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# Synthesis of Ni and NiO nanowires on nanoporous Alumina templates and their characterization

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**Abstract**

This work explores the fabrication and characterization of Ni and NiO nanowires. Ni nanowires were fabricated using electrochemical deposition into an AAO template. The techniques of sol-gel synthesis and template-directed growth are merged for the formation of NiO nanowires. When the porous templates of aluminium oxide were dipped in these solutions, the solution was captured in the pores. These templates were then heated at elevated temperatures to harden the nanowires. Different characterizations of Ni and NiO nanowires were carried out using, SEM, XRD and VSM to find out the morphology, behaviour and magnetic characteristics of nanowires formed. This new method for the preparation of NiO nanowires may be significant for the gas sensors to various engineering materials.

## 1. Introduction

Transition metals and their oxides contain a wide range of material applications. Intense attention has developed in the nanoscale-sized transition metal oxides in which the novel properties make them attractive for a wide variety of applications including magnetic materials, gas sensors, biomedical devices, and catalysis [1, 2]. Also, the nanostructures of antiferromagnetic transition metal oxides have been studied because of their vast variety of applications in magnetic random-access memory, and exchange bias properties to stabilize the magnetic properties of ferromagnetic properties [3, 4]. The significance of the study of magnetic properties of nanostructured metallic oxides is from the application point of view as well as the understanding of fundamental science of the structure-property relationship [5]. When compared with their bulk counterparts the magnetic properties of metallic oxide nanostructures show quite different behaviour. The exchange-coupled spins within the particle core reduce and the structural anisotropy increases remarkably in the case of nanostructures as compared to their bulk counterparts.

NiO has attained much consideration among its family of various antiferromagnetic transition metal oxides like CuO, CoO, MnO, and α-Fe2O3 [6, 7]. Nanowires can be manufactured within AAO (aluminium oxide) template by using several different methods, like chemical vapour deposition (CVD), sol-gel, electrodeposition, and non-electrodeposition [8]. Of these methods, the most promising one is the deposition of sol-gel inside the pores of the AAO template due to its benefits such as easier fabrication, easily controlled components and the ability to fabricate multi-component materials. In this work, nanowires of Ni and NiO were fabricated inside the pores of the AAO template using a sol-gel solution based on nickels nitrate and citric acid [9, 10]. The pore diameter of these fabricated AAO templates was of the order of 50 nm, so the nanowires formed had the same diameter as that of pores. Nanowires were collected carefully by dissolving the alumina templates using some etching solution i.e., NaOH [11]. Different characterizations of Ni and NiO nanowires were carried out using, SEM, XRD and VSM to find out the morphology, behaviour and magnetic characteristics of nanowires formed.

## 2. Materials and methods

### 2.1. Electro-polishing of Aluminum

The pre-treatment of the workpiece (a piece of aluminium sheet) was carried out by an electro-polishing process. The battery's positive (or anodic) terminal was connected to the Al piece, while a suitable conductor was connected with the negative (or cathodic) terminal. The solution (electrolyte) was prepared by mixing 100 ml per-chloric acid ($HClO_4$) with 400 ml of ethanol. The whole setup was dipped in the electro-polishing solution in a beaker. The voltage of about 12 V is applied to the two terminals of the anode and cathode. After 3 to 4 minutes the impurities were removed from the aluminium foil and a clean shining surface was obtained. The purpose of electro-polishing is to obtain a bright and attractive finish. It also reduces the effects of high-temperature distortions in the material. Figure 1 shows the schematic diagram of the electro-polishing cell.

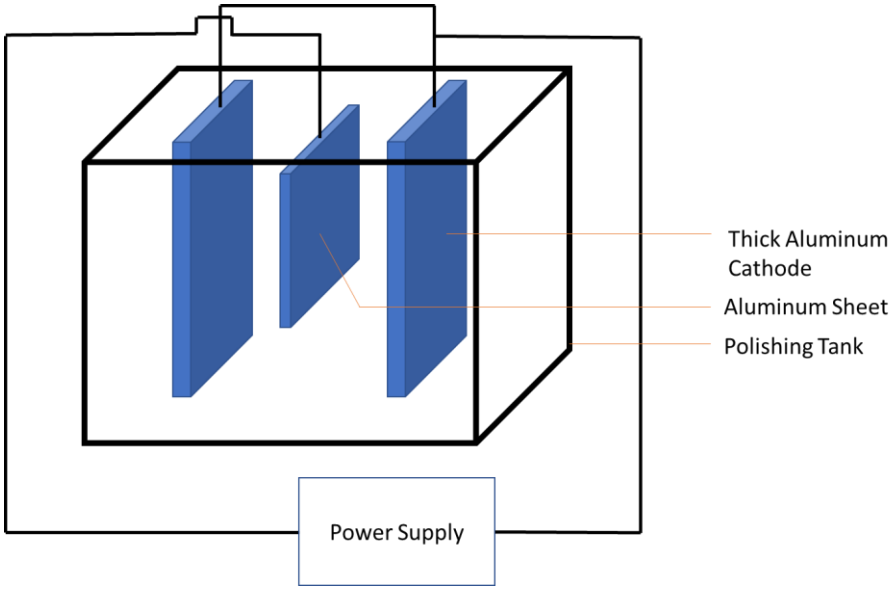



Figure 1: Schematic diagram of electro-polishing.

