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Properties of VN Coatings Deposited by ICP Assisted Sputtering: Effect of ICP Power

Sung-Yong Chun†

Department of Advanced Materials Science and Engineering, Mokpo National University, Muan 58554, Korea

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ABSTRACT

Vanadium nitride (VN) coatings were deposited using inductively coupled plasma (ICP) assisted sputtering at different ICP powers. Microstructural, crystallographic and mechanical characterizations were performed by FE-SEM, AFM, XRD and nanoindentation. The results show that ICP has significant effects on coating's microstructure, structural and mechanical properties of VN coatings. With an increase in ICP power, coating microstructure evolved from a porous columnar structure to a highly dense one. Single- phase cubic (FCC) VN coatings with different preferential orientations and residual stresses were obtained as a function of ICP power. Average crystal grain sizes of single phase cubic (FCC) VN coatings were decreased from 10.1 nm to 4.0 nm with an increase in ICP power. The maximum hardness of 28.2 GPa was obtained for the coatings deposited at ICP power of 200 W. The smoothest surface morphology with Ra roughness of 1.7 nm was obtained in the VN coating sputtered at ICP power of 200 W.

Key words : Inductively Coupled plasma, Vanadium nitride, Microstructure, Preferential orientation, Young's modulus

1. Introduction

Among nitride coatings utilizing transition metals, vanadium nitride (VN) is being utilized in diversified areas such as mechanical parts and jigs for surface protection, implant for dental care, computer hard disk, and micro electromechanical systems due to the excellent physical mechanical characteristics including corrosion resistance and high hardness.[1-5] In the present study, attention was given to power changes and applications of inductively-coupled plasma (ICP) capable of producing coatings having uniform thicknesses and excellent mechanical properties at high ion densities and low deposition temperatures. In general, plasma is generated in ICP by application of RF power supply to a circular, coil-shaped antenna. And, since the energy is easily transferred to charged particles inside the antenna through the inductive device of coil-shaped antenna, not only application of direct current magnetic field is unnecessary unlike internal electrode or ECR (Electron Cyclotron Resonance), but also utilization of plasma processing for relatively large-scale processing objects is possible, it is being widely noted.[6] As representative production methods reported thus far for the VN coatings, plasma spraying, DC sputtering and pulse DC magnetron sputtering may be considered.[7-8] Our laboratory has recently published the study articles stating that material properties such as microstructure, crystal structure, etc. could vary as a function of increase/decrease of plasma power by using pulse and ICP-assisted magnetron sputtering.[9-10] However, there has been almost no report made thus far on the effects of plasma power on crystalline phases or preferred orientation of the VN coatings which were produced by using ICP magnetron sputtering.

Thus, in the present study, an investigation has been conducted on the effects on VN coating's structure, crystal structure and mechanical characteristics of the ICP with an advantage of being able to produce excellent mechanical and physicochemical properties. Specifically, the VN coatings were produced by ICP, and particular attention has been paid to the effects of plasma power on grain size, surface and cross section structure, residual stress, preferred orientation, 3-dimensional topography and mechanical characteristics, etc.

2. Experimental Procedure

In the present experiment, Si (100) substrates were used, and were dried after being washed in acetone and ethyl alcohol for 10 minutes, respectively, by using an ultrasonic cleaner to remove impurities on the substrate surface. The coating equipment employed in the present experiment does not require any dielectric window since RF coil for ICP generation is inserted inside and can be directly mounted inside the chamber. Hence, the VN coatings were prepared by DC magnetron sputtering method using internal insertion-type of ICP having a favorable advantage for scale-up. As a starting raw material, V target with a diameter of 3", thickness of 1/4", (purity = 99.9%), and ultrahigh-purity N_2 and Ar

