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Effect of Sputtering Power on the Structure of DC Magnetron Sputtered Vanadium Nitride Thin Films

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Abstract

Vanadium nitride (VN) thin films were deposited on Si substrates by reactive DC unbalanced magnetron sputtering. Effect of sputtering power on the structure of the as-deposited films was investigated. The crystal structure, thickness, roughness, surface morphology and chemical composition of the films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS), respectively. The results showed that the as-deposited VN thin films had fcc structure with (111), (200) and (220) planes, varying with the sputtering power. The crystallite size and lattice constant of films were in the range of 16-49 nm and 4.119-4.147 Å, respectively. The film thickness and roughness increased with increasing of the sputtering power, from 275 nm to 830 nm and 3 nm to 12 nm, respectively. The as-deposited films compose of vanadium and nitrogen in different ratios, depending on the sputtering power. Cross section analysis by FE-SEM showed a compact columnar structure.

Keyword: Vanadium nitride; Thin films; DC magnetron sputtering; Sputtering power

Introduction

Surface modification by coating a thin layer on surface substrates is an important industrial process used to protect base material from many surface damages. Nowadays, most of machinery parts, cutting and forming tools are coated by hard coating or hard thin film, which increase in lifetime and more efficient compared to uncoated. The transition-metal nitrides such as TiN, CrN, and ZrN are known as the first generation of PVD hard coating, have attracted widely uses because of their outstanding physical and chemical properties, such as ultrahigh hardness, high melting point, high thermal stability, corrosion resistance, and metallic conductivity [(1)].

Among them, vanadium nitride (VN) thin film has been recently interested due to its excellent properties including wear resistance, high melting point, extreme hardness, high thermal conductivity, corrosion resistance, chemical stability, low electrical resistivity [(2)] and low friction coefficient at elevated temperatures caused by the formation of surface oxide phases which may act as self-lubricants [(3)].

Therefore, to deposited VN thin films with different structure or desired structure, several deposition techniques such as chemical vapour deposition.[(4)] pulse laser deposition,[(5)] ion beam assisted deposition,[(6)] reactive magnetron sputtering.[(7)] and reactive electron beam evaporation.[(8)] were used. Among them, sputtering is one of the preferred techniques for deposit of hard coatings due to advantages such as better control of process parameters and stoichiometry of the deposited coatings, low-temperature process, use of non-toxic gases and simple process [(9)].

It is common knowledge that the properties of thin films are related to certain characteristics, such as crystal structure, chemical composition, microstructure and surface morphology of the films which depend on deposition parameters such as gas flow rate, pressure, sputtering current, sputtering power, substrate heating, substrate-target distances and substrate bias. Therefore, the study of deposition parameters is useful to understand the structure and properties of the films to develop for desired characteristics. Until now, many researchers have been focused on the influences of the deposition parameters on the structure of VN thin films. However,

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current literatures report few results of the structure of VN thin films which deposited at various different sputtering powers.

In this research work, the effects of sputtering power on the structures of VN thin films, deposited by reactive DC unbalanced magnetron sputtering on crystal structure, thickness, roughness, microstructure, surface morphology and elemental composition were investigated.

Materials and Experimental Procedures

Thin films of VN were deposited on Si substrates by reactive magnetron sputtering from a homemade DC unbalanced magnetron sputtering system as show in Figure 1. The system is capable of creating a base pressure of 5×10^{-5} mbar in sputtering chamber using diffusion pump and rotary pump combination. The pressure in the chamber was measured by PFEIFFER Pirani–Penning gauge combination PKR 251 compact full range gauges with TPG 262 control and measurement unit. A circular planar magnetron of 50 mm diameter was used as the magnetron cathode. The magnetron target assembly was mounted on the top plate of the sputter chamber such that the sputtering could be done by sputter down configuration. Vanadium disk (99.95% pure) with 50 mm diameter and 3 mm thick was used as sputter target. A continuously variable dc power supply of 1,000 V and 3 A was used as a power source for sputtering. Pure Ar (99.999%) and N_2 (99.999%) were used as the sputtering and reactive gases, respectively. MKS type247D mass flow controllers were used to control the flow rate of both the argon and nitrogen gases individually.

