Study of Reactively Sputtered Nickel Nitride Thin Films

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Nickel nitride (Ni-N) thin film samples were deposited using reactive magnetron sputtering process utilizing different partial flow of N2 (R N2). They were characterized using x-ray reflectivity (XRR), x-ray diffraction (XRD) and x-ray absorption near edge spectroscopy (XANES) taken at N K-edge and Ni L-edges. From XRR measurements, we find that the deposition rate and the density of Ni-N films decrease due to successively progression in R N2, signifying that Ni-N alloys and compounds are forming both at Ni target surface and also within the thin film samples. The crystal structure obtained from XRD measurements suggest an evolution of different Ni-N compounds given by: Ni, Ni(N), Ni4N, Ni3N, and Ni2N with a gradual rise in R N2. XANES measurements further confirm these phases, in agreement with XRD results. Polarized neutron reflectivity measurements were performed to probe the magnetization, and it was found Ni-N thin films become non-magnetic even when N incorporation increases beyond few at.%. Overall growth behavior of Ni-N samples has been compared with that of rather well-known Fe-N and Co-N systems, yielding similarities and differences among them.

INTRODUCTION

The family of transition metal nitride (TMN) exhibits interesting electronic, optical, thermal and magnetic properties. In particular, the combination of various properties of 3d TMNs such as wear and corrosion resistant, exceptional hardness with excellent magnetic properties have attracted considerable attention [1-6]. However among those, early 3d TMNs (e.g. ScN, TiN, VN, and CrN) are well established and relatively more explored than late 3d TMNs (e.g. Mn-N, Fe-N, Co-N, and Ni-N).

For the early 3d TMNs, mostly the MN (M = metal) stoichiometry is prevalent but some reports of M2N phase has also observed e.g. Cr2N and Nb2N [3, 7, 8]. On the other hand, a significant change in stoichiometry is observed as M3N and M4N, etc. for late 3d TMNs. The increased M/N ratio for the late TMNs signifies the rejection of N by the metal atoms which reflected in their poor stability and challenging formation [3, 4, 7]. Nevertheless, the late 3d TMNs are largely investigated for their excellent electronic and magnetic properties [6, 9-15].

Unlike early, the late 3d TMNs have been known to possess several multi-nitride phases. For instance, in Fe-N, different crystallographic phases have been obtained: Fe16N2 [16], Fe8N [17], Fe2N [12], Fe5N [18], Fe2N [19], FeN [20], Fe2N, FeN4, FeN8 [21-23]. Similarly, in Co-N system, Co4N [24-27], Co3N [28], Co2N [29-31], CoN [32, 33] and CoN2 [21] phases have been synthesized. On the other hand, the nickel nitrides (Ni-N) is scarcest among the late 3d TMNs as only a handful of reports are available. However, Ni-N are potentially important metallic compound [34, 35] as they have been reported to serve as negative electrodes in lithium batteries and energy storage devices [35-39], dye or quantum dot solar cells [40, 41]. Ni-N compounds have been also found to exhibit superior (electro)catalytic activities in the reduction reactions and also demonstrated many other advantages over pure metals [34, 42]. Non-conventional insulating-metal transition properties have also been demonstrated by Ni-N [43-46]. With a good quality of interface, Ni-N demonstrates a high work function, low leakage current and therefore implemented as an electrode in GaN-based Schottky barrier diodes [36].

Notwithstanding the active experimental research work, relatively less information about the intrinsic properties of Ni-N is available. Even the phase-diagram information of Ni-N is ambiguous or scarce [47, 48]. Few phases in Ni-N system as; Ni4N(fcc) [49-53], Ni3N(hcp) [54, 55], Ni2N [56-58] have been reported to synthesized by chemical vapor deposition, sputtering and highly reactive azides or hydrazine. While some other phases Ni3N2 and NiN6, have also been reported to crystallize by chemical route methods [47]. On the other hand, the stoichiometric NiN has not been achieved yet. Recently, nickel pernitride (NiN2) phase is also synthesized at very high pressure of about 40 GPa [59]. Additionally, an ambiguity about the magnetic characteristic of Ni-N phases can also be seen from the available literature. Gajhiye et al., reported a ferromagnetic state in the Ni3N phase with Curie temperature of about 634 K [60]. On the other hand, the Ni5N phase (or mixed with Ni2N phase) was found to exhibit paramagnetic behavior, in some other reports [54, 55, 61]. Furthermore, the detailed information on the structural and the magnetic behavior of Ni-N thin films is still lacking. The dearth of such information about the Ni-N system is due to their metastability which is related to their high enthalpy of formation (H°f) and makes it rather difficult to synthesize [47]. This indicates that a relatively narrow window exists for the synthesis of various Ni-N phases.

