Phase formation, thermal stability and magnetic moment of cobalt nitride thin films

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Cobalt nitride (Co-N) thin films prepared using a reactive magnetron sputtering process by varying the relative nitrogen gas flow ($R_N$) are studied in this work. As $R_N$ increases, Co(N), Co$_3$N, Co$_2$N and CoN phases are formed. An incremental increase in $R_N$, after emergence of Co$_3$N phase at $R_N=10\%$, results in a continuous expansion in the lattice constant ($a$) of Co$_3$N. For $R_N=30\%$, $a$ maximizes and becomes comparable to its theoretical value. An expansion in $a$ of Co$_3$N, results in an enhancement of magnetic moment, to the extent that it becomes even larger than pure Co. Though such higher (than pure metal) magnetic moment for Fe$_3$N thin films have been theoretically predicted and evidenced experimentally, higher (than pure Co) magnetic moment are evidenced in this work and explained in terms of large-volume high-moment model for tetra metal nitrides.

Nitrides of 3d magnetic transition metals (TM=Cr, Mn, Fe, Co, Ni) are an interesting class of materials for applications in magnetic devices. With inclusion N atoms ($\sim 10-20\, \text{at.}\%$), TM become chemically inert and since they preserve the metallic character of the host metal, their structural and magnetic properties are superior. For example, a higher-than-Fe magnetic moment for iron nitrides ($\alpha''-\text{Fe}_1\text{N}$ [1] and Fe$_3$N [2, 3]), has been the driving force for the intense research work in this system. [4, 5] Specially, in case of tetra TM nitrides (TM$_4$N), such enhanced magnetic moment is caused by a volume expansion (compared to a hypothetical $fcc$ metal). [6] All TM$_4$N share a common $fcc$ structure, in which metal atoms are arranged in the $fcc$ positions and N atoms occupy the body centered positions. Such incorporation of N atoms results in an expansion of the $fcc$ lattice. [7]

Compared to the Fe-N system, the Co-N system has been relatively less explored. [8-16] Recent theoretical calculations predicted that the spin polarization ratio for Co$_3$N is even higher than that of Fe$_3$N. [17] This has lead to somewhat renowned interests in the Co-N system both theoretically and experimentally. [18-24] Though theoretical studies predict that under large-volume high-moment approach, the magnetic moment of Co$_4$N can be larger than Co, [7] experimental results always find a value much smaller than pure Co, for Co$_3$N thin films. [18] In this Letter we report more than Co magnetic moment for Co$_3$N thin films.

Co$_3$N thin film samples (200 nm thick) were deposited on glass substrate at room temperature using a direct current magnetron sputtering (dcMS) process operating at constant power of 50 W. A Co(purity 99.95\%) target (75 mm diameter) was sputtered using a mixture of N$_2$(99.9995\%) and Ar(99.9995\%) gases. Relative nitrogen gas flow defined as $R_N=\frac{p_{N_2}}{(p_{N_2}+p_{Ar})}\times100$ (where $p_{N_2}$ is N$_2$ and $p_{Ar}$ is Ar gas flow), was varied at 0, 5, 10, 20, 30, 50, 75 and 100\%. The total gas flow was fixed at 10 sccm. With a base pressure of $1\times10^{-7}$ mbar, the pressure during deposition was about $3\times10^{-3}$ mbar. The dcMS system was suitably modified to deposit all samples sequentially on a 25 cm long substrate kept at a distance of 7 cm from the target. The magnetron source was masked with a 10 mm wide slit. After the deposition for a $R_N$, substrate was moved linearly for deposition of next sample. X-ray reflectivity (XRR) and diffraction (XRD) measurements were carried out using laboratory x-ray systems equipped with a Cu k-\alpha x-rays. Thermal stability was studied after successive thermal annealing and XRD measurements.

XRR patterns of Co-N thin films deposited for various $R_N$ are shown in fig. 1(a), they were fitted using Parratt’s formulism. [25] Though total thickness oscillations could not be seen in XRR pattern due to large thickness, still a vital information about the film density is obtained, which decreases gradually as $R_N$ is increased. Obtained values of scattering length densities are plotted in fig. 1(b). Roughness of film surface was typically about 1.3-1.5 nm.

