Structural and magnetic properties of stoichiometric Co$_4$N epitaxial thin films

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In this work, we measured N self-diffusion in the Co-N system and found an unexpected result that N diffuses out almost completely around 500 K, leaving behind fcc Co irrespective of the amount of N used to deposit Co-N. On the other hand, in previous attempts the Co$_4$N phase has always been grown at 550 K or above. In view of our finding, it appears that fcc Co could have been mistaken for Co$_4$N, probably due to the closeness of their lattice parameters (LP; fcc Co = 3.54 Å, Co$_4$N = 3.74 Å). Therefore, Co$_4$N – an interesting material for its high spin-polarization ratio and high magnetic moment remained unexplored. By bringing down the growth temperature, we report the growth of stoichiometric Co$_4$N epitaxial thin films. Films were grown using a direct current reactive magnetron sputtering process on LaAlO$_3$ (LAO mismatch 1.4%) and MgO (mismatch 11.3%) substrates and their structural and magnetic properties were studied. Precise magnetic moment ($M_s$) of Co$_4$N samples were measured using polarized neutron reflectivity and compared with bulk magnetization results. We found that the $M_s$ of Co$_4$N is higher due to a magnetovolume effect. Unlike previous findings, we observed that substrates induce misfit strain and strain inhomogeneity is the cause of modifications in magnetic ensemble such as coercivity, saturation magnetization, and magnetic anisotropy. A consequence of incoherent strain present in our samples is also reflected in the magnetic anisotropy leading to a superposition of strong fourfold and a small fraction of uniaxial magnetic anisotropy. Obtained results are presented and discussed in this work.

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I. INTRODUCTION

Spintronics and high density magnetic memory devices demand a class of materials which primarily exhibit high spin polarization ratio (SPR), high saturation magnetism ($M_s$), low coercivity ($H_c$) etc. at room temperature [1]. In view of this, prominent ferromagnetic materials such as binary or ternary alloys of transition metals and rare earth intermetallic compounds, Heusler alloys, Mn and Cr based alloys [2–8] etc. have been actively pursued by several researchers. In addition, nitrides of 3d magnetic transition metals, binary and ternary rare-earth intermetallic compounds were also substantially investigated and recognized as efficient candidates for magnetic devices [5,9].

In particular, tetra metals nitrides (M$_4$N; M = Fe, Co, Ni, Mn) are a relatively new class of compounds that exhibit superior spintronic properties. They all share a similar type antiperovskite structure (space group; $Pm\bar{3}m$) in which the N atom occupies the central position as shown in Fig. 1. Such insertion of N increases the lattice volume leading to an enhancement in $M_s$ [9,10] and a strong hybridization between N and M atoms results in high SPR [11]. Among M$_4$N, Fe$_4$N is well studied and predicted to have $M_s$ $\approx$ 2.5 $\mu_B$/Fe atom [12], SPR $\approx$ 60% [11,13] and a gigantic value of tunnel magnetoresistance (TMR) ratio $\approx$ 24 000% [14]. Most of these have been verified experimentally in epitaxially grown Fe$_4$N thin films [15–17].

