Synthesis of Highly Pure and Hydrophilic Metal-Nitride Thin Films Using Reactive High-Frequency Magnetron Sputtering

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Abstract

The increasingly widespread innovation of nanotechnology significantly affects our society, especially its contribution to economies. Nanosized metal nitrides possess interesting properties (e.g., highly corrosive resistant, good electrical properties, great metallic conductivity, etc.) that are capitalized, resulting in numerous applications. The thin film preparation procedure is an important step that determines the film's characteristics, such as crystallographic orientation. Hence, this study pursues the synthesis of metal-nitride thin films and characterizes their properties for future possible applications. Vanadium nitride (VN) and aluminum nitride (AlN) were synthesized and deposited on silicon substrates via high-frequency magnetron sputtering. The crystalline structure of the thin films was characterized using X-ray diffraction (XRD), and the wettability was determined using static contact angle measurement. Accordingly, the (311) phase of vanadium nitride and the (100) and (004) phases of aluminum nitride were observed with no impurities. Meanwhile, the static water contact angle indicated a hydrophilic property in both thin-film samples, as the values were observed to be less than 90°.

Keywords: contact angle, metal nitrides, nanotechnology, sputtering, thin film

Introduction

The bonding of a specimen at the micro or nano level is different from that of the bulk level; hence, there are entirely novel physical and chemical properties. Indeed, there is a size-dependent effect from previous works of literature(Roduner, 2006, 2007). Moreover, magnetron sputtering as a synthesis method has gained attention from several researchers due to its reputation and advancement as an industrial coating method (Gudmundsson, 2020; Gudmundsson & Lundin, 2020; Rossnagel, 2020). Studies about metal nitride thin films produce interest among researchers due to their application as microelectronic device diffusion barriers, wear-resistant coatings, protective coatings in surgical types of equipment, electrode material in supercapacitor devices, energy harvesting, and transducers.(Hajihoseini & Gudmundsson, 2017; Huang et al., 2019; Iqbal & Mohd-Yasin, 2018) Several periodic table elements, particularly metals, can produce compounds with nitrogen. Stable compounds emerge mostly from nitrogen, forming bonds between low electronegativity elements (i.e., transition metals) (Chen et al., 2012; Hugosson et al., 2004). Metal nitrides such as tungsten nitride, chromium nitride, and molybdenum nitride were synthesized, and their mechanical and structural properties were examined with the influence of partial pressures. It was reported that morphological and compound electronic structure affected the material's hardness (Hones et al., 2003). The result of this research could contribute to the growing body of knowledge of nanotechnology applications, especially in the Philippines.

Framework of the Study

There are numerous synthesis routes to produce thin films (Chauhan & Rawal, 2014; Mohimi et al., 2019; Venkateshalu et al., 2020) and will play a significant role in terms of the thin film properties; nevertheless, for this particular study, high-frequency magnetron sputtering was utilized as a synthesis method. This particular machine is a project from DOST that is only available in Mindanao State University - Marawi City. Hence, this will open further research and development on nanotechnology in the Mindanao region.

Objectives of the Study

This study primarily aims to synthesize highly pure metal nitrides (i.e., vanadium and aluminum metals) on a silicon wafer via reactive high-frequency magnetron sputtering (SCOTT-C3 VTR-151M/SRF 27 ULVAC KIKO Inc) technique, examine the crystalline structure of the deposited films, and to analyze the thin film's wettability.

