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Characteristics of NbN Films Deposited on AISI 304 Using Inductively Coupled Plasma Assisted DC Magnetron Sputtering Method

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Abstract

Niobium nitride (NbN) films were deposited on AISI 304 stainless steels by inductively coupled plasma (ICP) assisted dc magnetron sputtering method at different ICP powers, and the effects of ICP power on the phase formation, mechanical and chemical properties of the films were investigated. X-ray diffraction analysis (XRD) and field emission scanning electron microscopy (FESEM) were used to analyze the crystal structure and micro-knoop hardness was used to measure the hardness of the films. Also, 3-D mechanical profiler and a ball-on-disk wear tester were used to measure the thickness of the films and to estimate wear characteristics, respectively. The thickness of the films decreased but their hardness increased with increasing ICP power, and it was confirmed that only cubic δ -NbN(200) remained at high ICP power. At lower ICP powers, a mixture of the hexagonal δ' -NbN and cubic δ -NbN phases was obtained in the films and the hardness decreased. The corrosion potential value increased gradually with increasing ICP power, but the changes of ICP power did not significantly influence the overall corrosion resistance.

Keywords : NbN thin films, Inductively coupled plasma (ICP), Reactive magnetron sputtering

1. Introduction

Transition metal nitrides coatings have many potential applications in instruments, molds, cars and vessels, thanks to their great mechanical properties, chemical stabilities and good corrosion resistance. Niobium nitride (NbN), as a transition metal nitride, is a very attractive material because of its high hardness, melting point, wear resistance, chemical inertness and superconducting properties. NbN thin films have good mechanical properties and high temperature stability. These films are used in semiconductors and electronic devices because they have superconducting properties in the temperature of 16-17 K with NaCl structure¹⁾.

NbN coating films have been produced by various deposition techniques such as magnetron sputtering²⁾, hybrid sputtering^{3,4)}, and vacuum arc^{5,6)}. Until now, most of the study on NbN was related to its super-

conducting properties rather than its mechanical properties. The different characteristics of NbN films produced by various deposition apparatus are well explained in Benkahoul *et al.*⁷⁾ An inductively coupled plasma (ICP) assisted sputtering is considered as a very efficient technique for the deposition of high quality coating at low temperatures due to its many beneficial properties. Especially, it is possible to form high-density plasma at the region between a target and a substrate in a chamber if an ICP is added to a conventional magnetron sputtering system⁸⁻¹⁴⁾.

In this work, NbN thin films are deposited on AISI 304 austenitic stainless steel in order to understand the influences of various ICP powers on the characteristics of the films, when a tube-shaped ICP source is added to a conventional magnetron sputtering chamber. Little studies have been reported on the mechanical and corrosion characteristics of the films compared with its superconducting properties. The present study aims to evaluate the mechanical properties

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and corrosion resistance of AISI 304 samples after NbN coating and to correlate the results of surface morphology, hardness and crystallographic information.

2. Experimental

NbN thin films were deposited on AISI 304 stainless steels and silicon (100) wafers by ICP assisted dc magnetron sputtering at room temperature. The magnetron sputtering chamber was equipped with an ICP source which was on the upper side of the chamber. And a pure Nb metal target (99.99%) of 220 cm² in area was located vertical to the chamber wall. The distance between the substrate holder and target was 13 cm, facing each other. The stainless steel specimens were disc-shaped with diameter of 22 mm and thickness of 6 mm, and they were polished to about 0.02 μm of surface roughness. 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 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. Deposition was carried out at different ICP powers with substrate bias voltage of -50 V, and without additional substrate heating. During deposition of NbN films, the working pressure was 0.4 Pa, and the N₂/(N₂+Ar) gas ratio was 0.2. The experimental conditions are shown in Table 1.

The hardness of the films was measured by a micro-knoop hardness tester (Mitutoyo, HM-124). The wear resistance of the films was evaluated using a ball-on-disk type wear tester with a Si₃N₄ ceramic ball, and wear test conditions were a 500 m distance, 3.6 cm/s speed with 5.9 N load. The residual stress and thickness of the films deposited on silicon wafers were measured by 3-D mechanical surface profiler (Veeco, Dektak 150). The surface morphology and microstructure of the films were observed by a field emission scanning electron microscopy (FESEM,

Table 1. Experimental conditions to deposit NbN films on AISI 304

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
ICP power (W)	0, 300, 500, 700 W

JEOL, JSM-820). The chemical composition of the films was analyzed by energy dispersive X-ray spectroscopy (EDX). The crystal phase of the films was investigated using X-ray diffraction (XRD) with Cu Kα₁ radiation. Corrosion behavior investigation of the deposited films was carried out using a potentiostat (WonATECH, WPG-100P). A three electrode system, in which saturated calomel electrode (SCE) as a reference, graphite as a counter and specimens as a working, was used to measure the electrochemical properties. Specimens were placed on the paint test cell (Gamry, PTC1) which was filled with 0.5 M sulfuric acid solution and this cell was put into a 70°C water bath. The polarization test was carried out after a stabilization period of 30 minutes. The exposed area of the specimen was 1 cm² in the test and the rest area was covered by electroplating tape. Polarization curves were obtained at a cathodic potential from -1000 to 2000 mV at 10 mV/s scan rate.