Recent theoretical reports on Co$_4$N predict even promising magnetic properties with SPR increasing to as high as $\approx$90% [13] with $M_s$ ($\approx$1.6 $\mu_B$/Co atom) [18] and TMR ($\approx$1260%) [14]. With low $H_c$ and corrosion resistance, Co$_4$N is poised to be a superior candidate in spintronic devices. Recently, in a theoretical study Meinert et al. studied exchange interactions and did Monte Carlo simulations to calculated the Curie temperature ($T_C$) and found it to be 291 K (Cr$_4$N), 710 K (Mn$_4$N), 668 K (Fe$_4$N), 827 K (Co$_4$N), and 121 K (Ni$_4$N) [10]. As can be seen here among these compounds the $T_C$ is highest in Co$_4$N at 827 K. Such multiple magnetic functionalities of Co$_4$N can harness the research in development of new families of spintronic devices and arise as rivals among promising ferromagnetic materials. However, as even the phase diagram of the Co-N has not been established yet, the recipe for formation of Co$_4$N phase is ambiguous. Due to this, the Co$_4$N has not been explored much experimentally and the available experimental reports are contradicting, e.g., the lattice parameter (LP) of Co$_4$N have been found between 3.59 to 3.52 Å [19–27] while its theoretical value is 3.735 Å [18]. Similarly, the $M_s$ of Co$_4$N was found to vary in a rather large range between 485 to 1300emu/cm$^3$ [20,21,23–28]. Since the LP of fcc Co is about 3.54 Å [18], it appears that Co$_4$N thin films prepared so far might have a significant fraction of fcc Co. Theoretically, it is expected that N at. % tend to decreases monotonically with LP [18,29] and therefore, a correlation can be made between the substrate temperature ($T_s$) used to deposit Co$_4$N and their corresponding measured LP. We find that $T_s$ between 435 to 725 K have been used and it apparently looks that as $T_s$ is raised N diffuses out from

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FIG. 1. Structure of M4N compound with M = Fe, Co, Ni, Mn. The two inequivalent metal sites M(I) and M(II) adopt an antiperovskite structure as M(I)M(II)3N.

the system, leaving behind fcc Co. But this is not unexpected, considering high (theoretical) enthalpy of formation, $\Delta H^f = 0 \pm 2.9$ kJ/mol for Co$_4$N [30,31]. Though the $T_c$ of Co$_4$N is quite high at 827 K, its poor thermal stability is a concern. It can be anticipated that by using suitable dopants, the thermal stability of Co$_4$N can be improved following a similar approach achieved in Fe-X-N [32].

In this work, we studied the N self-diffusion process and used it to grow stoichiometric Co$_4$N epitaxial thin films. We found that the substrate induced misfit strain is an important factor in affecting the structural and magnetic properties of Co$_4$N films. The effect of strain inhomogeneity on magnetic properties especially in terms of their magnetic anisotropy are presented and discussed.

II. EXPERIMENT

Co$_4$N thin films ($\approx$120 nm) were prepared on LaAlO$_3$ and MgO substrates using a direct current magnetron sputtering system (Orion-8, AJA Int. Inc.) at ambient temperature ($\approx$300 K). A Co target (99.95%) ($\phi$ = 1 inch) was sputtered. The partial pressure of nitrogen gas flow ($R_{N_2}$) was fixed at 12%; here $R_{N_2} = p_{N_2}/(p_{Ar} + p_{N_2})$; $p_{Ar}$ and $p_{N_2}$ are gas flow of Ar and N$_2$ gases, respectively. A base pressure of $1 \times 10^{-7}$ Torr was achieved before deposition and the working pressure was maintained at 3 mTorr during deposition. More details about sample preparation can be found elsewhere [33–35].

Deposited samples were characterized for their long range ordering and phase formation by x-ray diffraction (XRD) using a standard x-ray diffractometer (Bruker D8 Advance) having Cu-K$_\alpha$ x-ray source. Reciprocal space mapping (RSM) and Phi scans were performed with high resolution x-ray diffractometer (Bruker D8 Discover). N self-diffusion was measured on a separate sample in which a Co$_{15}$N layer was sandwiched between thick CoN layers. $^{15}$N depth profiles were measured using secondary ion mass spectroscopy (SIMS) in a Hiden Analytical SIMS workstation. A primary O$_2^+$ ions source was used for sputtering with an energy of 5 keV and beam current of 400 nA. The sputtered secondary ions were detected using a quadrupole mass analyzer. Polarized neutron reflectivity (PNR) measurements were performed at AMOR, SINQ, PSI Switzerland in time of flight mode using Selene optics [36,37], which allows us to focus a beam of neutrons so that PNR measurements can be done on smaller samples ($\leqslant 1$ cm$^2$). During PNR measurements, to saturate the sample magnetically, a magnetic field of 0.5 T was applied parallel to the sample surface. Magnetic anisotropy was studied using magneto-optical Kerr effect (MOKE) and Kerr microscopy (Evico Magnetics) equipment.

