

Mechanical and Chemical Characterization of NbN_x Coatings Deposited by ICP Assisted DC Magnetron Sputtering

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Abstract Niobium nitride coatings have many potential thin film applications due to their chemical inertness, good mechanical properties, temperature stability and superconducting properties. In this study, NbN_x coatings were prepared by inductively coupled plasma (ICP) assisted DC magnetron sputtering method on the surface of AISI 304 austenitic stainless steels. Effects of target power were studied on mechanical and chemical properties of the coatings. The coating structure was analyzed by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The coating hardness was measured by micro-knoop hardness tester. The coating thickness was measured using a 3D profiler and wear characteristics were estimated using a ball-on-disk wear tester. The thickness of the NbN_x coatings increased linearly from 300 nm to 2000 nm as the Nb target power increased, and it showed over HK_{0.005} 4000 hardness above Nb target power of 300 W. Hexagonal δ'-NbN phase and cubic δ-NbN phase were observed in the coating films and the hardness of the NbN_x coatings was higher when these two peaks were mixed. The corrosion resistance increased with the increase of the Nb target power. (Received October 30, 2013; Revised November 6, 2013; Accepted November 15, 2013)

Key words : NbN_x thin films, Inductively coupled plasma, Reactive magnetron sputtering

1. Introduction

Metal nitride coating is commonly used for a wide range of instruments, molds, cars and vessels, because it has great mechanical properties including high hardness, strong wear resistance and a low friction coefficient. It also shows good corrosion resistance.

Niobium nitride films have good mechanical properties and high temperature stability. NbN_x films can be used as wear resistant coatings due to their high hardness and good wear resistance. NbN_x is considered to be suitable for applications in microelectronics and sensors, and in micromechanics and superconducting electronics. Due to their high critical current density, good mechanical properties and transition temperature between 16 and 17 K, NbN_x films could be successfully used in several superconducting microelectronics applications

[1]. NbN_x thin films have been produced by various deposition techniques including reactive magnetron sputtering [2], ion beam assisted deposition [3], pulsed laser deposition [4] and cathodic arc deposition [5, 6]. Only few studies on NbN were emphasized on its mechanical properties. The NbN system consists of several phases and in most cases the NbN films show a mixed phase condition [7]. The different characteristics of NbN_x films produced by various deposition apparatus are well explained in M. Benkahoul *et al.* [8].

In the present study, a tube-shaped inductively coupled plasma source was added to a conventional magnetron sputtering system to study the influence of increase of applied Nb target power on NbN_x films. Generally, it is possible to form high density plasma in a chamber and to make high quality coating at low temperatures if an inductively coupled plasma (ICP) source is used [9-11]. FESEM, XRD, a

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surface profiler and a ball-on-disk wear tester were used to analyze mechanical and structural properties of the films. A polarization tester was used to identify the corrosion behavior of the films.

2. Experimental

The specimens used for the experiment were AISI 304 austenitic stainless steels and silicon (100) wafers. NbN_x coating films were deposited by using the inductively coupled plasma assisted DC magnetron sputtering method. The sputtering chamber was equipped with an inductively coupled plasma source which was on the upper side of the chamber. And a sputtering gun with Nb (99.99%) target of 220 cm² in area was located vertical to the chamber wall. Substrate holder to target distance is 13 cm, facing each other. The specimen was disc-shaped with a diameter of 22 mm and a thickness of 6 mm. It was made to have approximately 0.02 μm of surface roughness through mechanical polishing. Specimens were immersed in acetone and alcohol and went through 20 minutes of ultrasonic cleaning process to remove the pollutants and the grease.

The chamber was evacuated to a base pressure of 2.0×10^{-4} Pa using rotary and diffusion pumps. Before deposition, DC bias voltage of -100 V was applied to the substrate holder for 30 minutes in order to clean the surface of specimen. Experimental parameters were the N₂/ (N₂ + Ar) gas ratio, Nb target power, and working pressure. The variations of parameters for each experiment are shown in Table 1.

The hardness of the NbN_x films was measured by a micro-knoop hardness tester (Mitutoyo, HM-124). Wear resistance was measured using a ball-on-disk type wear tester with a Si₃N₄ ceramic ball, and wear test conditions were 500 m distance, 3.6 cm/s of rotation speed with 5.9 N load. A 3D profiler (Veeco, Dektak 150) was used to observe wear track and measure residual stress and thickness of the NbN_x

Table 1. Experimental conditions to deposit NbN_x films on AISI 304 stainless steels

| | |
|--|------------------|
| Substrate temperature | Room temperature |
| Distance of target-substrate | 13 cm |
| Working pressure | 0.4 Pa |
| Total gas ratio (N ₂ / (N ₂ + Ar)) | 0.2 |
| Substrate bias voltage | -50 V |
| Nb target power | 200, 300, 400 W |

films on silicon wafers. A field emission scanning electron microscope (FESEM, JEOL, JSM-820) was used to observe the surface morphology and growth structure of the NbN_x films. The chemical composition of films was analyzed by energy dispersive X-ray spectroscopy (EDX). The crystal phase of the films was investigated by X-ray diffraction (XRD) with Cu Kα radiation.

