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Structure and electrical characterization of VN_x prepared by reactive pulsed laser deposition

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Abstract. Epitaxial and stoichiometric VN_x films were prepared by reactive pulsed laser deposition (RPLD) with YAG:Nd laser on sapphire substrates. The film stoichiometry and structure were characterized by AES, XRD, RBS/channelling and XRD pole figures. It was found that epitaxially crystalline and nearly stoichiometric VN_x films with x of 0.96 on α-Al_2O_3 (0001) had been prepared by YAG:Nd laser at 450 °C with the mixed gas of nitrogen and 3% hydrogen at 2 mbar. Three methods, XRD, AES and RBS/channelling, surely confirm the nearly stoichiometric crystalline characteristics of the films. The XRD pole figures show the films have twinned structure. The electrical property relationship with the temperature in the range of 16 to 300 K has been measured by conventional four probe methods.

1. Introduction

The transition-metal nitrides and carbides (TMNCs) have long been of interest due to their unusual combinations of physical properties. These properties include extremely high melting points, extreme hardness and metallic conductivity. The vanadium–nitrogen system displays superconductivity [1–5]. It belongs to the group of refractory compounds with NaCl structure. It is a superconductor with the transition temperature T_c ranging from 2 to 9 K depending on the nitrogen content. Strong interest in VN has been stimulated by Rietschel *et al* who argue that spin fluctuations reduce the T_c of VN from 30 K to the observed bulk value of about 9 K [6]. Burnell *et al* concluded that T_c in V is indeed suppressed by up to 45% due to the spin fluctuations [7]. However the larger magnitude estimated [6] for VN makes it a natural choice to study spin fluctuations. The most direct evidence for spin fluctuations maybe comes from tunnelling measurement of the reduced density of states. Zasadzinski *et al* have made tunnel junctions on sputtered films of VN, and they also have demonstrated the importance and difficult of obtaining well ordered films [8, 9]. Therefore the preparation of high quality and stoichiometric VN films is not only of technological but also fundamental importance.

Pulsed laser deposition (PLD) is a relatively new means to fabricate superconducting thin films. The relative ease under which complex stoichiometry can be transferred from the target to the film, optimization of deposition pressure and temperature for epitaxial growth and subsequential deposition of multilayer films combine to give PLD unique advantages for thin film device fabrication. However most PLD prepared thin films are multi-elemental oxides,

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and there are only a few works on nitride thin films [10]. To our knowledge there was no published work on VN film preparation by pulsed laser deposition until our recent work [11].

We have reported our work on optimum conditions to prepare nearly stoichiometric and crystalline VN film by pulsed laser deposition [11]. In this article, we will report the structure and property characterization of vanadium nitride thin films. XRD, XRD pole figures, AES and RBS/channelling were used to characterize the structure of the thin films. The electrical properties of the films are also characterized.

2. Experiment

RPLD was performed by a second harmonic Q-switched Nd:YAG laser of 532 nm, 145 μs in pulsed width and 10 Hz in frequency. The average laser density of 2.5 J cm^{-2} was used for deposition. The laser beam was focused on a rotating disclike target within 2–3 mm in diameter. The base pressure was in the range of 10^{-7} Torr at room temperature, and the base pressure at deposition temperature (usually at around 450 °C) was in the range of 10^{-6} Torr. The substrate of α-Al_2O_3 (0001) was located at a distance of 5.5 cm from the target and it was heated during the deposition. In the process of deposition, the vanadium target (99.9999% pure) is rotated by a motor, and the partial gas pressure was controlled automatically by a MKS250 pressure controller by adjusting the in-flow gas flux. The temperature of the substrate was measured by a thermocouple affixed to the substrate directly. The temperature fluctuation during deposition can be controlled with an accuracy of 2 or 3 degrees, and the pressure fluctuation during deposition is less than 1%. The general deposition rate under the above conditions is around 20 Å min^{-1}, and the general ablation time is around 50–60 minutes. As soon as deposition was finished, the temperature was reduced slowly to the room temperature in several hours. During the process of decreasing temperature, the films were kept in the same partial pressure as that in which they were deposited. Different temperatures from 300 to 600 °C, different substrates and orientation and different partial pressure from 0.04 mbar to as high as 2 mbar of nitrogen have been used to prepare VN_x thin films. Our best film was $VN_{0.96}$ with lattice constant 4.130 Å, prepared at 450 °C in the ambient gas pressure of 2 mbar on α-Al_2O_3 (0001), and the mixed gas is nitrogen with 3% hydrogen. All experimental results presented in this paper are exclusively of this sample.