III. RESULTS AND DISCUSSION

In order to understand the formation of cobalt nitride (Co-N) phases, the knowledge of N self-diffusion process is essential but it has not yet been studied. Self-diffusion process is defined as the atomic diffusion in the absence of any chemical potential gradient. Recently, N self-diffusion was measured in FeN and it was found that the activation energy ($E$) was considerably lower as compared to other transition metal nitrides [38–40]. Adopting a similar approach [38–40], we prepared a sample [Si (sub.)$|$Co$_{40N}$(100 nm)$|$Co$_{15N}$(2 nm)$|$Co$_4$N$_{100N}$(100 nm)] at $T_c = 300$ K. Using SIMS, we measured $^{15}$N depth profiles from this sample as shown in Fig. 2. They were measured for the as-deposited sample and those annealed isochronally in a vacuum furnace at different temperatures (1 h at each temperature). Due to thermal annealing, $^{15}$N profiles get broadened and the width of $^{15}$N peak was used to deduce time average diffusivity $D(t) = (\sigma^2 - \sigma^0_0^2)/2t$ [38,39] where $\sigma_t$ is the standard deviation (before annealing, $t = 0$, and after an annealing time $t$) obtained after fitting $^{15}$N profiles by a single Gaussian function as shown in Fig. 2. Obtained diffusivity ($D$)
of \(N\) has been measured at different temperatures and follows an Arrhenius type behavior given by:

\[
D = D_0 \exp\left(-\frac{E}{k_BT}\right). \tag{1}
\]

Here, \(D_0\) denotes the pre-exponential factor, \(E\) the activation energy, \(T\) annealing temperature, and \(k_B\) is the Boltzmann’s constant.

Using Eq. (1), we get a straight line [as shown in inset (a) of Fig. 2], yielding \(E = 0.5 \pm 0.05 \text{ eV}\). A comparison of N self-diffusion data with other transition metal nitride (TMN) is given in Table I. As compared with other TMN, it can be seen that in CoN, \(E\) is smallest signifying that \(D\) will be fastest. A comparison of \(N\) self-diffusion in FeN [38] and CoN is shown in the inset (b) of Fig. 2. Here, it can be seen that substantial \(N\) diffusion already starts above 450 K, whereas in FeN this happens only above 550 K. In stable nitrides like CrN and TiN, appreciable \(N\) diffusion takes place at much higher temperatures (>1500 K) [41]. As we can see that \(15N\) profile disappears completely at 525 K (Fig. 2) indicating that \(N\) out-diffuses almost completely from CoN. The implication of high \(T_s\) on Co-N phases was also amply demonstrated recently [33]. Here, it was shown that when Co was sputtered with different amounts of \(N_2\) (and even with \(N_2\) alone) at 523 K, the resulting phase obtained was always fcc Co, independent of the amount of \(N_2\) that was used during the deposition [33]. This behavior can also be seen from the XRD, SIMS, x-ray photoelectron, and \(N\) K-edge x-ray absorption spectroscopy [42] results presented in the Supplemental Material [43] and references [44–50] therein.

