Effective role of deposition duration on the growth of V2O5 nanostructured thin films

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Effective Role of Deposition Duration on the Growth of V_2O_5 Nanostructured Thin Films

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Abstract. In this report, vanadium pentoxide nanostructured thin films (NSTs) with nanoplates (NPs) have synthesized on Ni coated glass substrate employing plasma assisted sublimation process (PASP), as a function of deposition/growth durations. The effect of deposition durations on the morphological, structural, vibrational, and compositional properties have been investigated one by one. The structural and vibrational studies endorsed that the grown NPs have only orthorhombic phase, no other sub oxide phases are recorded in the limit of resolution. The morphological results of all samples using SEM, revealed that the features, coverage density, and alignments of NPs are greatly controlled by deposition duration and the best sample is obtained for 25 min (S2). Further, the more insight information is accomplished by HRTEM/SAED on the best featured sample, which confirmed the single crystalline nature of NPs. The XPS result again confirmed the compositional purity and the nearly stoichiometric nature of NPs.

Keywords: Vanadium pentoxide, Nanoplates, Plasma
PACS: 68.55.-a, 81.07.-b, 78.67.-n

INTRODUCTION

Transition metal oxides have been a subject of research in recent years on the bases of their technological and fundamental aspects. Vanadium creates many oxides VO, V_2O_5, V_2O_3, V_4O_9, and VO_2 having different structural, optical, and chemical properties [1]. In the past decade, nanostructured vanadium oxide thin films have attracted interest due to their physical and chemical properties and their great potential for the applications in catalysts, gas sensors, Li^+-ion batteries, and electrochromic devices. Among various vanadium oxides, vanadium pentoxide is the most stable oxide phase with the highest oxidation state, having many interesting properties including multi-valance, layered structure, wide optical band gap (2.44 eV), good chemical and thermal stability, and excellent electrochromic properties [2]. Therefore, V_2O_5 have been excellently used in fabricating many solid state devices, such as high capacity lithium batteries, display systems, color filters, catalysts, smart windows, and gas sensors. So far, variety of deposition processes have been used to synthesize different kinds of V_2O_5 NSTs such as thermal evaporation, hydrothermal/solvothermal synthesis, sol-gel and electro-deposition techniques, etc. with or without post treatments. Most of the research groups employed chemical route and limited number of reports have been published on synthesis of V_2O_5 nanostructures using PVD approaches. Herein, we have investigated the effect of growth durations on the growth of V_2O_5 NSTs using PASP. Structural, morphological, vibrational, and compositional properties of V_2O_5 NSTs are studied systematically.

EXPERIMENTAL SETUP

The experimental setup of plasma assisted sublimation process (PASP) basically have two cup-shaped Al-electrodes facing each other and placed at separation of 7.5 cm. First, a 100 nm thick Ni film is deposited on glass substrate using thermal evaporation of 99.99% pure Ni powder at base vacuum of 7.5×10^{-6} Torr. After that Ni coated glass is placed over V-strip, held at 500 °C. The strip temperature is adjusted by the controlled current passing through it. In order to deposit V_2O_5 films, first the chamber is evacuated to 7.5×10^{-6} Torr, than high purity oxygen is inserted into chamber till the chamber attained pressure at 7.5×10^{-2} Torr. The plasma voltage is kept constant at its optimum values of 2500 Volts. Two separate thermocouples are adjusted inside vacuum chamber to read the substrate and metal strip temperatures simultaneously. In the present work, V_2O_5 NSTs are deposited for 15, 25, and 40

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minutes and named as samples S1, S2, and S3, respectively. The surface microstructure of films are studied by scanning electron microscope of model number ZEISS EVO (EVO-50 series). Structural studies are performed using Philips X-ray diffractometer equipped with Cu-K_α radiation (~ 1.54 Å) source keeping glancing angle at 1°. Photoelectron spectroscopic study is carried out by SPECS, with anode Mg/Al 25kV X-ray source of power 150 W. Micro-Raman measurements are performed to study the different vibrational modes of V and O atoms in all samples from 0-1000 cm^{-1} by employing Renishaw-inVia (excited with Ar^+ line at 514.5 nm). Transmission Electron Microscopy (TEM) study of V_2O_5 nanoflakes is carried out with Philips Model CM12 operated at 120 kV with HRTEM analysis. All the measurements are performed at room temperature.

