Structure and Magnetization of Co$_4$N Thin Film

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Abstract

In this work, we studied the local structure and the magnetization of Co$_4$N thin films deposited by a reactive dc magnetron sputtering process. The interstitial incorporation of N atoms in a fcc Co lattice is expected to expand the structure and such expansion yields interesting magnetic properties characterized by a larger than Co magnetic moment and a very high value of spin polarization ratio in Co$_4$N. By optimizing the growth conditions, we prepared Co$_4$N film having lattice parameter close to its theoretically predicted value. The N concentration was measured using secondary ion mass spectroscopy. Detailed magnetization measurements using bulk magnetization method and polarized neutron reflectivity confirm that the magnetic moment of Co in Co$_4$N is higher than that of Co.

Keywords: Co$_4$N thin films, reactive sputtering, Magnetization

1. Introduction

Transition metal nitrides (TMN) are an interesting class of compounds as N incorporation in metals make them less corrosive and results in interesting properties such as superhardness [1, 2, 3, 4], superconductivity [5], corrosion and wear resistance [6, 7]. In particular, tetra metal nitrides M$_4$N$_4$ generally formed only for late 3d TM (e.g. Fe, Co, Ni) [8] are somewhat unique in the sense that they share a common fcc structure. Due to a dominant metal-metal interactions in M$_4$N$_4$ they possess metal-like character (unlike metal oxides) [9]. In a metal fcc cage, the incorporation of N atoms at the interstitial positions, results in an expansion of the unit cell, which in turn affects the magnetic integrations [10, 11, 12, 13, 14]. Generally incorporation of a non-magnetic element in a magnetic one is expected to result in a loss of magnetic moment ($M$) explained by the well-known Slater-Pauling curve [9]. However, theoretical calculations predict $M$ to be larger for Fe$_x$N and Co$_4$N compounds. This is an interesting proposition as with larger than metal $M$, corrosion resistance and a metal-like character can make M$_4$N$_4$ compounds an alternative their pure metal counterparts. In addition, some recent theoretical predicted a very spin polarization ratio (SPR) for M$_4$N$_4$ compounds [10, 11]. Among them Co$_4$N is predicted to have SPR ~ 90% [11] which is among the highest values for any compound.

However experimental results obtained so far for Co$_4$N compounds does not seem to be as exciting as theoretical calculations. This can be understood from the fact that the value of $M$ found in most of the experimental works so far is perpetually less than that of pure Co. A closer look at the Co$_4$N thin films reveal that the values of lattice parameter (LP) obtained in most of the experimental works is typically 3.54 Å [15, 16, 17, 18, 19, 20, 21]. This is more close to theoretical values LP for fcc Co at 3.54 Å than that of Co$_4$N at 3.72 Å [10, 11]. Such a discrepancy in the experimental and theoretical values of LP for Co$_4$N requires attention. While investigating the recipes adopted for formation of Co$_4$N thin films, we found that Co$_4$N films were often deposited at substrate temperatures (T$_s$) similar to those used for Fe$_x$N thin films. This is convenient approach due to similarity between the Fe$_x$N and Co$_4$N and the absence of a phase diagram for the system Co-N, intuitively makes one to follow paths adopted for preparation of Fe$_x$N.

