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Effects of experimental parameters on the physical properties of non-stoichiometric sputtered vanadium nitrides films

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Abstract

Polycrystalline vanadium nitrides thin films were deposited onto (1 0 0)-oriented silicon wafers by reactive dc planar magnetron sputtering. The influence of the nitrogen gas flow (from 0 to 15 sccm) was studied. Several substrate temperatures were investigated: 150, 400 and 650 °C. Analytical techniques including X-ray diffraction and reflectivity, atomic force microscopy and optical photospectrometry were used to characterize the structure, the morphology and the optical properties of the films. The measured thickness indicates that the deposition rate is decreased (from 3.5 Å for 0 sccm to 1.5 Å for 15 sccm) with increasing nitrogen gas flow. Obtained structures depend on the substrate temperature. The structure of pure vanadium (0 sccm) varies from amorphous phase at 150 and 400 °C to α-V phase at 650 °C. The films crystallize dominantly in β-V_2N_{1-x} phase at low nitrogen gas flows and in δ-VN_{1-x} phase at high nitrogen gas flows. The as-deposited VN films were highly textured. The texture seems to depend on the nitrogen gas flow. The root mean square (rms) derived from atomic force microscopy (AFM) varies with the nitrogen gas flow. The optical reflectivity of VN films shows high values in the infrared region.

Keywords: Reactive sputtering; Vanadium nitrides; Crystallographic structure; Optical properties

1. Introduction

Among transition metal nitrides, thanks to their interesting properties (high melting point, hardness chemical stability and corrosion resistance), vanadium nitrides are promising materials in mechanics and microelectronics applications [1–6], although VN is recognized as a refractory compound and a superconducting material (transition temperature between 2 and 9 K) [5].

Following our previous literature [9,10], this study keeps going and investigating the effect of experimental conditions on the structural and physical properties of the IV and V groups transition metal nitrides. Because vanadium nitride has a defective structure, and deviations from stoichiometry are common, the properties of VN thin films are extremely sensitive to the microstructure and the growth morphology as well as deviations from stoichiometry. This deviation from the stoichiometry is the consequence of the presence of nitrogen vacancies in the structure and influences the phase stabilization. Vanadium nitride has been prepared as thin films by sputtering vanadium in a gas mixture of nitrogen and argon.

According to previous literature, the chemical composition, microstructure and hence, all properties (such as optical, electrical and magnetic) of VN films depend heavily on deposition parameters. In this work, we present preliminary results of the study of vanadium nitrides films which have been synthesized by reactive dc planar magnetron sputtering. We focus on structural and morphological changes under various N_2 gas flows, extending from 0 to 15 sccm on Si(1 0 0) substrates for two substrate temperatures, $T_s = 150$ and 400 °C. Some samples were only prepared at 650 °C but not extensively studied yet.

The synthesized VN films were characterized by means of X-ray diffraction (XRD) for phase identification and atomic force microscopy (AFM) for morphological analysis. The thickness of the films was derived from X-ray reflectometry. The optical reflectivity of these VN films was measured in the ultraviolet, visible and infrared regions.

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Table 1
Experimental conditions for the sputtered VN films deposition

N_2 gas flow (sccm)	$T_{\text{substrate}} = 150$ °C				$T_{\text{substrate}} = 400$ °C			
	Sample	Deposition time (s)	Thickness (Å)	Deposition rate (Å/s)	Sample	Deposition time (s)	Thickness (Å)	Deposition rate (Å/s)
0	VNF0	200	704	3.52	VNC0	200	767	3.49
1	VNF1	210	707	3.37	VNC1	230	759	3.30
2	VNF2	225	752	3.34	VNC2	240	791	3.17
3	VNF3	230	750	3.26	VNC3	250	732	2.93
4	VNF4	230	743	3.10	VNC4	240	692	2.88
5	VNF5	240	756	2.91	VNC5	230	606	2.63
6	VNF6	220	642	2.47	VNC6	260	656	2.52
7	VNF7	280	674	2.41	VNC7	300	721	2.40
8	VNF8	300	666	2.22	VNC8	275	599	2.18
9	VNF9	310	670	2.16	VNC9	330	669	2.03
10	VNF10	320	628	1.96	VNC10	330	652	1.98
11	VNF11	330	636	1.93	VNC11	340	636	1.87
12	VNF12	340	638	1.88	VNC12	350	591	1.69
13	VNF13	350	633	1.81	VNC13	360	590	1.64
14	VNF14	420	754	1.79	VNC14	380	579	1.52
15	VNF15	450	777	1.73	VNC15	380	566	1.49

2. Experimental

VN films were deposited onto n-type (1 0 0)-oriented silicon wafers by reactive dc planar magnetron sputtering. Using a vanadium target (82.5 mm in diameter, 3 mm thick and 99.95% pure) with nitrogen (99.99% pure) as the reactive gas and argon (99.99% pure) as the sputtered gas, VN films were deposited on Si(1 0 0) substrates.