RESULTS AND DISCUSSION

Figure. 1 shows the surface microstructures of vanadium oxide NSTs deposited for different growth durations (i.e. samples S1 to S3).

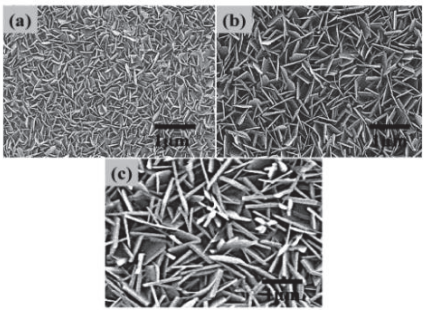

FIGURE 1. SEM micrographs of samples (a) 15 min, (b) 25 min, and (c) 40 min

All the recorded SEM micrographs depict the growth of well-defined nanoplates (NPs) with vertical alignments and their morphologies are greatly depend on deposition durations. Sample S1 shows the uniform growth of NPs having small dimensions owing to the lack of oxide vapor reaching onto substrate. As duration increases to 25 min, the dimensions and number density of NPs get enhanced because now more oxide vapor reaches on substrate.

TABLE 1. Dimensional details of NPs with growth duration

Deposition Duration (min)	Av. Width (nm)	Av. Thickness (nm)
15	300	50
25	600	50
40	1000	100

Since, it has been reported earlier [3] that the oxide volatilization rate depends on substrate temperature, which is fixed at 500°C. So, the dimensions of NPs will depend on durations. The dimensional details of NPs as a function of duration are given in Table 1. So, from SEM results it reveals that sample S2 is the best sample. Further, on increasing duration to 40 min dimensions of NPs again increases but number density of NPs gets decreased.

The X-ray diffractogram of vanadium oxide NPs formed at 25 min is shown in Fig. 2. The presence of sharp and intense diffraction peaks in diffractogram of sample S2 directly endorsed the polycrystalline nature of film. According to the standard JCPDS data, the recorded XRD peaks divulged that only orthorhombic oxide phase is present on the vanadium oxide NSTs and no other impurity phases are found under the resolution limit of XRD.

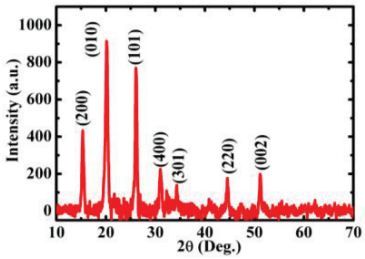

FIGURE 2. The X-ray diffractogram of V_2O_5 NPs grown for the deposition duration 25 min

The measured values of lattice parameters from XRD analysis are recorded to be a = 11.51 Å, b = 3.56 Å, and c = 4.37 Å, those are quite consistent with the reported values as given in JCPDS (Ref. Code No: 75-0457) for orthorhombic V_2O_5. Among all peaks, only the peak of (010) crystal plane is the most intense peak, which indicates that the preferential growth of V_2O_5 NPs is taking place along b-direction. Though the intensity of other peaks of (200) and (101) crystal planes are also relatively larger, confirming that NPs are slightly deviated from their vertical alignments, as also confirmed by the SEM micrograph of same film.

In further analysis, we selected the best sample (S2 in present case) in order to obtain more insight information of grown NPs through TEM analysis accompanied with HRTEM and SAED, as shown in Fig. 3.

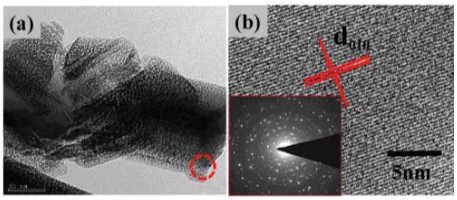

FIGURE 3. (a) Bright field TEM micrograph of a single nanoplate (b) HRTEM image with SAED pattern in inset

All the dimensions of NPs are nearly matched to that recorded from SEM images. The recorded fringe pattern using HRTEM form the encircled region, marked on NP in Fig. 3a, corroborated the single crystalline nature of NPs. In addition, the dot pattern in SEAD image again provide a strong base to justify the single crystalline nature of NPs.

