Impression of plasma voltage on growth of α-V2O5 nanostructured thin films

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Impression of Plasma voltage on Growth of α-V_2O_5 Nanostructured Thin films

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Abstract. In this communication, we synthesized vanadium pentoxide (α-V_2O_5) nanostructured thin films (NST_s) accompanied with nanoflakes/ nanoplates on the Ni-coated glass substrates employing plasma assisted sublimation process (PASP) as a function of plasma voltage (V_p). The effect of plasma voltage on structural, morphological, compositional, and vibrational properties have been studied systematically. The structural analysis divulged that all films deposited at different V_p have pure orthorhombic phase, no impurity phase is detected under resolution limit of XRD and XPS. The morphological studies of samples is carried out by SEM, revealed that features as well as alignment of V_2O_5 NST_s is greatly monitored by V_p and the film possessing the best features is obtained at 2500volt. In addition, XPS results reveal that V^{5+} oxidation state is the most prominent state in sample V_2, which represents better stoichiometric nature of film. The vibrational study of all samples is performed by FTIR and strongly support the XRD observations. All the results are in consonance with each other.

Keywords: Vanadium pentoxide, Plasma voltage, Plasma assisted sublimation process
PACS: 68.55.-a, 81.07.-b, 78.67.-n

INTRODUCTION

Transition metal oxides offer a wealth of unique physical, chemical, electronic, and optical properties, which have occupied the attention of scientists and engineers form last decade. Vanadium pentoxide (V_2O_5) especially in the form nanostructured thin film (NST_s) has attracted attention during the last decades primarily owing to its fascinating application in various kind of applications like in electrochromic devices, power storage devices (Li^+-ion batteries), gas sensing, and catalysis. Multivalency, layered structure, wide optical band gap, and good thermal and chemical stabilities are the characters, make a promising material in various applications mentioned above. For these applications, relatively large aspect and surface-to-volume ratio are found to be very important factors that greatly affect the efficient parameters, particularly at nano scale dimension of materials [1]. Up to now, several distinct approaches have been explored for the synthesis of V_2O_5 NST_s, such as thermal evaporation system, hydrothermal/solvothermal synthesis, sol-gel techniques, and electrodeposition etc. with or without post treatments. C. Diaz-Guerra et al. [2] have been reported the growth of V_2O_5 nanowires and nanotips on Si substrate using thermal evaporation and studied their cathodoluminescence behavior. M. Li et al. [1] have synthesized V_2O_5 nanobelts using sol-gel process coupled with hydrothermal process. Most of the research groups employed chemical route and very limited reports are published based on the synthesis of V_2O_5 nanostructure using PVD approaches. Herein, we have reported the growth of V_2O_5 NST_s by a facile PVD route named plasma assisted sublimation route (PASP) as a function of plasma voltage (V_p). All films grown at distinct value of V_p are characterized and analyzed systematically.

EXPERIMENTAL SETUP

The experimental setup of plasma assisted sublimation route basically have two cup-shaped Al–electrodes confronting each other and placed at an optimum separation of 7.5cm. First, nearly 100nm 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/glass substrate is placed on V-strip, held at temperature 500°C. The strip temperature is appropriately control by adjust current flowing across it. In order to deposit V_2O_5 NST_s at distinct values of plasma voltage (V_p), first the chamber is evacuated to 7.5×10^{-6}Torr, than high purity oxygen gas is inserted into the chamber and maintain the value of oxygen partial pressure at the level of 7.5×10^{-2}Torr to sustain stable plasma across electrodes. All the plasma parameters are kept constant

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at the time of film deposition except V_p. Three samples have prepared corresponding to three distinct value of plasma voltage of 2000, 2500, and 3500volts and are simply named as V_1, V_2, and V_3 respectively. Thermocouple arrangement is adjusted inside vacuum chamber to read the substrate/growth temperature. The surface microstructure of all the deposited films at different V_p values is studied with scanning electron microscope ZEISS EVO series scanning electron microscope model EVO-50. Structural studies are carried out using Philips X-ray diffractometer equipped with Cu-K_α radiation (λ~1.54Å) source keeping the glancing angle constant at 1°. Photoelectron spectroscopic studies is carried out by Perkin Elmer Model PHI 1257 spectrometer, with anode Mg/Al 25kV X-ray source of power 150W. Infrared (IR) measurements are performed to study the different vibrational modes of V and O atoms in all samples from 400-2000cm^{-1} by employing Perkin Elmer make (Model BX2) spectrophotometer. Transmission Electron Microscopy (TEM) study of V_2O_5 NST_s is carried out with Philips Model CM12 operated at 120kV with HRTEM analysis. All the measurements are performed at room temperature.