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†Corresponding author : Sung-Yong Chun
E-mail : sychun@mokpo.ac.kr
Tel : +82-61-450-2495 Fax : +82-61-450-2498

gases with the injected amounts of Ar and N_2 fixed at 31 sccm and 5 sccm, respectively. Upon vapor deposition, the distance between substrate and target was maintained at 60 mm, and the substrate was rotated at a speed of about 10 rpm for uniform vapor deposition. Initial pressure of the chamber was lowered to about 1.3×10^{-3} Pa through exhausting by using a rotary pump and a turbomolecular pump, and an ion gauge together with a baratron gauge were employed for vacuum measurement. Also, for cleaning of the target and the substrate prior to vapor deposition, Ar plasma was produced and vapor deposition was conducted in the same manner for 30 minutes at ICP powers of 50 W, 100 W, and 200 W. For analyses of crystal structure, preferred orientation and half width of the nano-crystalline VN coatings obtained, high-resolution XRD (PAN Analytical Company/ X'pert- pro MRD) was used, while microstructures of surface and cross section for the coatings were observed by using FE-SEM (Hitachi Company/ S-3500N). For 3-dimensional topography and surface roughness measurement, Auto Probe Atomic Force Microscopy (AFM) (Digital Instruments Company / Nanoscope a) was used. For measurement of nanohardness of the coatings, a precision hardness tester of nanoindenter (MTS System Company/ MTS XP) was used. Hardness was obtained as an average value through experiments for 16 times by using Berkovich diamond indenter. More than 10 μm was maintained for measurement intervals of nanoindenter to avoid being affected by the already-conducted hardness measurement tip. Also, to measure hardness within the range of not affecting the parent material, the depth of indentation was fixed to be about 10% of the coating.

3. Results and Discussion

To investigate the effects of ICP on average grain size, surface and cross section microstructure, crystal structure, preferred orientation, 3D topography, surface roughness and mechanical characteristics of coatings, the VN coatings were produced by varying ICP power from 0 W to 50 W, 100 W, and 200 W.

3.1. Surface and cross section microstructures

Observation was made on the microstructures of the VN coatings produced by ICP magnetron sputtering under FE-SEM, and pictures of the surface and the cross section are shown in Fig. 1. First, in the case of the VN coatings produced at the ICP power of 0 W, large grains containing multitude of pores and rough surface were observed in the surface, while a microstructure of typical porous columnar structure was observed from the substrate surface to the film surface in the cross section. However, in the case of surface of the VN coatings produced at the ICP power of 200 W, dense fine grains and smooth surfaces were observed while the porous columnar structure disappeared in the cross section with a very dense microstructure being observed from the substrate surface to the film surface. Thus, as a result of using ICP magnetron sputtering which allows high ionization rates and high-density plasma, kinetic energy of particles was increased and adatom mobility on the substrate surface was improved due to high ionization rates of particles and high-density plasma, leading to formation of dense coatings through reduction of pore generation. Consequently, the average grain size of the VN coatings is considered to have been reduced with the microstructure becoming dense.

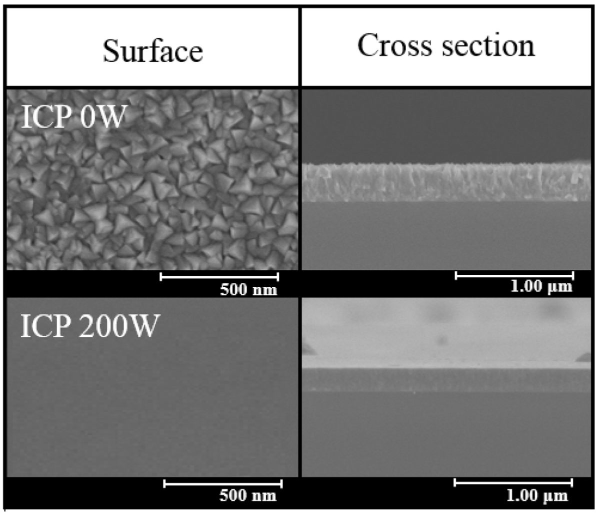

Fig. 1. Surface and cross-section FE-SEM image of VN coatings deposited using ICP assisted sputtering at various ICP powers.