## 2.2. Anodization of aluminium

After electropolishing of aluminium foil, the process of adonization was carried out for the fabrication of the AAO template. An oxide layer is grown on the aluminium foil, which contains a high density of nano-sized pores. Adonization of aluminium is a two-step process in which the aqueous solutions of three acids were used for the preparation of AAO templates. The aluminium foil was attached to the positive terminal of the battery and the electric current was passed across the electrolyte through the cathode. The temperature during anodization was maintained at about 0oC. The template was then immersed in the etching solution. The etching solution was formed by mixing 6 wt% phosphoric acid ($H_3PO_4$) and 1.8 wt % chromic acid ($H_2Cr_2O_4$). After etching the AAO template was again anodized using the same procedure mentioned above. Hence the regularly arranged pores with definite pore diameters were formed. The overall progress of two-step anodization and etching is shown in Table 1.

*Table 1: Table for anodization and etching time and voltage.*

| Sr No. | Acid used | Time for 1st step (hours) | Time for yellow solution (hours) | Time for 2nd step (hours) | Voltage (V) |
|---|---|---|---|---|---|
| 1 | Oxalic Acid | 5 | 12 | 5 | 40 |
| 2 | Sulfuric Acid | 5 | 4 | 5 | 20 |
| 3 | Phosphoric Acid | 4 | 4 | 3 | 120 |

## 2.3. Sol-gel Solution

Sol-gel solution of nickel oxide was prepared by mixing the aqueous solutions of nickelous nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) and citric acid. Firstly the aqueous solution of citric acid was prepared by mixing 2.10 g of citric acid in 50 ml water on a hot plate magnetic stirrer at 80 °C. Then nickelous nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) (11.63 g) was dissolved in 50 ml distilled water. This solution was green in colour. This green solution was then placed in a burrete and added drop-wise in the citric acid solution with constant stirring. The molar ratio of citric acid to nickel nitrate was 1:4. This mixed solution was again kept on magnetic stirrer with constant stirring at 80 °C for two hours.

## 2.4. Nanowires formation

The AAO templates were immersed in the sol-gel solution after specific amount of time. First two templates were immersed after half an hour one of them was taken out after 2 mins and the other was kept in the solution till gel formation. Then after one hour two more AAO templates were immersed; again one of them was taken out after 2 mins and the other was kept placed in the gel. Then during the gel formation some more templates were immersed and were taken out after the gel formation. The templates were then allowed to dry at room temperature so that the polymerization reaction took place inside the pores of the template. The templates were then calcinated in a furnace at 500°C for 1 hour. The heating rate was 10 °C/min. The sample was allowed to cool down at room temperature to avoid quick cooling fracture. The solution on the template surface was then removed by polishing it off with 1200 grit sandpaper.

### 2.5. Etching

To collect the NiO nanowires the AAO template was dissolved. This process is necessary for SEM analysis. The etching of AAO template was carried out by adding several drops of 6M NaOH solution on the template. Within a few seconds the AAO template begun to dissolve and the NiO nanowires were collected on conducting tape.

## 3. Results and Discussion

### 3.1. FESEM analysis of AAO Templates

The SEM images of AAO templates fabricated by the two step anodization are shown in Figure 2. The pores formed in the template have ordered hexagonal structure. The diameter of pores ranges from 50 to 70 nm and the density of pores was 1011 $cm^{-2}$. The pores are uniformly distributed over the surface of aluminum plate and each pore is surrounded by six aluminum oxide pores, which form a network of pores throughout the template. The pores formed are straight and parallel to each other in the whole length and have a uniform distribution. The geometry of nanowires was consistent with the pores of AAO template as it was expected from the method of template synthesis.