Pontentiostat (WonATECH, WPG-100P) was used to measure the corrosion behavior of deposited NbN_x films. A three electrode system, which includes saturated calomel electrode (SCE) as a reference, graphite as a counter and specimens as a working electrode, was used for measuring the electrochemical properties. Specimens were placed on the paint test cell (Gamry, PTC1) which was filled with 0.5 M sulfuric acid solution and contained in a water bath to proceed with the experiment. The paint test cell was put into a 70°C water bath. The polarization test was carried out after stabilization of 30 minutes. The area of the specimen that was exposed to the experiment was 1 cm² and the rest was covered by electroplating tape. Polarization curves were obtained at a cathodic potential from -1000 mV to 2000 mV at 10 mV/s scan rate.

3. Results and discussion

Fig. 1 shows the changes in the hardness and thickness of the NbN_x films when the target power was increased from 200 W to 400 W. During the deposition the N₂ / (N₂ + Ar) total gas ratio was

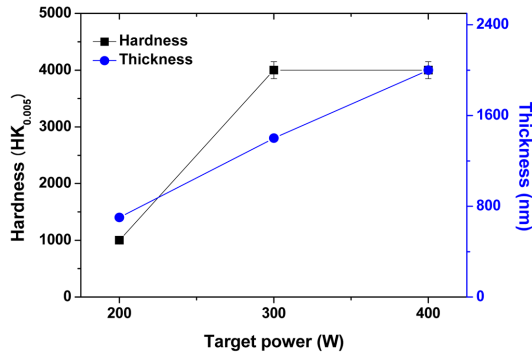


Fig. 1. Hardness and thickness of NbN_x films deposited at various target powers.

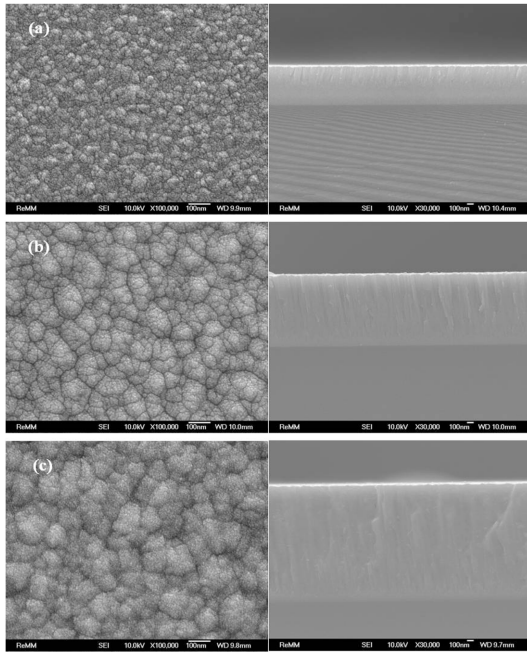


Fig. 2. FESEM images of NbN_x films deposited at various Nb target powers. (a) 200 W, (b) 300 W, (c) 400 W.

fixed to 0.2. The changes of film morphology are shown in Fig. 2. As shown in Fig. 1, the increase of the target power caused a linear increase in thickness of NbN_x films, but the hardness of the films was not changed significantly over 300 W. The cross section structure of NbN_x films confirmed that there was no special structure in the low Nb target power, while the film was developed into a columnar structure and its surface also showed a coarsening

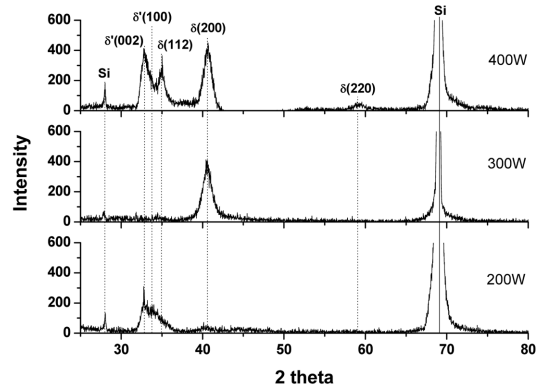


Fig. 3. X-ray diffraction patterns of NbN_x films deposited at various Nb target powers.

of crystal grains in the high target power. This can be confirmed in Thornton's structural zones in condensates [10] and it can be inferred as being changed from Zone T to Zone 2. In the other words, the increase of the applied target power would accelerate the ionized gas species that crashes against the Nb target surface and increase its collision energy, so the Nb⁺ ion that will be sputtered later would also have high energy. When this Nb⁺ ion with high energy starts to evaporate onto the surface of specimen, it will result in increasing the surface activity energy. Therefore, increased crystal grains are formed on the surface.