3.2. 3D topography and surface roughness

To investigate the effects of ICP power on 3D topography and surface roughness of VN coatings, a non-contact type of AFM analysis was conducted with the results shown in Fig. 2. When a comparison is made on the results for surface roughness (Ra) of the VN coatings produced by an increase in ICP power upon coating, topography and surface roughness can be seen to vary greatly as a function of ICP power. It can be seen that the VN coatings produced by ICP magnetron sputtering are much flatter than the VN coatings coated at the conventional ICP power of 0 W. For instance, average values of surface roughness (Ra) of the VN coatings produced at the ICP power of 0 W and 200 W were 9.3 nm and 1.7 nm, respectively, being reduced by the

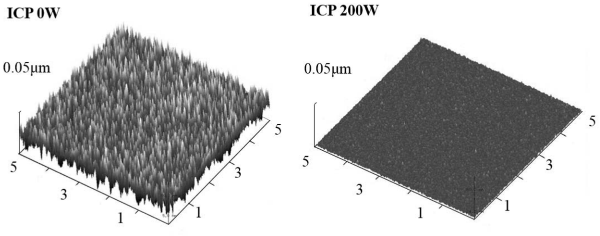

Fig. 2. AFM surface morphologies of VN coatings deposited using ICP assisted sputtering at various ICP powers.

maximum of 80% depending on the ICP power. As the causes for surface flattening and reduction of surface roughness of the VN coatings produced by such ICP magnetron sputtering method, an increase in mobility of adatoms of the accelerated ions and in nuclei generation density may be considered to be the result of increased ion energy due to generation of high-density plasma. In particular, the present laboratory has recently published a study article showing that generation of high-density, high-ionization plasma is closely related to the reduction in surface roughness of the coatings. Taking the transition metal nitride of NbN with a similar crystal structure as an example, the surface roughness of coatings was reduced by up to about 67% as a function of ICP power.[11]

3.3. Refinement of average grains

In Fig. 3, changes in the average grain size are shown for the VN coatings produced by ICP magnetron sputtering. More on-average and accurate calculation of grain sizes for the coatings is possible not only according to the measurement by an electron microscope but also to the size of half width of X-ray diffraction analysis peaks. In general, the smaller is the grain size, the larger the size of half width. In the present study, average grain sizes were calculated by using the Scherrer method[12] with the expression being as shown by the equation (1).

$$t = K \cdot \lambda / B \cdot \cos\theta \qquad (1)$$

where B is the half width of Bragg peak, K the constant dependent on grain shape, λ the wavelength of X-ray, and θ the Bragg angle. As shown in the figure, the average grain size for VN coatings can be seen to be decreased from 10.1 nm at the ICP power of 0 W to 4.0 nm at 200 W by about 60% as a result of using ICP and an increase in ICP power upon coating. Therefore, the change of ICP power can be seen to be a very important process variable as a technique to control the microstructure of VN coatings having nano-scale grain sizes. As the cause for nano conversion of the grain sizes in such multi-functional nitride coatings utilizing transition metals, the effects of combined elements such as an increase in flux ratio (J_i/J_N) compared with neutral particles resulting from incorporation of ECR (Electron Cyclotron resonance) or of ICP may be considered. In particular, the rise in ion flux density resulting from an increase in ICP power has been reported to be capable of improving the microstructure of coatings, especially columnar structure as well as the properties such as density, surface morphology and preferred orientation, etc.[12]

3.4. Crystal structure and preferred orientation

X-ray diffraction analysis results of the VN coatings produced by ICP magnetron sputtering are shown in Fig. 4. In all coatings, single-phase VN coatings of cubic (FCC) structure have been produced. Among the films, the following change in preferred orientation was observed, although crystalline phases of the VN coatings obtained by an increased power of ICP consisted of a single phase of VN without any change. In all VN coatings, the peaks of cubic (FCC) (111) face, (200) face, (220) face, and (311) face were observed (JCPDS 25-1252). However, in the coatings employing ICP, relatively high X-ray intensities were observed for the peaks of (111) face at 0 W, (200) face at 100 W, and (220) face at 200 W as a function of an increase in ICP power. Namely, the preferred orientation of VN coatings was changed in the order of (111) face, (200) face, and (220) face with an increase in ICP power. While many of such changes in crystal structure and preferred orientation of coatings as a function of process variables have been reported in the past, most process variables here included the mixing ratio of Ar/N_2, the axial direction change for application of external magnetic field and the substrate bias voltage, etc. during coating. Such study results as above showing the change in preferred orientations for the VN coatings as a function of ICP power have not been reported thus far, and more systematic additional studies in the future are deemed necessary concerning its causes.