In view of this, we synthesized the entire spectrum
of Ni-N films with the successive increase of the partial flow of nitrogen (in the window 0 to 100%) by reactive magnetron sputtering and investigated their structural and magnetic properties.

**EXPERIMENTAL PROCEDURE**

A set of Ni-N thin films were prepared on amorphous quartz (SiO$_2$) substrates using direct current magnetron sputtering system (Orion-8, AJA Int. Inc.) at room temperature. High purity Ni target (99.993% pure) φ 1 inch was sputtered in the presence of different partial gas flow of nitrogen ($R_{\text{N}_2} = p_{\text{N}_2}/(p_{\text{Ar}}+p_{\text{N}_2})$, where $p_{\text{Ar}}$ and $p_{\text{N}_2}$ are gas flow of Ar and N$_2$ gases, respectively). $R_{\text{N}_2}$ was varied at 0, 5, 10, 15, 20, 50, 75, and 100%. A base pressure of $1 \times 10^{-7}$ Torr was achieved before deposition and the working pressure was maintained at 3 mTorr during deposition. No intentional substrate heating was provided during and after deposition.

The density and deposition rates were measured using x-ray reflectivity (XRR) measurements using Cu K-α x-ray source. Samples were characterized for their crystal structure and phase formation by x-ray diffraction (XRD) using a standard x-ray diffractometer (Bruker D8 Advance) using Cu K-α x-ray source. X-ray absorption near edge spectroscopy (XANES) measurements were performed in the total electron yield (TEY) mode at BL-01 at the Indus-2 synchrotron radiation source at RRCAT, Indore [62]. Polarized neutron reflectivity (PNR) measurements were performed at AMOR, SINQ, PSI Switzerland in time of flight mode using Selene optics [63, 64]. During PNR measurements, to saturate the sample magnetically, a magnetic field of 0.5 T was applied parallel to the sample surface.

**RESULTS AND DISCUSSION**

**Phase formation and electronic structure**

XRR patterns of Ni-N thin films deposited at different $R_{\text{N}_2}$ are shown in the fig. 1. The thickness, roughness and density of these films have been extracted from the fitting of the XRR patterns using Parratt32 software [65]. We can see from the XRR patterns that with an increase in $R_{\text{N}_2}$, the critical edges shift towards the lower value (shown by dashed line) which indicates a gradual drop in scattering length density ($X_{\text{std}}$) due to the increased incorporation of nitrogen in Ni films as shown in the inset (a) of fig. 1. From the table. I, a significant reduction in $X_{\text{std}}$ (compared to the pure Ni film) can also be clearly seen. Similar behavior of $X_{\text{std}}$ with $R_{\text{N}_2}$ has also been previously obtained for Co-N films (not shown here) [66]. However, roughness remain nearly constant at about 5 Å. Apart from this, the deposition rates ($D_R$) have been measured using the thickness and the deposition time and shown in the inset (b) of fig. 1. For comparison, the normalized $D_R$ obtained from the Fe-N and Co-N films are also included.

