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Abstract. This paper investigates the influence of the electrolytic bath temperature on the morphology and physical properties of nickel (Ni) nanowires electrochemically deposited into the anodic alumina oxide porous membrane (AAO). The synthesis was performed using nickel sulfate hexahydrate ($NiSO_4.6H_2O$) and boric acid (H_3BO_3) as an electrolytic bath for the electrochemical deposition of Ni nanowires. During the experiment, the electrolyte bath temperature varied from 40°C, 80°C, and 120°C. After the electrochemical deposition process, AAO templates cleaned with distilled water preceding to dissolution in sodium hydroxide (NaOH) solution to obtain free-standing Ni nanowires. Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive Spectroscopy (EDX) and X-ray Diffraction (XRD) analysis were employed to characterize the morphology and physical properties of the synthesized Ni nanowires. Finding reveals the electrodeposition bath temperature significantly influences the morphology and physical properties of the synthesized Ni nanowires. Rougher surface texture, larger crystal size, and longer Ni nanowires obtained as the deposition bath temperature increased. From the physical properties properties analysis, it can be concluded that deposition bath temperature influence the physical properties of Ni nanowires.

1. Introduction

Template-assisted electrochemical deposition is one of the dependable technique for synthesizing metallic nanomaterials with controlled shape and size [1]. This method is known for its simplicity, high-throughput and cost-effectiveness which allow the duplication of complex topology present on the surface a template in a single step [2-4]. The method typically operates at ambient temperatures and pressure as well as can be used for mass production of nanowires with controlled geometry and morphology [5-8]. For example, the diameters of nanowires can be well determined and maintained by the diameter of template pores, and the lengths determined by the thickness of template [9]. The process is relatively straightforward as the template serves as a scaffold within or around which nanowires can be shaped with the morphology complementary to the template used.

Miguel García et al. [10] describes that during the electrochemical deposition process, the template pores were initially filled with liquid precursor from the chemical reaction of the electrochemical deposition process. Later, solidification of the filled liquid precursor takes place. These are a very simple route, but it is critical to ensure that the pores are filled with the fluid. If a solution has an excellent wettability for the template, it can diffuse through the membrane producing an enrichment of

the solid component in the interior of the pores. Once the pores filled, the template is removed from the solution, dried and further processed.

It is a well-established fact that synthesis process during the electrochemical deposition in porous templates initiates from the cathode at the bottom surface of the pore. The high surface area and the presence of sites with low coordination number in the porous part of the alumina provide energetically favorable sites for initiating the metal adsorption during the electrochemical deposition [11]. The metal ion M^{n+} is transferred from the electrolyte into the ionic metal lattice. Where else, the electrons are provided from the external electron source (power supply) to the electron gas of the metal M. Ohgai [12] in their study of Ni nanowires and Cobalt (Co) nanowires synthesis has explained that during the electrochemical deposition process, Ni^{2+} ions and Co^{2+} ions in the electrolyte of $NiSO_4.6H_2O$ and $CoSO_4.7H_2O$ respectively are surrounded by a hydration shell. This hydration layer will reduce the metal ion mobility, and the component of metal ion velocity become almost equal. The degree of reduction of metal ions thus becomes equal in both directions, resulting in the formation of nanowires.

Among the available synthesis method, Ni nanowires can be consistently synthesized using electrochemical deposition method [13]. The properties of synthesized nanowires by this approach significantly influenced by the processing parameters, such as solution pH, deposition bath temperature, magnetic field [14] and current density [15]. In this present study, the influence of the electrodeposition bath temperature on morphology and physical properties of the Ni nanowires synthesized is investigated. The synthesis performed using Ni Sulfate Hexahydrate ($NiSO_4.6H_2O$) as an electrolyte and boric acid (H_3BO_3) as a stabilizer. The deposition bath temperature was varied from 40 °C, 80 °C, and 120 °C, while other synthesis parameters were kept constant.

2. Experimental Details

Commercial Whatman, AAO membrane with a pore size of 200 nm was used as a template for electrochemical deposition of Ni nanowires. These templates have the advantage in controlling the diameter of nanowires precisely, as the diameter dictated by the pore size of the AAO membranes. In this study, the commercial template is employed to avoid the template fabrication step and emphasize more towards achieving the main objective the research.

