Co-based full heusler alloy nanowires: Modulation of static and dynamic properties through deposition parameters

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ABSTRACT
In this work, a successful fabrication of Co$_2$MnAl heusler alloy nanowires in anodic alumina templates has been demonstrated using simple and low-cost electro-deposition technique at room temperature. The role of deposition parameters, such as pH of the electrolyte solution were investigated on the structural and magnetic properties of Co$_2$MnAl nanowires. It is observed that the crystallinity improves with the increase of pH of the solution till around pH=3.0 where the best crystallinity is achieved. The X-Ray diffraction pattern confirms the formation of B2 crystal type in the Co$_2$MnAl heusler alloys which is further verified by high-resolution transmission electron microscope images. The static magnetic properties were explored by the VSM analysis which revealed that the saturation magnetization, squareness, coercivity and uniaxial anisotropy of the nanowires increase with the increase in pH value. The highest remanent squareness of 76% is observed for pH=2.9. The dynamic measurements of heusler alloy nanowires have been studied by ferromagnetic resonance technique using the flip-chip method in the field-sweep mode at different applied frequencies ranging from 20-40 GHz. It is observed that the resonance field increases linearly with the increase in frequency for all samples. Further, the resonance field decreases up to 35% with the increase of pH value of electrolyte, resulting in an increase in the effective field.

INTRODUCTION
Full Heusler alloys, with stoichiometric composition X$_2$YZ (X and Y are transition metals and Z is a p-block element) have emerged as a fascinating multifunctional materials. They are known to possess excellent magnetic and electrical properties which can be endorsed for fundamental physics research and technological applications such as spintronics, thermoelectric, ferromagnetic shape memory and superconductors. Co-based heusler alloys are appraised to be exemplary candidates for magnetic tunnel junction (MTJ) electrodes applicable in spintronic devices since they possess high spin polarization at room temperature due to their high Curie temperature above 500 K. These alloys are promising materials for long range spin wave propagation with low threshold current, ultra fast magnetization reversal and large microwave power emission due to their low magnetic damping. Recently a large number of groups have investigated various properties of heusler alloys in thin film. However, to meet the requirement of high performance and miniaturization of devices, materials with nanoscale dimensions are attracting interest. The nanoscale dimensions can enhance the typical properties of heusler alloys usually exhibited in the form of bulk and offers opportunity to incorporate these novel nanoscale materials into the products of industrial technologies. One dimensional nanowires are especially shown prospects in miniaturization of devices. In nanowires geometry, two directions are confined to nanoscale whereas the third dimension is unconfined. The magnetic properties of nanowires are strongly affected by its high aspect ratio, finite size effects and shape anisotropy. These nanowires can be fabricated by a variety of techniques, such as molecular beam epitaxy, electro-deposition, and ball milling. Among these techniques, electro-deposition is a low-cost and efficient way of obtaining high aspect ratio nanowires.
where the structural, magnetic and compositional properties of the samples can be modulated in a controllable way by changing various deposition parameters such as deposition potential, concentra-
tion, frequency, current density, pH, etc. In the present work, we have utilized this promising electro-deposition technique to fabricate one-dimensional $\text{Co}_2\text{MnAl}$ heusler alloy nanowires using anodic aluminium oxide (AAO) as template for the first time.

A well-established and powerful microwave technique to probe the dynamic properties is ferromagnetic resonance (FMR) and is useful to determine various magnetic properties such as magnetic anisotropy, effective magnetization, magnetic damping, etc. Complex dynamics of magnetic nanowires which are reflected in FMR spectra have been earlier studied in our previous works. Here, we report the fabrication of one dimensional $\text{Co}_2\text{MnAl}$ nanowires in AAO templates with pore diameter of 200 nm and thickness of 60 $\mu$m by electrochemical deposition technique. Moreover, we investigated the effect of deposition parameters such as pH of the electrolyte solution on the structural as well as static and dynamic magnetic properties of the nanowires. In order to characterize the microstructural, and static magnetic properties of the nanowires, we have employed X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM) and vibrating sample magnetometry (VSM). To study the dynamic magnetic properties we have used field-sweep mode FMR in flip-chip geometry.