Prior to deposition Si(1 0 0) substrates were ultrasonically cleaned for 10 min successively in acetone and ethanol and then dried quickly under a nitrogen gas flow. The vacuum chamber was evacuated by a rotary mechanical pump associated to a cryogenic pump. The argon gas flow and the nitrogen gas flow were controlled by flowmeters. The pressure in the chamber was monitored by a Pirani–Penning gauge combination. Before deposition, the sputtering chamber pressure was reduced to 2×10^{-8} mbar. Then a constant argon gas flow of 20 sccm was let into the chamber and the targets as well as the substrates were pre-sputtered in a pure argon atmosphere in order to remove carbon contamination and surface oxide layers. The amount of nitrogen in the working gas was changed in the range 0–15 sccm and the corresponding samples were labelled from VNF0 to VNF15 (150 °C substrate temperature) and VNC0 to VNC15 (400 °C substrate temperature). The target to substrate distance was approximately 200 mm and the dc discharge power was approximately 285 W. Table 1 summarizes the sputtering conditions for the synthesized VN films.

The crystal structures of the films deposited on a Si(1 0 0) substrate were identified by X-ray diffraction, with a monochromatic Cu $K\alpha_1$ incident beam (35 kV, 25 mA and $\lambda = 0.154056$ nm) in the symmetric $\theta/2\theta$ geometry. The apparatus used is a Siemens D-5000 diffractometer. The thicknesses of the films, still deposited on a Si(1 0 0) substrate, were determined by X-ray reflectometry operated with an X'Pert Philips apparatus using a monochromatic Cu $K\alpha_1$ radiation (40 kV, 50 mA and $\lambda = 0.154056$ nm). Optical reflectance spectra were measured in the 2500–200 nm range using a Perkin-Elmer Lambda 19 UV–VIS–NIR photospectrometer. A commercial barium sulfate ($BaSO_4$) paste was used as blank reference for reflectance spectra measurements. The surface morphology and roughness were analyzed by atomic force microscopy using a Nanoscope III from Digital Instruments.

3. Experimental characterization and results

3.1. Thickness and deposition rate

Thickness was measured by X-ray reflectometry. Let us recall here that Kiessig's fringes are the result of interferences between beams reflected at the film surface and beams reflected at the film–substrate interface. They appear in the low-angle reflection domain and allow the determination of the thickness with high

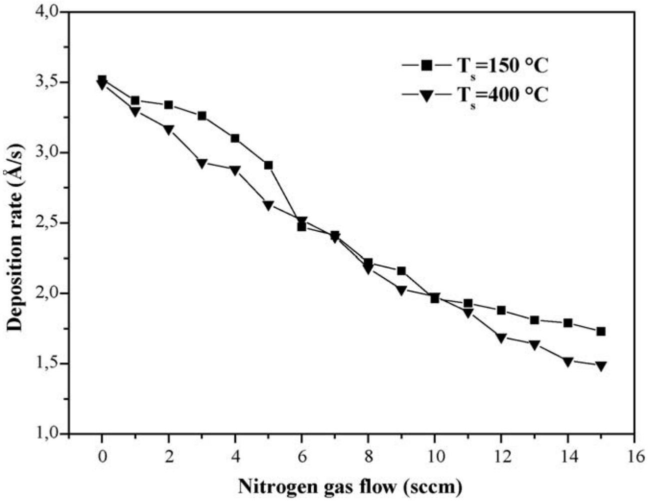

Fig. 1. Deposition rate vs. nitrogen gas flow derived from X-ray reflectivity measurements for the VN films obtained at $T_{\text{substrate}} = 150$ °C (■) and 400 °C (▼), respectively.

accuracy, as long as the film thickness remains below approximately 120 nm. Values derived from X-ray reflectometry are displayed in Table 1. The time deposition was chosen to obtain the same thickness (about 80 nm) for all samples. Fig. 1 represents the variation of the deposition rate as a function of the nitrogen gas flow. One observes that the deposition rate decreases with the increase of the nitrogen gas flow. We have observed this phenomenon in our previous works concerning zirconium [9] and niobium nitrides [10]. As generally assumed, the decrease in the deposition rate is correlated with the decrease in the sputtering rate of the target because several sites on it are occupied by V and N_2, thereby diminishing the ion efficiency. Fig. 1 also shows that the influence of the substrate temperature on the deposition rate is very weak.

