

INFLUENCE OF N₂ FLOW RATE ON THE PROPERTIES OF VANADIUM NITRIDE THIN FILMS DEPOSITED BY REACTIVE DC MAGNETRON SPUTTERING

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Abstract

Vanadium nitride (VN) thin films have been deposited on silicon wafer substrates by reactive DC magnetron sputtering with varied nitrogen (N₂) flow rates from 5.0 to 8.0 sccm without substrate heating. The crystallinity, morphology, and optical properties of the prepared VN films were investigated by grazing-incidence X-ray diffraction (GIXRD), field emission scanning electron microscope (FE-SEM), and UV-Vis-NIR spectrophotometer, respectively. The GIXRD pattern shows that the crystal structure of the films is consistent with the face-centered cubic VN structure. An increase in N₂ led to a decrease in film thickness and sheet resistance. On the contrary, the reflectance percentage tends to increase with the increase of N₂ flow rate. [Copyright information to be updated in the production process].

Keywords: Reactive DC magnetron sputtering; thin film; vanadium nitride

Introduction

Transition metal nitride thin films such as TiN, CrN, and ZrN were known as the first generation of physical vapor deposition (PVD) hard coating and they have been widely used in many industrial applications due to their outstanding properties such as high hardness, good wear resistance, corrosion resistance, high chemical stability and sometimes, the beauty of their apparent colors (Chou *et al.*, 2002; Niyomsoan *et al.*, 2002; Wang *et al.*, 2015).

In addition to the traditional transition metal nitride thin film, vanadium nitride (VN) has recently gained interest due to its excellent physical properties including high hardness, wear resistance, high melting point and low electrical resistivity (Chu *et al.*, 1996; Aissani *et al.*, 2019; Wu *et al.*, 2019). One additional highlight property of vanadium nitride film is its ability to decrease the friction coefficient when the temperature is increased,

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which is a result of the formation of surface oxide phases (V₂O₅) at a high temperature that acts as self-lubricants (Gassner *et al.*, 2004; Glaser *et al.*, 2007).

VN thin films can be prepared by various techniques such as reactive DC magnetron sputtering (Gassner *et al.*, 2004; Glaser *et al.*, 2007; Wu *et al.*, 2019), reactive RF magnetron sputtering (Aissani *et al.*, 2019), chemical vapor deposition (Parkin and Elwin, 2001), pulsed laser deposition (Guo *et al.*, 2016) and ion beam assisted deposition (Ma *et al.*, 2000). Among these methods, sputtering is the common technique to provide good film adhesion and high film crystalline due to the fact that this technique can effectively control deposition parameters and stoichiometry of the coating films. Moreover, this method can be applied to large-area coating for industrial applications. This paper focuses on the study of the influence of nitrogen on the properties of VN thin films deposited by reactive DC magnetron sputtering technique, by varying the nitrogen gas flow rate while the sputtering current of V target was kept constant. The properties of the prepared VN thin films including crystal structure, morphology, optical and electrical property have been investigated.

Experimental Details

The thin films of VN were prepared by a homemade reactive DC magnetron sputtering system without substrate heating and no substrate bias. The metallic vanadium disk (99.99% in purity), with a diameter of 3 inches was used as a sputtering target. The pre-cleaned Si wafer (100) was used as a substrate for thin film characterization. Ultra-high purity Ar (99.999%) and N₂ (99.999%) were used as the sputtering and reactive gas, respectively. The N₂

flow rate was precisely controlled by independent mass flow controllers (KOFLOC DF-300).

Prior to the deposition, the chamber was evacuated to the base pressure of 5×10^{-5} mbar. The V target was pre-sputtered by Ar for roughly 5 min to remove the possible surface contaminations. During the deposition, the sputtering current of the V target was kept constant at 800 mA. The flow rate of Ar was fixed at 45 sccm while the flow rate of N₂ was varied from 5 to 8 sccm, as a result, the working pressure was approximately 5×10^{-3} mbar. The deposition time was fixed at 30 minutes for all samples.

The crystal structure of the obtained VN thin films was characterized by grazing incidence X-ray diffraction (GIXRD, Rigaku) using Cu K α radiation at 40 kV and 30 mA. The thickness and surface morphology of thin films were determined by field-emission scanning electron microscopy (FE-SEM; Hitachi S8080) operated at 5 kV. Optical properties were investigated by UV-Vis-NIR spectrophotometer (Agilent, Cary 7000). The electrical sheet resistance of the prepared films was measured by the typical 4-point probe measurements.

