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The effect of Cr substitution on the structural, electronic and magnetic properties of pulsed laser deposited $NiFe_2O_4$ thin films

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ABSTRACT

We have studied the structural, electronic and magnetic properties of pulsed laser deposited thin films of $Ni_{1-x}Cr_xFe_2O_4$ (x=0.02 and 0.05) on Si (111) and Si (100) substrates. The films reveal single phase, polycrystalline structure with larger grain size on Si (111) substrate than that on Si (100) substrate. Contrary to the expected inverse spinel structure, x-ray photoemission (XPS) studies reveal the mixed spinel structure. XPS results suggest that Ni and Fe ions exist in 2+ and 3+ states, respectively, and they exist in tetrahedral as well as octahedral sites. The deviation from the inverse spinel leads to modified magnetic properties. It is observed that saturation magnetization drastically drops compared to the expected saturation value for inverse spinel structure. Strain in the films and lattice distortion produced by the Cr doping also appear to influence the magnetic properties.

1. Introduction

AFe_2O_4 ("A" being transition metal cation) based spinel ferrites have attracted tremendous attention among condensed matter physicists owing to their wide range of physical properties. Such ferrites have huge relevancies in contemporary technologies such as spintronics, high-density data storage, microwave absorption, catalysis, hydrogen production, batteries, magneto-caloric refrigeration, as magnetostrictive phase in multilayer magneto-electric composites etc. [1–6]. Besides these technological implications, these materials are also a source of abundant fundamental physics related to magnetization as well as catalytic properties. Among many spinel based ferrites, $NiFe_2O_4$ (NFO) has been widely studied because of the low eddy current loss, low magnetostriction and rather high Curie temperature which makes it suitable candidate for soft magnets and low loss materials at high frequency. To further extend its application domain, efforts are being made to modulate its structural, electrical and magnetic properties by doping of magnetic or non-magnetic impurity, where the dopant ions are expected to modify the exchange interaction among Ni and Fe ions of the host matrix [7–10]. NFO is mostly considered to be an inverse spinel structured ferrimagnetic material where the tetrahedral (A) sites are occupied by half of the Fe^{3+} cations, and the octahedral (B) sites are occupied by the rest of Fe^{3+} and Ni^{2+} ions. However, it has been found that in such spinel ferrites, the cationic distribution can deviate from perfect inverse spinel depending upon the growth parameters. It is to be noted that the magnetic moments of transition metal ions at the A and B sites interact antiferromagnetically, while the ions at the same site have a ferromagnetic interaction. It suggests that the magnetic property is immensely governed by the distribution of Ni and Fe ions at the A or B sites. Any alteration in distribution of these ions at these sites would hence affect the various functional magnetic features such as Curie temperature, saturation magnetization, magnetic anisotropy constant, coercivity, remanent magnetization, etc. [5–13].

Most of the previous studies are related to the nanoparticles of NFO, which show super paramagnetic behavior [14–17]. However, for better prospects in devices, study on thin film based structure of NFO is crucial. In thin film form, the structure of these ferrites depends upon the technique used for deposition, type of substrate, strain in the film, substrate temperature, etc. [18–22]. Moreover, its integration with technologically important Si substrate will be a key to realize its relevance in device. In spite of this, there are few reports in literature related to growth and properties of NFO films on Si substrate [3,18,22]. However, there are large discrepancies regarding the cation distributions among the various sites and the observed magnetic moments in these reports.

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In this milieu, we present structural and magnetic study of effect of Cr doping in $NiFe_2O_4$ thin films on the same substrate with different orientation; Si (100) and Si (111).

2. Experimental

The bulk target of $Ni_{1-x}Cr_xFe_2O_4$ (x=0.02 and 0.05) (NCFO) in pellet form used for the deposition was synthesized by standard conventional solid state route. NCFO films were deposited on chemically cleaned Si (100) and Si (111) substrates using pulsed laser deposition technique. KrF excimer laser source (λ=248 nm, pulse width=20 ns) was used for growing the films. During growth, substrate temperature was kept at 700 °C and base pressure was kept as the growth pressure. No additional gas was passed in the chamber. The temperature of the substrate was measured by thermocouple, mounted on the back side of the substrate holder. The substrate to target distance was fixed at 5 cm. The base pressure was kept to be 5×10^{-6} Torr. After the deposition, film was cooled under the same pressure. Thickness of the films was measured by Talystep profilometer and found to be ~70 nm. 2θ–ω X-ray diffraction measurement (XRD) was carried out using Brooker D2-Phaser with Cu-K_α source. Fourier transform infrared spectroscopy (FTIR) measurement was performed using Bruker model vertex 70. X-ray photoemission spectroscopy (XPS) was performed using Omicron energy analyzer (EA 125, Germany) with Al-K_α lab source (hν=1486.6 eV) Raman spectroscopy consisting of 200 mW Ar- laser (488 nm) was also used to characterise the films. Magnetization measurements as a function of temperature and magnetic field were carried out by employing a commercial 7-Tesla SQUID-vibrating sample magnetometer (SVSM; Quantum Design Inc., USA).