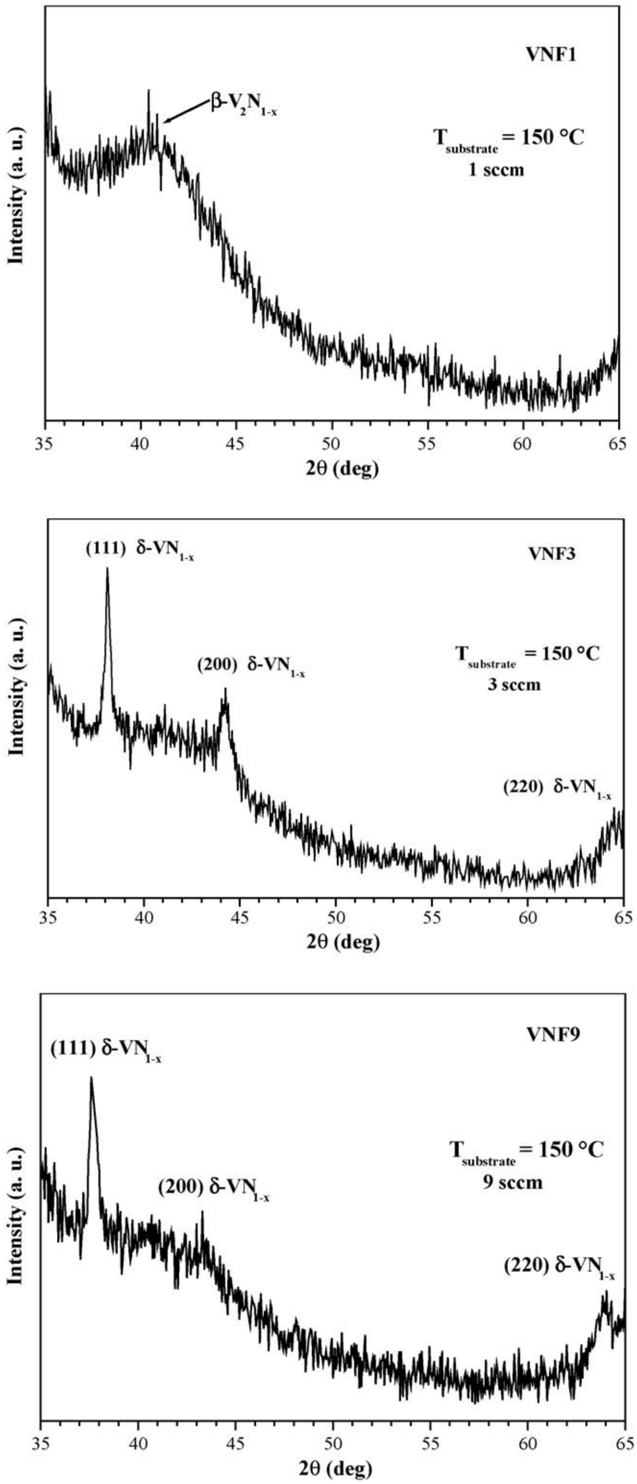

Fig. 2. XRD patterns of selected VN samples synthesized at $T_{substrate}$ = 150 °C with 1, 3 and 9 sccm N_2 gas flow, respectively (λ = 0.154056 Å).