Results and Discussion

The GIXRD patterns of VN thin films deposited at different N₂ flow rates from 5 to 8 sccm are shown in Figure 1(a). The crystal structure of all the prepared VN thin films was found to be the face-centered cubic (fcc) structure with the lattice constant of ~ 4 Å, which corresponds to the reported VN structure (JCPDS No. 025-1252). The Bragg peaks at 38.1° and 64.4° can be indexed as the (111) and (220) planes, respectively. The diffracted peak intensities were approximately constant throughout

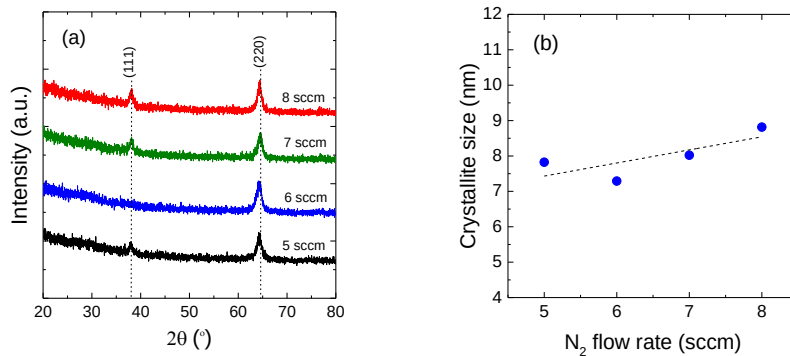
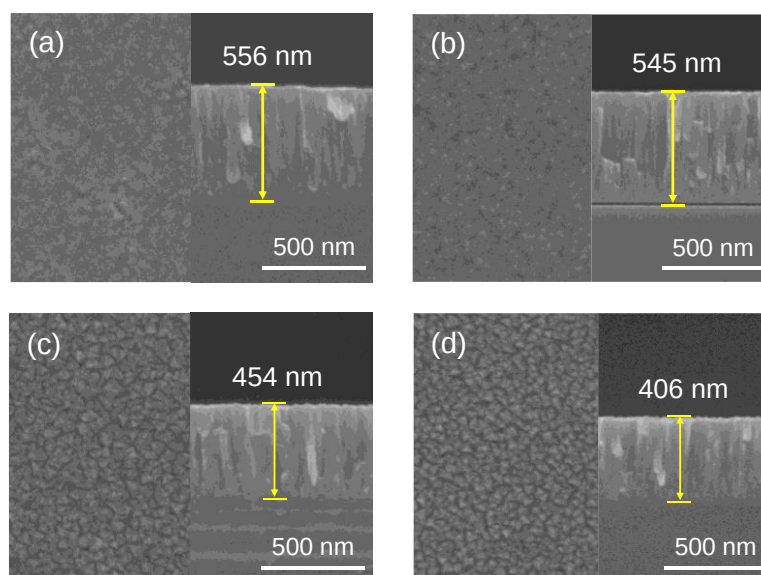


Figure 1. (a) GIXRD patterns of VN thin films deposited at N₂ flow rate of 5 (black), 6 (blue), 7 (green), and 8 sccm (red). (b) Calculated crystallite sizes from the (220) Bragg peak as a function of N₂ flow rate. The dashed line is a guide to the eye

Table 1. Lattice constant, crystallite size, thin film thickness, and sheet resistance of the VN thin films with N₂ flow rate of 5, 6, 7, and 8 sccm

N ₂ flow rate (sccm)	Lattice constant (Å)	Crystallite size (nm)	Thickness (nm)	Sheet resistance (Ω/sq)	Resistivity (μΩ-cm)
5	4.094	7.8	556	70.11	38.98
6	4.097	7.3	545	42.31	23.06
7	4.085	8.0	454	21.30	9.67
8	4.091	8.8	406	12.59	5.11

**Figure 2. Cross-sectional and surface FE-SEM images of VN thin films deposited at (a) N₂ = 5 sccm, (b) N₂ = 6 sccm, (c) N₂ = 7 sccm and (d) N₂ = 8 sccm**

the entire range of N₂ flow rate suggesting that the lattice constant is not noticeably changed. In fact, we calculated the values of the lattice constant and approximated the crystallite sizes using the well-known Scherrer's equation from the (220) Bragg peak, which is summarized in Table 1.

As expected, the lattice constants' values are in the range of 4.085-4.097 Å, very close to the reported value of 4.090 Å and independent of the N₂ flow rate. However, the calculated crystallite sizes tend to be slightly increased with the increase of N₂ (Figure 1(b)). It can also be seen from the FE-SEM images in Figure 2(a)-(d) that as the flow rate increases the film surface was formed into clear grain which might explain the increment of the crystallite size values upon N₂ flow rate. In addition, the columnar feature can be clearly seen in all samples suggesting the quality of the obtained VN thin films. The thin film thicknesses with the 30-min deposition time are drawn to the scale of the FE-SEM images as shown in Figure 2. At the lowest N₂ flow rate of 5 sccm where the thickness is 556 nm, it decreases by 27 % to 406 nm at N₂ = 8 sccm. This suggests that, with the same deposition time, the N₂ flow rate only slightly affects the thickness of

the film. The thin film thickness, with the same deposition time, linearly decreases with the increase of the N₂ flow rate (Figure 3(a)). This is typically due to target poisoning, a process in which an excess of N₂ interacts with the target. As a result, the target becomes nitride itself leading to a decrease in the sputtering yield of the target.