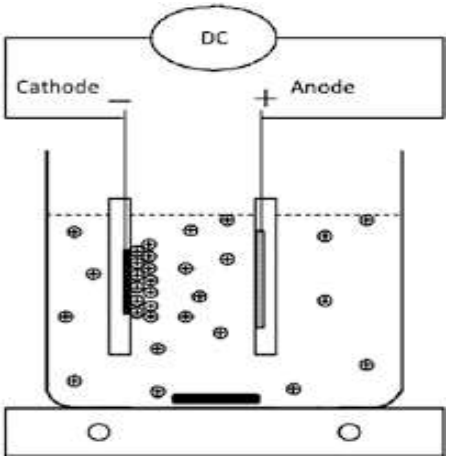

Figure 1. Electrochemical cell setup.

Figure 1 show the schematic illustration of the electrochemical cell setup. In cathode, the Copper tape attached to AAO template, where else, in the anode, the Copper tape is attached to Ni plate for the electrical connection in an electrolytic cell. The anode is placed into the electrolyte, parallel to the cathode. When an electric field is applied, cations diffuse through the channels and deposit on the cathode, resulting in the growth of nanowires inside the template.

The electrochemical cell placed on top of the heater and magnetic stirrer from Heidolph Instruments GmbH & Co. The whole system placed inside the fume hood to limit exposure to

hazardous gasses released during the synthesis. The magnetic stirrer used to stir the electrolyte to keep the reaction active. As the deposition bath temperature act as manipulated parameter in this study, three different heating temperatures exploited at 40 °C, 80 °C, and 120 °C.

The electrolyte prepared by mixing the 176.8 g/L of nickel sulfate hexahydrate ($NiSO_4.6H_2O$) solution with 60 g/L boric acid (H_3BO_3) solution. The two solutions were combined and stirred for 30 minutes at 25 °C till all the chemical completely dissolved. The Keithley 2400-C systems voltage/current source meter used as the power supply and as an effective equipment that could be utilized both as potentiostat and amperostat. The applied current was set at 3.0 mA for all the cases. During the electrochemical deposition process, we closely monitor the current for continuous deposition. The sudden rise or decline in current gives an indication that the growth of nanowires has increased or decrease significantly, and the process needs to be terminated to prevent the excessive and non-growth of nanowires and also to avoid the collapse of the pore walls due to excessive growth pressure.

The electrochemical deposition duration is set at 1 hour for all the cases. The duration of electrochemical deposition determines the growth length of the nanowires. As a precaution, during the synthesis process, it is important to ensure copper tape on both cathode and anode not immersed in the electrolyte to avoid reduction and plating of copper in the template. The deposited template finally dissolved in NAOH solution and further cleaned using methanol to obtain freestanding nanowires for characterization. JOEL JSM-7800F FESEM equipped with EDX system was used to investigate the morphology characteristics and the elemental composition of the synthesized Ni nanowires. Where else, the crystallographic information of the synthesized Ni nanowires obtained by X-ray diffraction analyses conducted using Bruker D8Advance diffractometer.

3. Results and discussion

3.1. Effect of deposition temperature on Crystal Orientation

Figure 2 shows the XRD spectrum of Ni nanowires array grown at 3.0 mA at three different deposition bath temperatures: 40°C, 80°C and 120°C. For all cases, XRD spectrum shows the presence of multiple XRD peaks which suggest that the obtained Ni nanowires are polycrystalline in nature. Also, the XRD spectrum shows there was no a significant influence of deposition bath temperature on the orientation of the crystals. The preferred orientation of synthesized Ni nanowires in all cases was found to be (1 1 1), followed by (2 0 0) and (2 2 0) planes. However, obtained Ni nanowires with a deposition bath temperature of 120°C present the highest intensity of diffraction peaks demonstrating a better crystalline structure. From the obtained XRD spectrum pattern, the increase of bath temperature gives a strong advantage to the crystalline structure of the Ni nanowires. These are due to the effect of high deposition temperature on the crystalline structure enhancement of electrochemical deposition growth.

From the spectrum, the obtained 2-theta peak angle used to calculate the spacing between atoms for the nanowires synthesized at a deposition temperature of 40 °C, 80 °C, and 120 °C. Table 1 presents the calculated d-spacing for Ni nanowires synthesized at this process parameters as compared with bulk Ni literature data. Bragg's formulation was used to determine the d-spacing for Ni nanowires.

$$\lambda = 2d \sin \theta$$

where, d is the space between atomic planes in the crystalline phase, λ wavelength of incident X-ray and θ is the angle between incident X-ray and diffraction plane.

