Effect of nickel seed layer on growth of α-V2O5 nanostructured thin films

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Citation: AIP Conference Proceedings **1675**, 030052 (2015); doi: 10.1063/1.4929268
View online: http://dx.doi.org/10.1063/1.4929268
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1675?ver=pdfcov
Published by the AIP Publishing

Effect of Nickel Seed layer on Growth of α-V_2O_5 Nanostructured Thin films

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Abstract. In this communication, we reported the role of Ni seed layer on the growth of vanadium pentoxide (α-V_2O_5) nanostructured thin films (NSTs) using plasma assisted sublimation process (PASP). Two different substrates, simple glass substrate and the Ni coated glass substrate (Ni thickness ~ 100 nm) are employing in the present work. The influence of seed layer on structural, morphological, and vibrational properties have been studied systematically. The structural analysis divulged that both films deposited on simple glass as well as on Ni coated glass shown purely orthorhombic phase, no other phases are detected. The morphological studies of V_2O_5 film deposited on both substrates are carried out by SEM, revealed that features of V_2O_5 NSTs is completely modified in presence of Ni seed layer and the film possessing the excellent growth of nanorods (NRs) on Ni coated glass rather than simple glass. The HRTEM analysis of NRs is performed at very high magnification, shows very fine fringe pattern, which confirmed the single crystalline nature of nanorods. The vibrational study of NRs is performed using micro-Raman spectroscopy, which strongly support the XRD observations.

INTRODUCTION

Now in these days, the current research is mainly focused on the fabrication and the application of nanomaterials, has rapidly extended with the controlling the shape of materials and understanding the correlations between the material properties and their nanostructures of different surface morphologies. Among the transition metal oxide semiconductors, vanadium pentoxide (V_2O_5) has drawn significant interest over the past decades owing to its novel characteristics. Its multivalence nature, layered structure, wide band gap, excellent chemical and thermal stability, and good thermoelectric property make V_2O_5 a promising material for the variety of technological applications like in microelectronics and optoelectronic devices. Vanadium pentoxide is also widely used as a catalyst, gas sensors, electrochromic devices, and in electronic and optical switches. It is well established that for these applications, the nanostructures with excellent aspect and surface-to-volume ratio are most required and greatly affect the efficient parameters, particularly at the nano size of materials [1]. So far, numerous deposition techniques have been employed for the synthesis of variety of V_2O_5 NSTs, such as thermal evaporation route, hydrothermal/solvothermal synthesis technique, sol-gel route, and electro-deposition etc. D. Su et al. synthesized by layered vanadium pentoxide oxide nanobelts using simple solvothermal method and used them successfully in sodium ions batteries. Alexey M. Glushenkov et al. [2] reported the growth of V_2O_5 nanorods using the two stages procedure of ball milling and annealing in air and used them in the application of Li- ion batteries. M. Li et al. [1] have synthesized V_2O_5 nanobelts using sol-gel process coupled with hydrothermal process. It is to be noted that most of the synthesis of V_2O_5 NSTs have been carried out using chemical routes and very few reports are published based on the synthesis using PVD approaches. In the present work, we have reported the effect of nickel of seed layer on the growth of V_2O_5 NSTs using a simple PVD route called plasma assisted sublimation route (PASP). The films grown with and without Ni layer on glass substrate are characterized and studied systematically.

EXPERIMENTAL SETUP

Vanadium pentoxide nanostructured thin films are deposited on two types of substrates: bare glass and Ni coated glass substrates by plasma assisted sublimation process (PASP). First, the nickel film of thickness ~ 100 nm is deposited on glass substrates by the thermal evaporation of pure nickel powder (99.99% Aldrich) at the

Advanced Materials and Radiation Physics (AMRP-2015)
AIP Conf. Proc. 1675, 030052-1–030052-4; doi: 10.1063/1.4929268

base vacuum of 7.5 x 10^{-6} Torr. Then substrates are hanged between electrodes at a distance of ~ 1 mm from source (act as a sublimation source), shown in Fig. 1. The source temperature increase with the rate of 2°C/sec up to 500°C by monitoring the current flowing through the V-strip.

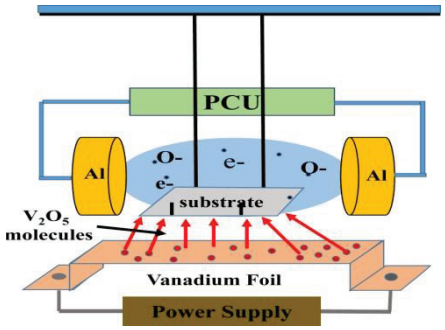

FIGURE. 1 The schematic diagram of experimental setup of PASP with plasma setup

Thermocouple arrangement is used to measure the substrate as well as source temperature during deposition. The recorded temperature of substrate in this cases was ~ 300°C. Rectangular shaped vanadium strip along with substrate was placed between electrodes and then keep oxygen plasma on. The optimum plasma parameters, plasma voltage, electrode separation and oxygen partial pressure are maintained at 2500 Volts, 7.5 cm, and 7.5 x 10^{-2} Torr, respectively during growth. The duration of deposition is kept fixed at 30 min in both cases. After deposition that samples are allowed to cool naturally at room temperature in the Ar atmosphere. The V_2O_5 films deposited on Ni coated glass substrates and bare glass are abbreviated as S1 and S2.