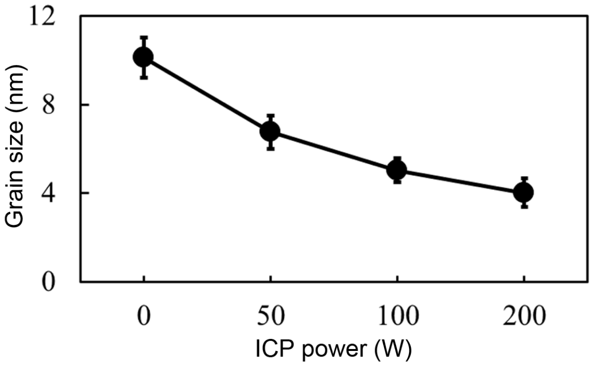

Fig. 3. Crystal grain size of VN coatings deposited using ICP assisted sputtering at various ICP powers.

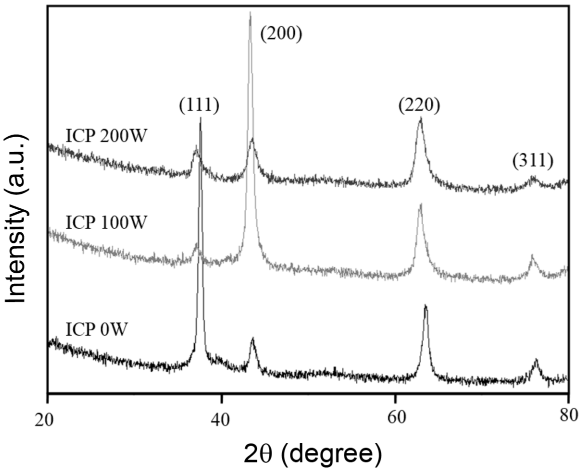

Fig. 4. XRD data of VN coatings deposited using ICP assisted sputtering at various ICP powers.

3.5. Residual stress

To study the effects of ICP power during coating on residual stresses inside the VN coatings, the changes in 2θ values for the X-ray peak of (220) face as a function of ICP power are shown in Table 1. To easily represent the effects of the VN diffraction peaks on position changes, the standard 2θ value for the (220) face obtained from JCPDS card (#25-1252) is displayed in Fig. 5. The measured 2θ value for the (220) face can be seen to be continuously reduced in comparison with the standard 2θ vale of JCPDS card with an increase in ICP power. Such shift in 2θ values to a lower angle is reported to be originating from an increase in compressive stress of the residual stresses.[13] In general, adhesion is reduced whereas wear resistance and hardness are increased, since a considerable amount of residual stress exist in the coatings produced by PVD process. Compressive stresses present in the coatings produced by such PVD process are closely related to the point defects produced by Ar^+ ion bombardment. To produce coatings with a dense microstructure free of columnar structures, ion bombardment is required, and such ion bombardment has large effects on the refinement of grain sizes and the improvement of adhesion. Although absolute values cannot be known since no quantitative analysis of compressive stresses was made, a considerable amount of residual stress is considered to exist inside the coatings obtained in the present experiment, based on the results of Table 1 and Fig. 5.

Table 1. XRD Data for VN Coatings Produced by ICP Assisted Sputtering

VN	Peak position				
	(220)				
ICP power (W)	0	50	100	200	standard
2θ (°)	63.37	63.10	63.03	62.86	64.35

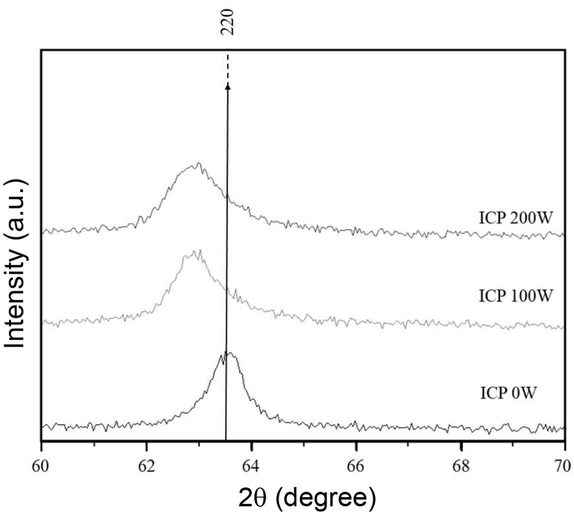

Fig. 5. XRD patterns of maximum peak with shift toward low angles in relationship to the increase in applied ICP powers.