From Table I, an analogy can be made between \(E\) and enthalpy of formation (\(\Delta H_f\)) for several TMN. Thermally stable compounds like TiN and CrN have high \(E\) and low \(\Delta H_f\). For the CoN phase, \(\Delta H_f \approx 0 \pm 2.9 \text{ kJ mol}^{-1}\) [30,31]. This is quite high as \(\Delta H_f \approx -338, -125, \text{ and } -47 \text{ kJ mol}^{-1}\) for TiN, CrN [51], and FeN [52], respectively. Our experimental results on \(N\) self-diffusion correlate well with theoretical estimates of \(\Delta H_f\) and clearly show that Co-N phases cannot be formed at high \(T_s\). A comparison of \(15N\) depth profiles in FeN and CoN shows that they both look similar and can be fitted to a single Gaussian function even after thermal annealing (Fig. 2). Therefore, \(N\) self-diffusion mechanism in CoN should be conventional volume type, similar to FeN [38]. However, in the case of FeN, an anomalous behavior was observed in Fe self-diffusion and explained in terms of fast grain boundary diffusion of Fe [38]. A similar case might also be applicable in CoN, but as no suitable isotope of Co is available, self-diffusion of Co could not be measured.

The \(N\) self-diffusion process obtained for the Co-N system can now be used to understand the formation of CoN thin films. We find that in previous works the CoN phase was always synthesized at \(T_s \geq 525 \text{ K}\) [20–27]. Comparing the LP of CoN films obtained in those works, we find that the LP was much smaller than the theoretically predicted value of 3.735 Å [18]. For example, Oda et al. found LP \(= 3.59 \text{ Å}\) at \(T_s = 435 \text{ K}\) [19], Silva and Pandey et al. found LP \(= 3.54 \text{ Å}\), at \(T_s = 525 \text{ K}\) [20,33]. In several other studies also, when \(T_s > 525 \text{ K}\), LP remained at 3.54 Å [21,22]. Therefore, it appears that \(N\) diffuses out from Co-N leaving behind fcc Co. The LP of fcc Co is 3.52 Å and the closeness between the LP of CoN and fcc Co has lead to the situation in which the fcc Co phase was mistaken for CoN. To further prove this analogy, we also deposited samples at different \(T_s\) (between 300–400 K) and found that as \(T_s\) increases, LP decreases linearly as shown in the Supplemental Material [43].

Under optimized conditions, epitaxial CoN thin films were grown on LaAlO\(_3\) (LAO) (100) and MgO (100) substrates. They were chosen to understand the role of lattice (mis)matching with CoN. The mismatch between CoN and LAO is about 1.4% and with MgO it is about 11.3%. XRD patterns show that the films are grown in a single CoN phase and highly oriented along the substrate (100) direction, depicted in Fig. 3(a). Out-of-plane LPs come out to be 3.63 and 3.7 Å, for films grown on LAO and MgO substrates, respectively. To further confirm the epitaxial nature of these films, phi scans along the (111) plane are shown in Fig. 3(b).
Occurrence of fourfold equispaced reflections at 90° in both films confirms the cubic symmetry and epitaxial growth. Moreover, peak positions of films are completely overlapping the substrates peaks, confirming that the unit cell of Co4N unambiguously grown as cube-on-cube with LAO and MgO unit cells.

Crystalline quality, strain state etc. were investigated using reciprocal space mapping (RSM) measurements illustrated in Figs. 3(c) and 3(d). RSM collected along asymmetric (111) reflection demonstrated that the maps of Co4N films are far from the pseudomorphic line of the LAO and MgO substrates and corroborate that these films are in a nearly relaxed state with respect to the substrates. Using RSM mapping, we can deduce in-plane LPs. We find that in-plane (out-of-plane) LPs are 3.7(3.63), 3.65(3.7) Å for films deposited on LAO and MgO, respectively. This difference between in-plane and out-of-plane LP can be understood due to tensile strain along the out-of-plane direction for the film grown on LAO and vice versa for the MgO case. Relatively larger lattice mismatch between Co4N and MgO substrate (−11.3%) is expected to cause an in-plane tensile strain. On the contrary, our film showing a small tensile strain along the out-of-plane direction indicates the existence of strain reversal in Co4N film grown on the MgO substrate. In addition, the RSMs of these films show some salient features such as elongation of the map in qX and qZ directions. Such a larger width of the map can be a characteristic of mosaicity and defined in terms of structural parameters such as lateral correlation length (L), microscopic tilt, and twist disorder etc. [53,54]. Out of these L can be estimated using [53]:

\[
L = -\frac{\sin \varphi}{L_3 \cos (\xi + \varphi)}
\]

where, \(\varphi = \tan^{-1}(\frac{q_z}{q_x})\), \(\xi = \tan^{-1}(\frac{\Delta q_x}{\Delta q_z})\), and \(L_3 = \sqrt{\Delta q_x^2 + \Delta q_z^2}\).

