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Scratch Adhesion of Magnetron Sputtered NbN Films

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Abstract—*NbN films were deposited on SS-304 substrates by reactive DC magnetron sputtering at N_2/Ar flow ratios ranging 5-70% and at substrate bias varying 0 to -150V. Coatings were characterized for their thickness by weight gain and calotest methods, hardness by Knoop microhardness, phase analysis by X-ray diffraction, and adhesion by scratch tester. Scratch adhesion was performed using a Rockwell-C diamond indenter with a spherical tip radius of 200 µm. The starting load was 1N while maximum load was varied from 10 to 60N depending upon the load sustainability of the coatings. During scratch tests, coefficient of friction, depth of indentation and acoustic emission signals were recorded online. Optical microscopy was used to view the scratch tracks immediately after the tests to visualize the scratch patterns and to observe the critical loads for cohesive and adhesive failures. Loading rate during scratch tests was also varied and its effect was studied.*

Rate of deposition decreased from 20 to 8.4 nm/min with the increase in N_2/Ar flow ratio from 0 to 70%. Deposition rate decreased from 15.4 to 5.8 nm/min with the increase in bias from 0 to -150V. Maximum hardness of 1612 HK_{10} was obtained at a N_2/Ar flow ratio of 25% and it decreased gradually with further increase in N_2 flow. Hardness increased progressively from 1612 to 2044 HK_{10} with the increase in bias from 0 to -150V. X-ray diffraction analysis showed the presence of hexagonal βNb_2N, cubic δNbN and hexagonal δ'NbN phases with increasing N_2 flow. In the scratch tests, critical loads for cohesive and adhesive failures varied between 6-16 N and 11-24 N respectively. Coatings deposited at N_2/Ar flow ratio of 25% and bias of -75V, showed better adhesion. Critical loads for cohesive and adhesive failures both increased slightly at higher loading rates. Analyses for coefficient of friction, depth of penetration and acoustic signals were also performed.

1. INTRODUCTION

Transition metal nitrides possess high mechanical properties, high melting point, temperature stability and chemical inertness and therefore have a great potential for various applications. Reactive magnetron sputtering is commonly used for deposition of these transition metal hard nitride coatings [1-3]. NbN films have been deposited by different techniques which include reactive magnetron sputtering [4], ion beam assisted deposition [5], pulsed laser deposition [6] and cathodic arc deposition [7].

In the present study, NbN films were deposited by reactive magnetron sputtering on AISI-304 stainless steel (SS) substrates. During deposition, N_2/Ar gas flow ratio and substrate biasing were varied. Coatings were studied for their crystal structure, surface hardness and scratch adhesion. Scratch test was carried out with a Rockwell diamond indenter at various loads. Critical loads for cohesive and adhesive failure were observed. The effect of loading rate during scratch tests was also studied.

2. EXPERIMENTAL PROCEDURE

SS-304 rectangular samples of size 40×25 mm^2 of 3 mm thickness were prepared and polished metallographically to a surface roughness of 0.06 µm. The samples after polishing were cleaned thoroughly and degreased in alkaline solution prior to deposition. Deposition of NbN films was carried out by reactive DC magnetron sputtering using Nb (>99.9% purity) target of 160 mm diameter and 4 mm thickness. Chamber was evacuated to a base pressure of 2×10^{-6} mbar. Pressure during deposition was kept at 5×10^{-3} mbar by admitting high purity Ar and N_2 gases into the chamber. Flow of Ar gas was kept constant at 20 sccm and N_2 flow was varied between 0-14 sccm. Power to the target was supplied through a stabilized d.c. power supply of 0-1000V (6A maximum). Substrate bias was varied from 0 to -150V in a step of 25V (keeping the N_2/Ar flow ratio constant at 25%) by means of a stabilized d.c. power supply of variable voltage (0-300V) and current (0-500mA).

Weight gains of the coated samples were recorded and thickness of the coatings was calculated using bulk density value. Actual coating thickness was studied by Calotest technique using hardened 52100 steel balls rotated against coated samples in a suspension of diamond particles. The crystal structure was studied by X-ray diffraction (XRD) using CuKα radiation. Surface hardness was measured by a microhardness tester using Knoop indenter at 10 gf load. Adhesion tests were performed by scratch tester at different loading rates of 10, 30, 50 and 80 N/min. Scratch length was 3 mm. The scratch indenter used was a Rockwell-C diamond indenter with a spherical tip radius of 200 µm as per the ASTM standard. Tests were performed in a linearly progressive mode from 1N start load to a predefined maximum load. Maximum load was varied from 10 N to 60 N depending upon the load sustainability of the coating. During scratch adhesion tests, friction force, depth of indentation and acoustic emission signals were recorded online. The scratch tracks were seen in the attached optical microscope after the tests to visualize the scratch patterns and correlate the different phenomena occurred on the coated substrates at various loads.