Methods

The vanadium nitride (VN) and aluminum nitride (AlN) thin films were deposited on a silicon wafer substrate from 99.99% pure vanadium and aluminum metal via reactive high-frequency magnetron sputtering technique, respectively. A complete schematic diagram of the sputtering mechanism is shown in **Figure 1.**

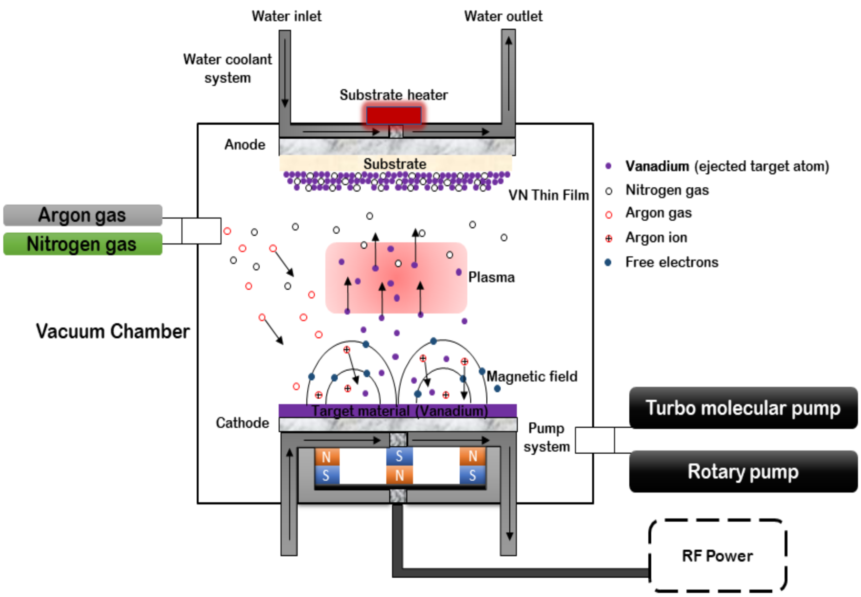

Figure 1. *High-Frequency Magnetron Sputtering Schematic Diagram*

To facilitate the deposition, the vacuum chamber was evacuated at a base pressure of $5x10^{-4}$ Pa to prevent contamination from unwanted, unnecessary gasses. Further, vanadium and aluminum metal were 5 cm relative to the silicon wafer substrate, wherein the substrate was heated at 300°C. The RF Power at 50 W was fixed among the samples. The crystalline structure of the VN and AlN thin film was examined using the x-ray diffraction technique (XRD) (X'pert Pro PANalytical PW 3040 MPD). Utilizing the Bragg's Law, lattice spacing was computed using the equation (Epp, 2016):

$$n\lambda = 2dsin\theta \quad (1)$$

where, $n\lambda$ is the wavelength, d represents the interplanar spacing, and θ is the critical angle. Lastly, Scherrer's equation was utilized to compute the crystallite size, the equation (Durai et al., 2019)

$$crystallite\ size\ (D) = \frac{k\lambda}{\beta cos\theta} \quad (2)$$

where, k represents the form factor, λ is the wavelength, and β represents the full width-half max. Furthermore, in obtaining the contact angle, the liquid drops were facilitated with 5 trials across all samples for its repeatability. Lastly, the wettability of the untreated substrate, VN, and AlN thin film was determined using public domain software (*ImageJ*) through static contact angle measurement wherein distilled water was utilized as a probe liquid. The contact angle mean and standard deviation were computed to show data variability and consistency.

Results and Discussion

Figure 2 provides the corresponding images of the synthesized pure metal nitride (i.e., vanadium nitride and aluminum nitride thin film)