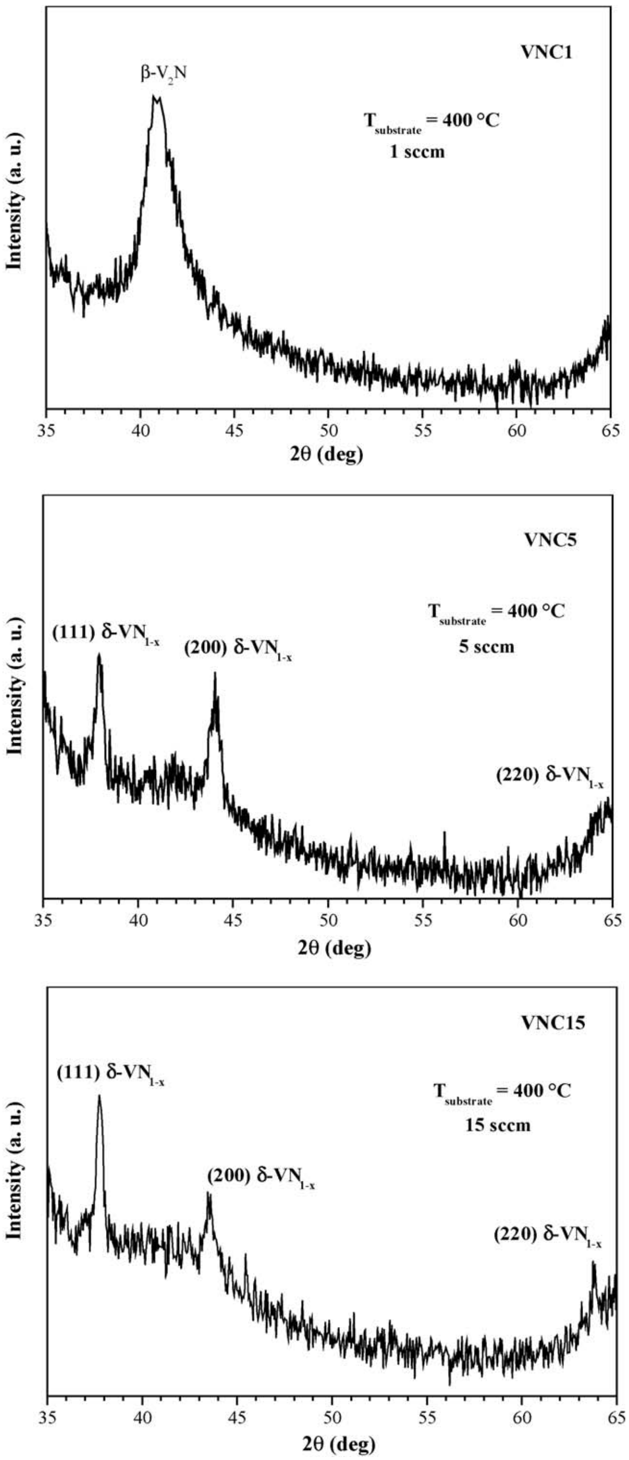

Fig. 3. XRD patterns of selected VN samples synthesized at $T_{substrate}$ = 400 °C with 1, 5 and 15 sccm N_2 gas flow, respectively (λ = 0.154056 Å).

3.2. Structural characterization

The V–N system presents, in addition to unstable phases, the following stable phases: the hexagonal subnitride phase β-V_2N_{1-x} and the mononitride δ-VN_{1-x} of NaCl-type of structure. These two phases exist over a wide range of composition [7,8]. The pure vanadium crystallizes in a bcc array noted α-V phase. XRD patterns of pure vanadium deposited at different substrate temperatures show that the structure of V films appears strongly depending on substrate temperature and exhibits an amorphous phase at $T_{\mathrm{substrate}}$ = 150 and 400 °C, respectively. The α-V phase appears only at 650 °C with (1 1 0) preferential orientation. Fig. 2 displays XRD patterns of some samples synthesized at 150 °C. At low nitrogen gas flows the VN films exhibit the hexagonal subnitride phase β-V_2N_{1-x}. From 3 to 15 sccm the dominant phase in the VN films is the δ-VN_{1-x} mononitride. The increasing of nitrogen gas flow induces a variation of the preferential orientation in the VN films. Fig. 3 shows the XRD patterns of several samples deposited at $T_{\mathrm{substrate}}$ = 400 °C. The effect of nitrogen gas flow is the same as in case of samples synthesized at $T_{\mathrm{substrate}}$ = 150 °C. Besides XRD patterns indicate that an amorphous phase is present in all VN films synthesized.