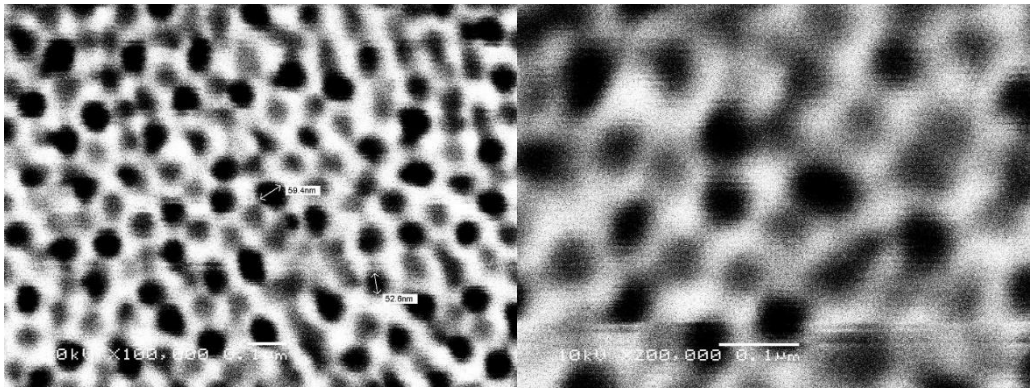



Figure 2: *SEM micrographs of AAO templates at different magnifications (a) ×100,000 (b) ×300,000*

### 3.2. SEM analysis of Ni and NiO nanowires

Figure 3 shows the SEM images of nanowires in which the template was partially dissolved in NaOH solution. The SEM analysis of nanowires fabricated by the sol-gel method showed that the material has been deposited on both sides of the AAO template. When the template was partially dissolved in NaOH solution for shorter interval of time ~60 seconds some rods were observed which have larger diameter nearly one micrometer. But these rods were well arranged and having a very regular geometry (cylindrical shape). The larger diameter of rods is alumina attached with nanowires, since AAO template is not fully dissolved. Figure 3 shows the micrographs of the rods at different magnifications.

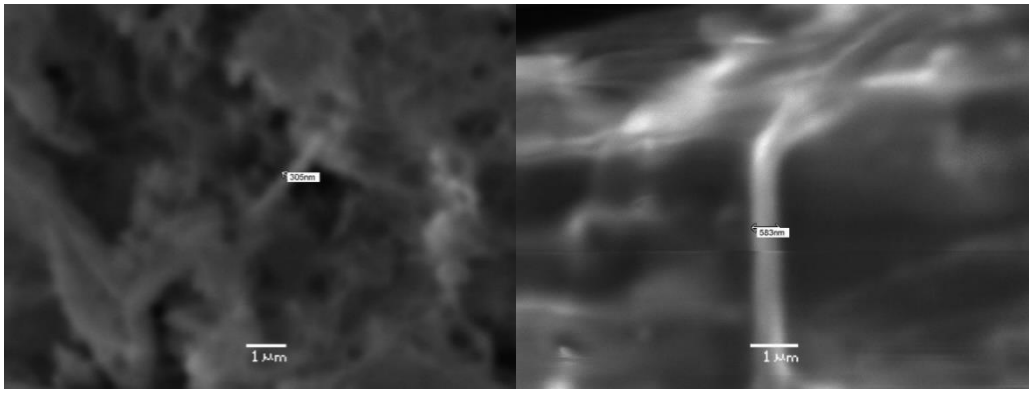


Figure 3: SEM images of sample 2 at magnification (a) ×5000 and (b) ×10000

When the etching time for AAO template is increased ~120 seconds the nanowires of rather smaller diameter were obtained. The diameter of nanowires obtained is 583nm (Figure 4 (a)) and 305nm (Figure 4 (b)).

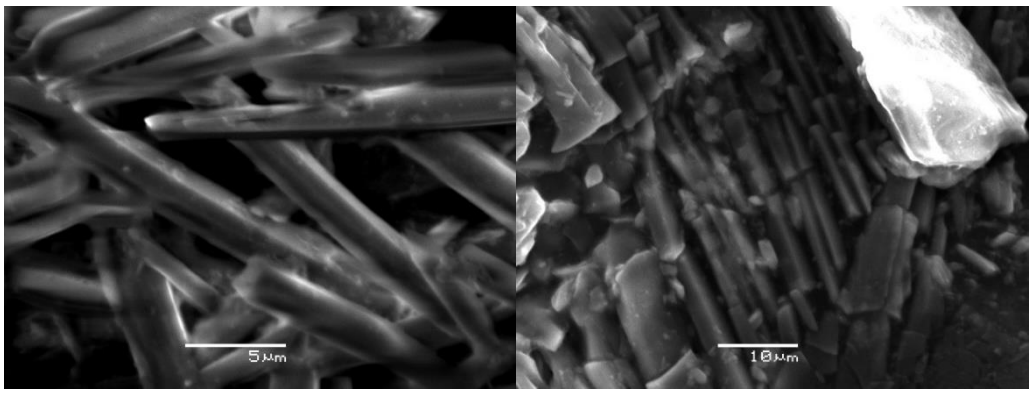


Figure 4: SEM micrographs taken at different magnifications (a) ×10,000 (b) ×12,000

The quality of AAO template formed was also found to have impact on the geometry of nanowires after the fabrication. As the template was etched for 3 minutes after the deposition of nanowires, some parts of alumina template were remained with nanowires, so the diameter of nanowires was larger than the pore size as shown in Figure 5.