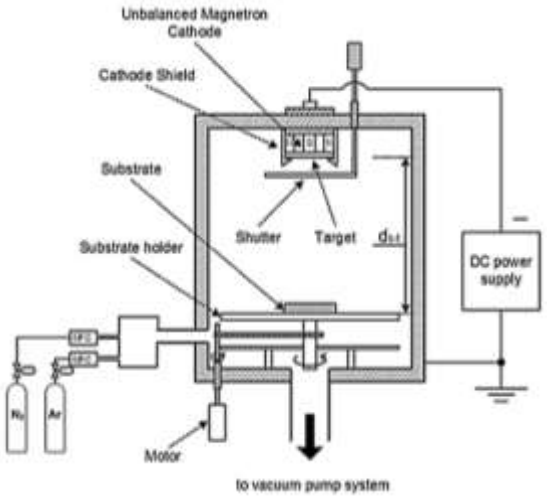

Figure 1. Schematic diagram of deposition system use in this work.

Before deposition of each VN film, the chamber was evacuated to a pressure below 5×10^{-5} mbar. The targets were pre-sputtering with the Ar gas atmosphere for 10 min while the substrate was shielded by shutters in order to remove the contaminant on the target surface contaminant. VN thin films were deposited at different sputtering power from 110 W to 280 W and remaining deposition parameters such as nitrogen gas flow rate, substrate temperature and sputtering pressure were constant. The deposition conditions as listed in Table 1.

Table 1. Thin films deposition conditions

Paremeters	Details
Sputtering target	Vanadium (99.95%)
Substrate temperature	room temperature
Substrate-target distances	10 cm
Base pressure	$5.0\text{x}10^{-5}$ mbar
Working pressure	$5.0\text{x}10^{-3}$ mbar
Sputtering power	110, 195, 280 W
Flow rate of Ar : N_2	20 sccm : 2 sccm
Deposition time	60 min

The as-deposited VN thin films were characterized by several techniques to studying crystallographic structure, surface morphology, and microstructure. The crystal structure was determined by glancing angle X-ray diffraction (GAXRD: Bruker D8). The incident angle of 3º with 2θ-scan varied from 20°-80°. The crystallite size can be calculated from the full width at half maximum (FWHM) in the XRD pattern using Scherrer's equation. The surface morphology and roughness were evaluated by Atomic Force Microscope (AFM: SEIKO SPA400). The thickness, microstructure, and cross-section structure were investigated by Field Emission Scanning Electron Microscope (FE-SEM: Hitashi s4700). The composition of the films was determined by energy dispersive X-ray spectroscopy (EDS: EDAX).

Results and Discussion

Deposition rate

VN thin films were deposited on Si by reactive DC unbalanced magnetron sputtering at various sputtering powers and keeping the other deposition parameters such as nitrogen flow rate, substrate temperature, and sputtering pressure as constant. Figure 2 show the variation

of deposition rates, which determined from the thickness divided by the deposition time, as a function of the sputtering power. The results show a significant increasing of the deposition rate with increasing the sputtering power. The deposition rate of the films increased form 4.6 nm/min to 13.8 nm/min with increasing the sputtering power from 110 W to 280 W. As the sputtering power increased, the argon ion bombardment rate increased on the surface target, increasing the deposition rate of the films.

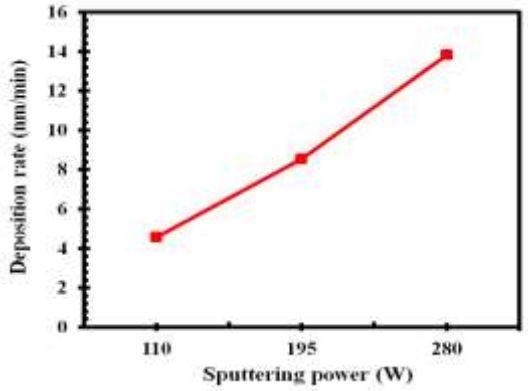

Figure 2. The deposition rate of VN films with different sputtering power

Chemical composition

An increase of the sputtering power affected the chemical composition (atomic concentrations of V and N) of the as-deposited thin films. In this work, it was found that as the sputtering power increased from 110 W to 280 W, the V content of the as-deposited films increased from 36.1 wt.% to 43.4 wt.%, while the N content decreased from 63.9 at.% to 56.6 at.% as show in Figure 3. The ratio of V:N was about 0.6 - 0.8, which increased with increasing of the sputtering power.