By utilizing the values of \(q_x\), \(q_z\) and \(\Delta q_x\), \(\Delta q_z\) from the RSM maps and using Eq. (2), values of L and microscopic tilt (twist) are calculated. L \(\approx 3.3\) for LAO and 1.6 nm for MgO case. Microscopic tilt (twist) disorder was about 0.07(5.3)° and 0.1(9.2)° for film grown on LAO and MgO substrates, respectively. As twist is larger than tilt disorder in both films, it signifies the presence of higher density of edge (as opposed to screw) dislocations in Co4N films. In order to measure the dislocation density accurately, one should draw the Williamson’s Hall plot for each reflection. However, in our case, a close estimation of these dislocation densities (\(\rho_{screw}, \rho_{edge}\)) can be extracted by utilizing the FWHM of (111) and (200) reflections, respectively, and using the following relations considering the random distribution of dislocations [55]:

\[
\rho_{screw(002)} = \frac{\Delta \Omega^2_{4\text{th}}}{4.35|b_{screw}|^2}
\]

\[
\rho_{edge(111)} = \frac{\Delta \Omega^2_{twist}}{4.35|b_{edge}|^2},
\]

where \(\Omega_{4\text{th}}\) is the tile and twist disorder (measured from the FWHM of the rocking curves of symmetric and asymmetric reflections, respectively), \(b_{screw/edge}\) are Burgers vectors of the screw and edge dislocations, respectively.

Using above Eqs. (3) and (4), screw (edge) dislocation densities are estimated about 3.4 × 10^{12} cm^{-2} (6.5 × 10^{13} cm^{-2}) for LAO and 7 × 10^{12} cm^{-2} (2 × 10^{16} cm^{-2}) for MgO grown Co4N films, respectively. Various reports are available on the heteroepitaxial growth of III-V nitride semiconductor films. Mostly, edge type dislocations densities (twist angle) was found to be higher than screw type dislocation (tilt angle). They are typically of the order of 10^{9} cm^{-2} for the screw type dislocation and 10^{11} cm^{-2} for the edge type dislocations [56,57]. Compared to these, our obtained values are much higher: 10^{12} cm^{-2} for the screw and 10^{16} cm^{-2} for the edge dislocations. On the other hand, the L in III-V nitrides is generally found to be two orders of magnitude higher compared to the value obtained in the present case. These higher values of dislocation densities and lower values of L obtained in the present study are not surprising as our films were grown at room temperature while the III-V nitride group films usually deposited at higher temperatures [56,57].

High substrate temperature will result in better crystallinity, whereas deposition at room temperature leads to a mosaic block epitaxial growth. Presence of mosaicity in both films could be due to the fact that at low \(T_s\) (300 K) adatoms would not have sufficient energy to establish the long range ordering to its fullest.

Moreover, difference in the values of L, tilt and twist disorder are subtle in both films (Co4N on LAO and Co4N on MgO). Since L is larger and tilt/twist disorder is smaller for the films grown on LAO than that in MgO, it reflects that lattice (mis)match affects the quality of grown films, as expected. In this scenario, we can clearly see that the Co4N film grown on the MgO substrate has a higher degree of local strain diversity. It is expected that such strain may also affect the magnetic properties and they were investigated using different methods like bulk magnetization, MOKE, and PNR.