A reduction in $D_R$ with an increase in $R_{\text{N}_2}$ can be seen in Ni-N films similar to that in Fe-N and Co-N obtained using the same sputtering system with similar φ 1-inch Fe and Co targets. Such behavior clearly indicates that some nitride formation is also taking place at target itself. Such compound formation in a reactive sputtering process is generally referred as ‘target poisoning’. However, it is contrary to a previous report which ruled out the possibility of target poisoning during the formation of Ni-N thin films [67]. Here, both Ni-N and Fe-N systems seem to follow a similar variation in $D_R$ with $R_{\text{N}_2}$, whereas the Co-N system shows a rather different behavior. The $D_R$ reduces about 16 to 42% respectively, at $R_{\text{N}_2} = 25$ to 100% compared to the $D_R$ of pure metallic state (i.e. $R_{\text{N}_2} = 0%$; $D_R = 41 \text{ Å/min}$) whereas, it drops at about 42 to 72% for Co-N. In addition, the poisoned state achieve at relatively higher $R_{\text{N}_2}$ in Ni-N and Fe-N system compared to Co-N. On comparing the behavior of $D_R$ in Ni-N, Fe-N system with the Co-N, it is interesting to note that the Co target is more prone to nitride formation at the target.

Using $D_R$ obtained from XRR measurements, a separate set of samples with a thickness of about 100 nm was prepared. The XRD patterns of these samples are
shown in fig. 2. Pure Ni films formed with \( R_{N_2} = 0\% \) exhibit peaks at 44.58 and 51.85° corresponding to fcc Ni (JCPDS No. 040850). On increasing the \( R_{N_2} \) to 5 and 12%, (111) and (200) peaks gradually shift to lower 2\( \theta \) values and also become slightly border, signifying an interstitial incorporation of N atom into fcc Ni lattice and can be assigned as Ni(N). Such behavior is usually achieved in the initial nitride formation of films as previously also seen in the Fe-N, Co-N and Cr-N systems. The incorporation of N into Ni lattice is also evident from the noticeable reduction in the \( D_B \) (inset (a) of fig. 1) and \( X_{std} \) (table. 1). On further increasing the \( R_{N_2} \) to 15%, the structure changes into Ni\(_x\)N phase with preferential orientation of (200) plane. However, the Ni\(_x\)N phase formation remains constant up to \( R_{N_2} = 20\% \) but with a shift towards lower angles in both (111) and (200) peaks, indicates a further expansion in Ni\(_x\)N phase with lattice parameter (LP) about 3.692 ± 0.005 Å. However, the obtained LP is still approximately 1% less than the theoretical value (3.732 Å) [13]. In addition, it may also be noted here that an asymmetry appears on the onset of (200) peak (shown by an arrow in fig. 2) which may be related to deformation in the cubic structure. On further increasing the \( R_{N_2} \) to 25%, the Ni\(_x\)N phase is accompanied by the Ni\(_3\)N phase. Whereas it completely get transforms into N rich phase, identified as hcp Ni\(_3\)N for \( R_{N_2} = 50\% \). Here, a strong reflection at about 44.25° indicates a preferential orientation with the (111) direction normal to the surface. However, a reactively sputtered Ni\(_3\)N film has previously been obtained with preferred orientation along (002) direction. Such differences in the preferred orientation directions can be due to high substrate temperature (475 K) and higher deposition rate (≈ 2.9 Å/sec) than the present work [50]. However, when \( R_{N_2} \) is increased to 75 and 100%, the (111) peak of the hcp Ni\(_3\)N phase gets slightly shifted to lower values along with an additional peak at about 45.5°. The shift in (111) peak indicates a further expansion in Ni\(_3\)N structure while the additional diffraction peak corresponds to the Ni\(_2\)N phase [56, 68]. Such transformation from the single phased Ni\(_3\)N to the mixed phase of Ni\(_2\)N and Ni\(_3\)N is also evident from the obtained density of the films. In table. I, a substantial drop in \( X_{std} \) can be seen when \( R_{N_2} \) is increased from 50 to 75%, indicating more nitrogen incorporation in the film and thus confirms the formation of N richer Ni\(_2\)N phase.

