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Study of magnetic iron nitride thin films deposited by high power impulse magnetron sputtering

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ABSTRACT

In this work, we studied phase formation, structural and magnetic properties of iron-nitride (Fe-N) thin films deposited using high power impulse magnetron sputtering (HiPIMS) and direct current magnetron sputtering (dc-MS) techniques. The nitrogen partial pressure during deposition was systematically varied both in HiPIMS and dc-MS processes. Resulting Fe-N films were characterized for their microstructure, magnetic properties and nitrogen concentration. We found that HiPIMS deposited Fe-N thin films show improved soft magnetic properties and likely to possess globular nanocrystalline microstructure. In addition, it was found that the nitrogen reactivity with Fe get suppressed in HiPIMS discharge as compared to that in dc-MS plasma. Obtained results can be understood in terms of distinct plasma properties of HiPIMS discharge.

1. Introduction

HiPIMS is a recently developed technique for the deposition of thin films. Unique plasma conditions associated with it, makes it a preferred choice over conventional deposition methods [1–4]. As compared to dc-MS technique, the plasma density in HiPIMS discharge is of the order of $10^{19}\ \mathrm{m}^{-3}$, about 2 orders of magnitude larger than that in dc-MS plasma [2]. In this technique a high power pulse is applied to a magnetron target at low duty cycle (between 0.1 and 1%) that produces a highly dense plasma. In such kind of situation it was observed that the number of sputtered ionized species exceeds neutrals. The volume fraction of ionized species depends on various process parameters such as pulse duration, gas pressure, and peak current [2,5]. These characteristic properties of HiPIMS plasma result in improving film qualities such as film density, hardness, surface roughness, better adhesion, and dense microstructure. Moreover, due to high metal ionization in HiPIMS process, it is expected that thin films deposited via reactive sputtering would display superior properties. As such HiPIMS technique has been frequently utilized for the deposition of metal nitrides such as Al-N [6], Cr-N [7–9], Ti-N [10], and Nb-N [11] and metal oxide thin films such as TiO_2 [12,13], Al_2O_3 [14,15], ZnO [16], ZrO_2 [17], and Fe_2O_3 [18,19]. In these studies, it was observed that properties of films deposited using reactive HiPIMS process are superior. Konstantindis et al. found that the formation of rutile phase in TiO_2 thin film is more favorable as compared to anatase phase when sputtered using HiPIMS technique. Moreover, HiPIMS deposited films show higher refractive index [13]. Ehiasarian et al. observed that pretreatment using HiPIMS process has improved the adhesion and mechanical properties of CrN thin films [20,21]. Similarly, Reinhard et al. observed improvement in corrosion resistance properties of HiPIMS treated CrN/NbN superlattice structure [11]. Recently, Zhao et al. observed that the optical transmittance of Zirconia thin films deposited using HiPIMS process is more as compared to dc-MS process [17].

Looking at the vast capabilities of HiPIMS technique in depositing various kinds of thin films, it is surprising to note that HiPIMS process has not yet been applied for the deposition of magnetic thin films. Very recently, HiPIMS process has been employed to deposit Fe_2O_3 [18,19] and FeCuNbSiB thin films [22]. Still magnetic nitride films have not yet been studied with HiPIMS technique. It is well known that transition metal magnetic nitrides are an important class of materials for their usage in various technological applications [23,24]. Therefore, it will be immensely useful to study magnetic nitride films deposited using HiPIMS technique.

It is well known that Fe-N compounds are interesting both from the basic and applied point of view. These compounds have a wide range of usage, such as in tribological coatings, magnetic read–write heads, and memory devices [25–27]. In the present work we deposited a series of Fe-N films using HiPIMS technique and compared them with films deposited using dc-MS technique. The structure (local and long range), growth and magnetic properties of the deposited thin films were investigated using various characterization techniques. We found that HiPIMS deposited Fe-N films show improved soft magnetic properties and likely to have a globular nanocrystalline microstructure. In addition, it was found that nitrogen reactivity with Fe get suppressed in HiPIMS process as compared to that in dc-MS process. The obtained

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Table 1
Deposition parameters for samples prepared using HiPIMS and dc-MS techniques. Here V_{av} is average voltage density (Vcm^{-2}), I_{av} is average current density (Acm^{-2}), P_{av} is average power density (Wcm^{-2}), V_p is peak voltage density (Vcm^{-2}), I_p is peak current density (Acm^{-2}), P_p is peak power density (Wcm^{-2}), ν is pulse frequency (Hz) and pulse duration is in (μs).

Process	V_{av}	I_{av}	P_{av}	V_p	I_p	P_p	Pulse	ν
HiPIMS	–	–	6.8	15.9	1.1	750	150	60
dc-MS	7.2	0.007	2.3	–	–	–	–	–

results are presented and discussed in terms of plasma properties of HiPIMS discharge.