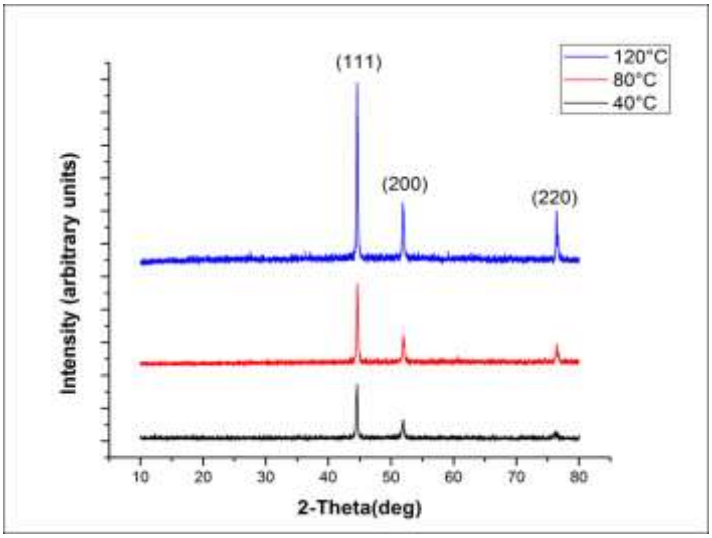

Figure 2. X-ray diffraction spectrum of Ni nanowires at different deposition temperature.

Table 1. 2θ angle and d-spacing for Ni nanowires synthesized at different deposition temperature compared with bulk nickel literature data.

Sample	(1 1 1)		(2 0 0)		(2 2 0)	
	2θ (deg)	d (Å)	2θ (deg)	d (Å)	2θ (deg)	d (Å)
Ni bulk (literature)	44.37	2.04159	51.596	1.77	76.0884	1.25098
Ni nanowires						
40°C	44.620	2.02836	51.979	1.75716	76.533	1.24329
80°C	44.639	2.02754	52.003	1.75641	76.487	1.24393
120°C	44.627	2.02805	51.976	1.75725	76.683	1.24124

3.2. Effect of deposition temperature on Crystal Size

The obtained XRD spectrums were further analyzed to study the effect of different deposition bath temperature on the formed crystallite size. For a specific material, if the individual crystallite size of the material is less than 1000 Å or 100 nm, then the crystallite size can be estimated using the Scherrer equation.

$$D = \frac{k\lambda}{\beta cos\theta}$$

where, D is the diameter of crystallites, λ is the X-ray wavelength, K is crystallites shape factors (for spherical crystallites, K = 0.9) and β is the full width at half maximum (radians).

Table 2. Crystal size of synthesized nickel nanowires.

Sample	Deposition Temperature		
	40°C	80°C	120°C
Crystal Size Sample 1(nm)	28.550	32.277	35.745
Crystal Size Sample 2(nm)	29.875	34.311	39.967
Crystal Size Sample 3(nm)	24.195	25.740	28.612
Average	**27.540**	**30.776**	**34.775**

To obtain the crystal size, three XRD experiments performed for each deposition temperature. The full width half maximum (FHWM) for each experiment is obtained using Origin Lab Software. Table 2 lists the average crystallite sizes obtained for all the deposition temperature. The results clearly show a significant increment in crystallite size when the deposition bath temperature increased.

From the crystal size obtained as shown in table 2, further investigation needed to understand the physics behind the increasing of the crystal size when the deposition temperature increased. According to the past results, the increase in bath temperature gives a strong benefit on the crystalline structure of the Ni nanowires [16]. The higher bath temperatures promote the surface diffusion of atoms, favoring the growth of preexisting nuclei established during the first stages of the electrochemical process [17].