However, the energetics of nitride formation for Fe$_x$N and Co$_4$N immediately indicates about the complexity for the later. Theoretical values of enthalpy of formation (Δ$H_f$) for Fe$_x$N is about -12 kJ mol$^{-1}$ [22], whereas those for Co$_4$N are slightly above or below 0 for hcp Co or fcc Co [11]. This also implies that at a higher T$_s$, Co$_4$N system will be less stable as compared to Fe$_x$N. In a recent work, we studied the phase formation process in the Co-N system at T$_s$ = 300 K [23] and 523 K [24]. We found that at T$_s$ = 523 K, N incorporation in the Co-N system is minimal and the phases formed are similar to a fcc Co having LP~3.52 Å. On the other hand when T$_s$ is lowered to 300 K Co$_4$N depicts a similar type of phase formation sequence as found for the Fe-N system [25, 26]. By optimizing the deposition
conditions, Co$_3$N film having LP as high as 3.68 Å can be deposited and the value of $M$ also supersedes that of Co. Since the Co$_3$N films deposited without any intentional heating are expected to have a large fraction of disorder, estimation of LP with x-ray diffraction alone may not be decisive, therefore in the present work, we investigate the local structure and $M$ of the Co$_3$N thin film deposited at $T_s = 300$ K using x-ray absorption based techniques. By doing measurements at Co K and L-edges and at N K-edge, we get valuable information about the local structure. In addition, by doing polarizer neutron reflectivity (PNR) measurements at low temperatures (∼20 K) we determined the value of $M$ for Co$_3$N thin film. Obtained results are presented and discussed in this work.

2. Experimental

We deposited Co$_3$N thin film with a nominal thickness of 120 nm at $T_s = 300$ K (without intentional heating) using a reactive direct current magnetron sputtering (dcMS) system (Orion-8, AJA Int. Inc.). A one inch diameter and 0.5 mm thick pure Co (purity 99.95%) target was sputtered using a gas mixture of Ar and N$_2$ (both 99.9995% pure) gases. With a base pressure of $1 \times 10^{-7}$ Torr, the pressure during deposition was about 3 mTorr. More details about deposition process can be found in [23]. Along with the Co$_3$N sample, we also deposited a pure Co thin film under identical conditions as a reference.

To investigate the local and electronic structure, x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure measurements (EXAFS) were performed in the total electron yield (TEY) and fluorescence mode at BL-01 [27] and BL-09 beamlines, respectively at the Indus-2 synchrotron radiation source at RRCAT, Indore. The measurements in TEY mode at BL-01 were carried out in a UHV chamber with a base pressure of $(2 \times 10^{-10})$ Torr. To avoid surface contaminations, samples were cleaned in situ using a Ar$^+$ source kept incident at an angle of 45°. The measurement in fluorescence mode at BL-09 were carried out at ambient conditions.

The composition of Co$_3$N thin film was measured using secondary ion mass spectroscopy (SIMS) depth profiling using a Hiden Analytical SIMS workstation. An oxygen ion beam of energy 4 keV and 200 nA was used as a primary source and the sputtered species were detected using a quadrupole mass analyzer. The SIMS depth profiles were compared with a reference sample as described in [23]. The magnetization measurements were carried out using a Quantum Design SQUID-VSM (S-VSM) magnetometer at room temperature. We did PNR measurements at AMOR reflectometer [28] in the time of flight mode at SINQ-PSI Switzerland. To saturate the sample magnetically, a magnetic field of 0.5 T was applied during the PNR measurements. The measurements at low temperature were carried out using a closed cycle refrigerator installed inside the electro magnet.

Figure 1: (Color online) SIMS depth profiles of Co and Co$_3$N thin films samples.

![Figure 1](image1.png)

Figure 2: (Color online) Normalized Co K-edge XANES spectra of Co$_3$N and Co foil samples (a). Fitted $k^2$ weighted spectra for Co$_3$N and a Co samples (b).

3. Results and Discussion

To quantify the N at.% in our samples, we did SIMS depth profiling measurements. The SIMS depth profiles for the Co$_3$N sample are shown in fig. I along with a Co reference sample. The depth profiles clearly reveal that N concentration in the Co$_3$N sample is more and the Co concentration is less as compared to Co sample. Following a procedure described in ref. [23] and measuring a reference sample with known concentration, we found that N at.% comes out to be $\sim 18(\pm 2)$ at.% indicating formation of Co$_3$N phase.