2. Experimental details

Fe-N thin films were deposited using HiPIMS and dc-MS techniques on Si(100) and float glass substrates using a AJA Int. Inc. make ATC Orion-8 series sputtering system. Pure Fe (purity 99.995%) target (diameter 75 mm, thickness 1 mm) was sputtered using a mixture of Ar and N_2 gases. Total gas flow was kept constant at 50 sccm and the relative partial pressure of nitrogen defined as $R_{N_2} = P_{N_2} \times 100\%/[P_{N_2} + P_{Ar}]$, (where P_{N_2} and P_{Ar} is nitrogen and argon gas flow) was kept at 0, 2, 5, 10, 20, 30, 40 and 50. Before deposition a base pressure of 2×10^{-6} Pa was achieved. During the deposition pressure was kept constant at 0.4 Pa using a dynamic throttling valve and substrate temperature was kept at 423 K. A substrate to target distance of 15 cm was kept fixed during all deposition sequences. Deposition parameters used in dc-MS and HiPIMS processes are listed in Table 1. To get nearly similar deposition rate average power in HiPIMS process was kept higher as compared to dc-MS process. For dc-MS process AJA DCXS 1500 power supply was used, whereas for HiPIMS process a Hüttinger Electronic TruPlasma Highpulse 4002 generator was used. Typical thickness of deposited films was about 80–100 nm. It is well know that the sputtering of a magnetic material using a magnetron source is rather difficult due to shunting of magnetic field lines of magnetron magnets by magnetic target. Therefore, magnetron source used in this work was specially configured for sputtering of Fe targets as shown in Fig. 1(a). The magnetic field strength of magnets in outer ring was about 4 kG with that of central magnet was about 2 kG. Fig. 1(b) shows a sketch of magnetic field lines from the magnetron source configured in un-balanced mode for sputtering of magnetic targets [28].

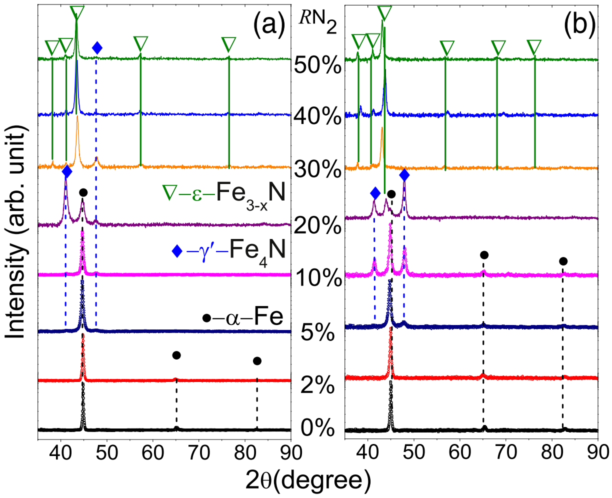

Fig. 2. X-ray diffraction patterns of Fe-N thin films prepared at varying R_{N_2} using HiPIMS(a) and dc-MS(b) techniques.

Structural characterizations of the samples were carried out with X-ray diffraction (XRD) using a standard X-ray diffractometer (Bruker D8 Advance) equipped with Cu *K-α* X-rays source in *θ–2θ* geometry. Surface morphology was obtained using atomic force microscopy (AFM) using a Digital Instruments make Nanoscope E AFM system with a Si_3N_4 cantilever. Magnetic properties were studied using a Quantum Design make superconducting quantum interference device-vibrating sample magnetometer (S-VSM) and polarized neutron reflectivity (PNR). PNR measurements were performed at Dhruva Reactor of Bhaba Atomic Research Center, Mumbai [29]. A magnetic field of strength 2000 Oe was applied along the films plane to saturate samples magnetically. The local structure of nitrogen atoms was studied using soft X-ray absorption spectroscopy (SXAS) at BL-1 beamline of Indus-2 synchrotron radiation source at RRCAT, Indore [30]. SXAS measurements were performed in an UHV chamber in total electron yield (TEY) mode. For accurate measurements of nitrogen concentration, ^{14}N depth profiles were measured using secondary ion mass spectroscopy (SIMS) technique (Hiden Analytical SIMS Workstation). For sputtering, O_2^+ primary ions were used with 5 keV energy and 400 nA beam current. SIMS measurements were performed in an UHV chamber with a base pressure of the order of 8×10^{-8} Pa and during measurements the chamber pressure was 8×10^{-6} Pa. In SIMS measurements quantification of N concentration was performed using well characterize reference samples: α-Fe(N) and ε-$Fe_{2.23}N$ with known nitrogen concentration as 11 at.% [24] and 30 at.% [31], respectively.

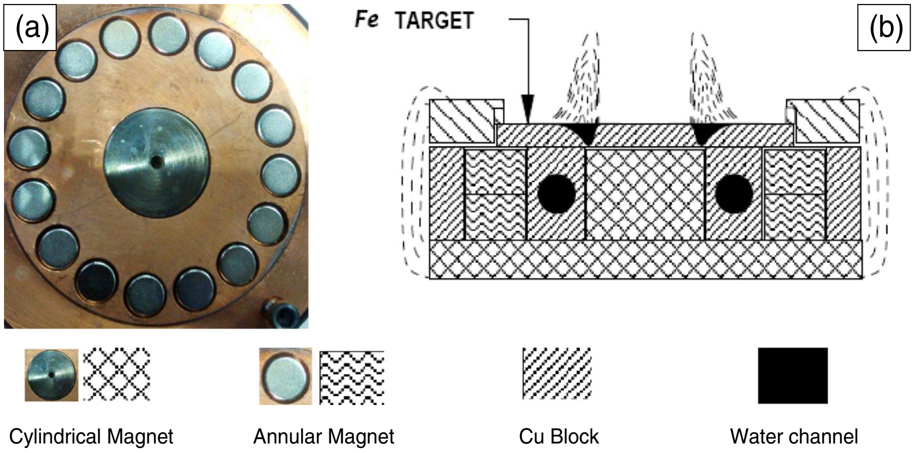

Fig. 1. A photograph of the magnetron source (AJA International Inc.) showing distribution of magnets (a) and a typical sketch of magnetic lines of force from a magnetron source configured for sputtering of magnetic targets (b).

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