The x-ray diffraction technique was explored for the crystallographic characterization of all films, and an x-ray diffractometer (XRD) (Rigaku: Cu Kα; 40 kV; 30 mA) was used for XRD measurement. Rutherford backscattering spectrometry was used to determine the chemical composition and the thickness of the film. Ion channelling was used to check the crystalline film quality. 2.0 MeV He^+ ions were incident on the sample in a normal direction, and the backscattered ions were detected at 165°. XRD pole figure measurement was also used to characterize the structure of laser ablated VN films. The RBS spectrum simulation program: RUMP [12] was used to obtain the thickness and stoichiometry of all films from RBS spectra. A 3000 eV electron beam was used in the AES measurement.

3. Results and discussion

The crystal structure of VN thin films was examined using a x-ray diffractometer (XRD) (Rigaku; Cu Kα; 40 kV; 30 A). Figure 1 shows an x-ray diffraction intensity versus incident angle plot showing (111) and (222) peaks from a vanadium nitride film on α-Al_2O_3 (0001) substrate, and the film was deposited in a mixed gas of nitrogen with 3% hydrogen of 2 mbar at temperature of 450 °C for 50 minutes. The figure shows only (111) and (222) peaks for VN_x

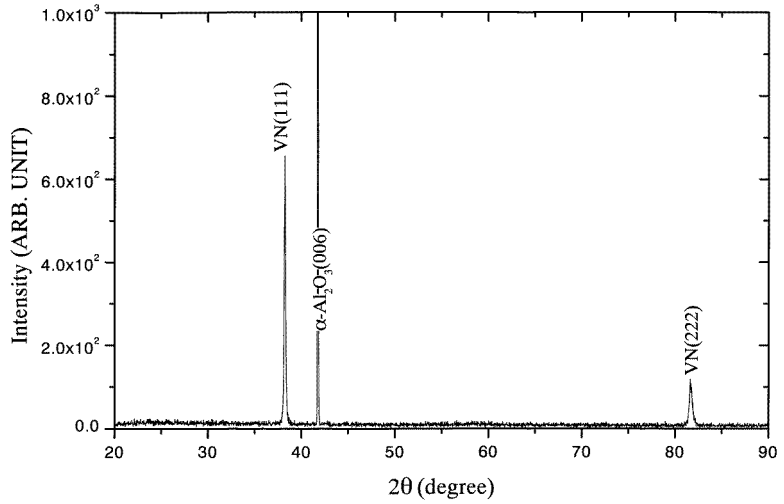


Figure 1. X-ray diffraction intensity versus incident angle plot showing only (111) and (222) peaks from VN film prepared at 450 °C on α-Al_2O_3 (0001) substrate.

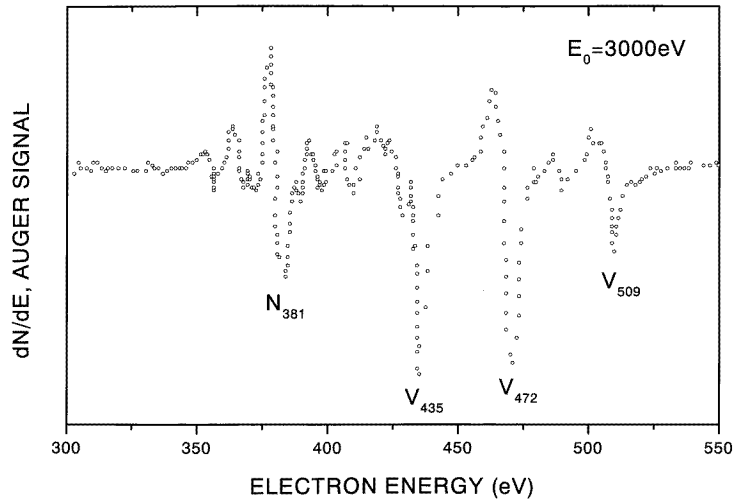


Figure 2. Auger spectra from the same vanadium nitride film prepared at 450 °C on α-Al_2O_3 (0001) substrate.