RESULTS AND DISCUSSION

The X-ray diffractograms have been recorded to study the composition and crystalline phase purity of the V_2O_5 NSTs deposited on bare glass and Ni coated glass, shown in Fig. 2 (S1 and S2). The recorded well indexed XRD peaks in the diffractograms of films S1 to S2 divulged the existence of pure orthorhombic phase in both V_2O_5 NSTs. No peaks corresponding to other impurity phase is found under the resolution limit of XRD technique.

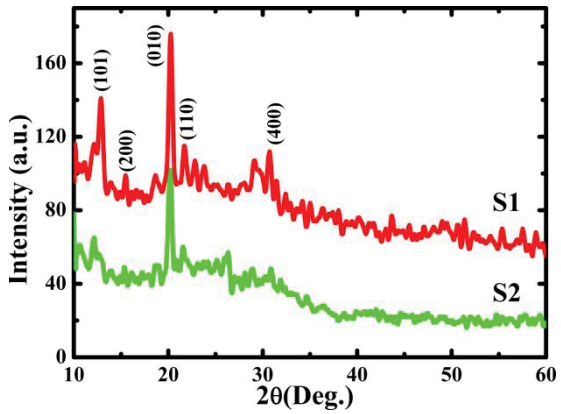

FIGURE 2. XRD of V_2O_5 NSTs deposited (S1) on bare glass substrate (S2) on Ni coated glass substrate

The measured values of lattice parameters from X-ray diffractograms are found to be: a = 11.48 Å, b = 3.53 Å and c = 4.35 Å, which is quite consistent with the reported values in JCPDS (Ref. Code: 75-0457) a = 11.48 Å, b = 3.55 Å and c = 4.36 Å for α-V_2O_5. As shown in Fig. 2, the X-ray pattern of sample S1 shows relatively more intense peaks than sample S2. In both samples the most intense peaks is recorded for [010] crystal direction, which reveal that V_2O_5 NSTs are growing preferentially along [010] crystallographic direction. The average value of crystallite/grain size of samples S1 and S2 is measured corresponding to the diffraction peak having the maximum intensity using the Debye-Scherrer formula. The measured crystallize of sample S1 and S2 are found to be 24.4 and 22.5 nm, respectively. So, it can be concluded that V_2O_5 film with better crystallinity is obtained in case of sample S1.

Figure 3 shows the surface morphology of samples S1 and S2 deposited on distinct substrates. The recorded micrograph of film deposited on Ni coated glass shows the growth of randomly aligned nanorods with average length and width of 500 nm and 50 nm, respectively (see in Fig. 3a). In contrast, the V_2O_5 film deposited on bare glass substrate (S2) showed no defined nanostructures, only a rough film is deposited (see in Fig. 3b).

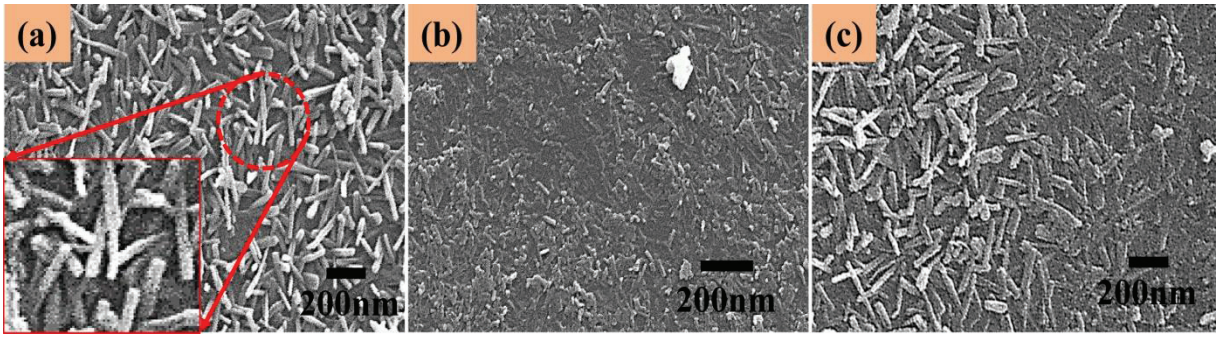

FIGURE 3. SEM images V_2O_5 nanostructured thin films: deposited on (S1) Ni coated glass substrate (S2) on bare glass substrate