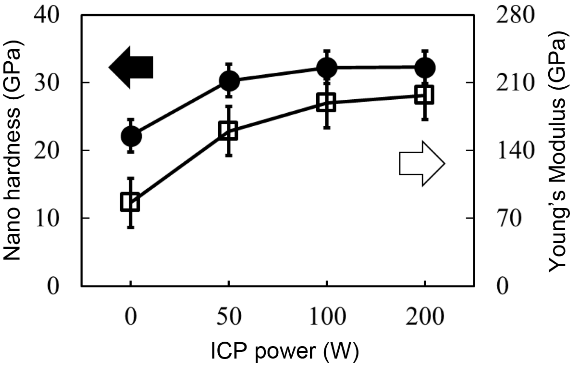

Fig. 6. Nanoindentation hardness and Young's modulus of VN coatings deposited using ICP assisted sputtering at various ICP powers.

3.6. Nano indentation hardness and Young's modulus

For mechanical hardness of the VN coatings produced by ICP magnetron sputtering, the results of average nanoindentation hardness and Young's modulus obtained by using the nano indentation equipment are shown in Fig. 6. Not only measurement of hardness for the thin coatings with a thickness only of a few hundred nm is impossible, but also precise measurement is very difficult due to the nanoindentation size effect.[14] Therefore, for precise nanoindentation hardness measurement for the coatings with a thickness less than 1 μm, the applied load for indenter was fixed at 5 mN, and the average measurement position was set to be the point of 1/10 of the total film thickness to exclude the indentation size effect where the greater tendency toward an increase in measured hardness values was exhibited, the shallower the indentation depth. As shown in the figure, nanoindentation hardness and Young's modulus for the VN coatings could be seen to be continuously increased with an increase in ICP power. While nanoindentation hardness and Young's modulus for the nano-crystalline VN coatings produced at the ICP power of 0 W in the present study were 12.3 GPa and 155.5 GPa, respectively, those for the VN coatings produced at the ICP power of 200 W were 28.2 GPa and 226.0 GPa, respectively, representing an increase of about 230% and 150%, respectively, compared with the coatings produced at the ICP power of 0 W. Such improvement of mechanical properties resulting from the use of ICP and an increase in ICP power is considered attributable to the combined elements including the Hall-Petch effect such as grain refinement of coatings due to ion bombardment of Ar^+ ions, continuous collision among neutral atoms and molecules, and change in internal stresses such as an increase in compressive stresses, etc.

4. Conclusions

In the present study, single-phase VN coatings were produced by using ICP (inductively coupled plasma)-assisted sputtering equipment. Observations were made with a particular emphasis on the effects of ICP on not only microstructural changes such as surface and cross section microstructure, 3D topography, and average grain refinement but also crystal structure change such as crystal structure, preferred orientation, residual stress as well as physical mechanical characteristics such as nanoindentation hardness and modulus of elasticity. With an increase in ICP power, the microstructures of VN coatings were changed from that of columnar structure including rough surfaces accompanied by a large amount of pores to the dense microstructure with dense and smooth surfaces where the columnar structure disappeared. While nanocrystalline, single-phase VN coatings of cubic (FCC) structure was obtained for all coating conditions, the preferred orientation was changed in the order of (111) face, (200) face, and (220) face with an increase in ICP power. Also, for the VN coatings produced at the ICP power of 0 W and 200 W, the corresponding average grain size was reduced from 10.1 nm to 4.0 nm, respectively, and the surface roughness (Ra) was reduced from 9.3 nm to 1.7 nm, while the nanoindenation hardness was correspondingly increased from 12.3 GPa to 28.2 GPa, and the modulus of elasticity was increased from 155.5 GPa to 226.0 GPa.

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