3. Results and Discussion

The changes of the thickness and hardness of the film when we applied 400 W to the Nb target are shown in Fig. 1. In this case, the total gas ratio was kept at 0.2 and ICP power was increased from 0 to 700 W. With the increase of ICP power, the hardness of the films reached the maximum value. The film showed the hardness over HK_{0.005} 4000 when 300 W of the ICP power was given, and it did not show any major differences in its hardness with the higher power. The deposition rate decreased as the ICP power increased, and it caused the thickness of the film to be decreased, too. In general, if ICP power is increased, the plasma density in a chamber would be

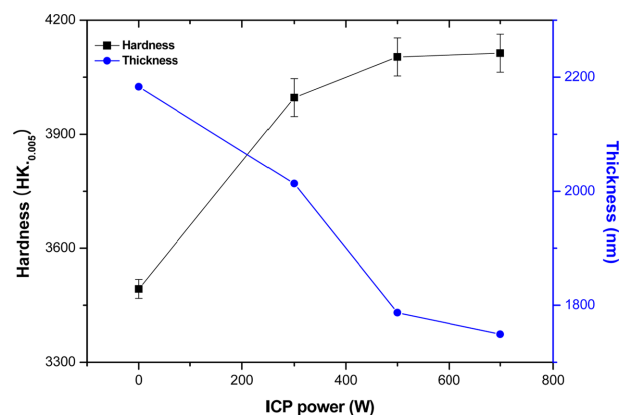


Fig. 1. Hardness and thickness of NbN films deposited at different ICP powers.

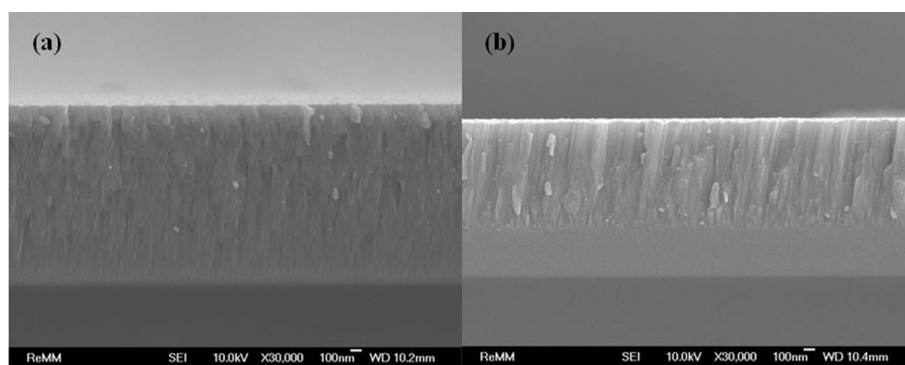


Fig. 2. FE-SEM image of the cross-section of NbN films deposited at different ICP powers (a) 0 W, (b) 700 W.

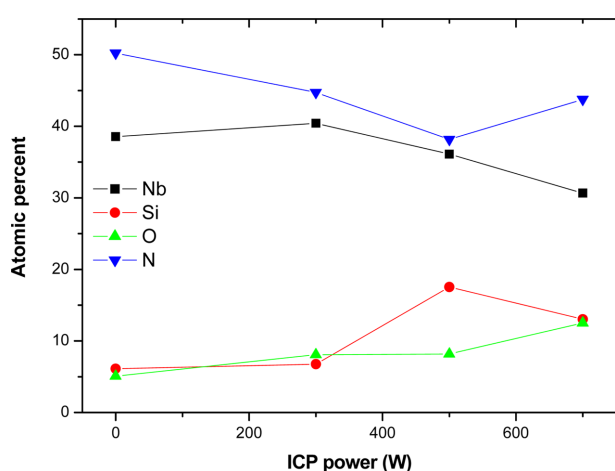


Fig. 3. Chemical composition of NbN films on silicon wafer as a function of the different ICP powers measured by energy dispersive X-ray spectroscopy.

