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Crystalline vanadium nitride ultra-thin films obtained at room temperature by pulsed laser deposition

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ABSTRACT

In this work the synthesis of vanadium nitride ultra-thin films by means of pulsed laser deposition technique is reported. The solid target used for laser ablation was prepared from vanadium nitride powder synthesised by sol–gel of V_2O_5 followed by temperature programmed reduction with ammonia. The films deposition was performed at room temperature and 500 °C on glass or Si substrates and the films were characterised by different techniques, i.e., Scanning and Transmission Electron Microscopy, X-Ray Diffraction, Atomic Force Microscopy and X-ray Photoelectron Spectroscopy. As a function of the deposition conditions, the films present different thicknesses, reveal a homogenous dense to slightly porous morphology and are highly crystalline. As determined by X-ray Photoelectron Spectroscopy analyses the VN films are nitrogen deficient due to the formation of an oxide layer on their surface. The possibility of depositing crystalline VN ultra-thin films at room temperature using a VN target is of great importance for several possible applications where low temperature substrates are employed.

1. Introduction

Due to its remarkable properties, i.e., hardness, chemical stability, high melting point, superconductivity, vanadium nitride in form of thin films has attracted great attention in different kinds of applications such as: optical devices [1–3], tribological utilisation [4], microelectronics [5], catalyse [6] etc. Moreover, recently VN thin films were successfully employed as electrodes for energy storage devices like batteries [7] and supercapacitors [8]. For supercapacitor applications the decrease of film thickness is of key importance in order to improve the capacitance performances. Therefore, to deposit VN films with different physico-chemical properties and characteristics, several deposition techniques like magnetron sputtering [9], chemical vapour deposition [1], rapid thermal processing [10], or reactive pulsed laser deposition (RPLD) [11–13] were used. As known, PLD can offer the advantage of depositing a wide range of complex materials at room temperature [14]. However, in order to get highly crystalline nitride and carbide thin films by PLD, substrate temperatures in excess of 700 °C, incident laser fluences of 10 J/cm^2 and 2×10^{-6} Pa vacuum conditions are usually required. It was recently shown that crystalline ZrC films could be obtained at moderate deposition temperature using for ablation a higher repetition rate excimer laser source [15]. However, we note that the few reports concerning the deposition of VN by RPLD [11–13] proceed by the ablation of metallic vanadium targets in nitrogen atmosphere. Consequently high deposition temperatures (around 500 °C) are required for complete transformation of V into VN. This inconvenience prohibits for instance the deposition on low temperature substrates and furthermore the application of these materials in specific fields. For instance, in the case of Al which is preferably used as current collector in the supercapacitors [16] and which have a low melting point (~660 °C), a deposition of VN films at high temperatures by PLD technique will not be convenient. Therefore, the aim of this work is to test the feasibility of this method to deposit VN films at low temperature (room temperature) using first classical substrates as glass or silicium wafers.

A VN target was used for the first time to deposit VN thin films by high repetition rate laser ablation in low pressure N_2 atmosphere. The influence of the deposition temperature (room temperature vs. 500 °C) and the substrate nature (glass vs. Si) on the structural, morphological and compositional properties of the films is evaluated.

2. Experimental

2.1. Film deposition

The target used for the deposition of the films was manufactured from VN powder synthesised by sol–gel technique as described elsewhere [17,18]. Usually, the V_2O_5 powder (Aldrich) is dissolved in H_2O_2 (30 wt.%, J.T. Backer) at 0 °C because of the high exothermicity of the reaction. The solution was stirred for about 1.5 h and the remaining H_2O_2 was decomposed by sonication. The resulting

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suspension was aged until a brown-dark gel was formed ($V_2O_5 \cdot nH_2O$) which was then dried, ground and thermally treated under NH_3 at 500 °C. The as-synthesised VN powder was subsequently pressed and sintered in N_2 atmosphere at 500 °C in order to obtain a 20 mm diameter VN target, used further for the deposition of VN films by PLD.

The deposition of VN films was carried out inside a stainless steel chamber. Before each deposition, the chamber was pumped down to the residual pressure of 4×10^{-6} Pa. A UV COMPEXPro 205 KrF* excimer laser source ($\lambda = 248$ nm, $\tau_{FWHM} \approx 25$ ns) was used for the ablation of the VN target. The target was rotated at 0.4 Hz and translated during the multipulse laser irradiation in order to avoid drilling and to obtain a highly uniform film on 10×10 mm^2 areas. Before the deposition of thin films, the target surface was "cleaned" with 1000 laser pulses by collecting the ablated material on a shutter interposed between the target and collector. The ablation was performed in 10^{-3} Pa nitrogen for confining the expulsed material and compensating the possible N_2 losses. The ablated material was collected on immobile glass or (100) silicon substrates positioned plane parallely 50 mm apart from target. Before introduction into the deposition chamber, the substrates were ultrasonically cleaned in acetone and ethanol, rinsed with deionized water and blown dried with high purity N_2 gas. During the deposition/ablation process the substrate were kept at either RT or 500 °C. The incident laser fluence was set at 5 J cm^{-2} and the laser was operated at 40 Hz repetition frequency. For the deposition of each structure, 3000 subsequent laser pulses were applied. The films are denoted VN-500G, VN-25G and VN-25S (as explained in Table 1).