3.3. Effect of Deposition Bath Temperature on Surface Morphology

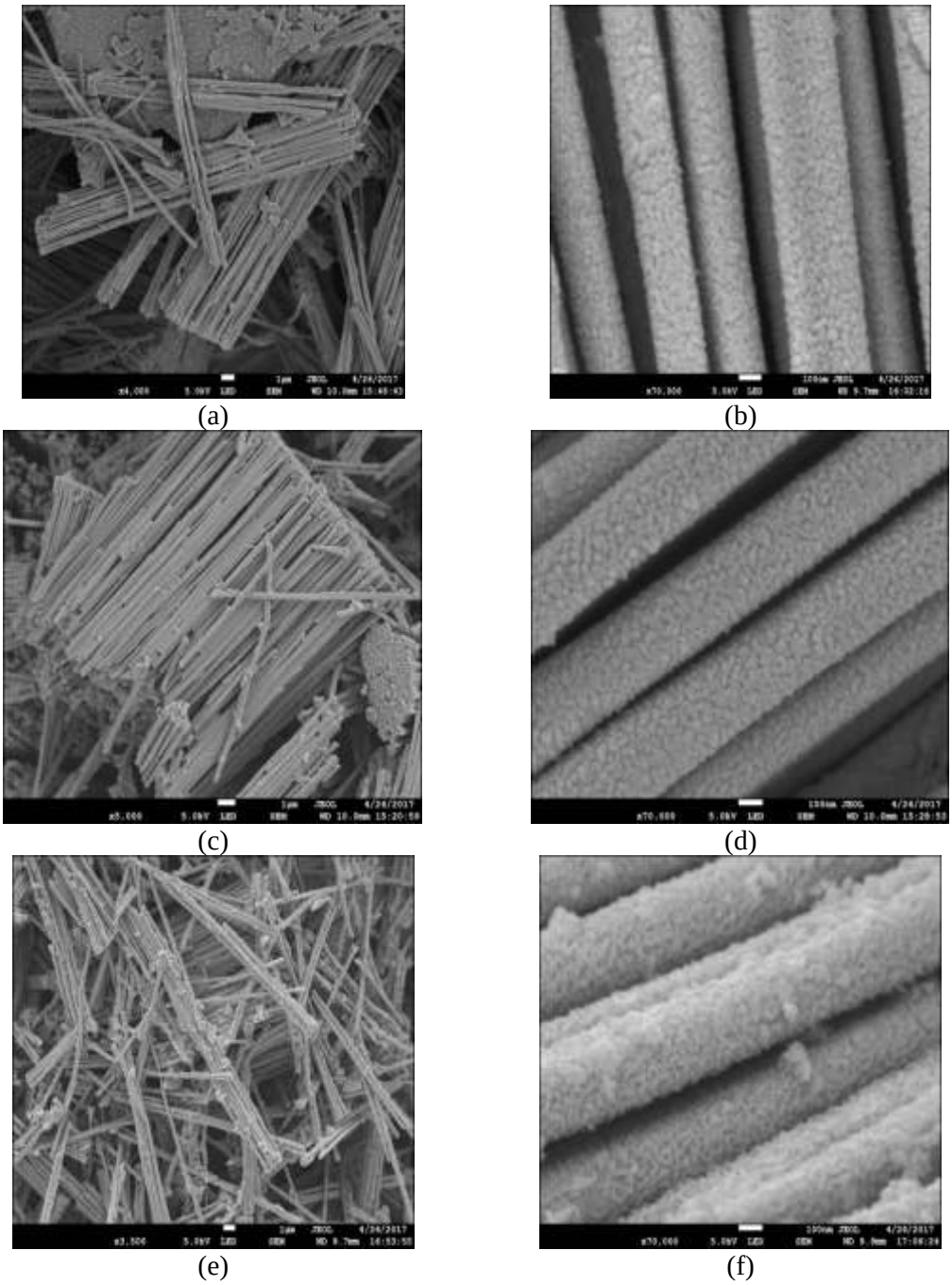

Figure 3. FESEM surface texture images of grown Ni nanowires at a deposition temperature of 40 °C, 80 °C, and 120 °C.

FESEM (JOEL JSM-7800F) used to study the structure and morphology of the grown Ni nanowires. The study was performed through qualitative observation from a series of images taken using FESEM. The morphology imaging carried out at a beam source of 5 kV, and a working distance of 10 mm. Figure 3 (a-b) show the FESEM surface morphology images of Ni nanowires electrodeposited at a temperature of 40 °C. Figure 3 (c-d) and Figure 3 (e-f) show the FESEM surface morphology images of Ni nanowires deposited at a temperature of 80 °C and 120 °C respectively.

From the obtained FESEM images, the surface texture and roughness found to increase as the deposition temperature increase. The surface texture change to be very rough at the deposition temperature of 120 °C. The possible reasons for the formation of the rough surface are possibly due to the formation of larger grain size as the deposition temperature increased. Thus, the large Ni grains could not uniformly fill the AAO template pores during the deposition process. Typically, smooth surface textured nanowires are preferred since it is suitable for many applications, including sensing of electrical or optical signals. However, in some circumstances, an increased surface roughness is of interest [18]. Hochbaum et al. and Boukai et al. recently reported that rough textured Si nanowires exhibit a thermal conductivity up to 100 times smaller than their smooth counterparts, becoming promising objects to be implemented in thermoelectric devices [19, 20].