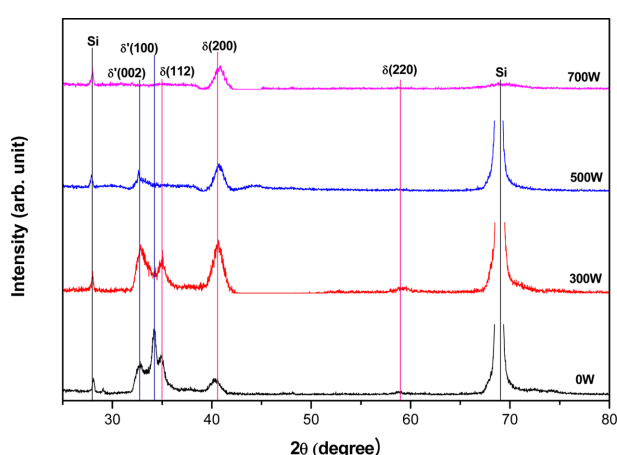


Fig. 4. X-ray diffractograms of NbN films deposited at various ICP powers.

increased, and the collision rate of ion is increased, too^{10,15}. This causes the hardness and Young's modulus of a film to be increased and it will influence the surface roughness and density of film.

The growth structure of the film was changed to a columnar grain from a fibrous grain as shown in Fig. 2. The structure of the part that was in contact with the silicon wafer had a very elaborate form, and this section confirmed by EDX that silicon existed in the film as shown in Fig. 3. This phenomenon is considered to be produced by recombined silicon that has been bounced off from the surface of specimen by sputtering because of growing ICP power which caused high energy ions to be formed inside the chamber.

Fig. 4 shows the crystal structure of the film analyzed by XRD. In this work, only two phases of the NbN system, cubic δ -NbN and hexagonal δ' -NbN, were observed. It could be seen that cubic δ -NbN was the main phase of NbN films. At low ICP powers, the hexagonal δ' -NbN phases were found and the cubic

δ -NbN showed a (200) preferred growth orientation. The crystal structure with hexagonal δ' (100) of preferred growth orientation formed in the absence of ICP power, but it disappeared when ICP power was applied. And the peaks of δ' (002), δ (112), δ (220) gradually vanished, leaving only δ (200) orientation. At lower ICP powers the hardness was low, which was attributed to the existence of softer hexagonal δ' -NbN phases. At the ICP power of 700 W, the films were single-phase cubic δ -NbN. From these results, it can be concluded that single-phase NbN films have higher hardness¹⁾.

The cross section of the track that was formed as a result of abrasion tests was achieved by a mechanical profiler. Fig. 5 shows the abrasion properties as a function of ICP power applied. The better abrasion properties were shown when ICP power was 0, 300 and 500 W. Comparing to the XRD analysis results, it is considered that the film shows surpassing abrasion properties when δ' (002) and δ' (100) peaks exist together. According to the experimental results, the ICP power obviously affected the phases and