The changes in the XRD pattern of NbN_x films by the increase of the target power are shown in Fig. 3. The peaks of hexagonal δ'-NbN (002) and (100) were shown from the NbN film deposited on the silicon wafer with the target power of 200 W, but with the power of 300 W only cubic δ-NbN (200) was confirmed while hexagonal δ'-NbN phase disappeared. The peaks of δ'-NbN (002), (100) and δ-NbN (112), (200), (220) were shown when 400 W was applied. This shows that as the target power is increased, the compositional ratio of the Nb ion will be increased rather than nitrogen ion in the film, and it is easier to observe the intensity of the Nb ion which contains high energy caused by ion collisions.

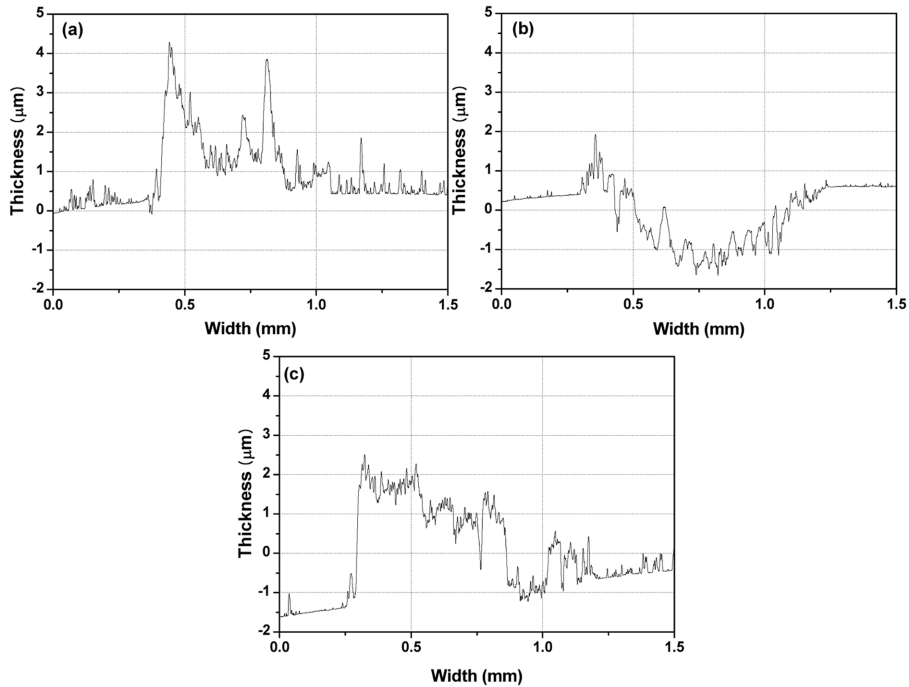


Fig. 4. 2D tracks of NbN_x films deposited on AISI 304 stainless steels as a function of the Nb target power. (a) 200 W, (b) 300 W, (c) 400 W.

As shown in Fig. 4, the surface profile of a cross section on the track that has been formed as a result of abrasion test was acquired by a mechanical profiler. Fig. 4 shows the abrasion properties of the NbN_x films as a function of the target power applied. The better abrasion properties were shown when the power of 200 W and 400 W were applied to the Nb target. In the Fig. 4(b), it could be seen that the film was worn away. On the other hand, in the Fig. 4(a) and 4(c), it is possible to observe that the surface of the coated sample was covered with some debris. This is attributed to the interaction of coating and the ball material that led to the transfer of material from ball to the coated surface. Comparing to the XRD analysis results, it is considered that the film shows surpassing abrasion properties when hexagonal δ' (002) and δ' (100) peaks exist together.