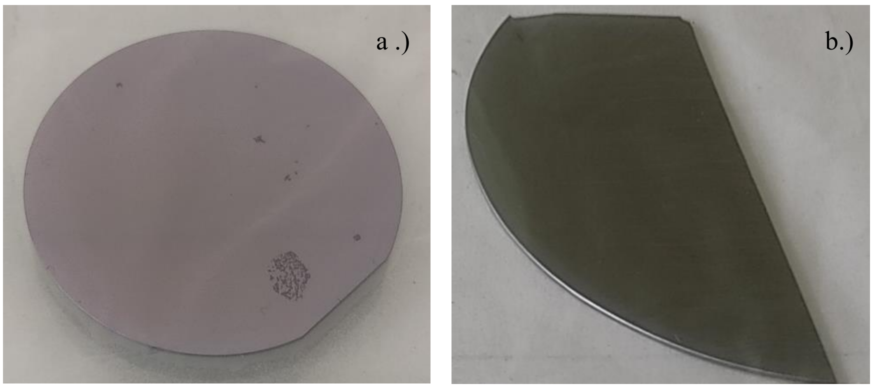

Figure 2. *Synthesized thin films* a) *Vanadium Nitride* b) *Aluminum Nitride*

Conditions for all the metal nitrides are identical. Collectively, however, the diffractogram shown in **Figure 3** exhibits different crystal structures (miller indices) due to property discrepancy between metal targets per se i.e., metal targets material strength and original orientation. It is noteworthy that the deposition parameters (i.e., substrate temperature, flow rate, power, etc.) mainly influence the crystallographic orientation and, thus, determine its physical properties.(Achour et al., 2018) Observed from the diffractogram, the VN thin film displayed a Bragg peak at $2\theta = 76.9°$ which denotes a (311) diffraction pattern that reflects a VN fcc structure (JCPDS ICDD no. 00-035-0768) (Escobar et al., 2013; Robert et al., 2018). The (311) crystallographic orientation was also observed in the work of Aissani et al. in 2021 (Aissani et al., 2021) wherein they varied the nitrogen gas flow rate to study its effects on the structure and tribo-mechanical properties of vanadium nitride. In our work, we achieved growing a (311) crystallographic orientation despite with a total sputtering gas flow rate of 20 sccm compared to their work at 100 sccm. On the other hand, the AlN thin film showed a Bragg peak at $2\theta = 32.9°$ and $2\theta = 75.5°$ which represents a (100) and (004) crystallographic orientation of AlN structure, respectively. The obtained peaks were also observed in the work of Tarala et al. in 2016 (Tarala et al., 2016). In their work, they have utilized the plasma-enhanced atomic layer deposition (PEALD) method to synthesize AlN thin film by varying the substrate temperature below 300°C. In contrast with our work, we managed to obtain the peak using high frequency magnetron sputtering method despite the difference in the experiment conditions and method. AlN with a highly c-axis crystallographic orientation is known for its piezoelectric application since it appears to have the most practical solution to a wide array of transducers (Iqbal & Mohd-Yasin, 2018). It can be observed in the diffractogram that we have grown a (004) c-axis crystallographic orientation known as the higher-order reflection of (002) which reflects a c-axis orientation of AlN. Hence, the synthesized AlN has the potential use for piezoelectric application. The Bragg peaks of vanadium nitride (311) and aluminum nitride (100) and (004).