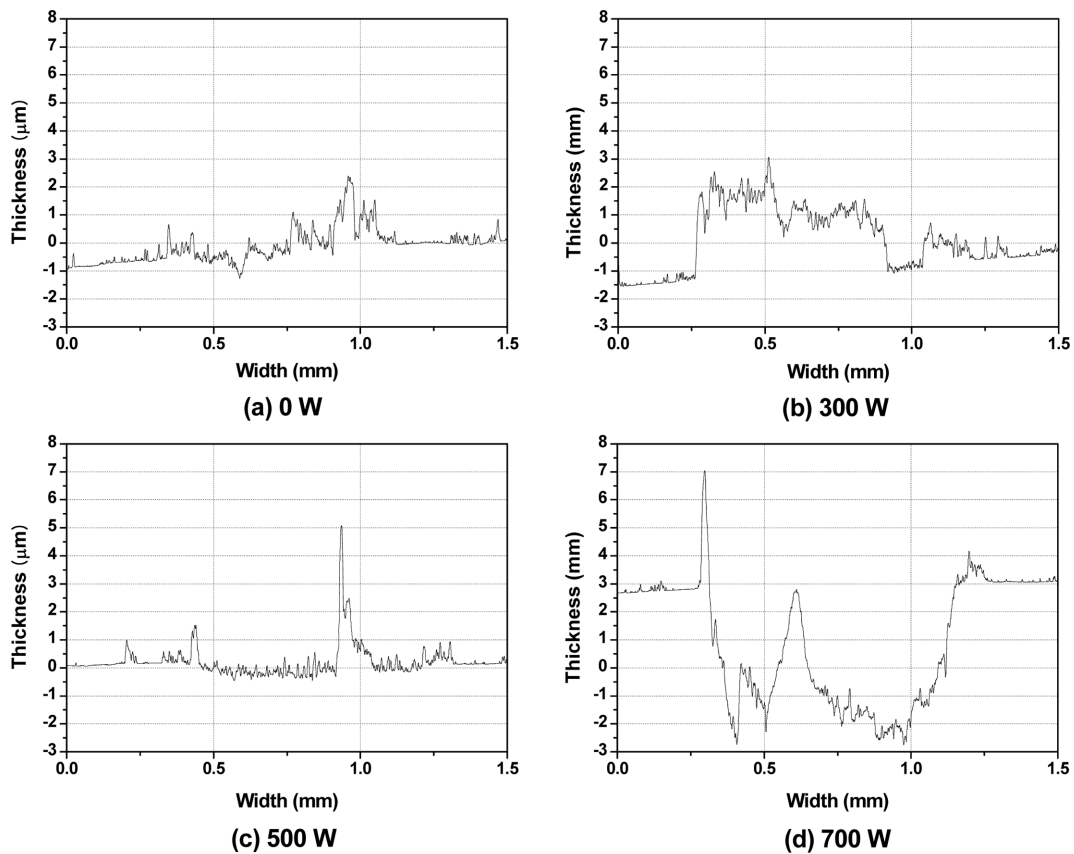


Fig. 5. Wear tracks of NbN films as a function of the ICP power measured by mechanical profiler.

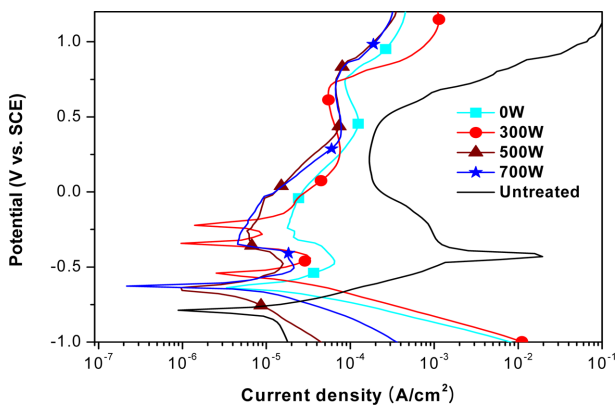


Fig. 6. Polarization curves of NbN-coated AISI 304 stainless steels after 30 min immersion in 0.5 M H_2SO_4 at 70°C.

mechanical properties of the films. And preferred orientation in the coatings also changed with ICP power, exerting an effective influence on film hardness¹⁶⁾: while cubic δ -NbN was the main phase of the magnetron sputtered films, at lower ICP powers, hexagonal δ' -NbN and cubic δ -NbN phases existed together in the films¹⁾.

Fig. 6 shows the polarization curves taken by the potentiodynamic test which indicate the corrosion

behavior of NbN coated AISI 304 in 0.5 M H_2SO_4 solution. The untreated AISI 304 curve is for comparison. Although the corrosion resistance of the films deposited at ICP power over 300 W increased gradually, the ICP power of 300 W showed unusual polarization behavior. At low potentials, the polarization curve of the power of 300 W was similar to that of the others. However, just above the active-passive transition, a second E_{corr} appeared followed by a loop and yet a third E_{corr} before the passive region was observed. The portion between the first and the third E_{corr} of the anodic curve at the active-to-passive transition, where current decreases with increasing potential, is an artifact of the instrumental measurement. Thus, the second E_{corr} 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. The origin of the cathodic loop is the fact that at these potentials, the rate of the cathodic reaction is greater than the passive current density. Thus the net current is cathodic over that range of potential. At the power of 300 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 300 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 one always conservatively choose the active state as the one most likely in cases of borderline passivity^{17,18}. As shown in Fig. 6, the increase of ICP power could not decrease the corrosion density, but the corrosion potential value increased gradually. The rest ICP powers except 500 W, showed similar corrosion behavior, but it entered passive area with lower current density compared to untreated AISI 304 stainless steels.

4. Conclusion

NbN films were successfully deposited on 304 stainless steel substrates using the ICP assisted dc magnetron sputtering techniques, and mechanical and chemical properties evaluated. The experiment investigated the influence of changes in ICP power applied to deposit the films, and we were able to draw the following conclusions:

The thickness of the film decreased, but the hardness increased with increasing ICP power. Lower ICP powers caused hexagonal δ' -NbN to appear in the films. Accordingly, hardness of the films decreased. Also, with over 500 W power, hexagonal δ' -NbN (002), (100) and cubic δ -NbN (112) disappeared and only cubic δ -NbN (200) peak remained. Analyzing the abrasion properties of the films confirmed that the ICP power of 0, 300 and 500 W showed hexagonal δ' -NbN (002), (100) peak and they had a great abrasion-resistance. The result of the potentiodynamic test showed that the changes in ICP power did not significantly influence corrosion resistance.

Our study on the characteristics of sputtered NbN films revealed a correlation between the applied ICP power and an excellent improvement of the mechanical properties. We show that it is possible to obtain excellent film properties, especially hardness and wear resistance, at a relatively low ICP power using ICP assisted dc magnetron sputtering. Although there are few publications on the mechanical behavior of NbN coatings, comparing our results obtained for the coatings, those prepared at a relatively low ICP power seem to be the promising for technical applications

as hard and wear protective coatings.

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