Fig. 5 shows the polarization curves taken by the potentiodynamic test which indicate the corrosion

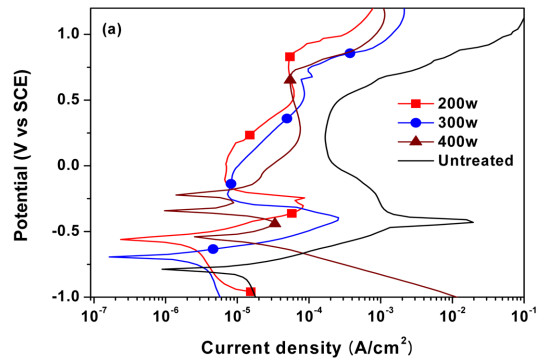


Fig. 5. Polarization curves of NbN_x-coated AISI 304 stainless steels after 30 min immersion in 0.5 M H₂SO₄ at 70°C.

behavior of NbN_x-coated AISI 304 stainless steel in 0.5 M H₂SO₄ solution. The curve of untreated AISI 304 stainless steel is for comparison. The films that have been produced with the target power of 200 W, 300 W and 400 W have the higher corrosion resistance than untreated AISI 304, overall. And the corrosion resistance of the NbN_x films deposited at target power over 200 W increased gradually. But,

in the case of the polarization curve for the target power of 400 W, there are three E_{corr} above the active-passive transition. Another E_{corr} appears followed by a loop and yet a third E_{corr} before the passive region is observed. The second E_{corr} between the first and the third E_{corr} of the anodic curve at the active-to-passive transition, is not a stable potential state and is never observed when passivity is established in practice. Generally, either the uppermost or lowermost E_{corr} is the most stable, and the material exhibits that corrosion potential spontaneously.

At the power of 400 W, the coating may exist in either the active state or the passive state, that is, the coating is in a state of borderline passivity with both active and passive state. Consequently, the film deposited at the power of 400 W is not appropriate for a corrosion resistant coating. Because the borderline passivity should be avoided in which either the active or the passive state may be stable, and the active state is always chosen as the one most likely in cases of borderline passivity [12, 13].

It was confirmed that the corrosion rates of all films increased at potential value over 0.74 V. The rest except the target power of 400 W showed similar corrosion behavior, but it entered the passive area with lower current density compared to untreated AISI 304 stainless steel.

4. Conclusion

The experiment investigated the influence of changes in the target power applied to Nb target on the mechanical and chemical properties of NbN_x films deposited on AISI 304 stainless steels. The growth structure of the film was changed by increasing the target power from columnar to fibrous, and the morphology of the crystal grains

increased gradually. With target power over 300 W, the film showed hardness value over $\text{HK}_{0.005}$ 4000 and its thickness increased linearly. The result of XRD analysis confirmed that only hexagonal δ '-NbN phase and cubic δ -NbN phase increased, and δ '-NbN (002), (100) and δ -NbN (112), (200), (220) peaks were shown in 400 W. From the potentiodynamic test, the corrosion resistance increased with increasing the Nb target power.

References

1. Kulwant Singh, N. Krishnamurthy and A. K. Suri : Tribology International **50** (2012) 16-25.
2. J. J. Olaya, S. E. Rodil and S. Muhl: Thin Solid Films **516** (2008) 8319.
3. M. L. Klingenberg and J. D. Demaree : Surface and Coatings Technology **146** (2001) 243.
4. G. Cappucio, U. Gambardella, A. Morone, S. Orlando and G. P. Parisi : Applied Surface Science **109** (1997) 399.
5. N. Cansever, M. Danisman and K. Kazmanlı : Surface and Coatings Technology **202** (2008) 5919.
6. J. L. Mo and M. H. Zhu : Applied Surface Science **255** (2009) 7627.
7. C. S. Sandu, M. Benkahoul, M. Parlinska-Wojtan, R. Sanjinés and F. Lévy : Surface & Coatings Technology **200** (2006) 6544-6548.
8. M. Benkahoul, E. Martinez, A. Karimi, R. Sanjines and F. Levy : Surf. Coat. Technol. **180-181** (2004) 178-183.
9. H. D. Na, H. S. park, D. H. Jung, G. R. Lee, J. H. Joo and J. J. Lee : Surf. Coat. Technol. **169-170** (2003) 41-44.
10. Rointan F. Bunshah : Handbook of deposition technologies for films and coatings, NOYES PUBLICATIONS, New Jersey (1994) 194-210.
11. J. J. Lee and J. H. Joo : Surf. Coat. Technol., **169-170** (2003) 353-358.
12. Denny A. Jones: Principles and prevention of corrosion, 2nd ed. Prentice Hall, New Jersey (2011) 116-132.
13. Robert G. Kelly, John R. Scully, David W. Shoesmith and Rudolph G. Buchheit : Electrochemical techniques in corrosion science and engineering, Marcel Dekker, Inc., New York (2003) 55-69.