One of the highlight properties of VN film is its low electrical resistivity. Here we measure the sheet resistance using the typical four-probe method. As can be seen from Figure 3(a) and the summation in Table 1, the sheet resistance is in the approximate range of 12-70 Ω/sq. The higher the N₂ flow rate, the lower the sheet resistance. These values are considerably lower than the typical metal nitrides e.g., TiN, ZrN (Kim *et al.*, 2000; Signore *et al.*, 2010). When the N₂ flow rate increases, thickness and sheet resistance both decreases. As a result, the resistivity substantially decreases with the increase of N₂ flow rate from 5 to 7 sccm at which the resistivity tends to be constant afterward. It is suggested that the resistivity of VN thin film might not drastically change with a further increase in the N₂ flow rate.

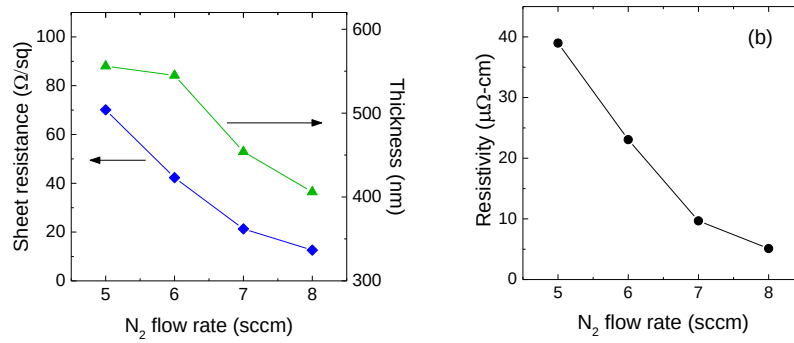


Figure 3. (a) Sheet resistance (blue diamond, left axis), thin film thickness (green triangle, right axis), and (b) the resistivity of VN films as a function of N_2 flow rate

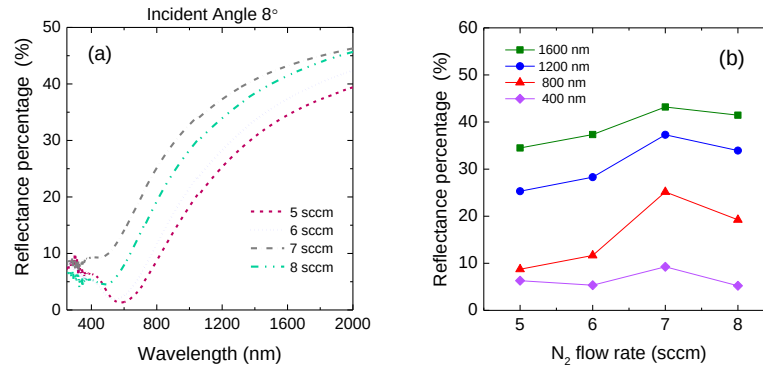


Figure 4. (a) UV-Vis-NIR reflectance spectra of the VN thin films. (b) Reflectance percentage of the VN thin films as a function of N_2 flow rate at the wavelengths of 400 nm (purple diamond), 800 nm (red triangle), 1,200 nm (blue circle), and 1,600 nm (green square)

Lastly, we investigate the influence of N_2 flow rate on the reflectance spectrum from UV to near IR wavelength at the incident angle of 8° . The results are shown in Figure 4(a). The reflectance of all samples increases with the longer wavelength. However, on the $N_2 = 5$ and 6 sccm samples, the reflectance drops to almost zero at the wavelength of approximately 600 nm i.e., the orange color region. It can be seen from Figure 4(a) that the reflectance minimum moves toward a lower wavelength as the N_2 flow rate increases. This feature therefore could be applied to reflective color filter applications. The reflectance over the visible light region tends to increase with the increase of N_2 flow rate, and with the decrease of film thickness, except for an anomaly at $N_2 = 7$ sccm which the reflectance jumps above the highest $N_2 = 8$ sccm as can be seen from Figure 4(b). It should be noted that the reflectance typically decreases as the increase of surface roughness. This is due to the formation of granules, which causes non-uniform light scattering. This suggests that the surface roughness tends to

decrease with the increase of the N_2 flow rate. Therefore, despite the same crystal structure, the influence of the N_2 flow rate seems to impact more on the resistivity and the reflectance but not on the crystal structure.

Conclusions

We successfully prepare VN thin films with varying N_2 flow rates using a homemade reactive DC magnetron sputtering system without substrate heating. All the prepared VN thin films exhibited fcc structure. With an increase in N_2 flow rate, the film thickness decreases while the crystalline increases. The four-point probe analysis revealed a decrease in sheet resistance from 70.11 to 12.59 Ω/sq and the resistivity from 38.98 to 5.11 $\mu\Omega\text{-cm}$. The reflectance percentage monotonically increases with the wavelength increase, reaching the UV region plateau. With the very low resistivity in VN thin film and its possibility for use as the reflective color

filter in the yellow-orange region, these properties are left for future detailed investigations as well as their possible applications in the field of optoelectronic devices.

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