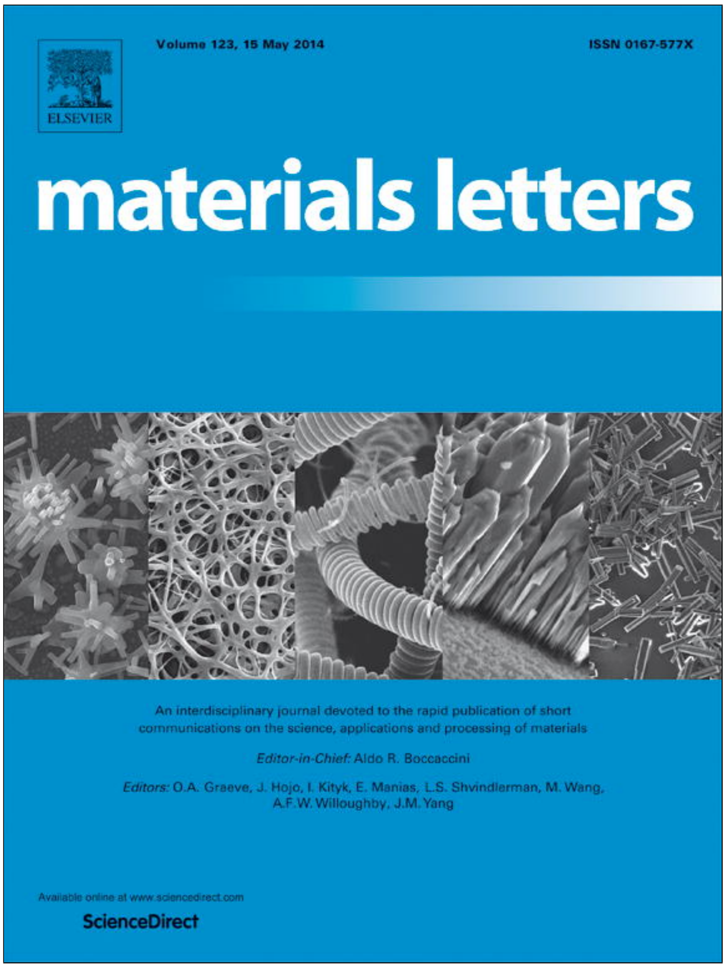
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Epitaxial growth of vanadium nitride thin films by laser molecule beam epitaxy

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ABSTRACT

Vanadium nitride thin films were epitaxially grown on $SrTiO_3$ and sapphire substrates by ablating vanadium target in activated N_2 atmosphere. The epitaxial orientation relationships of film/substrate are $[001]_{VN}//[001]_{SrTiO_3}$ and $[111]_{VN}/[0001]_{\alpha-Al_2O_3}$. Atomic force microscope measurements show the smooth surfaces of the films. High-resolution transmission electron microscope measurement was performed on the cross-section of VN/$SrTiO_3$ sample, which shows a good epitaxial growth. Temperature-dependent resistance measurements demonstrate that the films have typical metallic conductivity.

1. Introduction

The transition-metal nitrides (TMNs) have attracted widely attentions because of their outstanding physical and chemical properties, such as ultrahigh hardness, high melting point, high thermal stability, corrosion resistance, and metallic conductivity. Vanadium nitride (VN) is one of the typical TMNs, which has been extensively studied as additive in steels to enhance their hardness, tenacity and abrasive resistance [1–3]. With the exception of mechanical properties, superconductivity is another interesting property of VN, whose transition temperature (T_c) is ranging from 2 to 9 K, depending on the nitrogen content and residual stress strongly [4]. Recently, VN has been attracting increasing attention because it is a promising candidate for electrode material of supercapacitor [5,6], taking the advantage of the excellent conductivity and chemical stability.

In order to explore the potential applications of TMNs, film materials were extensively developed. It is known that most of TMNs are interstitial compounds; they can crystallize into various structures in a very wide range of *N* content [7]. Therefore, the obtainment of single phase TMNs film is not easy. Magnetron sputtering and pulsed laser deposition (PLD) are two common methods for preparing TMNs films [8,9]. The targets used in these two methods are either binary TMNs ceramics or pure metal bulks. Some of the TMNs ceramic targets are very difficult to be sintered, or the cost is too high, so they are not the first choice for magnetron sputtering and the PLD method. The process of sputtering/ablating pure metal targets in nitrogen atmosphere is widely adopted, whose advantage is that we can control the *N* content in the films easily by adjusting the nitrogen pressure of the chamber. But its disadvantage is also remarkable, that is the possible emergence of impurity phase in the product [10–12]. Recently, we try to explore the preparation of high quality TMNs films using the laser molecule beam epitaxy (Laser-MBE) method with pure metal targets. We have successfully grown epitaxial NaCl-type CoN films on different substrates, which show antiferromagnetic property [13]. In this work, we report the epitaxial growth of VN films on $SrTiO_3$ and sapphire substrates by ablating vanadium target in activated N_2 atmosphere.