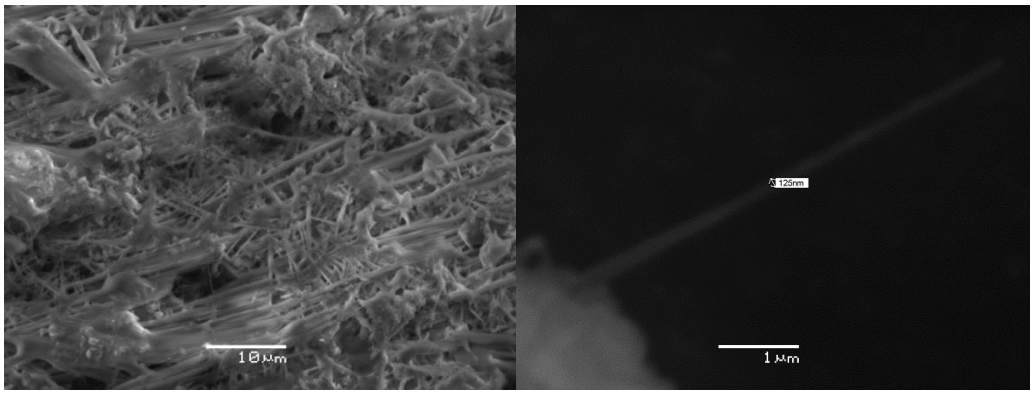


Figure 5: SEM images at magnifications (a) ×10,000 (b) ×20,000

When the etching time was further increased to 5 minutes, nanowires with small diameter ranging from ~250 to 80nm were obtained. The arrangement of these nanowires was disturbed during etching

process. The length of these nanowires was quite large because the time of immersion of AAO template in sol-gel solution for this sample was large. The SEM micrographs of at different magnifications is shown in Figure 6.

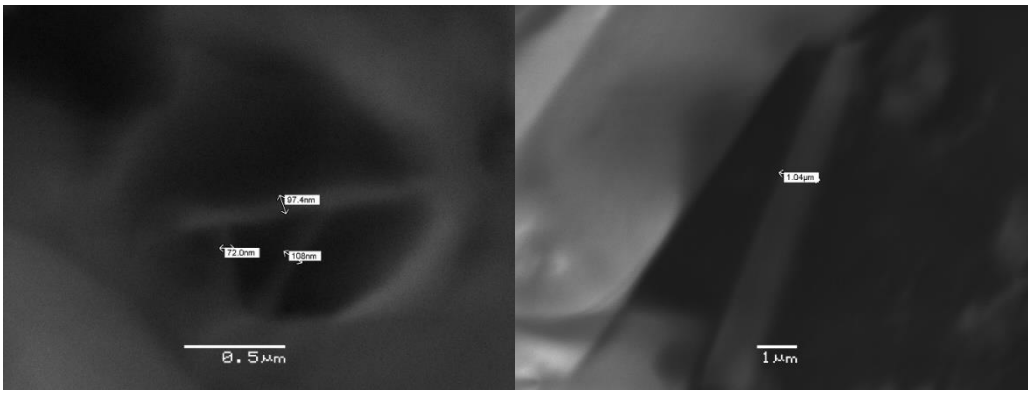



Figure 6: SEM images at different magnifications (a) ×10,000 (b) ×50,000

The SEM images of nanowires formed after the 90 minutes immersion of AAO template in the sol-gel solution are shown in Figure 7. After the exposure of NaOH to the sample for 10 minutes, removal of AAO template was taken place and the bundle of nanowires were formed. The diameter of nanowires ranged from ~80-40 nm. Figure 7 shows the clusters of nanowires formed and the diameter of some isolated magnified nanowires.