In order to study vibrational properties NPs the Raman spectrum of V_2O_5 NPs growth for 25 min is recorded in the wavelength range of 0 to 1000 cm^{-1} and shown in Fig. 4.

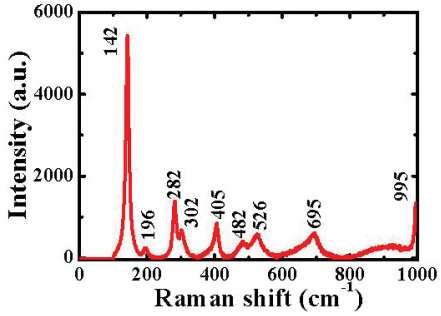

FIGURE 4. Raman spectrum of V_2O_5 nanoplates

All the Raman peaks as shown in spectrum again confirm the presence of only orthorhombic phase as per reported results. Among all the peaks, the most intense Raman peak at 142 cm^{-1} is attributed to the skeleton bent vibration. Whereas, the other peaks of relatively lesser intensity predominantly observed at 196, 282, 302, 405, 482, 526, 695, and 995 cm^{-1} are associated to the bending vibrations of O_c-V-O_b and V-O_b-V bonds (called A_g and B_{2g} modes) and the stretching vibrations of V-O_c bond [3]. In addition, the presence of relatively intense peaks correspond to skeleton bent mode and stretching mode at 147 cm^{-1} and 995 cm^{-1}, respectively are strongly evidenced the existence of layered structure in V_2O_5 [4].

To study the material quality and the relative compositions the best sample has been selected (sample S2) for the XPS analysis.

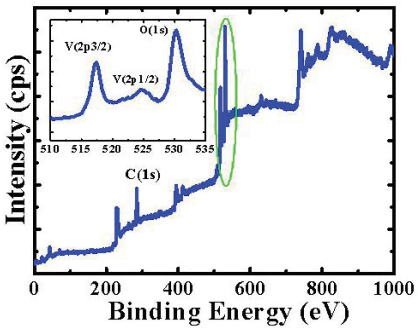

FIGURE 5. XPS of sample V_2 deposited with survey spectrum and highly resolved spectrum of V (2p) and O (1s) bands ranging from (500-540) eV

The general XPS survey scan of sample S2 is shown in Fig. 5, which displaying only three intense bands of V (2p), O (1s) (as shown in the inset), and C (1s) almost matched to the reported values of core level binding energies (BEs).The absence of other extra elements in our survey scan infers the compositional pureness of V_2O_5 nanostructured thin film. The amplified view of V (2p) doublet peaks positioned at 517.3 and 524.5 eV are representing to doublet states of V^{5+} ($2p_{3/2}$) and V^{5+} ($2p_{1/2}$), respectively with the typical spin-orbit splitting of 7.2 eV and nearly consistent with the reported results [5]. The symmetric nature of doublet peaks corresponding to V (2p) assured the maximum percentage of highest oxidation state of V^{5+} in sample S2 and lead to the better stoichiometric ratio (i.e. V/O).But the asymmetric nature of O (1s) band evidenced the presence of –OH bonds on the surface of NPs.

CONCLUSIONS

In summary, vertically aligned and uniformly distributed vanadium pentoxide NPs with very large surface area have synthesized on Ni coated glass substrates as a function of deposition duration using PASP. The recorded morphological results demonstrate that the growth of single crystalline V_2O_5 NPs with one of the best coverage and uniformity is took place for sample S2 (25 min). Both the features and the coverage density of grown NPs are found to be strongly depend on deposition duration. The structural and the Raman results endorsed that the V_2O_5 NPs have only orthorhombic phase, no other oxide phases are recoded under the XRD resolution limit. According to XPS results, it is confirmed that NPs are compositionally pure, means only the signature corresponds to V, O, and C are recorded in general survey scan. This novel architectures of α-V_2O_5 grown using PASP

might be a better candidate in various applications such as energy storage devices (Li-ion batteries), display devices, and gas sensors etc.

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