and (0006) from α-Al_2O_3 (0001) substrates. This indicates the film is highly orientated in the (111) direction. The high intensity and narrow half-width suggest the film has good quality. Since the (111) plane is one of the closest packed for fcc structure, it is not surprising that the (111) growth is preferred. From the well established linear relationship between lattice parameter and nitrogen content [2, 13, 14] found in vanadium nitride, we have determined the x value in VN_x is around 0.96. This suggests the thin vanadium nitride film is nearly stoichiometric.

AES was used to characterize the stoichiometry of the films more directly and accurately, as XRD is not a direct way to determine the stoichiometry of the film and the subsequent RBS

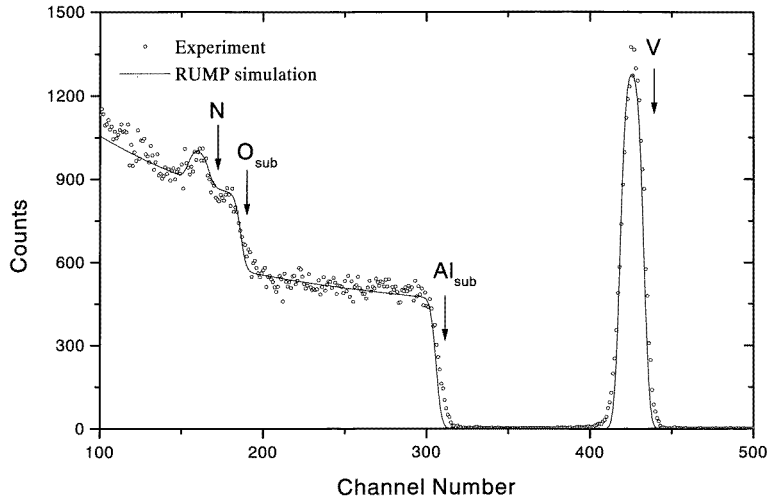


Figure 3. RBS experimental spectrum of the VN film on α-Al_2O_3 (0001) substrate with that from RUMP simulation. The simulation result suggests a near-stoichiometric film deposited by RPLD.