3. RESULTS AND DISCUSSION

3.1 Thickness

Weight gain of the coatings was recorded and thickness was calculated using bulk density (8.4 gm/cc) of NbN. Actual coating thickness was found out by using Calotest technique as described above. Coating thickness as observed by the Calotest technique was higher by about 5-20% than the coating thickness calculated using the bulk density value. This is due to the lower density obtained in the coatings deposited by physical vapour deposition (PVD) techniques than the bulk value. Lower density is due to the porosity, voids and columnar grain growth structure obtained in PVD coatings [8]. Coatings deposited at various N_2 flows and substrate biasing had different deposition rates. Therefore, deposition time was adjusted for coating deposited at different processing parameters so as to get the coating thickness of 1µm. Actual coating thickness obtained were 1 µm ±10%.

3.2 Deposition Rate

Coatings were deposited at 0, 5, 10, 20, 30, 40, 50, 60 and 70% of N_2/Ar flow ratios. No external heating or substrate biasing was applied. Deposition rate decreased almost linearly from 20 to 8.4 nm/min with the increase in N_2/Ar flow ratio from 0 to 70% and has been reported earlier [9]. Deposition rate decreases with increasing N_2 flow due to the combined effect of increased collision frequency (between ions, N_2 molecules and target atoms) and increased flux of N_2^+ ions (lower momentum transfer as compare to Ar^+) which reduces deposition rate [10].

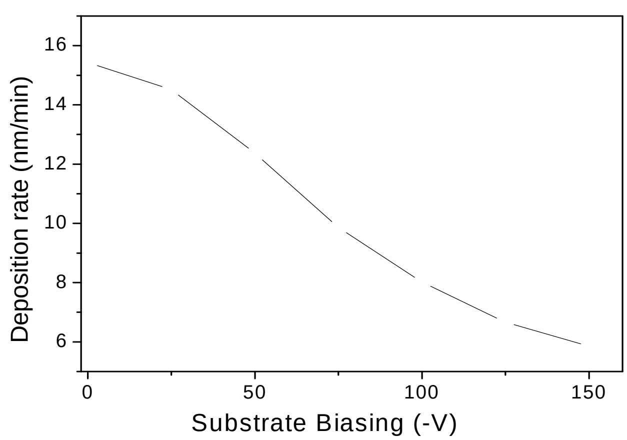

Fig. 1: Deposition rate Vs substrate bias (N_2/Ar=25%)

Coatings were deposited at negative substrate bias of 0, 25, 50, 75, 100, 125 and 150V (N_2/Ar flow was kept constant at 25%). Deposition rate decreased progressively from 15.4 to 5.8 nm/min when the bias was increased from 0 to -150V (Fig.1). Substrate bias during deposition causes the ion bombardment at the substrate, which imparts energy and thus improves adhesion and coating density. However, deposition rate is reduced. Deposition rate decreased with the increase in bias due to the resputtering at the substrate. With every increase in substrate bias increased ion bombardment at the substrate takes place causing the removal of entrapped gas atoms and lower energy particles from the substrate surface resulting in decreased deposition rate.

3.3 Hardness

Knoop microhardness was measured at a load of 10 gf. Fig.2 shows the microhardness of NbN coated samples with increasing N_2 flow. Hardness increased rapidly with the increase in N_2 flow. It reached a maximum value of 1612 HK_{10} at a N_2/Ar flow ratio of 25% and then decreased gradually with further increase in N_2 flow. The change in hardness is attributed to changes in grain size, stoichiometry, phase, residual stress or the appearance of texture [11].