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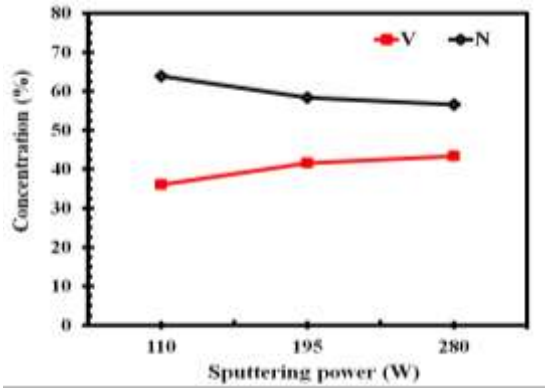


Figure 3. Chemical composition of VN films with different sputtering power.

XRD results

Figure 4 shows the XRD patterns of the as-deposited VN thin films deposited on Si substrates for different the sputtering power from 110 W to 280 W. The diffraction pattern at 2 θ of 43.9° which corresponded to the VN structure (JCPDS card No. 35-0768) was only observed at the sputtering power 110 W. At 195 W, the 2θ peak at 37.79°, 43.9° and 63.89° which respect to the (111), (200) and (220) planes of VN structure with prefer orientation at (111) plane (JCPDS card No. 35-0768). As sputtering power reach to highest value of 280 W, the (111) and (220) planes were still performed whereas (200) plane was disappeared.

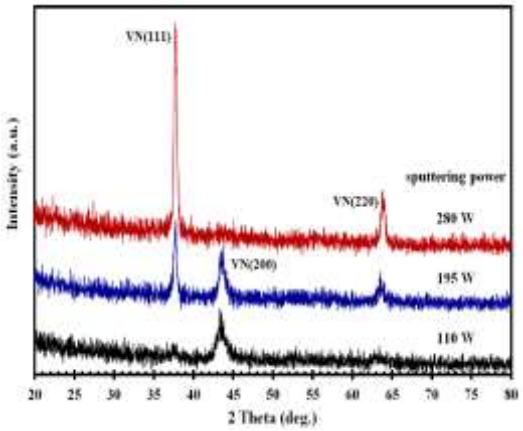


Figure 4. XRD patterns of VN thin films deposited with different sputtering power.

It can be implied that the plane evolution from only (200) plane to the planes of (111) and (200) was direct influenced by sputtering power. The X-ray intensities of all planes were increased with sputtering power increased to 195 W. The crystallinity of (111) and (220) were still improved but the (200) plane was suddenly disappeared which obtained for sputtering power of 280 W.

The film crystallinity at higher sputtering power stronger respected to the films deposited at lower sputtering power was clearly observed. It can conclude that the sputtering power raised the film crystallinity which attributed to larger impact energy of the bombarding particles, which leads to better adatom mobility on surface, therefore forming highly crystalline films [10].

The calculated crystal size and lattice constants of the as-deposited the films as a function of sputtering powers were reported in