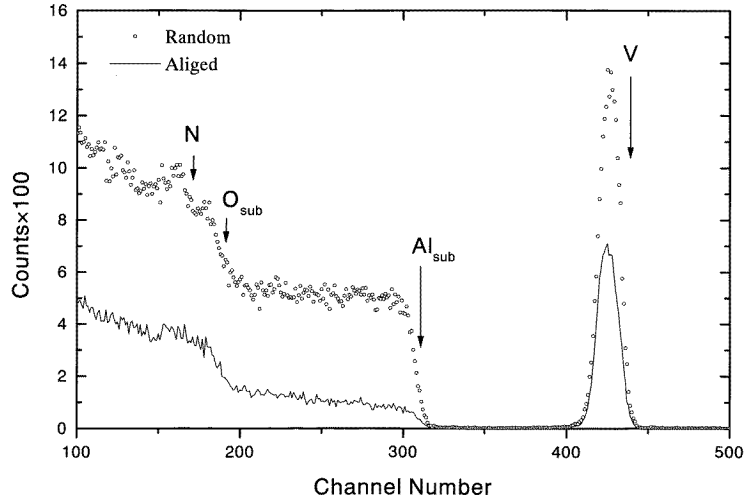
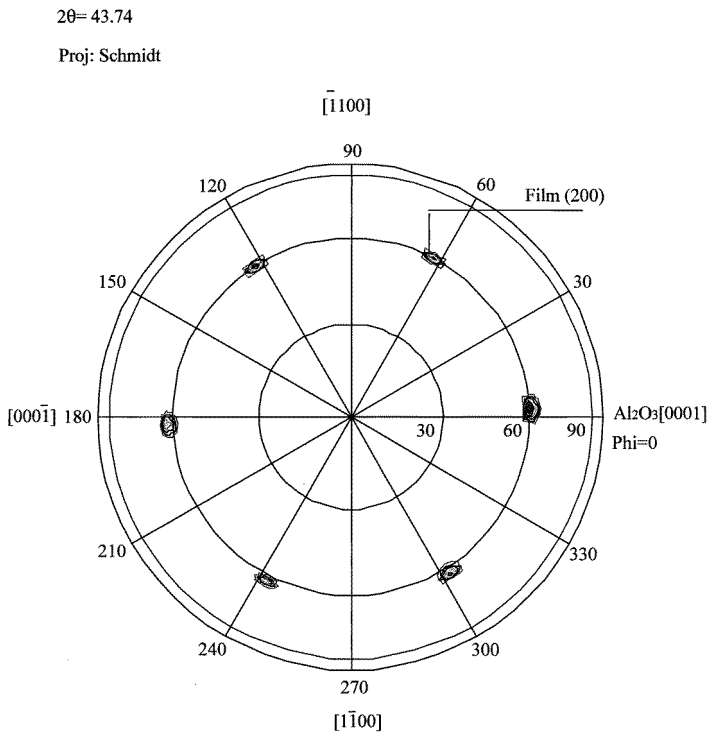


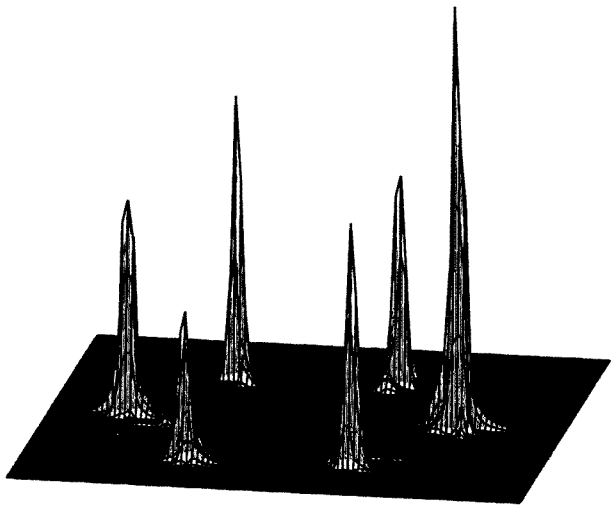
Figure 4. RBS spectrum of the VN film on α-Al_2O_3 (0001) substrate in aligned and random directions.

technique is not so sensitive to light elements such as nitrogen. Figure 2 shows the Auger electron spectroscopy spectrum from the same sample. The spectrum only shows nitrogen and vanadium signals. We did not find any signal from oxygen. Therefore we believe there are no significant problems with oxygen contamination in our films. By using sensitivity factor means, we obtained the relative concentration of each element. The measured value of x in VN_x of this film is 1.04. The result agrees well with the value calculated from XRD analysis: 0.96.

RBS measurements were taken to determine the chemical composition and the thickness of the film. A RBS experimental spectrum of the same vanadium nitride film and a RUMP [12]



