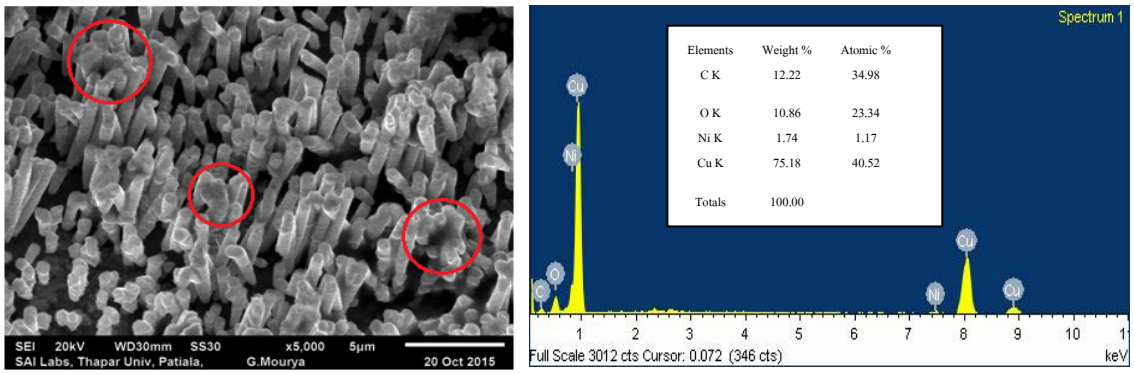
(a) (b)

Figure 7 (a) SEM image (b) EDS results of Ni/Cu multilayer nanowires deposited at pH 2.8/ 3.1.



(a) (b)

Figure 8 (a) SEM (b) EDS results image of Ni/Cu multilayer nanowires deposited at pH 3.2/3.5.



(a) (b)

Figure 9 (a) SEM image (b) EDS results of Ni/Cu multilayer nanowire deposited at pH 4.1/3.7.

Conclusions

Metallic nickel and copper multilayer nanowires have been fabricated using electrodeposition technique into the pores of polycarbonate membranes. The effect of pH of the solution on the growth of Ni and Cu nanowires was studied successfully. Decrease in charge transfer resistance (R5) confirms the growth of nanowires in pores of membrane. Structural analysis of the fabricated multilayer nanowires at different pH value through X-ray diffraction reveals that Ni and Cu both shows FCC structure and the preferred orientation is along with (200) plane at low pH values, which is calculated by using texture coefficient equation. SEM images show different morphology of multilayer nanowires fabricated at different pH values. The comparison of morphology revealed that at low pH values nanowires formed are dense, uniform and there is a proper growth of multilayer nanowires. At high pH values, formation of hemispherical caps and nanowires collapsed with each other. EDS revealed the effects of pH values on the composition of fabricated multi-layer nanowires, which shows that weight percentage of both Cu and Ni decreases with increase in pH value. It means that, by lowering the hydrogen ion concentration in the electrolyte, an increase in the current efficiency of the nickel deposition is expected that would also lead to an increase in the Ni content of the deposit.

Acknowledgements

The authors thankfully acknowledge Dr. Anup Thakur, Department of Basics and Applied Sciences, Advanced Materials Science Lab., Punjabi University, Patiala, Punjab, India for extending laboratory facility, allowing the use of 'Gamry reference 600 3-electrode system'.

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