2. Experimental details

VN films were grown on $SrTiO_3(001)$ and α-$Al_2O_3(0001)$ substrates by means of Laser-MBE, with a XeCl excimer laser (wavelength = 308 nm, repetition = 2 Hz, and energy density = 1.5 J/cm^2). A high-purity vanadium disk (purity $>99.99\%$) was employed as target. Before deposition, gas pipes and epitaxy chamber had been carefully cleaned using high-purity N_2 ($>99.999\%$). After that, the epitaxy chamber was pumped to $<5\times10^{-6}$ Pa. N_2 was introduced into the epitaxy chamber, and nitrogen partial pressure was kept at 0.5 Pa. A home-made glowing discharge unit was employed to activate N_2. Activated N_2 sprayed to the substrate surface directly. The substrate temperature during the growth

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process was maintained at 400 °C after excluding other temperature prudently. As soon as the growth was finished, the temperature was reduced down to room temperature naturally. The nitrogen source was turned off after the samples were cooled down to 150 °C. The growth time was 4 h, and growth rate was estimated to be 3.3 Å/min.

The surface quality of the VN films was monitored by *in situ* reflection high energy electron diffraction (RHEED). The crystallization was characterized by X-ray diffraction (XRD) with Cu $K\alpha$ radiation. The surface morphology was observed by an atomic force microscope (AFM). The microstructures of VN film on $SrTiO_3$(100) was measured by a transmission electron microscope (TEM). The measurement of electric properties was carried out by a physical property measurement system (PPMS-9T).

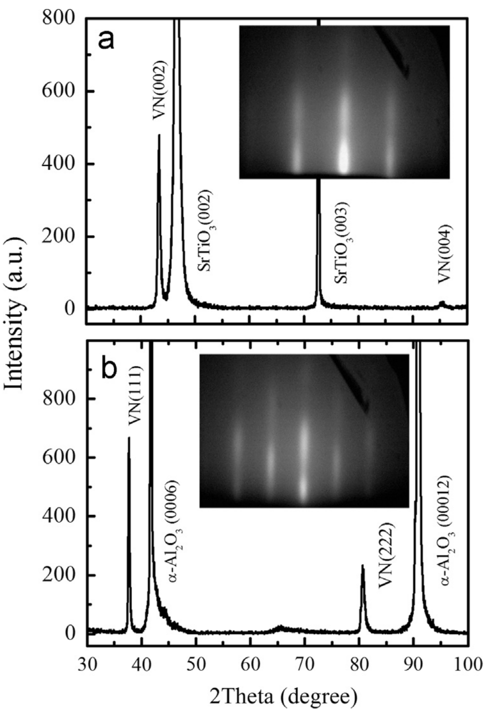

Fig. 1. XRD θ–2θ scan profiles of VN films on (a) $SrTiO_3$(001) and (b) α-Al_2O_3(0001) substrates, the insets are RHEED patterns obtained at room temperature.

3. Results and discussion

The RHEED pattern provides us useful information about the surface quality of films. The insets in Figs. 1(a) and 1(b) are the RHEED patterns of VN films on $SrTiO_3$(001) and α-Al_2O_3(0001) substrates, respectively, which are obtained when the substrate temperature has cooled down to room temperature. The bright and sharp diffraction streaks reveal the smooth surfaces. Fig. 1 shows the XRD θ–2θ scan profiles of VN films on different substrates. Except for the diffraction peaks ascribed to the substrates, the XRD profiles show (002) and (004) peaks (2θ=43.41°, 95.43°) for VN on $SrTiO_3$(001), (111) and (222) peaks (2θ=37.72°, 80.78°) for VN on α-Al_2O_3(0001). It indicates that VN orients in [001] direction when grows on $SrTiO_3$(001), whereas grows along [111] direction on α-Al_2O_3(0001). And it also indicates that the as-prepared VN films have pure phases for no extra peaks were observed in the XRD curves.