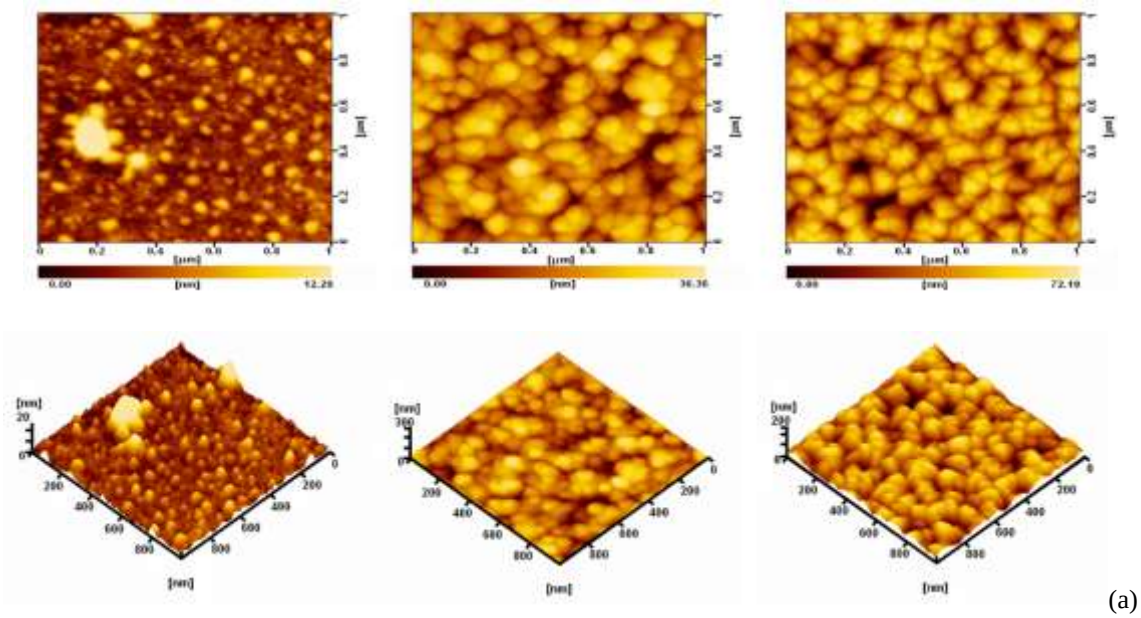
Table 2. The crystallite sizes which obtained from the Scherrer's equation were increased from 16.3 nm to 49.4 nm as increasing sputtering power. The larger of crystallite size through the sputtering power implied that the high adatom kinetic energy induced higher surface mobility resulting improved the strengthen crystallinity of the VN thin films at higher sputtering power as evidence from XRD results [11]. In addition, the lattice constant of the as-deposited thin films which calculated fromdiffraction plane were almost constant in the range of 4.145 Å to 4.124 Å as increasing sputtering power from 110 W to 280 W. This results are good agreement compared to the standard lattice constant value (4.145 Å) from JCPDS card no. 35-0768.

Table 2. Deposition conditions and some properties of VN films at different sputtering power

Sputtering power (W)	Thickness (nm)	Roughness (nm)	Crystal size (nm)	Lattice constants (Å)	Composition V (wt%)	N (wt%)	V:N
110	275	3	16.3	4.145	36.09	63.91	0.6
195	513	5	41.9	4.147	41.61	58.39	0.7
280	830	12	49.4	4.124	43.40	56.60	0.8

Surface morphology

Figures 5 show the surface morphologies as two dimension and three dimension AFM images with the same squared size (1 μm^2) of VN thin films deposited at different sputtering powers. The small grains with triangle shape spread across the surface were investigated at low sputtering power of 110 W (Figures 5(a)). At 195 W, the spherical structure of grain sizes were gradually increased (Figures 5(b)). The grains aggregation with facet structures were found as sputtering power increased to highest value of 280 W (Figures 5(c)). The RMS roughness values which obtained from AFM images were significantly increased from 3 to 12 nm as a function of sputtering powers. It can be noticed that the evolution of surface morphology and surface roughness were dependence on sputtering power. According to result above, it indicates the changes of surface morphologies and RMS roughness are according to the fact that sputtering power helps to increase the atomic mobility on the growing surface which resulting the grain size enhancement [12].