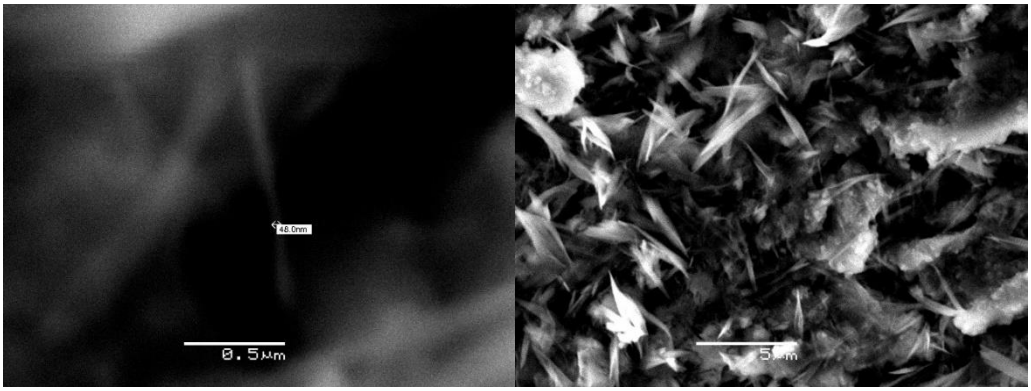



Figure 7: SEM images at magnifications (a) ×40,000 (b) ×55,000

### 3.3. X-Ray Diffraction Analysis

The structural and phase analysis of Ni and NiO nanowires were determined by X-ray diffraction technique. The XRD pattern of four samples of Ni and NiO nanowires deposited in AAO template was taken by using Rigaku XRD D/Max-II a diffractometer equipped with Cu Kα radiation with wavelength λ =1.5405Å. The X-ray diffraction pattern of samples S1, S2, S3 and powder sample synthesized for different durations of time i.e., for t=30, 60, 90, 120 minutes are shown in Figure 8. In all these patterns the angle 2θ is varied from $0^o$ to $120^o$ having a step width of 0.2 $\theta$ and the maximum intensity obtained for different samples is different. The XRD patterns of Ni and NiO nanowires formed at different intervals were analyzed and the results for different samples are discussed below.

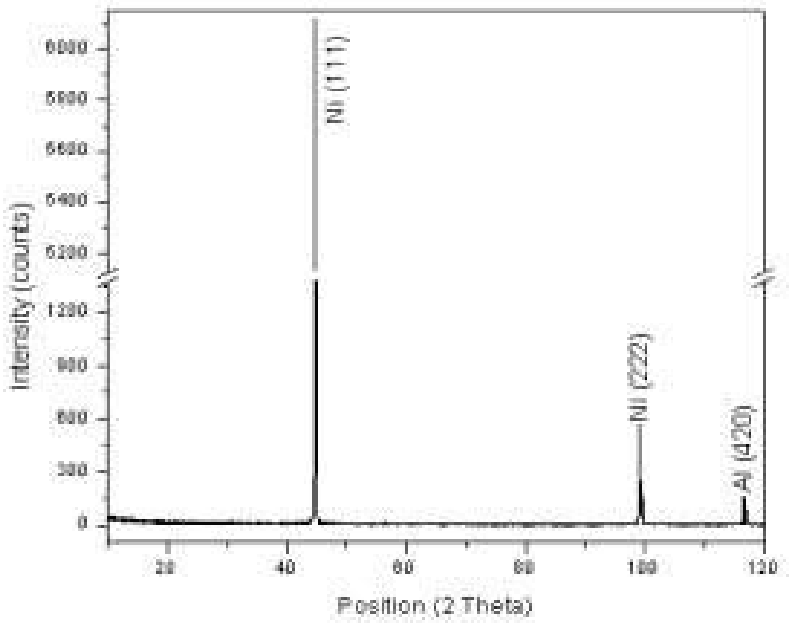



Figure 8: XRD pattern of the sample S1 formed after 30 min of sol-gel formation.

Figure 9 shows the XRD patterns of the nanowires formed by immersing AAO template after 30 min heating of the sol-gel solution. When compared with the reference peaks of aluminum it is verified that the diffraction peaks (420) at position 2θ ~116.52 with d-spacing 0.905 is due to aluminum element. The diffraction peak (111) and (222) at position 2θ ~44.53 and 98.43 respectively correspond to the Ni nanowires. Hence it is verified that at the early stage of sol-gel formation Ni nanowires are deposited in the pores of AAO template.

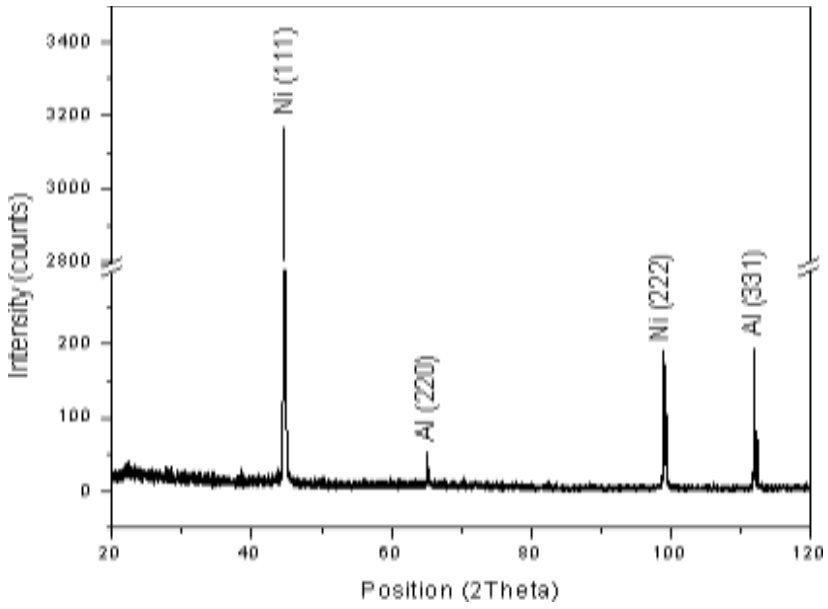



Figure 9: XRD pattern of the sample S2 formed after 60 min of sol-gel formation.