3.3. Surface morphology and roughness

Fig. 4 displays the surface AFM micrographs of several VN samples synthesized at $T_{\mathrm{substrate}}$ = 150 °C. With increasing nitrogen gas flows the surface morphology of samples becomes denser. The root mean square (rms) values derived from AFM measurements were 2.8 nm (for 0 sccm), 0.7 nm (for 2 sccm), 3.4 nm (for 8 sccm) and 3.7 nm (for 12 sccm), respectively. These variations can be related to crystallographic structure of the VN films. The first value (for 0 sccm) is measured on pure vanadium as an amorphous phase. The second value (2 sccm) is related to the subnitride phase β-V_2N_{1-x}. The last values (for 8 and 12 sccm) were very close because the concerned samples exhibit the δ-VN_{1-x} mononitride phase as pointed out in Section 3.2.

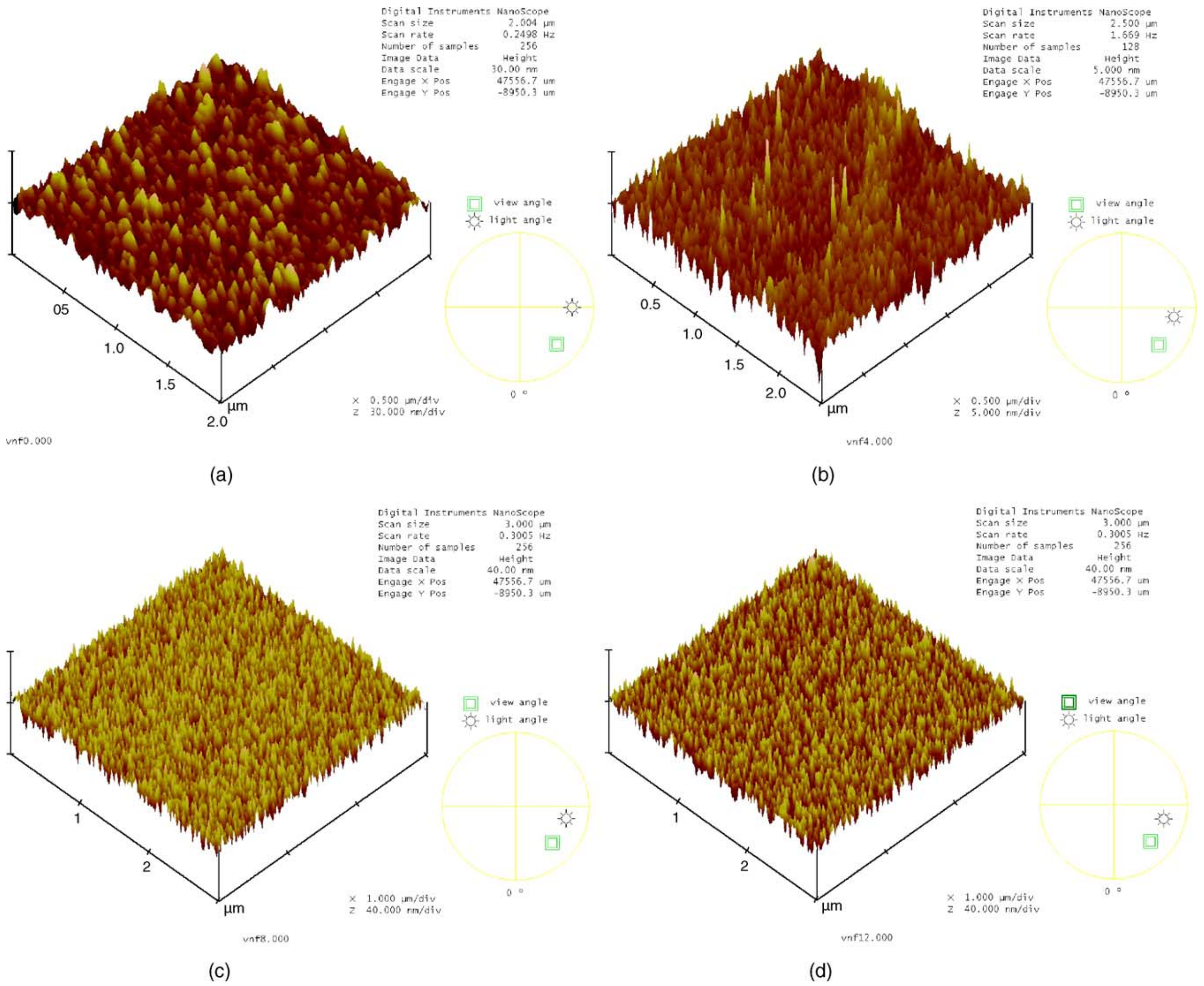

Fig. 4. Surface AFM micrographs showing the morphology of VN films deposited at $T_{\mathrm{substrate}}$ = 150 °C: 0 sccm (a), 4 sccm (b), 8 sccm (c) and 12 sccm (d).