3. Results and discussions

In Fig. 1, we show the XRD patterns of $Ni_{1-x}Cr_xFe_2O_4$ (x=0.02 and 0.05) films grown on Si (100) and Si (111) substrates. Mainly three intense peaks are observed which correspond to planes of $NiFe_2O_4$ structure as reported in PCPDF card (PCPDF no – 862267), while other remaining peaks match well with the Si substrates. Here, if we compare the growth of Cr doped NFO on Si substrates with the growth of magnetite (Fe_3O_4) which also has a cubic inverse spinel structure consisting of Fe^{2+} and Fe^{3+} ions, it turns out that the growth nature of NCFO films is different than that of Fe_3O_4. Fe_3O_4 grows along [111] direction irrespective of the choice of orientation of Si substrate [18] whereas, in the present case, of NCFO films, it turns out to be a polycrystalline growth of the films on both orientations of Si substrate. Further, when we compare the patterns of films on Si (100) and Si (111) substrates, it is revealed that for both the doping concentrations, full width at half maxima (FWHM) of the peaks is smaller for the films grown on Si (111) substrate than that of Si (100), suggesting larger grain size in films grown on Si (111) than the corresponding films on Si (100). FWHM values given in Table 1 correspond to the most intense peak (111) in θ–2θ scan lying between 18 to 19° as shown in inset of Fig. 1.

After confirmation of phase, we calculated the grain size (D) of the films following the Debye-Scherrer formula,

$$D = 0.94 * \lambda / (B \cos \theta)$$

where, λ is the wavelength of the x-ray source and B is the FWHM of individual peak at 2θ (where θ is Bragg angle). Lattice strain (T) in the material also causes broadening of diffraction peak, which can be represented by the relationship

$$T \tan \theta = (\lambda / D \cos \theta) – B$$

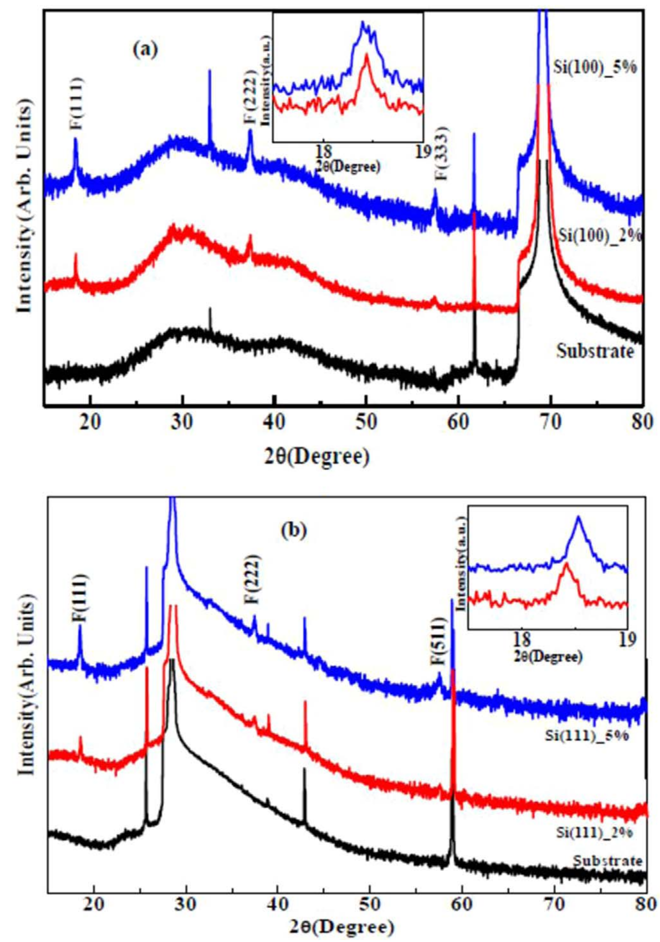

Fig. 1. The XRD patterns of $Ni_{1-x}Cr_xFe_2O_4$ (x=0.02, 0.05) films grown on (a) Si (100) and (b) Si (111) substrates along with those of the bare substrates. Here *F* corresponds to the peaks arising from the film. The inset shows a zoomed view of the most intense film peak (111).

Table 1
XRD method based lattice parameters and other parameters of Cr doped $Ni_{1-x}Cr_xFe_2O_4$ (x=0.02, 0.05) films grown on Si (111) and Si (100) substrates.

Substrate	Doping % (x)	Lattice parameter (Å) (±0.003)	FWHM (deg)	Grain size (Å)	Strain
Si(100)	0.02	8.330	0.43	324	5×10^{-3}
Si(111)	0.02	8.325	0.22	425	3.4×10^{-3}
Si(100)	0.05	8.345	0.91	167	12×10^{-3}
Si(111)	0.05	8.330	0.20	293	5.7×10^{-3}

Various XRD based parameters for the present films are given in Table 1. Consequently, it is revealed that grain size decreases with Cr doping for films on both the substrates. It is also observed that films deposited on Si (111) substrate for both the doping concentration reveal larger grain size value than the respective films grown on Si (100) substrate.

We shall like to mention here that initially we tried to deposit the films at lower temperature also, but single phase was not observed. We could get the single phase of $NiFe_2O_4$ (undoped as well as doped) at 700 °C only. Substrate temperature is used to provide sufficient kinetic energy to the adsorbent atoms/ions so that they can diffuse at the substrate surface and get into a crystalline form with the required phase.

To find out the thickness of the films, we have performed x-ray reflectivity (XRR) measurement. As an example, the XRR patterns of 2% Cr doped NFO film on Si (111) substrate is shown in inset of