Figs. 2(a) and (b) presents two-dimensional AFM images of the VN films grown on $SrTiO_3$(001) and α-Al_2O_3(0001). The sapphire substrate used in this work has been processed in advance to get the step-and-terrace surface [14]. And it is noted that the step-and-terrace structure is still obvious after the coverage of VN. The root-mean-square (Rms) surface roughness within a $5\times5\ \mu m^2$ area is 0.189 and 0.219 nm for VN/$SrTiO_3$ and VN/Al_2O_3, respectively. Fig. 2 (c) and (d) shows height profiles corresponding to the solid lines in the AFM images. We can see that the height fluctuations of both samples are limited into 0.5 nm, which is close to the size of one VN unit cell (a=0.413 nm). The results demonstrate that the as-grown films have smooth surfaces. The surface roughness of VN/$SrTiO_3$ is slightly smaller than that of VN/Al_2O_3, which may be related to the different strain from their respective substrate.

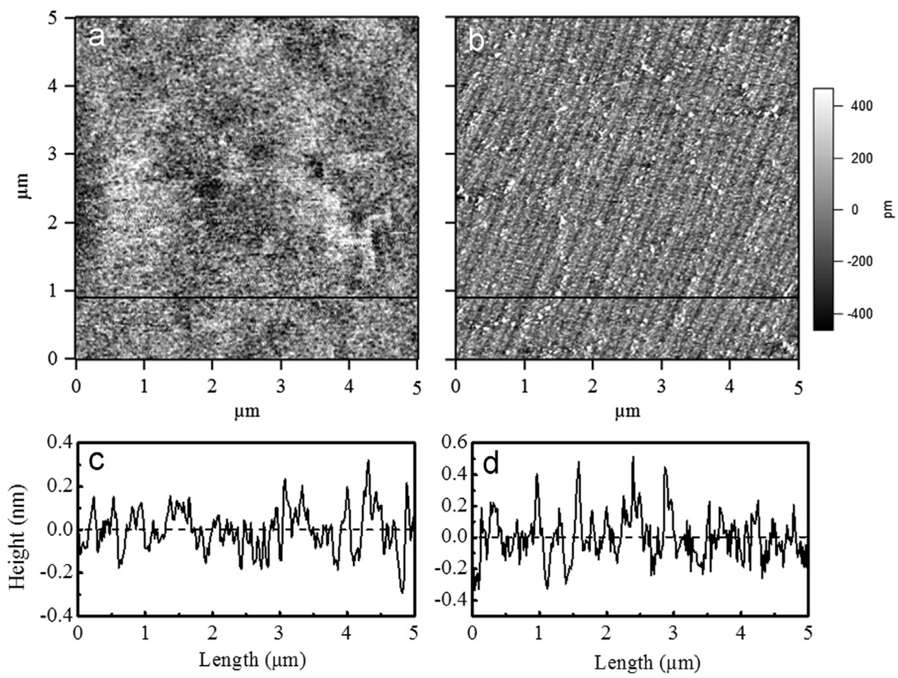

Fig. 2. (a) and (b) present the two-dimensional AFM images of the VN films grown on $SrTiO_3$(001) and α-Al_2O_3(0001), within a $5\times5\ \mu m^2$ area, (c) and (d) show height profiles corresponding to the solid lines in (a) and (b).

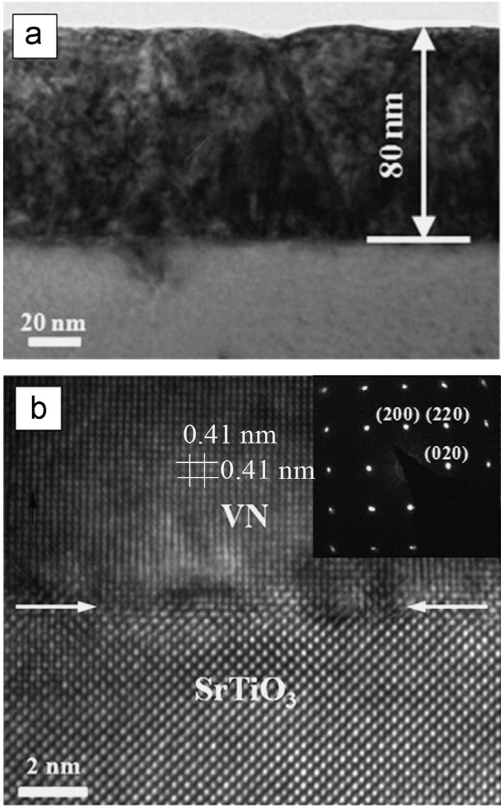

Fig. 3. (a) Cross-sectional low-resolution TEM image of the VN(001)/$SrTiO_3$(001) sample, (b) HRTEM image of VN(001)/$SrTiO_3$(001) interface, the inset is a SAED pattern of VN film.