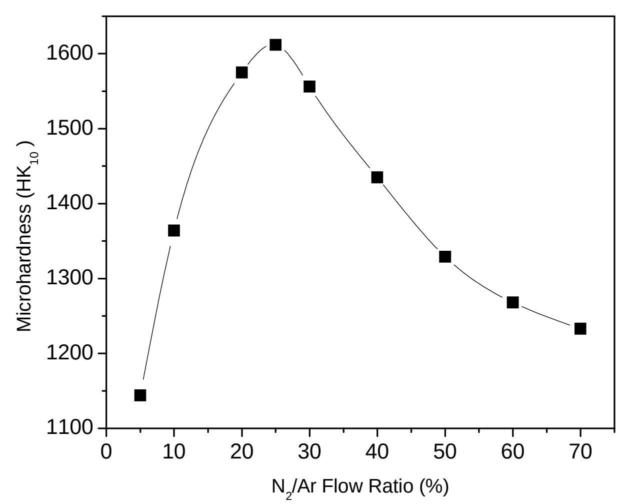

Fig. 2: Surface hardness Vs N_2/Ar flow ratio

Fig. 3 shows the hardness of NbN coatings with variation in substrate bias voltage. N_2/Ar flow ratio was fixed at 25%. Hardness increased continuously with the increase in substrate bias voltage. Increased bias causes increased ion bombardment at the substrate. Due to increased ion bombardment coating density increases, grain size reduces and residual stress increases; which lead to increased strength and hardness [12-13]. Hardness increased consistently from 1612 HK_{10} for coatings deposited without bias to 2038 HK_{10} for coatings deposited at -150V substrate bias.

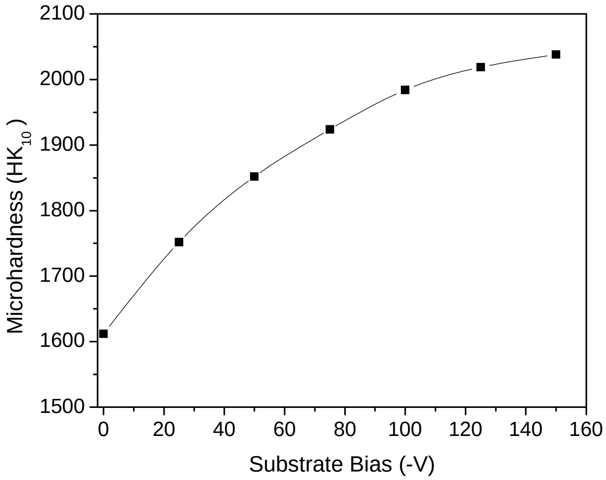

Fig. 3: Surface hardness Vs substrate bias

3.4 Crystal structure

Crystal structure of the Nb-N films deposited at various N_2 flow ratios were analyzed by XRD and have been reported earlier [9]. Coatings deposited at N_2/Ar flow ratio of 5% had hexagonal β Nb_2N as the major phase. At N_2/Ar flow ratio of 10%, the major phase was cubic δ NbN. At N_2/Ar flow ratio of 30%, hexagonal δ' NbN phase appeared, though the major phase was still cubic δ NbN but with preferred orientation of (200). With further increase in N_2 flow the hexagonal δ' NbN phase increased and appeared as the major phase.

3.5 Scratch Adhesion

During scratch tests, loading force, friction force, depth of penetration and acoustic emission signals all were recorded online along with the indenter movement. Micrographs were taken at different loads and various failure events were observed during scratch tests. These events include top layer removal, pile-up on the sides, small cracks, long wide cracks, chipping, partial and complete delamination of the coatings. Fig.4 shows the scratch micrographs at 10, 15, and 30N loads for coatings deposited at N_2/Ar flow ratio of 20, 25, 30 and 40%. Various failure events can be observed from the figures with increasing load. Coating deposited at N_2/Ar flow ratio of 25% showed better adhesion.

Fig.5 shows the scratch micrographs at various loads for coatings deposited at substrate biasing of 0, -25, -50, -75 and -100V. Coating deposited without substrate bias (Fig.5a) showed poor adhesion, cracks appeared at 5N load and delamination occurred at 10N load. With increase in substrate bias voltage adhesion increased and cracks and delamination occurred at higher loads. Coatings deposited at -50 and -75V substrate bias showed better adhesion. However, coatings deposited at -100V (Fig.5e) and above showed large cracks in the coatings around scratch path. This can be attributed to the generation of excessive stresses in the coatings deposited at higher substrate bias.