**EXPERIMENTAL**

AAO templates with specifications of cylindrical pores of height around 60 $\mu$m, pore radius 100 nm and inter-pore spacing ~300 nm were purchased from Whatman Ltd. Prior to electro-deposition, one side of the AAO template was sputtered with a conducting layer of gold of thickness around 200 nm using an RF-sputtering system (Alcatel, QM-311). The gold-coated AAO template serves as a working electrode in a three-electrode electrochemical cell. A platinum wire was used as the counter electrode and a silver rod serves as a reference electrode. For the fabrication of $\text{Co}_2\text{MnAl}$ heusler alloy nanowires, we used an electrolyte solution containing 0.1 M cobalt sulphate, 0.05 M of manganese sulphate, 0.05 M of aluminium sulphate and boric acid 0.05 M. The pH of the solution was adjusted in the range of 2.0 to 3.5 by adding small amount of NaOH or HCl in the solution and the pH was monitored by a pH-meter. DC electro-deposition was done at room temperature for electrolyte solution of various pH at a fixed cathode potential of -1.4 V. The samples were labelled as S1 to S5 (for pH 2.0, 2.5, 2.9, 3.2 and 3.5, respectively).

After electro-deposition, the samples were characterized by various techniques to study their morphological, structural and magnetic properties. We used scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) to study the morphology and crystallinity of nanowires and vibrating sample magnetometer (VSM) to study the static magnetic properties. For XRD and VSM, the heusler alloy nanowires were kept in the AAO template whereas for SEM, the nanowires were partially eman-
cipated from AAO templates by etching the AAO template in 3M NaOH solution for 15 minutes. The liberated nanowires were decanted by a perma-
ent magnet and thoroughly rinsed with de-ionized water for several times before drop-casting on the carbon coated copper grid. VSM measurements were performed under an applied magnetic field of 1 Tesla. A broad-band FMR measurement system (Keysight, PNA Network Analyzer, N5224A) was used to study the dynamics of nanowires at microwave frequencies ranging from 1 to 43 GHz and with external magnetic field from 0 to 10 kOe. To allow the propaga-
tion of the rf signal through nanowires, we used a flip-chip technique in which the nanowires, embedded in AAO template, was flipped on to top of a one-side shorted coplanar waveguide. The ferromag-
netic resonance (FMR) spectra were measured in reflection mode from port 2 ($S_{22}$). The magnetic field was swept from 0 to 10 kOe at a fixed frequency to obtain the field dependent FMR. Field sweep measurements were done for various frequency ranges from 20 GHz to 40 GHz. The reflection coefficient of scattering parameters ($S_{22}$) was traced using a vector network analyzer.

**RESULTS AND DISCUSSION**

**Crystal structure characterization**

The crystal structure of Co-based heusler alloy nanowires were analysed by X-ray diffraction by acquiring the spectra in the two-theta range of 20$^\circ$–80$^\circ$. Fig. 1 shows the XRD patterns of samples S1 to S5 prepared at different pH value from 2.0 to 3.5. It is observed that all the samples show (220) and (420) reflection peaks whereas (400) reflection plane appears at higher pH of the electrolyte i.e. for S4. However, the crystallinity of S5 degrades due to the fact that at higher pH of the electrolyte the aluminium in the solution starts precipitating. So, we considered further studies for samples S1 to S4. The observed spectra demonstrate B2 type crystal structure in the deposited nanowires. The strongest reflection intensity peak was recorded from (220) plane in the diffraction spectra. We observed that the crystal structure of nanowires improves with the increase of

![FIG. 1 XRD spectra of Co2MnAl nanowires fabricated by electrodeposition at various pH of the solution.](image-url)
the pH value of the electrolyte. The crystalline size of the deposited samples is calculated using Scherer formula and found to be 2.03 Å and the lattice constant is calculated to be 5.76 Å which is in agreement with the bulk value of 5.79 Å.

**Morphological characterization**

Fig. 2 shows the SEM image of the Co$_2$MnAl heusler alloy nanowires after partial etching of the AAO templates. It is clear from the images that the nanopores are uniformly filled by the deposited material and closely arranged with the average diameter of about 200 nm. Fig. 3(A) shows the TEM image of a nanowire released completely after etching in NaOH solution for sample S3 (pH 2.9). It is clear from the HR-TEM image (Fig. 3(B)) that the inter-planar spacing are 0.27 nm and 0.14 nm which corresponds to planes (220) and (420) of Co$_2$MnAl nanowires. The selected area electron diffraction (SAED) patterns as shown in Fig. 3(C) identify the polycrystalline nature of the nanowires due to concentric rings formations.