XRD pattern of samples deposited for different $R_N$ are shown in fig. 2. For $R_N=0\%$, pure Co $hcp$ phase is observed however a faint peak at 20=51.4 degree corresponding to $fcc$ (200) reflection can also be seen. Co is known to stabilize in $hcp$ phase below 690 K and above it, in $fcc$ phase. [26, 27] However, co-existence of both phases in thin films is also seen.[28, 29] For the sample prepared at $R_N=5\%$, the structure remains similar to 0\% sample, but peak widths become broader due to interstitial incorporation of N atoms. [30] As $R_N$ increases to 10\%, the structure changes and reflection corresponding to Co$_4$N(200) can be seen. A rather broad tail on the onset of this peak, is due to Co$_4$N(111) (discussed later). An increase in $R_N$ for 20 and 30\%, leads to shift in this peak towards lower angles indicating an expansion in $a$ of Co$_4$N(see table I). For $R_N=50\%$, the phase identified is $hcp$ Co$_3$N and for $R_N=75\%$, the structure changes again to $fcc$ cobalt mononitride(CoN). For $R_N=100\%$, Co$_3$N(200) peak gets broadened due to nanocrystallization. [30] To correlate N at.\% with the structure of samples, secondary ion mass spectroscopy measurements

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were performed. Using a procedure adopted for Fe-N thin films, we find N at.% for R_{N_2}=30 and 100% samples is 20±3 and 50±4, respectively, which is expected for Co_{4}N and CoN structures. Grain sizes and a obtained from the most intense peak in XRD pattern are given in table I.

| R_{N_2} (%) | crystal structure | grain size(nm) | a (nm) | magnetic moment(µB) |
|-------------|------------------|----------------|--------|-------------------|
| 0           | hcp + fcc        | 33             | 0.407  | 1.7               |
| 5           | hcp + fcc        | 22             | 0.406  | 1.6               |
| 10          | fcc              | 6              | 0.358  | 1.6               |
| 20          | fcc              | 9              | 0.362  | 1.75              |
| 30          | fcc              | 7              | 0.370  | 1.85              |
| 50          | hcp              | 7              | 0.431  | 1.5               |
| 75          | fcc              | 19             | 0.418  | 0                 |
| 100         | fcc              | 10             | 0.423  | 0                 |

To resolve the structure and to study the thermal stability, annealing of selected samples deposited for R_{N_2}=20, 30, 50 and 100% was carried out. Samples were annealed in a vacuum furnace (pressure 1×10^{-6} mbar) for about 1 hour and XRD measurements were carried out after each annealing as shown in figure 3(a)-(d), for R_{N_2}=20,30,50 and 100%, respectively. For R_{N_2}=20 and 30%, XRD pattern are identical to pristine state up to 423 K. Above it, there are notable changes: (i) the peak corresponding to (200) reflection of Co_{4}N shifts towards higher angles (ii) a new peak corresponding to Co_{4}N (111) starts to emerge. The peak shift upon annealing is more for R_{N_2}=30% sample and the intensity of (111) reflection is also more prominent in this case. The peak shift towards higher angle is a clear signature of contraction in a. The value of a remains constant at 0.370 nm up to 423 K and at 573 K it becomes 0.356 nm for R_{N_2}=30% sample. On the other hand, the sample deposited at R_{N_2}=50%, show very little changes with annealing temperature, only peak width decreases, signifying grain growth with annealing. For R_{N_2}=100% sample, we find that the structure is stable only up to 423 K and at 473 K, the broad peak observed for the pristine sample, splits into two peaks, one corresponding to CoN(200) and other to Co_{4}N(111). Further annealing at 573 K results in formation of pure Co hcp phase.

The XRD measurements carried out in the pristine and annealed samples provide an insight about the phase formation the thermal stability of samples. Broadly, observed behavior is in line with those reported by Fang et al.
The magnetic potential for such kind of interaction is given by [16]

\[ a(x) = a_A (1 - x) + a_B x + C \mu, \]