Figure 10 shows the XRD patterns of the nanowires formed by immersing AAO template after the 60 min of heating of the sol-gel solution. The diffraction peaks (220) and (331) at position 2θ ~65.11 and 116.53 respectively are due to aluminum element. The (111) and (222) diffraction peak at position 2θ

~44.56 and 98.52 respectively correspond to the Ni nanowires. It is obvious that Ni has not been oxidized after one hour of heating the solution. Hence Ni nanowires are formed.

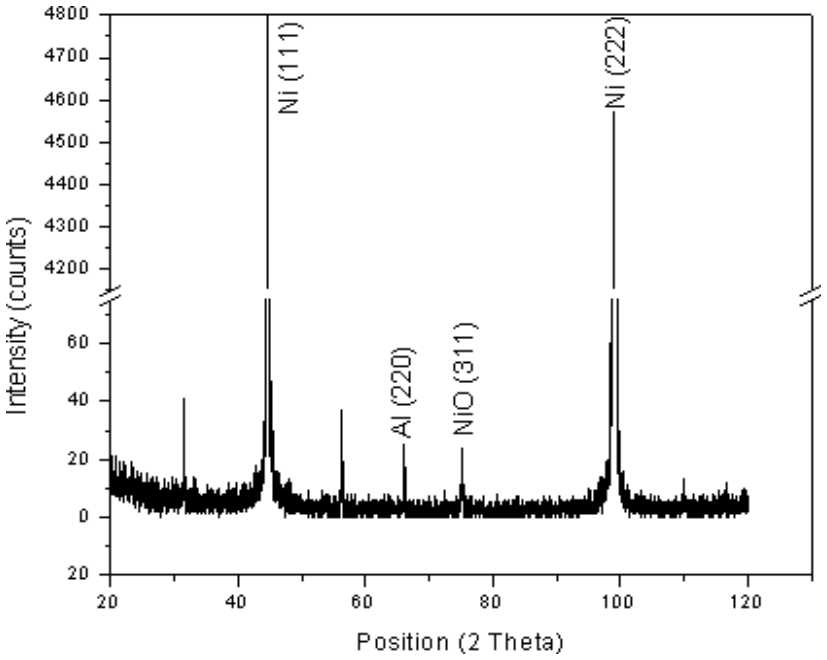



Figure 10: XRD pattern of the sample S3 formed after 90 min of sol-gel formation.

The XRD patterns of the Ni and NiO oxide nanowires formed by immersing AAO template after the 90 min of heating of the sol-gel solution is shown in Figure 11. The aluminum peak was seen at (220) diffraction plane. The diffraction peak (111) and (222) at position 2θ ~44.53 and 98.52 correspond to the Ni nanowires. The formation of NiO nanowires was verified at plane (311) corresponding to the position 2θ ~75.44 with d- spacing value 1.259.