Figure 3c presents the morphology of V_2O_5 film deposited on patterned glass having half portion is coated with Ni. The difference in the surface structure on simple glass and the Ni coated glass can be recorded clearly. The difference in morphology is mainly because of unavailability of proper nucleation site on bare glass substrate (sample S2). In case of sample S1 the strain is developed on Ni film because of unbalanced expansion of Ni and glass at 500°C due to the difference in thermal expansion coefficients of Ni and glass. Since the substrates are positioned directly in front of V-strip the direct impingement of V_2O_5 molecules will also favored the growth of nanorods after getting a proper nucleation site [3-4].

In order to study the more insight information of NRs grown in sample S1, TEM and HRTEM measurements are performed, shown in Fig. 4. The TEM analysis also confirmed the formation of NRs with well-defined features. The recorded length and the width of NRs form TEM image are found to be nearly 500 nm and 90 nm, which are nearly in consistent with the SEM results from the dimensions prospective.

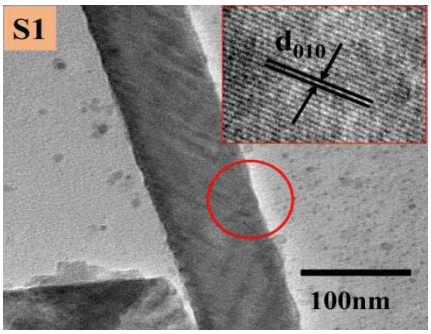

FIGURE 4. TEM and HRTEM images of V_2O_5 NRs grown on Ni coated glass substrate using PASP

The HRTEM image in inset of Fig. 4 shows a fine fringe pattern recorded from encircled part on NRs, which confirmed the single crystalline nature of NRs. The measured spacing between lattices fringes are nearly matched with the spacing of d_{010} interplanar spacing, and strongly evidenced the preferential growth of NRs along b-direction.

The Raman spectra of V_2O_5 NRs (Sample S1) shows several prominent Raman peaks positioned at 146, 213, 284, 405, 530, 705, 995 cm^{-1}. All the observed peaks are corresponding to the different vibrational modes of V and oxygen atoms coordinated in different fashions.

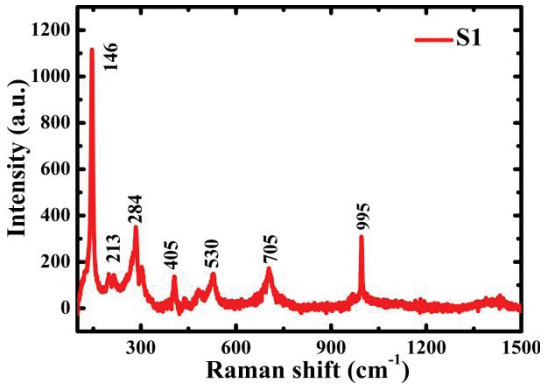

FIGURE 5. Micro-Raman spectrum of α-V_2O_5 NRs grown using PASP

All the recorded Raman peaks are perfectly matched with the position of α-V_2O_5 peaks reported earlier and further confirmed the presence of pure orthorhombic phase of V_2O_5 NRs. The most intense and shape peaks centered at 146 and 995 cm^{-1} are attributed to the skeleton bending mode and the stretching mode of vanadium atom connected to oxygen atoms by double bonds. The presence of these two peaks are strongly evidenced the existence of layered structure in α-V_2O_5. Finally, the recorded Raman results are well in consonance with the XRD results.

CONCLUSIONS

In summary, the effect of nickel seed layer has investigated on the growth of V_2O_5 NSTs. For that V_2O_5 films are deposited on two different substrates: bare glass substrate and Ni coated glass substrate. The structural results endorse the existence on only orthorhombic phase of vanadium pentoxide with the preferential orientation along [010] crystallographic direction. No other phases are found in both cases. The morphological results show that the presence of Ni coating on glass substrate is favorable for the growth of well-defined NRs, while in case of bare glass substrate no structure is found under the same deposition conditions. Further, more insight characterization of NRs is performed using HRTEM, which shows a clear fringe pattern and confirm the single crystalline nature of NRs. The vibrational analysis of NRs using Raman further confirm the polycrystalline nature of film with pure orthorhombic nature and quite consistent with XRD results. The nanorods of α-V_2O_5 grown using PASP might be a good candidate in variety of applications such as energy storage devices (Li^+ - ion batteries), display devices, and gas sensor devices etc.

ACKNOWLEDGMENT

We acknowledge the financial support from CSIR grant 086(0950)/09/EMR-I.

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