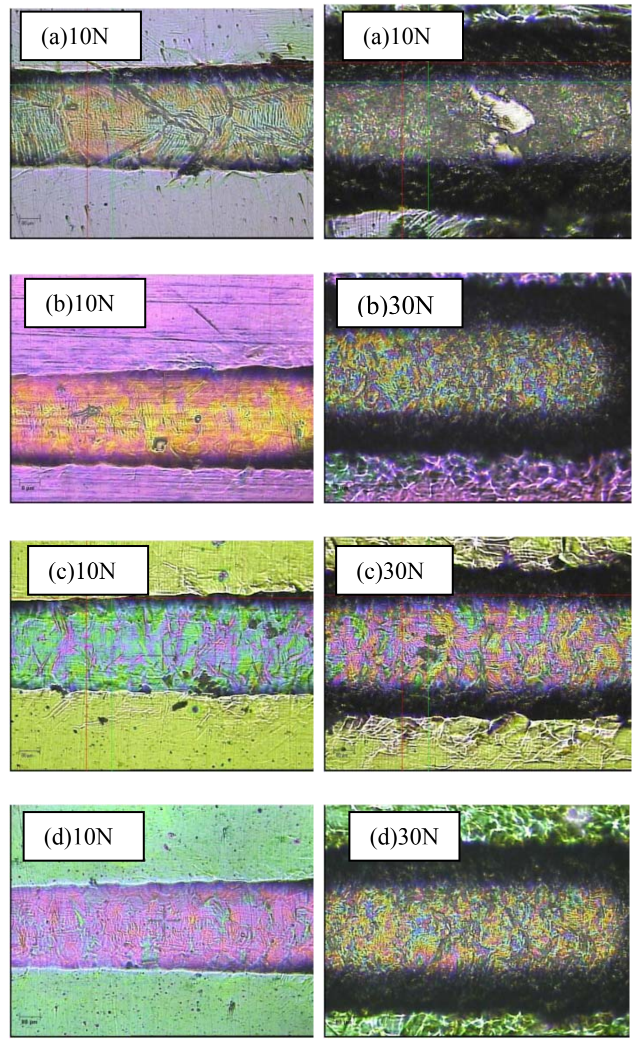

Fig. 4: Scratch micrographs of NbN coatings deposited at N_2/Ar flow ratio of (a) 20, (b) 25, (c) 30, and (d) 40%

Fig.6 shows the typical graphs for loading, coefficient of friction, depth of indentation and acoustic emission obtained during scratch test. From these spectra, depth of indentation and coefficient of friction data were evaluated. Acoustic emission signals showed small peaks wherever cracks occurred and big peaks where coating delaminated. For brittle coatings the height of the peaks increased. Acoustic emission signals confirmed the critical loads for various failure events as observed in the scratch micrographs (Fig.4, 5).

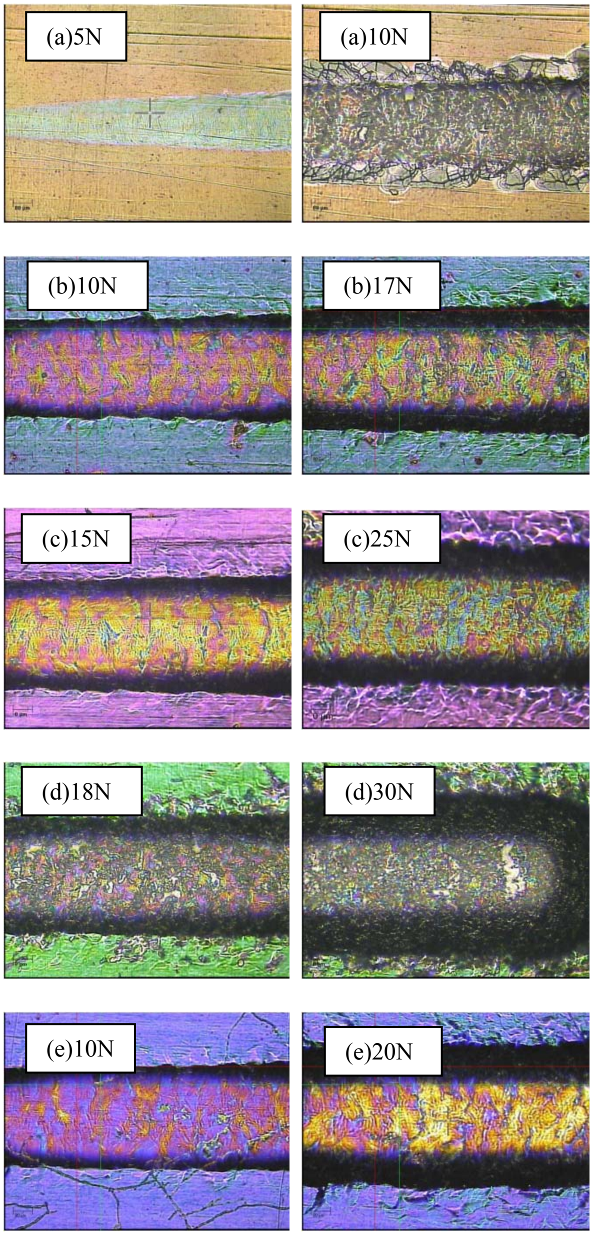

Fig. 5: Scratch micrographs of NbN coatings deposited at substrate bias of (a) 0V, (b) -25V, (c) -50V, (d) -75V, and (e) -100V (N_2/Ar flow ratio=25%)