The grain size calculated from the XRD peak width using Scherrer formula is plotted as a function of \( R_{N_2} \), is shown in fig. 3. For the Ni film deposited to \( R_{N_2} = 0\% \), the grain size obtained is about 23 nm. On slightly increasing the \( R_{N_2} \) to 5%, the grain size decreases to about 19 nm. The grain size decreases further on increasing \( R_{N_2} \) and found to be the smallest for \( R_{N_2} = 25\% \). Such variation in grain sizes with \( R_{N_2} \) signifies the formation of nanocrystalline grains due to the formation of the Ni\(_2\)N phase with the smaller grains. However, the grain size increases rapidly on further increasing the \( R_{N_2} \) at 50% which indicates the well-crystalline single
phase Ni$_3$N formation in the films and the grain size increases. However, a further increase in $R_{N_2}$ would cause the degradation of crystalline quality and enhance the formation of the Ni$_2$N phase which is mixed with the Ni$_3$N therefore, the grain size decreased slightly again. A similar variation in grain sizes as a function of $R_{N_2}$ has also been previously obtained in a recent report [36].

XANES measurements were performed at N $K$ and Ni $L_−$ edges of Ni-N samples, shown in fig. 4. For $R_{N_2} = 5\%$, a prominent peak around 398.eV along with some other features can be seen in the N $K$− edge spectra indicating the presence of incorporated nitrogen in Ni-N sample, can be seen in fig. 4 (A). However, the features get more pronounced at $R_{N_2} = 20\%$ due to the enhanced incorporation of nitrogen in sample. Here, the four feature structures around the main peak at energies of 397.eV, 398.5.eV, 400.eV, and 401.2.eV can clearly be seen in the derivative of N $K$− edge spectra, assigned as $a′, a, b'$ and $b$ respectively, shown in the inset of fig. 4 (A). Similar behavior has previously also been probed in the N $K$− edge spectra for Fe$_4$N thin films [69]. By calculating the partial densities of states in Fe$_4$N, the origin of different features present in N $K$− edge spectra has been well explained in term of hybridization between Fe 3$d$ and N 2$p$ orbitals [69]. By comparing the N $K$− edge spectra obtained for Ni-N sample deposited at $R_{N_2} = 20\%$ with those obtained for Fe$_4$N thin film in a work by Ito et. al. [69], the formation of Ni$_4$N phase can also be confirmed which is evident from the XRD results as well. The origin of feature $a′$ can be explained in terms of $π^*$ anti-bonding, and features $a, b'$ and $b$ are explained by $σ^*$ anti-bonding states arises due to dipole transition from the N 1$s$ core-level to the hybridized states of Ni 3$d$ and N 2$p$. For $R_{N_2} ≥ 50\%$, a noticeable change in N $K$− edge XANES spectra appears which may be due to the phase transformation from Ni$_4$N phase to other Ni-N phases. At $R_{N_2} = 50, 75$ and 100%, now the features $a, b$ may be attributed to the $π^*$ anti-bonding formed by hybridization between Ni 3$d_{xy}, 3d_{yz, 3d_{zx}}$, and N 2$p$ orbitals, and the $σ^*$ anti-bonding due to Ni 3$d_{x^2−y^2}$ and N 2$p$ hybridization, respectively. While the feature $c$ and above may attributed to transition from N 1$s$ to hybridized states of Ni 2$p$ and Ni 4$s$ orbitals states.

The Ni $L_−$ edge spectra shows two main peaks at about 852.5 and 870.eV correspond to $L_3$ and $L_2$ edges arises due to well-known spin-orbit interaction, shown in fig. 4 (B). A weak satellite feature around 858.5.eV assigned as $a$ can also be seen which corresponds to hybridization between valence $d$ and unoccupied $sp$ states. A gradual shift in the peak position of $L_3$ edge centroid to higher energy side can be seen with increasing $R_{N_2}$ compared to 5% spectra. Such behavior again signifies the increased oxidation state of Ni in different Ni-N phases. In addition, a small feature appears at about 2.eV above the $L_3$ edge assigned as $β$ in fig. 4 (B) which is prominently present in $R_{N_2} ≥ 75\%$. This feature $β$ has previously been obtained for Ni $+2$ state species and arises due to strong interactions between core holes and 3$d$ orbitals of Ni [70]. In the present study also, we have seen that at $R_{N_2} ≥ 75\%$, a mixed phase of Ni$_2$N and Ni$_3$N is present in the sample and the oxidation state of Ni is 1.5 in Ni$_2$N phase [68]. Therefore, the presence of this feature $β$ and upshift of the $L_3$ edge centroid directly reflects nearly $+2$ chemical valency of Ni in $R_{N_2} ≥ 75\%$ and supports the formation of Ni$_2$N phase as well.