RESULTS AND DISCUSSION

In order to study the composition and phase purity of the V_2O_5 NST_s, X-ray diffraction pattern of samples have been recorded, can be seen in Fig. 1(V_1-V_3). The sharp diffraction peaks in the diffractograms of sample V_1 to V_3 are directly endorsed the polycrystalline nature of films. The obtained XRD pattern divulge the single orthorhombic nature of all the V_2O_5 NST_s and no other impurity phase is found under the resolution limit of XRD.

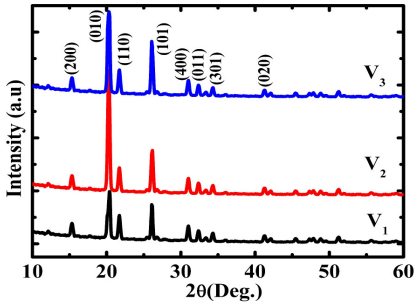

Figure 1. XRD of V_2O_5 NST_s deposited at different value of V_p: 2000volt (V_1), 2500volt (V_2), and 3500volt (V_3)

The obtained values of lattice parameters from XRD analysis are a = 11.51Å, b = 3.56Å and c = 4.37Å, which are quite in good agreement with the reported values as given in JCPDS (Ref. Code: 75-0457) a = 11.48Å, b = 3.55Å and c = 4.36Å for α-V_2O_5. It is worth noted that X-ray pattern of sample V_2 among all, reveal the highly preferred orientational growth along [010] crystallographic direction. Even other samples are also give a good signature of crystallinity, but film grown at 2500volt expresses good degree of crystallinity with relatively better preferential growth. The mean crystallite size of samples V_1, V_2, and V_3 is estimated corresponding to the diffraction peak having the highest intensity using the Debye-Scherrer formula can be seen in Table 1. According to our observations the crystallite size for all samples are nearly same but the growth accompanied with better alignment will be observed in case of V_2.

TABLE 1. Shows the dimensional analysis of samples V_1, V_2, and V_3

Plasma voltage (V_p) in volts	Average length (nm)	Average Thickness (nm)	Crystalline Size (nm)
2000	200	50	28.2
2500	1000	30	29.1
3500	900	60	27.5

Figure 2 depicts the surface microstructure of V_2O_5 NST_s of samples V_1, V_2, and V_3 fabricated at distinct plasma voltage. The obtained results endorse that in sample V_1 nanoflakes like morphology is formed having small dimensions with undeveloped features, may be owing to the low plasma density. Which leads to the lack of energetic oxygen ionic species at smaller value of V_P during growth. On increasing plasma voltage upto 2500volt (V_2) completely developed nanoplates is formed with vertical alignment as confirmed by XRD results. This well-established nanoplates like features in case of V_2 is mainly due to improved plasma density at relatively high V_p in plasma discharge and also furnishes enough energetic oxygen ions for oxidation (volatilization) of V-metal (V_2O_5) throughout deposition.

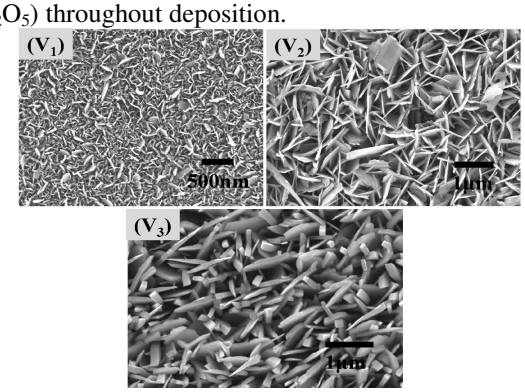

Figure 2. SEM images V_2O_5 nanostructured thin films: deposited at different value of V_p: 2000volts (V_1), 2500volts (V_2), and 3500volts (V_3)

Further increment in plasma voltage upto 3500volt offer more number of energetic O-ions in plasma column as a result, oxidation and volatilization of V-metal and V_2O_5 get prominently enhanced, but at the same time presence of more O-ions interrupt the alignment of nanoplates because of their collision with the impinging V_2O_5 molecular species on substrate as

can be seen in Fig.3 (V_3) [3-4]. Therefore, it can be concluded that optimum value of plasma voltage should be required in order to achieve better features as well as alignment of NST_s. The observed SEM result are verify the XRD outcomes.