2.2. Film characterisation

The film morphology was observed by scanning electron microscopy (SEM, FEI Quanta 400) while their topography and thickness were evaluated by atomic force microscopy (Nanoscope IV-Multimode Veeco Instruments, USA) operating in a tapping mode regime. A part of the film was scratched from the substrate and subsequently was laid on a carbon grid and their microstructure was investigated by transmission electron microscopy (TEM, Philips CM200).

The crystallinity and structure of the films were evaluated by X-ray diffraction (XRD, Philips X'pert MPD, $\lambda_{CuK\alpha1} = 0.15406$ nm).

The XPS spectra were acquired on a SCIENTA 200 X-ray photoelectron spectrometer equipped with a conventional hemispherical analyser and operating at constant pass energy of 100 eV in the fixed transmission mode. A monochromatic Al Kα (1486.6 eV) incident beam operated at 420 W (14 kV; 30 mA) was used. The survey and multiregions spectra were recorded and CasaXPS software was used to deconvolute the peaks.

3. Results and discussion

As showed elsewhere [19], the VN powder prepared by sol–gel of V_2O_5 and thermal treatment with NH_3 (500 °C) presents a porous morphology and a crystalline structure. The structure characteristics of the VN target and the VN films deposited on different substrates and temperatures were investigated by XRD diffraction. For all samples, the XRD patterns (Fig. 1) show well defined peaks suggesting

Table 1
Film characteristics obtained by AFM characterisations.

Sample	Substrate	Temperature (°C)	Thickness (nm)	Roughness, Ra (nm)
VN-500G	Glass	500	30	0.46
VN-25G	Glass	25	15	0.37
VN-25S	Si	25	17	0.15

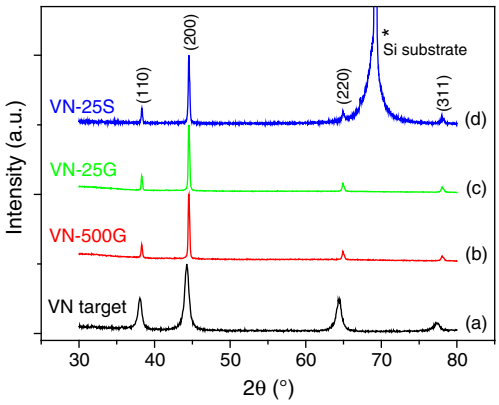

Fig. 1. X-ray diffraction patterns of (a) VN target and VN films, (b) VN-500G, (c) VN-25G, and (d) VN-25S (* — Si substrate).

their highly crystalline nature. The peak position corresponds to VN cubic phase. Compared with the VN target XRD patterns, it can be remarked that the prepared films (Fig. 1b–d) exhibit a preferential orientation on the substrate to (200) direction plane. The calculated texture coefficient [I (110)/I (200)] for the films deposited on glass substrate is 0.28 no matter what the deposition temperature is while that of the film growth on Si is 0.23, which is clearly smaller than that of VN powder (0.5) or a VN reference powder (0.6) which has no preferred orientation. As suggested by Ma et al. [20] the preferential orientation of the films on the (200) direction is mainly due to highly energetically conditions used in the PLD process, this direction being thermodynamically preferred to bring the system to an equilibrium state.

Moreover the film patterns are less broad and slightly shifted to the higher 2θ values compared to the target ones, suggesting a slight increase in the particles size during the deposition process. Furthermore, no significant structural differences between the films prepared at different temperatures (Fig. 1b, c) or on different substrates (Fig. 1c, d) could be remarked. The lattice parameter, a, calculated for the (200) peak of the films is about 4.068(9) Å while for the VN target is 4.093 Å. By corroborating these values with the linear relation between the lattice parameter and the nitrogen content found in the vanadium nitride [13,21], the x value in VN_x can be estimated to be around 0.72 for the VN films and 0.82 for the VN target. This reveals a deficiency in nitrogen and a slightly oxidised surface. The presence of oxygen was also proved by EDX measurements (not shown here). This is often seen in the case of VN materials as already reported in the literature [1,20]. It should be mentioned that the crystalline structure of the VN target was well transferred to the films even at room temperatures which represents one of the main advantages of the applied method. As it has been already demonstrated [22] with the PLD method the target stoichiometry is congruently transferred to the coating. Nevertheless, important modifications in the bonding configuration of the coatings compared to the bulk target can be produced during the PLD process. Complex physical phenomena such as dynamic expansion of the plasma plume and the plume–sample interaction, which are involved in the growth of the PLD films, could however contribute to different rearrangements of the ablated material on the substrate surface.

The morphology of the films as visualised by SEM technique can be seen in Fig. 2. Thin scratches were made to verify the film adhesion as well as scotch tape test. The surface was found homogenous and smooth while the coating exhibited good adhesion to the substrate. Some spherical particulates, characteristic to PLD [11,23–26], with sizes between 0.1 and 0.5 μm can be observed on the surface of the films. At this level no major differences can be seen between the morphologies of the films deposited in different conditions. The TEM pictures show a quite dense morphology for the films deposited at room