Critical loads (Lc_1 and Lc_2) have been defined for the failure of the coatings. Lc_1, the first critical load is the initial cohesive failure such as first cracks observed within the coating. Lc_2, the second critical load is the initial adhesive failure of the coating i.e. chipping, or delamination, where substrate beneath coating gets exposed. Lc_1 and Lc_2 were between 6-16N and 11-24N respectively for NbN coatings deposited at different processing parameters. Best adhesion was obtained with coatings deposited at N_2/Ar flow ratio of 25% and substrate bias of -50 and -75V having highest values of Lc_1 and Lc_2. Lc_1 and Lc_2 both dropped for coatings deposited at substrate bias of -100V or more, revealing the coatings became brittle.

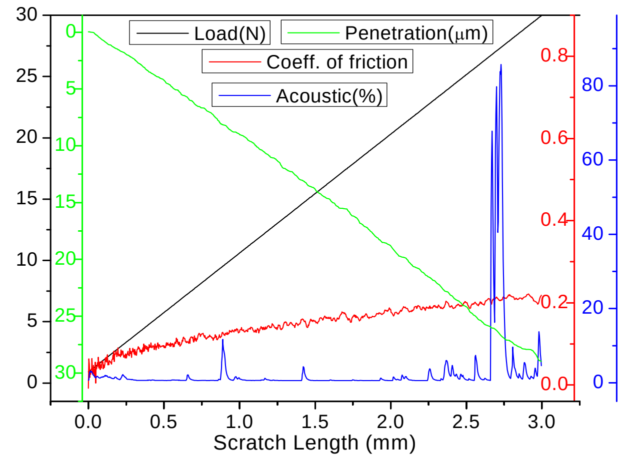

Fig. 6: Load, coefficient of friction, depth of indentation and acoustic emission graphs obtained during scratch test for NbN coating (N_2/Ar flow ratio=25%, bias -50V)

Coefficient of friction (μ) during scratch tests increased with the load. μ was 0.08 at 1N, 0.13 at 10N, 0.18 at 20N, 0.22 at 30N, 0.28 at 40N and 0.4 at 60N loads. At any particular load, μ varied within a narrow range for coatings deposited at different N_2 flows. For example μ varied between 0.20-0.24 at 30N load for coatings deposited at different N_2 flows.

Loading rate during scratch tests was varied for few samples, keeping other parameters constant. The effect of loading rate on critical loads was found to have some impact. Lc_1 increased from 12N at 10 N/min to 12.5N at 30 N/min and further to 13.1N at 50 N/min and to 13.9N at 80 N/min. Similarly, Lc_2 increased progressively from 20N to 22N with the successive increase in loading rate from 10 N/min to 80 N/min.

Depth of penetration increased with the increase in applied load. For coatings deposited at various processing parameters, depth of penetration was between 5-7 μm, 9-13 μm and 13-23 μm at 10, 20 and 30N load respectively. Hard coatings had low depth of penetration. Depth of penetration includes elastic and plastic deformation.

4. CONCLUSIONS

NbN coatings were deposited on SS substrates by reactive DC magnetron sputtering. N_2/Ar flow was varied from 0 to 70% and substrate biasing from 0 to -150V. Coatings were characterized for their thickness by weight gain and Calotest methods, hardness by Knoop micro hardness, crystal structure by X-ray diffraction technique, and adhesion by scratch tester. Deposition rate decreased from 20 to 8.4 nm/min with the increase in N_2/Ar flow from 0 to 70%. Deposition rate decreased from 15.4 to 5.8 nm/min when the bias voltage was increased from 0 to -150V. Surface hardness increased with the increase in N_2 flow, a maximum value of 1612 HK was obtained at a N_2/Ar flow ratio of 25%. It decreased gradually with further increase in N_2 flow. Increase in substrate bias from 0 to -150V increased the hardness consistently from 1612 to 2044 HK. With increasing N_2 flow, hexagonal β Nb_2N, cubic δ NbN and hexagonal δ' NbN phases were revealed by the XRD. Critical load for cohesive failure varied between 6-16N and critical load for adhesive failure varied between 11-24N. Coatings deposited at N_2/Ar flow ratio of 25% and substrate bias of -75V, showed better adhesion with higher critical loads. Increase in loading rate from 10 to 80 N/min during scratch tests increased the critical loads by 2N. Depth of penetration increased with the increase in applied load and decreased with the increase in hardness of the coatings. Coefficient of friction (μ) during scratch tests varied between 0.08-0.4 with the increase in load from 1N to 60N. At any particular load, μ varied within a narrow range for coatings deposited at different N_2 flows.

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