For further analysis, we have selected the best sample, which is V_2 in this case. In order to obtain the material quality and the relative compositions, XPS analysis of sample V_2 is carried out. Figure 3 depicts the general XPS survey spectrum of V_2 which, displaying only three intense bands of V(2p), O(1s), and C(1s) almost matching to the reported values of core level binding energies (BE_s). The absence of other extra elements in our survey scan infers the compositional pureness of V_2O_5 nanostructured thin film. The amplified veiw of splited V(2p) levels positioned at 517.2 and 524.7eV 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 7.4eV and quite matched with the results reported earlier [3] (see in the inset of Fig.3).

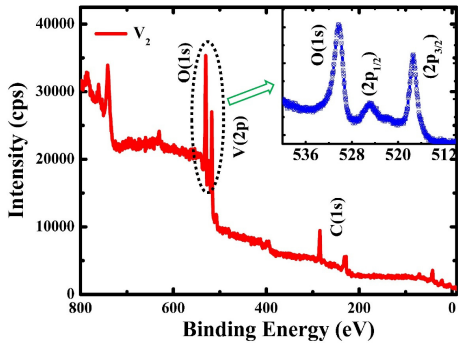

Figure 3. XPS of sample V_2 deposited with survey spectrum and highly resolved spectrum of V(2p) and O(1s) bands ranging from (510-537)eV

The nearly symmetric nature of doublet peaks corresponding to V(2p) assured the promenient percentage of higest oxidation state of V^{5+} in sample V_2 and lead to the better stoichiometric ratio of V and O. FTIR spectra are recorded to investigate vibrational modes of vanadium and oxygen atoms coordinated in distinct fashion for all samples (V_1-V_3) in the spectral regime from 400 to 2000cm^{-1} can be seen in Fig. 4. The IR reflectance spectra of samples reveal four prominent absorption peaks positioned at 1025, 859 730, and 492cm^{-1}, attributed to different vibrational modes. The strong absorption peak at 1025cm^{-1} particularly in V_2 indicates the presence of V=O stretch mode of terminal bond, which is mainly responsible for layered structure in α-V_2O_5. The comparatively weak IR-peak corresponding to 492cm^{-1} and 730cm^{-1} represents the symmetric and asymmetric vibrations (ν_s and ν_{as}) of O-V-O stretching in V_2O_5. Whereas, the peak positioned at 859cm^{-1} is due to the bending mode of bridge-oxygen in V-O-V entity [1&5]. The relatively intense and sharp IR peaks in V_2 further confirmed the betterment in degree of crystallinity and strongly support XRD and SEM outcomes as well.

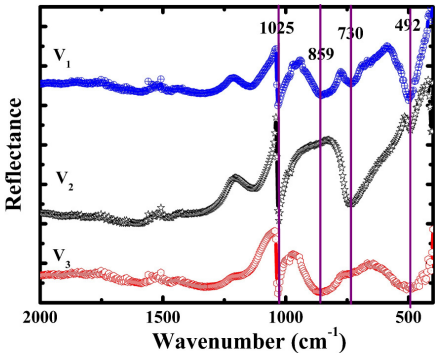

FIGURE 4. FTIR spectra of V_2O_5 NST_s: 2000volts (V_1), 2500volts (V_2), and 3500volts (V_3)

CONCLUSIONS

In summary, vanadium pentoxide NST_s accompanied with vertically aligned nanoflakes/nanoplates with very high reactive surface area are synthesized on Ni coated glass substrates using plasma assisted sublimation process (PASP). The obtained structural and morphology outcomes endorsed that the growth of α-V_2O_5 nanoplates of better homogeneity as well as alignment on very large area scale took place only when plasma voltage is maintained at 2500volts. Both the features and alignment of grown nanostructure are found to be strongly dependent on plasma voltage (V_p). In addition, the XPS results divulged that V_2O_5 nanoplates (in sample V_2) are nearly stoichiometric from the compositional prospective. These grown novel architectures of α-V_2O_5 grown by PASP might be a better candidate in variety of applications such as energy storage devices (Li^+-ion batteries), display devices, and gas sensor devices etc.

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