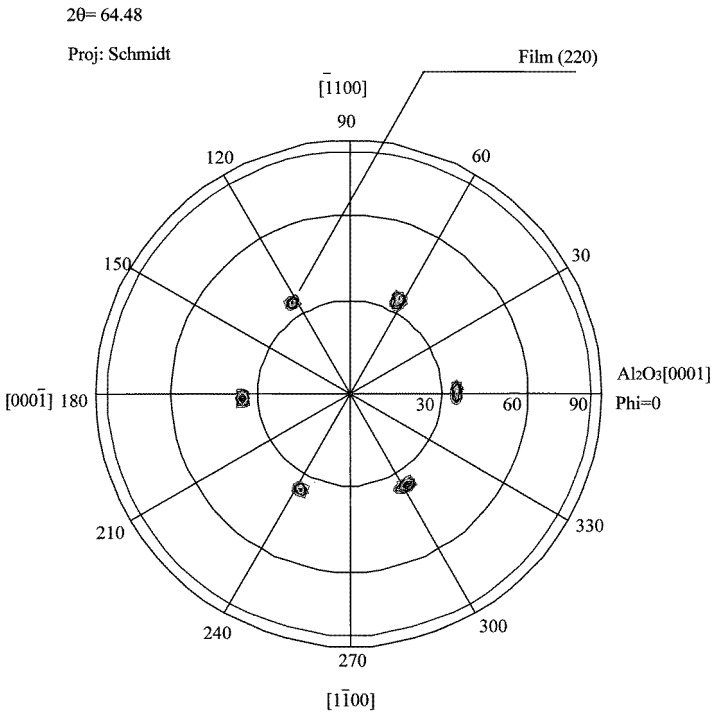
(*a*)



(*b*)

Figure 5. (*a*) (200) pole figure of (111) oriented VN film deposited on α-Al_2O_3 (0001) substrate; (*b*) (200) surface peak of (111) oriented VN film deposited on α-Al_2O_3 (0001) substrate.

simulated spectrum are shown in figure 3. The RBS analysis was carried out using 2.0 MeV $^4He^+$ ions from a 3 MV single stage accelerator at TIARA in JAERI Takasaki. The spectra were taken with the detector set at 165°. The simulated film thickness of 850 Å with atomic fraction



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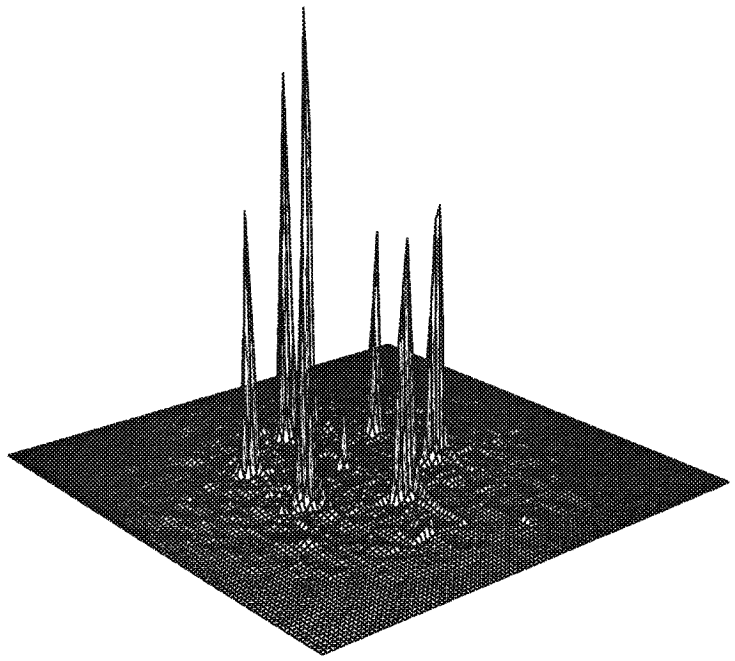

(*b*)

Figure 6. (*a*) (220) pole figure of (111) oriented VN film deposited on α-Al_2O_3 (0001) substrate; (*b*) (220) surface peak of (111) oriented VN film deposited on α-Al_2O_3 (0001) substrate.