where \( x \) is the atomic fraction, \( a_A, a_B \) and \( C \) are parameters. For precise measurement of \( \mu \), polarized neutron reflectivity (PNR) is a well-known technique. Unlike bulk magnetization techniques, it is independent of substrate magnetization and sample mass. [33] It is surprising to note that PNR has not yet been used for quantification of \( \mu \) in Co-N thin films. Neutrons being spin ½ particles have two states of quantization, parallel (+) or antiparallel (−) to applied external field (\( H \)). Neutrons interact with the magnetic field generated by unpaired spins on an atomic magnet via dipolar interaction. The magnetic potential for such kind of interaction is given by [34] \( V_m = -\mu_m \cdot \mathbf{B} \). Where magnetic induction \( \mathbf{B} = H + 4\pi M \), \( \mu_n \) is neutron magnetic moment and \( \mathbf{M} \) is sample magnetization. We did PNR measurements at Narziss neutron reflectometer at SINQ/PSI, Switzerland. During measurements a magnetic field of about 0.2 Tesla was applied (parallel to sample surface) to saturate them magnetically. Measured PNR for spin-up (\( R^+ \)) and spin-down (\( R^- \)) can be directly used for the two spin states of neutron using spin asymmetry (\( SA \)), given by: [33]

\[ SA = (R^+ - R^-)/(R^+ + R^-). \]

PNR pattern and \( SA \) for samples prepared using different \( R_{N_2} \) are shown in fig. 4 (a) and (b), respectively.

Since \( SA \) is a directly proportional to \( \mu \), it can be compared to see the relative changes as \( R_{N_2} \) increases. Compared to \( R_{N_2} = 0\% \) sample, \( SA \) decreases marginally for \( R_{N_2} = 5 \) and 10% samples. However for \( R_{N_2} = 20 \) and 30% samples, \( SA \) takes an upturn and its maximum shifts towards lower \( q_z \). While the shift to lower \( q_z \) is due to overall reduction in film density, an increase in the maximum value of \( SA \) is a direct measure of enhanced \( \mu \) as compared to pure Co films. When \( R_{N_2} \) is increased to 50%, the maxima in the \( SA \) drops-off rapidly and for \( R_{N_2} = 75\% \), \( R^+ = R^- \) and \( SA \sim 0 \), indicating that the sample has become non-ferromagnetic. For \( R_{N_2} = 100\% \), results (not shown) are similar to \( R_{N_2} = 75\% \) case.

To get qualitative information of \( \mu \), PNR pattern were fitted using SimulReflect software [35] and density of films obtained from XRR measurements was taken as a input. Obtained values of \( \mu \) are given in table I. It can be seen as \( R_{N_2} \) is increases, first \( \mu \) decreases and than it increases for \( R_{N_2} = 20 \) and 30% samples. For \( R_{N_2} = 50\% \), it decreases again and finally becomes zero for samples prepared at \( R_{N_2} = 75 \) and 100%. From eq.1, it is expected as \( a \) increases, \( \mu \) should increase. Although such enhancement is theoretically predicted [6, 7, 15], it is evidenced experimentally in this work for Co-N thin films.

It may be noted that the experimentally obtained values of \( a \) for Co-N are typically 0.357 nm [9, 19, 21], much smaller than the theoretically predicted value at 0.373 nm [7]. While for pure Co (fcc), \( a = 0.354 \). We find that for \( a = 0.358 \)nm (\( R_{N_2} = 10\% \) sample), the value of \( \mu \) is lower than that of pure Co, as observed in other studies. However, for \( R_{N_2} = 30\% \), \( a = 0.370 \)nm and in this condition, it is expected that \( \mu \) of Co in Co-N should be larger than that of pure Co. Here it is interesting to note that in most of the studies, Co-N films have always been deposited at elevated temperature between 433-723 K. Calculational prediction that the heat of formation (\( \Delta H_f \)) for Co-N system are even larger than that of Fe-N system [36]). In this situation, when deposited at elevated temperature, nitrogen deficient Co-N films are obtained characterized by smaller than theoretical values of \( a \). When deposited at room temperature, nitrogen incorporation within Co-N can be maximized leading to enhanced the magnetic moment as observed in our samples.

In conclusion we studied the phase formation, thermal stability and magnetization of Co-N thin films prepared using dcMS at room temperature. We find that Co-Co,N,Co-N and Co phases are formed as \( R_{N_2} \) increases. While Co-N and Co phases are stable only up to about 423 K, Co,Co,N phase is more stable. More remarkable results are obtained for Co,N films. As Co,N phase is formed, an incremental increase in \( R_{N_2} \) results in an expansion of lattice constant, which in turn results in an enhanced Co magnetic moment in Co,N phase.

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