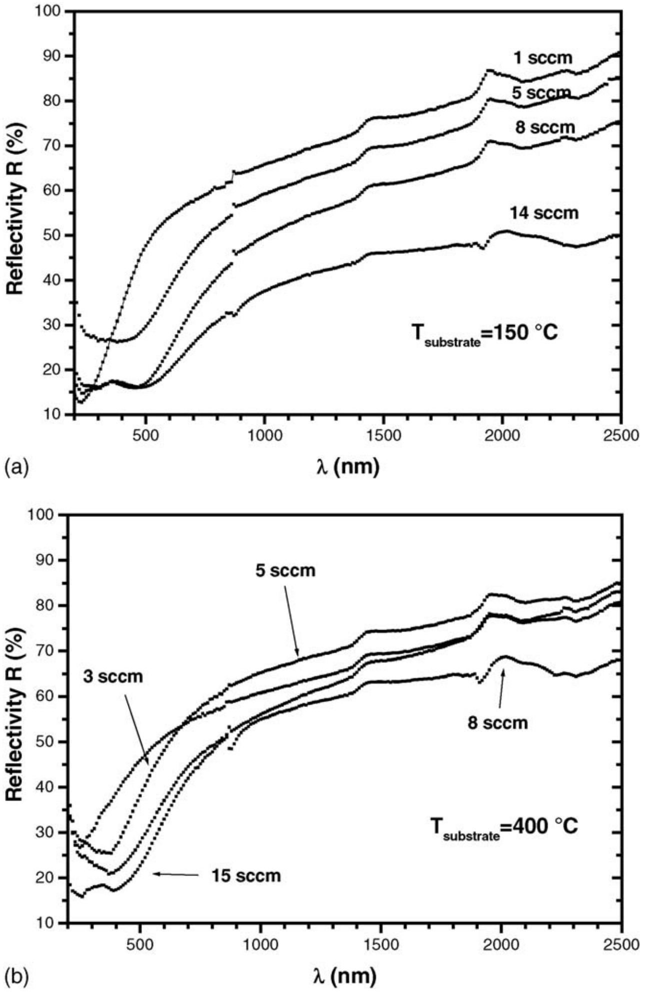

Fig. 5. Reflectivity spectra of selected VN films at $T_{\text{substrate}} = 150$ °C (a) and 400 °C (b).

3.4. Optical properties

The reflectivity spectra of a selected set of VN films are shown in Fig. 5. The highest reflectivity is observed in the infrared region for all samples.

For VN films synthesized at $T_{\text{substrate}} = 150$ °C the reflectivity R, in infrared region, decreases with increasing nitrogen gas flow. Samples synthesized at low nitrogen gas flow exhibit a reflectance minimum in ultraviolet region. This behaviour is probably related to the existence of β-V_2N_{1-x} subnitride as pointed out in Section 3.2. The same conclusion is valuable for VN films synthesized for low nitrogen gas flows at $T_{\text{substrate}} = 400$ °C. The minimum is displaced to the visible region for high nitrogen gas flows.

In case of samples fabricated at 400 °C the decrease of reflectivity with increasing nitrogen gas flow is not as pronounced as in case of $T_{\text{substrate}} = 150$ °C. The full analysis of all reflectivity spectra is still under investigation and will be published elsewhere.

4. Conclusion

Using reactive dc planar magnetron sputtering and varying nitrogen gas flow we prepared non-stoichiometric vanadium nitride films onto Si(1 0 0) substrate at 150, 400 and 650 °C. XRD measurements show that the structure of the films depends on the nitrogen gas flow. At low nitrogen gas flows (below 4 sccm) the crystalline phase observed was β-V_2N_{1-x}, and at high nitrogen gas flows (over 4 sccm) the crystalline δ-VN_{1-x} phase appeared. However, an amorphous phase was present in all VN samples. The roughness (rms) derived from AFM measurements varies with the microstructure of samples. The optical reflectivity shows that vanadium nitrides films of NaCl structure have a high reflectivity in the infrared region and a low reflectivity in the visible and ultraviolet regions.

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