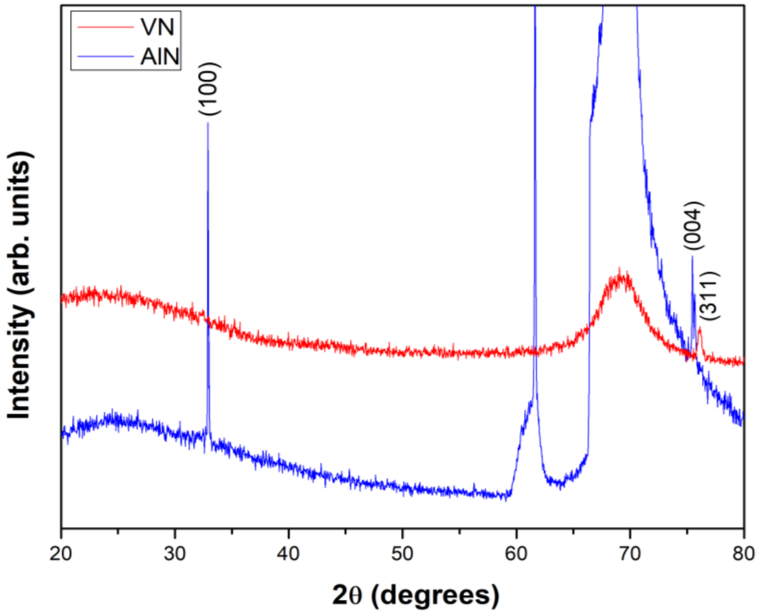

Figure 3. *Diffractogram of VN and AlN*

Comprehensive crystallographic information of the synthesized VN and AlN thin film is shown in **Table 1**. Given the computed results that correspond to crystal orientations of the following thin films using **Eq. 1** and **Eq. 2**, The VN thin film displayed a lower crystallite size and interplanar spacing (d-spacing) than that of the AlN thin film. Conversely, VN thin film displayed more broad FWHM relative to AlN. Thus, this deposition parameter creates more crystalline AlN compared to VN. Nevertheless, both samples displayed a crystalline thin film.

Table 1. *Crystallographic properties of VN and AlN thin films*

Samples	*hkl*	Full width at half max (FWHM)	d-spacing (Å)	Crystallite size (nm)
VN	3 1 1	0.316800	1.25004	33.2554
AlN	1 0 0	0.18	2.72032	46.0217
AlN	0 0 4	0.1512	1.25861	66.4376

The wettability of the untreated substrate in comparison to VN and AlN thin film is presented in **Figure 4**. As depicted, there is a significant difference between the untreated silicon wafer substrate and metal nitrides thin film, especially, VN thin film at 22.77° contact angle. It can be identified that these metal nitrides are hydrophilic, particularly in this experiment's implemented deposition conditions since their contact angles are less than 90° (Marmur et al., 2017). Surface roughness could be a further explanation as to why these metal nitrides are dissimilar in terms of their wettability according to Wenzel state theory (Gorodzha et al., 2015; Wenzel, 1949). A study published in 2016 by Vadyiar et. al. (Vadiyar et al., 2016) reported that they utilized static contact angle measurement or surface wettability as a cost-effective approach in running an investigative assessment on the capacitive property of a supercapacitor. It was found that there was an increase in specific capacitance with increasing wettability (low contact angle). A correlation between wettability and specific capacitance was reported. In Figure 4, vanadium nitride thin film displayed a hydrophilic property which makes it a great candidate for a potential supercapacitor electrode. The mean and standard deviation contact angle of untreated and metal nitride samples is shown in **Table 2**.

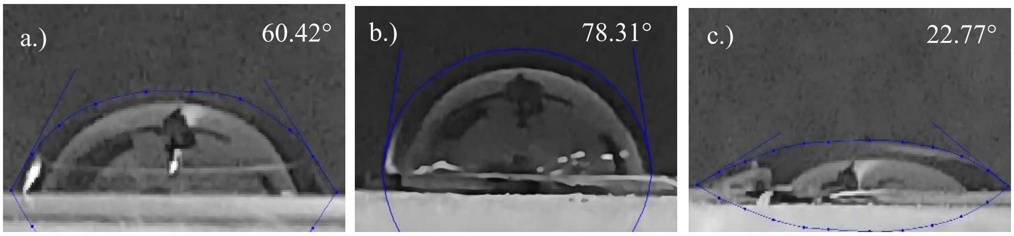

Figure 4. *Static contact angle measurement from ImageJ* a.) *untreated* b.) *AlN* c.) *VN*

Table 2. *The mean contact angle of untreated, AlN, and VN thin films*

Samples	(°)
Untreated	60.42° ± 3.20
AlN	78.31° ± 2.56
VN	22.77° ± 8.58

Conclusion

Pure vanadium nitride and aluminum nitride were successfully synthesized via high-frequency magnetron sputtering method. A particular deposition condition produced crystalline film according to the diffractogram i.e., VN and AlN, respectively. A significant distinction of metal nitride-coated thin film from the untreated silicon substrate is observed. VN and AlN exhibit a contact angle of 22.77° and 78.31°, respectively. From the wettability results, a hydrophilic VN showed high cohesive characteristics which can be used as corrosive-resistant coating and can be incorporated into increasing the capacitance of supercapacitors. Meanwhile, AlN characteristics showed a potential that can be used in piezoelectric applications.

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