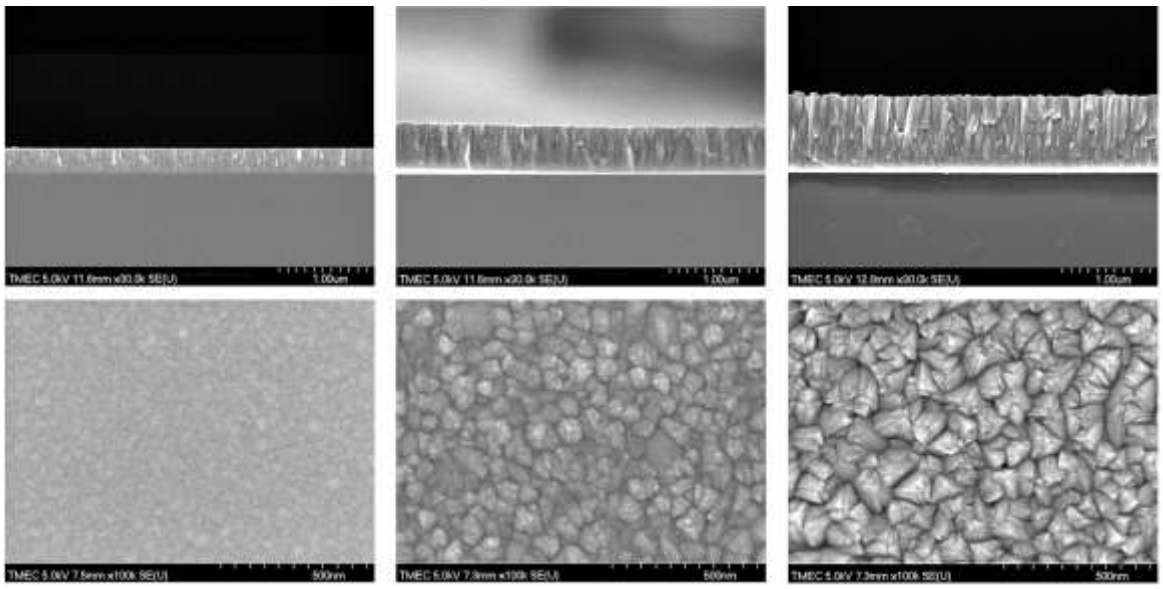
(a) power = 110 W (b) power = 195 W (c) power = 280 W

Figure 5. AFM images of VN thin films deposited with different sputtering power.

Microstructures

Figures 6 illustrated microstructure and the cross-sectional SEM micrographs of the as-deposited VN thin films. It is evident that films sputtered at low sputtering power (110W) contain small spherical grains but the grains boundaries along the coating surface are not clear. As the sputtering power reached to 280 W, the grain size become bigger and the facet structure were obtained with clearly seen the void between the columnar grains compared to the films deposited at low sputtering power of 110 W. It was evident that with high DC sputtering power, the larger kinetic energy of the sputtered particles arriving at substrate surface and can migrate to more lattice site which helpful for nucleation and growth consequently the grain size was increased [13]. The cross-sectional FE-EM images of VN thin films deposited at various sputtering power were investigates as shown in Figures 6. The development of grain structure from dense microstructure to porous columnar grain structure, which contains long columnar grains and clear grain boundaries throughout the film thickness were clearly seen as increased sputtering power from 110 W to 280 W. The film exhibited similar columnar structure were consistent with the Thornton model [14].

The film's thicknesses were increased from 275 nm to 830 nm. It was due to the kinetic energy of the sputtered particles enhanced which in turn multiplies flux of the deposition atoms reaching to the substrate per time unit by increasing the sputtering power, therefore increasing film thickness [15].



(a) power = 110 W (b) power = 195 W (c) power = 280 W

Figure 6. FE-SEM micrograph of VN thin films deposited with different sputtering power.

Conclusions

VN Thin films were deposited by DC unbalanced magnetron sputtering technique of pure metallic vanadium target on Si substrates in a mixture of argon and nitrogen atmosphere at different sputtering powers in the range of 110-280 W. The effect of sputtering power on the structure of films was systematically studied. According the XRD results, the as-deposited VN thin films had fcc structure with (111), (200) and (220) planes, through the sputtering power. The evolution of diffraction plane was also observed. Moreover, when sputtering power increased it produced an increased of the crystallinity and crystallite size from 16 nm to 49 nm. The lattice constant were in the range of 4.119 –4.147 Å. The higher the sputtering power, the deposition rate of the VN film is higher. The as-deposited films compose of vanadium and nitrogen in different ratios, depending on the sputtering powers which identified from EDS. The AFM results indicate that an increase of sputtering power promoted grains enhancement with RMS roughness increased from 3 nm. to 12 nm. Cross section analysis by FE-SEM show thicknesses were enhanced from 275 nm. to 830 nm. A uniform compact columnar structure was observed.

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