3.4. Effect of Deposition Bath Temperature on Growth Length

The growth length of Ni nanowires at different deposition temperature was measured. The measurement performed after dissolving the AAO templates in NaOH solution after the deposition to obtain freestanding nanowires. A total of 10 length measurement was taken for each deposition temperature. The measured growth length of deposited Ni nanowires for all deposition temperature listed in table 3. These are used to examine the influence of deposition temperature on the growth length of the nanowires.

Table 3. Measured length of grown Ni nanowire at different deposition bath temperature.

Heating Temperature (°C)	**Ni nanowires Length (µm)**
40	11.321
80	12.600
120	16.860

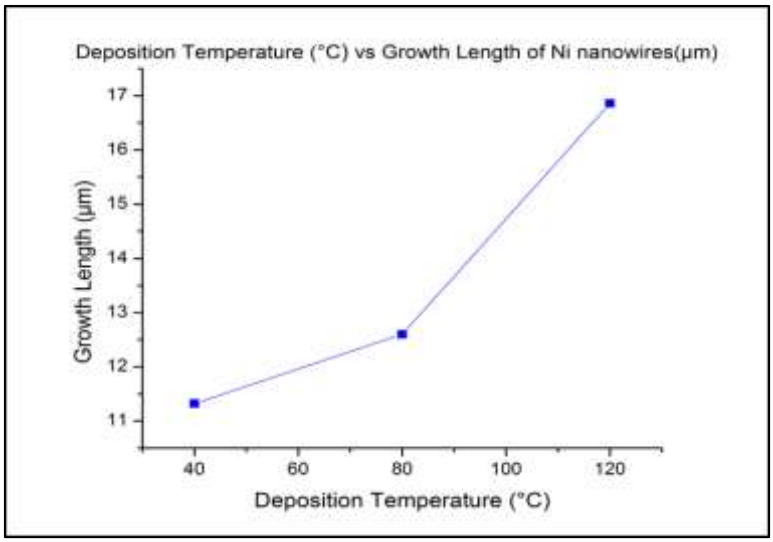

Figure 4. Deposition temperature versus Growth Length curve of synthesized nickel nanowires.

The grown length of the Ni nanowires is found to increase significantly as the deposition bath temperature increased. These are due to the higher rate of nanoparticles diffusion when the temperature increased [16]. Higher temperature promotes atomic diffusion on the growing face of the nanowires and thus accelerates growth relative to the nucleation of new grains [21]. The higher rate of nanoparticles diffusion improves the degree of growth of Ni nanowires. Apart from that, the length improvement with an increase in the temperature is due to the lowered energy barriers [22]. However, when the nanowire length increases, creates a higher center of gravity which makes their position unbalanced and easy to angle during the washing and processing stage [23].

3.5. Energy Dispersive X-Ray (EDX) Analysis

A quantitative EDX analysis is performed on all the samples to determine the elemental composition of the Ni nanowires deposited on the AAO templates at different bath temperatures and the results shown in Table 4. The EDX analysis is performed using Oxford Instruments EDX attached to JOEL JSM-7800F FESEM at a beam source of 15kV. The EDX analysis demonstrates that the synthesized Ni nanowires were consistently composed of 97.97 % of Ni and 2.04 % of oxygen. The small amount of oxygen observed in the entire spectrum indicates potential absorption from the air on the surface of Ni nanowires.

Table 4. EDX elemental composition of synthesized Ni nanowires

Elements	Value (%)	Standard deviation (%)
Nickel (Ni)	97.97	0.4
Oxygen (O_2)	2.04	0.4

4. Conclusions

The present research has focused on the effect of deposition bath temperature on the morphology and physical properties of electrodeposited Ni nanowires. Ni nanowires were synthesized using template-assisted electrochemical deposition method at a deposition bath temperature of 40 °C, 80 °C, and 120 °C. From the obtained trend of XRD spectrum, the increase of temperature gives a strong benefit on the crystalline structure of the Ni nanowires. These are due to the effect of high deposition temperature on the crystalline structure enhancement of electrochemical deposition growth. The crystal was also found to increase as the electrodeposition bath temperature increased. Qualitative FESEM image analysis has shown that the surface roughness increased as the deposition bath temperature increase. Overall growth length found to be significantly better as the deposition bath temperature increased. EDX analysis showed the synthesized structure was composed of 97.97 % of Ni and 2.04 % of Oxygen. The observed oxygen is primarily due to absorption from the air on the surface of the nanowires after synthesis. From the physical properties properties analysis, it can be concluded that deposition bath temperature influence the physical properties of Ni nanowires.

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