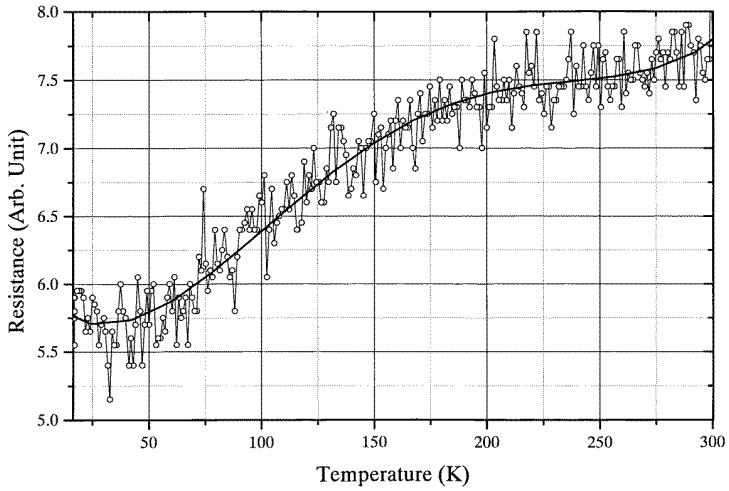

Figure 7. The relationship between resistance and the temperature in the high and low temperature range.

ratio V:N = 1:0.95 suggests a nearly stoichiometric film has been prepared by RPLD. The RBS analysis result also confirms the result of XRD analysis, i.e. $VN_{0.96}$, a nearly stoichiometric film, has been prepared by pulsed laser deposition on α-Al_2O_3 (0001).

To examine the crystalline perfection of the film ion channelling was also used. Figure 4 shows RBS spectra of the same vanadium nitride film on α-Al_2O_3 (0001) substrate in aligned and random directions. These spectra were also obtained using 2.0 MeV $^4He^+$ ions. The figure suggests a crystalline VN(111) thin film is epitaxially grown on α-Al_2O_3 (0001) substrate, although the aligned minimum yield χ_{min} is very high, around 50%. The strong aligned yields are likely related to a very high density of misfit locations arising from a complete different structure between VN and Al_2O_3. The further work will be on improving crystalline quality by changing substrate and optimize the deposition conditions.

A relation between the crystal axes of VN and the in-plane vectors of the sapphire substrate can be obtained from the x-ray diffraction pole figure. An untwinned single crystal should show threefold symmetry in the (200) pole figure in the plane of VN(111). Figure 5(*a*) shows the (200) pole figure in the plane of (111) oriented VN film deposited on α-Al_2O_3 (0001) substrate. It shows two groups of VN (200) poles: one group located at $\phi = 0^\circ$, 120° and 240°, and the other group at $\phi = 60^\circ$, 180° and 300°. This suggests that the (111) oriented film is grown epitaxially; however, there are two kinds of twin that are rotated by 60° about the film normal. The relative intensities of these two groups are quite similar, which can be seen clearly in figure 5(*b*). The (220) x-ray pole figure in the plane of the (111) oriented VN film deposited on a α-Al_2O_3 (0001) substrate is also shown in figure 6(*a*). An untwinned single VN crystal should also show three peaks for (220) poles. The (220) pole appears as sixfold symmetry. This also suggests the VN has twinned structure. Figure 6(*b*) shows the surface peak of the (220) pole figure.

Figure 7 shows the temperature dependence of the electrical resistance measured by standard four probe techniques. A convenient measure of disorder is the residual resistance ratio, r_R, equal to the ratio between the electrical resistance at 300 and 10 K. Our best films have r_R 1.4–3, which is lower than the value, 2–5, reported by Zasadzinski *et al* [8]. This is possibly because our film, usually less 1000 Å, is rather thinner compared to theirs, 4000 Å [8], as we noted that bulk vanadium nitride has a higher r_R value compared with vanadium nitride film [8].

4. Conclusions

In summary, epitaxial crystalline and stoichiometric vanadium nitride films were prepared on α-Al_2O_3 (0001) by second harmonic Nd:YAG reactive pulsed laser deposition, and characterized by XRD, XRD pole figures, AES and RBS/channelling techniques. The best film, $VN_{0.96}$ with lattice constant 4.130 Å, was prepared in a mixed ambient of nitrogen and 3% hydrogen at 2 mbar and 450 °C for 50 minutes. XRD, AES and RBS techniques surely confirm the stoichiometry of the vanadium nitride film and show there is no significant oxygen contamination in our film. The XRD pole figure shows twinned structure although the film is epitaxially grown on sapphire substrate. The resistance dependence on temperature also show the film having good quality.

Acknowledgment

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