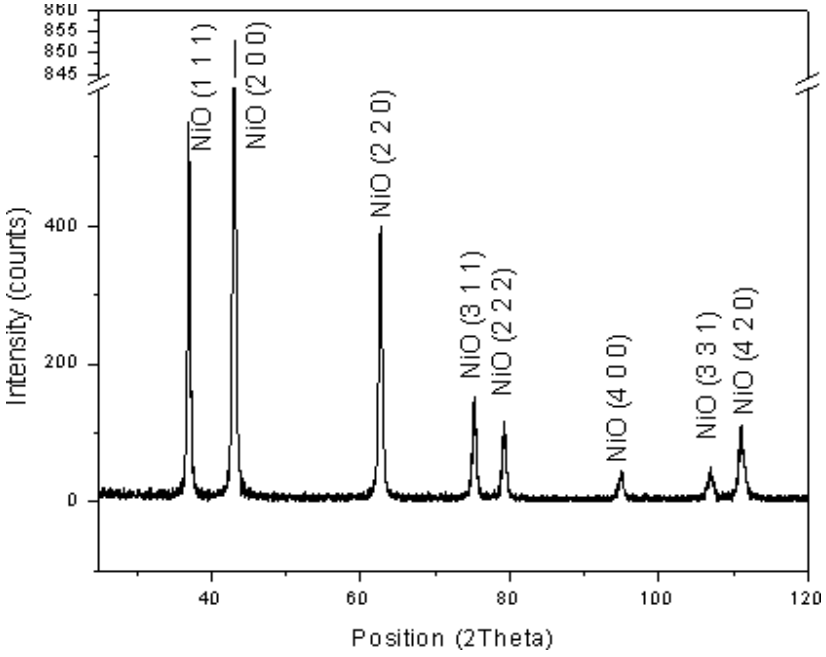
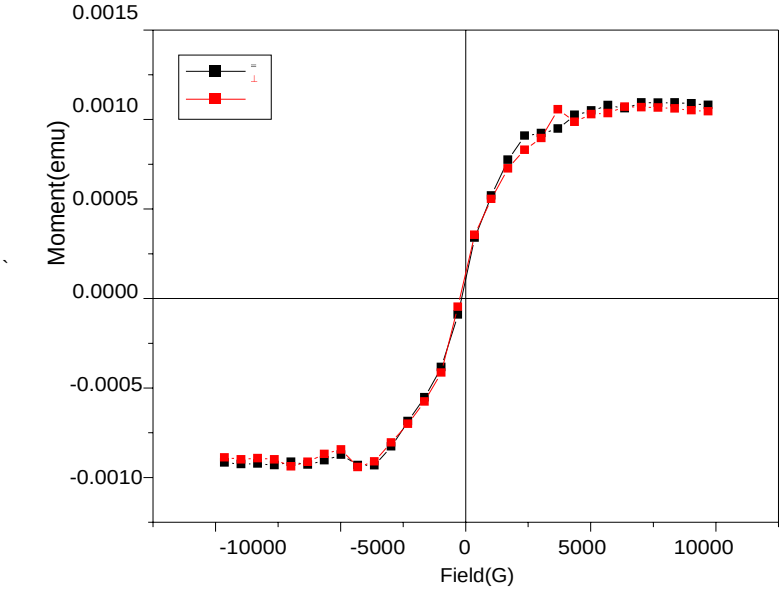



Figure 11: XRD pattern of NiO powder.

The XRD patterns of NiO nanowires in Figure 11 has peaks at 75.05 which is in good agreement with the peaks of Figure 3.10 having the diffraction peaks (111), (200), (220), (311), (222), (400), (331) and (420) at 2θ ~37.23, 43.25, 62.79, 75.46, 79.41, 95.13, 106.96, 111.35 respectively. Also, the d-spacing at intensity 75.05 for both graphs were confirmed as 1.26. These results confirmed the formation of NiO nanowires in AAO templates.

### 3.4. Magnetic properties of Nanowires

The magnetic properties of Ni and NiO nanowires deposited in AAO template were measured by using vibrating sample magnetometer. Figure 12 shows the VSM graphs of Ni and NiO nanowires synthesized for different durations. The magnetization of the samples was measured for the in-plane (parallel) and out-plane (perpendicular) applied magnetic field to the direction of nanowires formed. The VSM graphs of the samples S1 and S2 for which the template was immersed in the solution for 30 and 60 minutes respectively, show that Ni nanowires show ferromagnetic behavior and the in-plane and out- plane magnetization are almost same which shows the isotropic nature. The VSM graph of S3 and S4 are for NiO nanowires and showed different behavior as compared to Ni nanowires. NiO in bulk shows antiferromagnetic nature but in case of NiO nanowires shows a ferromagnetic trend as shown in Figure 12. The in-plane and out-plane saturation magnetization for NiO nanowires have noticeable difference that shows the anisotropic behavior. Out plane saturation magnetization has larger value ($1.6606\times10^{-3}$emu) as compared to in- plane saturation magnetization ($1.0040\times10^{-3}$emu). The reason for this change in behavior for NiO is that as the particle size is reduced to nanometer size, the surface to volume ratio increases, and number of uncompensated spins at the surface shell will increase resulting in net magnetization. Such behavior has been already discussed in case of nanoparticles of NiO [58], CuO [59] and β-MnO2 [60], which are bulk antiferromagnetic materials. NiO nanowires have promising applications for storage devices.



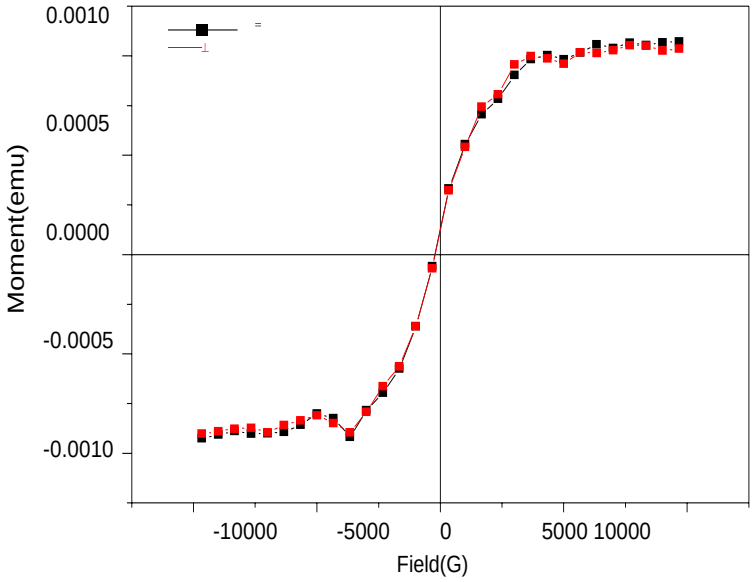



Figure 12: VSM graph of Ni and NiO nanowires at different time of sol-gel formation.