From bulk magnetization measurements (shown in Supplemental Material [43]), we found that saturation magnetization (\(M_s\)) of both samples is about \(\approx 1200\text{ emu/cm}^3\) (1 emu/cm³ = 10³ A/m). Comparing the experimental values of \(M_s\) for Co4N films obtained so far in the literature, a large variation can be seen ranging between 485–1300 emu/cm³ [19–21,23–25,28]. As pointed out before, the formation of stoichiometric Co4N phase itself is questionable, the large difference in \(M_s\) can stem from: (i) error in volume measurement of film, (ii) intermixing taking place at the substrate-film interface, (iii) surface oxidation/contamination etc. Among these while (i) may not have a greater influence provided the thickness of film is known accurately, other factors cannot be eliminated when \(M_s\) is estimated by bulk magnetization methods. By using magnetic circular dichroism (MCD), \(M_s\) can be measured accurately [58]. However, even in a MCD measurement, surface contaminations can affect it. On the other hand, polarized neutron reflectivity (PNR) is a technique which can provide the magnetic depth profile in a nondestructive way and therefore \(M_s\) can be measured accurately independent on sample volume etc. In view of this, it is surprising to note that PNR has not been used to measure \(M_s\) in Co4N films.
FIG. 4. Fitted PNR spectra of epitaxial Co$_4$N thin film on LAO and MgO substrates (a). Inset showing the enlarged view of PNR spectra. Respective nuclear SLD (N$_{SLD}$) and magnetic SLD (M$_{SLD}$) of epitaxial Co$_4$N thin films (b).

PNR data of samples grown on LAO and MgO substrates are shown in Fig. 4. Here, the splitting in the reflectivity for spin up ($R^+$) and down ($R^-$) neutrons is a measure of magnetization [59]. We can see that at the critical $q_z$, $R^+$ and $R^-$ can be distinguished clearly for LAO case but not for MgO. This can be understood by comparing the neutron scattering length density (SLD). The SLD of LAO and MgO is $5.4 \times 10^{-6}$ and $6.1 \times 10^{-6} \text{ Å}^{-2}$, whereas that of Co$_4$N (including magnetic SLD) is about $6.2 \times 10^{-6}$ and $0.4 \times 10^{-6} \text{ Å}^{-2}$ for spin up and down neutrons. Since the SLD of substrate exceeds the SLD of Co$_4$N for the spin down case, $R^-$ will be dominated by the substrate. Nearly comparable values of SLD for MgO and spin up SLD of Co$_4$N will result in similar $R^+$ and $R^-$. Still, the differences in $R^+$ and $R^-$ at higher $q_z$ would get influenced by $M_s$ and fitting of PNR data (using GenX software [60]) can be used to get both nuclear and magnetic depth profiles as shown in Fig. 4(b). The nuclear density of the Co$_4$N samples was accurately extracted from the x-ray reflectivity (not shown here) and XRD measurements and used as an input to fit PNR data. From the fitting, we get $M_s = 1.55$ and $1.52(\pm 0.03) \mu_B/\text{Co atom}$ for films on LAO and MgO, excluding the magnetically dead film-substrate interface ($\approx 5$ nm) and surface contaminations ($\approx 3$ nm). On the basis of obtained results, we can conclude that the $M_s$ in Co$_4$N does not get influenced substantially by substrate-film lattice (mis)matching in agreement with previous experimental observations on Fe$_4$N [61] and Co$_4$N [20] films grown on different substrates.