**Magnetic characterization**

Fig. 4(A) shows the room temperature hysteresis loop of Co$_2$MnAl nanowires with externally applied magnetic field along parallel orientation of the nanowire’s long axis for samples S1 to S3. It can be depicted from the results that saturation magnetization ($M_s$), remanent magnetization ($M_r$), squareness, coercivity, and uniaxial anisotropy of the nanowires increases with the increase of pH value of electrolyte. Fig. 4(B) shows the magnetic behaviour of heusler alloy nanowires with external magnetic field applied perpendicular to nanowire’s long axis. It can be seen that the easy magnetization axis is parallel to the wire axis which can be attributed to the dominance of shape anisotropy as compared to magnetostatic interaction. Fig. 4(C) shows the variation of coercivity ($H_c$) of all the samples and corresponding squareness which is the ratio of remanent to saturation magnetization ($M_r$/M$_s$) in parallel orientation as a function of pH value of the electrolyte. With the increase of pH value coercivity increases from 0.23 kOe to 0.53 kOe and squareness increases from 0.1 to 0.8 respectively. Remanent magnetization for parallel orientation is 76% of the saturated magnetization for
maximum pH value as shown in Fig. 4(C) by blue dots. It is observed that the coercivity and squareness decreases with further increase of pH value.

Magnetization dynamics: Ferromagnetic resonance characterization

The dynamic properties of heusler alloy nanowires were measured by vector network analyzer using flip-chip based ferromagnetic resonance. Prior to measurements, standard through-open-line (TOL) calibrations have been performed using NIST Multical® software. At a fixed microwave frequency $f_r$, the FMR spectra was recorded by sweeping the external dc magnetic field which is kept parallel to the nanowires long axes. Fig. 5(A–D) shows the reflection coefficient ($S_{22}$) as a function of applied magnetic field at various frequencies from 20–40 GHz. We observed a notch at a specific frequency which corresponds to absorption of power at the resonance. It was observed from the FMR spectra that the resonance field increases with the increase in operational frequency for all the samples.

We derived the in-plane resonance field $H_r$ by fitting the FMR spectra by the Lorentzian function at constant frequencies. The observed resonance field as a function of operational frequency along the parallel direction of nanowires can be computed using the Kittel’s equation

$$\frac{\omega}{\gamma} = H_r + H_{\text{eff}}$$

where $\omega = 2\pi f$ and $\gamma = g\mu_B/\hbar$ is the gyromagnetic ratio. $H_{\text{eff}}$ is the effective field can be expressed as

$$H_{\text{eff}} = 2\pi M_s(1 - 3P)$$

where $P$ is the porosity which can be written in terms of nanowires radius ($r$) and interwire spacing ($S$), as $P = 2\pi r^2/\sqrt{3}S^2$. 

![FIG. 5. Reflection coefficient ($S_{22}$) versus magnetic field as a function of frequency for Co2MnAl nanowires, fabricated at pH (A) 2.0, (B) 2.5, (C) 2.9 and (D) 3.2 of the electrolyte solution.](image)

![FIG. 6. Resonance field versus operational frequency for various pH values of the electrolyte.](image)
Table I. The intrinsic material parameters for Co₃MnAl nanowires.

| Samples | pH value | Hᵣ (kOe) at 0° | γ’ (GHz/kOe) | Hₘ0 (kOe) |
|---------|----------|----------------|--------------|------------|
| S1      | 2.0      | 4.88           | 3.54         | 2.79       |
| S2      | 2.5      | 3.58           | 3.29         | 4.57       |
| S3      | 2.9      | 3.39           | 2.99         | 6.33       |
| S4      | 3.2      | 3.16           | 3.01         | 6.5        |

Fig. 6 shows the resonance field as a function of frequency for various pH value of the electrolyte. It is clear that the resonance field decreases with the increase in pH value, which can be attributed to the decrease in shape anisotropy as compared to magnetostatic interactions (also depicted from the hysteresis plots in Fig. 4(A)). The red line corresponds to the theoretical fits using equation (3). Table I shows all the intrinsic parameters derived from the pH variation of electrolyte.

CONCLUSION

In the present work, we successfully fabricated ordered Co₃MnAl heusler alloy nanowires by electro-deposition in anodic alumina templates. A contribution to the knowledge of the dependence of structural, compositional, morphological, and static and dynamic magnetic properties of the nanowires on pH of the electrolyte solution during electro-deposition is reported. The Co₃MnAl heusler alloy nanowires with B2-type cubic structure were obtained with improved crystallinity at pH value of around 3.0. The SEM and TEM images confirm the morphology and SAED pattern revealed the static phase structure which is in agreement with XRD. The static magnetic properties revealed that the saturation magnetization, squareness, coercivity and uniaxial anisotropy of the nanowires increase with the increase in pH value. The dynamic measurements revealed that the resonance field decreases to 35% with the increase of pH value of electrolyte. The proposed Co-based full heusler alloy nanowires are promising candidates for future spintronics applications and high frequency S-G technology materials.

ACKNOWLEDGMENTS

This work is supported by the MHRD-IMPRINT grant, DST-SERB, DST-AMT grant of Govt. of India.

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