Fig. 3(a) shows a low-resolution TEM image of cross-section of VN (001)/$SrTiO_3$(001) sample. It is obvious that VN film has grown on the substrate, and film thickness is 80 nm. High-resolution TEM (HRTEM) image (in Fig. 3(b)) shows the interface of film/substrate is very clear. The highly ordered atom arrangement in the film region indicates the good crystallinity and well epitaxy. The inset of Fig. 3(b) displays a selected area electron diffraction (SAED) pattern of VN film which shows a group of bright and well-ordered spots, meaning that the VN film has a very good single crystal structure. This SAED pattern can be indexed as a cubic lattice, which is in accord with the NaCl-type structure of VN. Both VN and $SrTiO_3$ are cubic lattice, and the mismatch between VN and $SrTiO_3$ is only $(a_{VN}-a_{STO})/a_{STO}\times 100\%=(4.13-3.905)/3.905\times 100\%=5.8\%$, so VN can grow on $SrTiO_3$ substrate in a cube-on-cube epitaxy mode. We can determine that the epitaxial relationship of VN(001)/$SrTiO_3$(001) is $[001]_{VN}//[001]_{STO}$ and $(100)_{VN}//(100)_{STO}$. With regard to the VN(111)/α-Al_2O_3(0001) system, VN(111) plane is a closest packed plane and has threefold symmetry, which is similar to the α-Al_2O_3(0001) plane, so it is expected that $\langle 111\rangle$ orientation is preferred.

The electrical resistance measurement of VN films was performed by the traditional four-probe method. Fig. 4 shows temperature dependent resistivity of VN films on $SrTiO_3$ and Al_2O_3 substrates, in the temperature range of 10–300 K. The films show typical metallic conductivity for their resistivity increase with the increasing temperature monotonously. The films have excellent conductivity. In the case of VN on $SrTiO_3$, the values of resistivity are approximately 89 and 123 μΩ cm at 10 and 300 K; for VN/Al_2O_3, the values are 49 and 105 μΩ cm at 10 and 300 K, respectively. It is widely accepted that residual resistance ratio (r_R) is able to express the degree of disorder in the lattice. Herein, the magnitudes of r_R are 1.38 and 2.14 for VN on $SrTiO_3$ and Al_2O_3 substrates, respectively. These values are similar to the reported values by Dai et al. [15]. In addition, we note that the

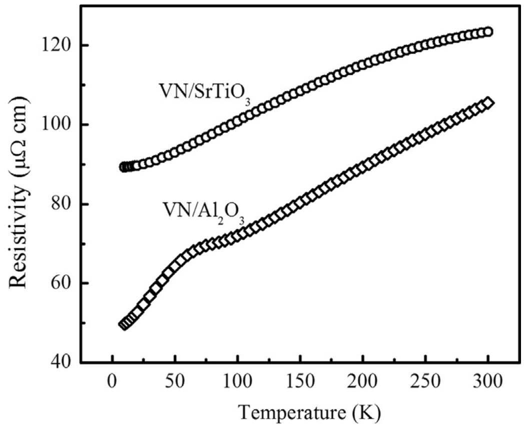

Fig. 4. The ρ–T curves of VN films on $SrTiO_3$ (circles) and Al_2O_3 (squares), in the temperature range of 10–300 K.

resistivity of VN/Al_2O_3 is a bit smaller than that of VN/$SrTiO_3$, and the resistivity of VN/Al_2O_3 increases more sharp than VN/$SrTiO_3$ when the temperature is lower than 60 K. The crystal anisotropy and different substrate-induced strain are the potential reasons for the difference in electrical property.

4. Conclusions

In summary, high-quality epitaxial vanadium nitride films were prepared on $SrTiO_3$(001) and α-Al_2O_3(0001) substrates by ablating vanadium target in high-purity activated nitrogen atmosphere using the Laser-MBE method. It is observed that the epitaxial relationships between film and substrate are $[001]_{VN}//[001]_{STO}$ and $[111]_{VN}//[0001]_{\alpha-Al_2O_3}$. VN films show excellent electrical conductivity. Our results suggest that the epitaxial VN film is very suitable for applications on electrode material for solar cells and supercapacitors.

Acknowledgments

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