Obtained values of $M_s$ are slightly lower than the theoretical value expected for Co$_4$N. In Co$_4$N, different Co sites (Fig. 1) show different values of magnetic moments. Corner Co(I) atom exhibits an enhanced moment of 1.967 $\mu_B$ and for the face centered Co(II) atoms, it gets reduced to 1.486 $\mu_B$ due to hybridization between Co(II) and N. Therefore, the average magnetic moment will be 1.62 $\mu_B$/Co atom in Co$_4$N (neglecting N moment) [18]. However, in the absence of such enhancement, the magnetic moment of Co(I) site would remain at 1.6 $\mu_B$ as in bulk Co, and the average magnetic moment would then get reduced to about 1.5 $\mu_B$/Co atom. In the present case, we obtained the average magnetic moment of Co at about 1.55 $\mu_B$/Co atom, which is somewhere between the two cases discussed above. Therefore it can be anticipated that indeed there is some enhancement of the magnetic moment at the Co(I) site. However, as the LP of our samples at 3.70 Å is still lower than the theoretical value of 3.74 Å and significant presence of mosaicity (due to absence of substrate heating) may be the cause of such reduction in $M_s$.

To study the effect of epitaxy and strain on the magnetic anisotropy, we did MOKE measurements in longitudinal mode. By varying the angle of applied magnetic field direction with reference to sample surface, M-H loops were measured and are shown representatively for 0 and 40° for the film deposited on LAO and MgO in Figs. 5(a) and 5(c). As can be seen, the coercivity ($H_c$) is much larger in the film deposited on MgO (e.g., at 0°; $H_c \approx 12$ and 130 Oe for films LAO and MgO) and can be understood from the fact that larger local strain diversity would lead to enhanced pinning domains as observed from RSM results discussed above. In addition, the...
shape of M-H loops suggests that two components are present and they can be quantified using [62]:

$$M(H) = \sum_{i} \frac{2Ms}{\pi} \left( \frac{H \pm Hc}{Hc} \right) \tan \left( \frac{\pi S}{2} \right). \quad (5)$$

From the fitting of M-H loops [using Eq. (5)] for the LAO sample, we obtain these magnetic contributions having $Hc \approx 15$ and 40 Oe and their relative fractions amounting to about 90 and 10%. From the polar plot of squareness ($S = M_R/M_s$; here $M_R$ is the remanence magnetization), it can be seen from Figs. 5(b) and 5(b') that the major component demonstrates a fourfold, whereas the minor one, a twofold (uniaxial) magnetic anisotropy (MA). The existence of fourfold MA is expected in the cubic symmetry with easy and hard axes [16]. This can be evidenced in Kerr microscopy images as shown in Fig. 6. Images were captured at points $a (= e)$, $b$, $c$, and $d$ and shown there for an applied field angle of 20°. The 180° magnetization reversal can be clearly seen from the image $a$ to $e$ followed by two consecutive 90° domain wall nucleation in image $b$ and $d$ (shown by arrow) for film grown on the LAO substrate. Overall, from the MOKE measurements we can see that strain clearly affects MA in CoN films. Greater strain diversity arises due to substrate induced misfit strain observed in films grown on MgO (as compared to LAO) results in loss of fourfold MA giving rise to substantial UMA.

IV. CONCLUSION

In conclusion, we performed N self-diffusion measurements in CoN thin films. We found that N out-diffuses almost completely from CoN at 525 K. Detailed analysis of diffusion data suggests that extrapolated N self-diffusion at 300 K in CoN is more than 10 orders of magnitude faster than that in FeN. Therefore, when the CoN phase is grown at $T_s \geq 525$ K, N diffuses-out leaving behind fcc Co. Due to the closeness of LP of CoN and fcc Co, it appears that fcc Co was mistaken for CoN. By reducing the $T_s$ to 300 K, we have grown stoichiometric CoN epitaxial thin films on LAO and MgO substrates. Detailed study of structural and magnetic properties of thus grown CoN films suggests that LAO with smaller lattice mismatching (1.4%) has stronger fourfold magnetic anisotropy. Film grown on MgO with about 11% lattice mismatch shows prominent strain diversity resulting in higher UMA and coercivity. The effect of surface contaminations and the interaction between film-substrate interface were quantified by measuring magnetic depth profile using PNR. We found that the magnitude of magnetization does not seem to be greatly affected by lattice mismatching.

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