X-ray diffraction measurements (not shown) carried out in our samples resulted in similar patterns as observed in an earlier work [23]. Since samples are deposited without any intentional heating, the long range structure is expected to somewhat disordered and more reliable information about the structure can be obtained from a local probe like x-ray absorption spec-

Figure 3: (Color online) XAS spectra of Co$_3$N and Co thin film at Co-L-edge (a) at N K-edge (b). The inset in (b) shows the derivative of N K-edge in Co$_3$N.
weighted EXAFS data for Co$\text{$_2$}$ EXAFS measurements. Fig. 2(b) shows the modulldie of $k$ for the Co$\text{$_4$}$ results obtained from XAS measurements provide a strong evidence for enhanced transitions from N 1s to hybridized states of face centered Co 3d and N 2p orbitals through $\sigma^*$ anti-bonding and an enhancement in density of states in Co$\text{$_2$}$N as compared to Co. Such effects are even more pronounced at Co L-edges as shown in fig. 3(a). Here presence of N in Co$\text{$_2$}$N thin film can also be confirmed by comparing the N K-edge spectrum of Co$\text{$_2$}$N with that of a Co reference sample as shown in fig. 3(b). The features in N K-edge spectra are labelled as A, B, C and D. Here the feature A is attributed to a dipole transition from N 1s to hybridized states of face centered Co 3d and N 2p orbitals through $\pi^*$ anti-bonding. Features B and C represents the dipole transition from N 1s to hybridized states of face centered Co 3d and N 2p orbitals through $\sigma^*$ anti-bonding in Co$\text{$_2$}$N thin films. We find that LP and the $M$ values of $M$ obtained in most of the works were closer to pure Co. To measure $M$ in our samples we did bulk magnetization and PNR measurements. Inset of fig. 4 shows M-H loop measured using S-VSM at room temperature for a Co$\text{$_2$}$N thin film. We find that $M = 1195\textrm{ emu/cc}$ which approximately corresponds 1.6$\mu_B$ per Co atom, which is slightly lower than the theoretically predicted value of $M$ for pure Co. Exact determination of $M$ from bulk magnetization measurements in a thin film sample require precise values of sample volume and density. While the former can be measured with a great accuracy, estimation of later is not easy due to relatively large fraction of defects etc. in thin films. In addition diamagnetism of substrate always interferes with sample magnetization.

It is well-known that in a PNR measurement, absolute value of $M$ can be measured as in PNR technique, measurement of $M$ is not influenced by sample volume and substrate magnetism. On the other hand density of the film is inherently measured in PNR. In this context it is surprising to note that PNR has not
been used to measure $M$ in Co$_3$N thin films. In most of the works available so far, $M$ was measured using bulk magnetization methods and there seems to be a large variations in estimation of $M$ for Co$_3$N thin films ranging from 1.3 to 1.6$p$/$atom.

We performed PNR measurement at room temperature and at 17 K (to minimize thermal fluctuations) under an applied magnetic field of 0.5 T, which is sufficient to saturate sample magnetically (see inset of [3]). The spin-up down reflectivities clearly show a separation typically expected for a ferromagnetic sample. The fitting of PNR patterns was carried out using SimulRelec programme [31] and the obtained values of $M$ are 1.73$\pm$0.05$p$/$atom at 300 K and 1.75$\pm$0.05$p$/$atom at 17 K. This clearly shows that $M$ is larger than Co in Co$_3$N thin film. Though such enhancement in $M$ was theoretically predicted, it has been unambiguously demonstrated in this work.

4. Conclusion

In conclusion, by measuring the local structure and a we found that LP of Co$_3$N thin films far exceeds that of previous works and is more closer to its theoretical value. For Co$_3$N thin films an enhancement in $M$ was expected. By doing precise magnetization measurements using PNR we found enhancement in the Co magnetic moment. In addition, our SIMS depth profile measurements clearly reveal the formation of Co$_3$N phase and N K-edge measurements further confirms the formation of Co$_3$N phase.

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