## 4. Conclusions and Future Work

Alumina templates were fabricated using two-step anodization at low temperature. The SEM images of template showed that the hexagonal and uniformly ordered pore arrangement was developed on the alumina surface. The average diameter of the pores was measured about 50nm and the distance between the pores as 100nm. Ni and NiO nanowires were successfully synthesized within the pores of AAO template. The formation of Ni and NiO was carried out by a sol-gel process. In the first part of sol-gel reaction Ni is produced and when the AAO template was dipped in the solution Ni nanowires were generated. While after passage of time for the sol- gel reaction NiO was produced which was a thick green jelly like liquid with high viscosity. When the AAO template was dipped in this solution, NiO nanowires were obtained. The collection of nanowires was quite a hard task and was carried out by etching of AAO template by using NaOH solution (etching solution). The SEM images of nanowires showed that the thickness of the nanowires was very much dependent on the etching time and the concentration of etching solution. Formation of Ni and NiO was verified from X-ray diffraction technique that showed that at the first stage of sol-gel process. The magnetic properties of nanowires were determined by the vibrating sample magnetometer graphs. The in-plane and out-plane graphs for samples were investigated and it was found that the Ni shows the isotropic nature while NiO show remarkable difference for different directions of magnetic fields and shows anisotropy. This explains that when the material was fabricated at the nanometer scale there occurred a remarkable difference in the magnetic properties. Which is due to the reason that surface to volume ratio of the material increased.

## 5. References:

[1] Lu, G. Q. & Zhao, X. S. Nanoporous materials- an overview. Series on Chemical Engineering, 1-13 (2004).

[2] Rao, C. N. R., Mueller, A. & Cheetham, A. K. Nanomaterials - An introduction. Chemistry of Nanomaterials 1, 1-11 (2004).

[3] Tolles, W. M. & Rath, B. B. General overview on nanomaterials. Nanomaterials: Synthesis, Properties and Applications, 545-553 (1996)

[4] Liu, M., Li, X., Imrane, H., Chen, Y., Goodrich, T., Cai, Z., ... & Sun, N. X. (2007). Synthesis of ordered arrays of multiferroic Ni Fe 2 O 4-Pb (Zr 0.52 Ti 0.48) O 3 core-shell nanowires. Applied physics letters, 90(15), 152501.

[5] Sharma, G., Kripesh, V., Sim, M. C., & Sow, C. H. (2007). Synthesis and characterization of patterned and nonpatterned copper and nickel nanowire arrays on the silicon substrate. Sensors and Actuators A: Physical, 139(1-2), 272-280.

[6] Ali, H., Soleimani, H., Yahya, N., Khodapanah, L., Sabet, M., Demiral, B. M., ... & Adebayo, L. L. (2020). Enhanced oil recovery by using electromagnetic-assisted nanofluids: A review. Journal of Molecular Liquids, 309, 113095.

[7] Soleimani, H., Ali, H., Yahya, N., Guan, B. H., Sabet, M., Lee, K. C., ... & Kakooei, S. (2020). Transport modelling of multi-phase fluid flow in porous media for enhanced oil recovery. In Defect and Diffusion Forum (Vol. 400, pp. 38-44). Trans Tech Publications Ltd.

[8] Yang, Q., Sha, J., Ma, X., & Yang, D. (2005). Synthesis of NiO nanowires by a sol-gel process. Materials Letters, 59(14-15), 1967-1970.

[9] Shumskaya, A. E., Kaniukov, E. Y., Kozlovskiy, A. L., Shlimas, D. I., Zdorovets, M. V., Ibragimova, M. A., ... & Kadyrzhanov, K. K. (2017). Template synthesis and magnetic characterization of FeNi nanotubes.

[10] Zheng, M., Li, G., Zhang, X., Huang, S., Lei, Y., & Zhang, L. (2001). Fabrication and structural characterization of large-scale uniform SnO2 nanowire array embedded in anodic alumina membrane. Chemistry of materials, 13(11), 3859-3861.

[11] Bentley, A. K., Farhoud, M., Ellis, A. B., Nickel, A. M. L., Lisensky, G. C., & Crone, W. C. (2005). Template synthesis and magnetic manipulation of nickel nanowires. Journal of chemical education, 82(5), 765.