Hence, from XANES results also, it is clear that with the successive increment in the $R_{N_2}$, different Ni-N phases get formed which is well-consistent with our XRD results.

**Magnetization Measurements**

We performed magnetization measurements along out-of-plane direction in the Ni-N samples using SQUID-VSM and magnetooptical Kerr effect (not shown here) measurements. We found the absence of out-of-plane magnetization component in the samples. Therefore, to probe the in-plane magnetization in the Ni-N samples, PNR measurements were carried out as PNR is ideally favorable to determine the nuclear and the averaged in-plane magnetization depth profile of the film. The PNR patterns of Ni-N films are shown in fig. 5. We can see that the splitting between spin-up ($R^+$) and down ($R^−$) reflectivities in PNR patterns are only visible for $R_{N_2} = 0$ and 5% while disappears afterwards. Since, it is known that the splitting between $R^+$ and $R^−$ reflectivity in the PNR pattern clearly indicates the fer-
TABLE I. Parameters, $R_{N_2}$, roughness obtained from XRR, phase identified by XRD, scattering length density ($N_{slid}$) measured from XRR, theoretical $N_{slid}$, nuclear $slid$ ($N_{slid}$) obtained from PNR, theoretical $N_{slid}$ and magnetic moment ($M_s$) of Ni-N thin film samples.

| $R_{N_2}$ (%) | Roughness (Å) | Phase(s) identified | XRR | XRD | $N_{slid}$ Exp. | $N_{slid}$ Theo. | $N_{slid}$ Exp. | $N_{slid}$ Theo. | $M_s$ (µB/Ni) |
|---------------|---------------|---------------------|-----|-----|---------------|---------------|---------------|---------------|-------------|
| 0             | 4             | Ni                  | 6.3×10^{-9} | 0.44×10^{-9} | 9.1×10^{-6} | 9.41×10^{-6} | 0.48          |
| 5             | 5             | Ni(N)              | -          | -          | 9.0×10^{-6} | -          | 0.18          |
| 12            | 5             | Ni$_{4+3}N_1$      | 5.9×10^{-5} | -          | 8.9×10^{-6} | 9.66×10^{-6} | 0             |
| 20            | -             | Ni$_3$N           | -          | -          | 9.1×10^{-6} | -          | 0             |
| 25            | 5             | Ni$_3$N + Ni$_1$N | 5.8×10^{-5} | -          | 9.1×10^{-6} | -          | 0             |
| 50            | 6             | Ni$_3$N           | 5.6×10^{-5} | 5.7×10^{-5} | 9.2×10^{-6} | 1.02×10^{-5} | 0             |
| 75            | 8             | Ni$_3$N + Ni$_2$N | 4.8×10^{-5} | -          | 9.5×10^{-6} | -          | 0             |
| 100           | 7             | Ni$_3$N + Ni$_2$N | 5.2×10^{-5} | 5.52×10^{-5} | 7.0×10^{-6} | 1.03×10^{-5} | 0             |

*For the pure Ni$_2$N phase.

Conclusion

We have successfully synthesized the different phases of the Ni-N system by reactive magnetron sputtering process. The deposition rates and densities of Ni-N films decreases with increasing $R_{N_2}$, indicates the target poisoning behavior and gradual incorporation of N in Ni-N thin films, respectively. Evolution of different Ni-N phases; Ni(N)→Ni$_4$N→Ni$_3$N→Ni$_2$N phases obtained with successively increasing $R_{N_2}$, confirmed by XRD results. The transformation into different Ni-N phases is also reflected in their corresponding grain sizes. The formation of different Ni-N phases with varying $R_{N_2}$ is also further supported by XANES results. PNR measurements reveal the presence of ferromagnetism only in pure Ni ($R_{N_2} = 0$%) and in Ni-N sample deposited at a very smaller value of $R_{N_2} = 5$%, while the Ni-N samples become non-magnetic for $R_{N_2} > 5$%.

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