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Oxidation of vanadium metal in oxygen plasma and their characterizations

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In this report, the role of oxygen plasma on oxidation of vanadium (V) metal and the volatilization of its oxides has been studied as a function of source (V metal strip) temperature (T_{ss}) and oxygen partial pressure (P_{O_2}). The presence of O_2 -plasma not only enhances the oxidation rate but also facilitates in transport of oxide molecules from metal to substrate, as confirmed by the simultaneous deposition of oxide film onto substrate. Both the oxidized metal strips and oxide films deposited on substrates are characterized separately. The structural and vibrational results evidence the presence of two different oxide phases (i.e. orthorhombic V_2O_5 and monoclinic VO_2) in oxide layers formed on V metal strips, whereas the oxide films deposited on substrates exhibit only orthorhombic phase (i.e. V_2O_5). The decrease in peak intensities recorded from heated V metal strips on increasing T_{ss} points out the increment in the rate of oxide volatilization, which also confirms by the oxide layer thickness measurements. The SEM results show the noticeable surface changes on V-strips as the function of T_{ss} and P_{O_2} and their optimum values are recorded to be 500 °C and 7.5×10^{-2} Torr, respectively to deposit maximum thick oxide film on substrate. The formation of microcracks on oxidized V-strips, those responsible to continue oxidation is also confirmed by SEM results. The compositional study of oxide layers formed on V-strips, corroborates their pureness and further assures about the existence of mixed oxide phases. The effect of oxygen partial pressure on oxidation of V-metal has also been discussed in the present report. All the results are well in agreement to each other. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4931997>]

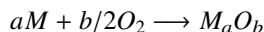
INTRODUCTION

Oxidation is the most crucial high temperature process in metals. The oxidation of metals and alloys takes place when they are heated in a highly oxidizing atmosphere like air and oxygen. The oxidation process of refractory metals has been the subject of numerous past studies and reviews.¹⁻⁷ It is well known that most of metals except noble metals, form tarnishing oxides layers even at low temperatures. Their reaction with oxygen at high temperature is expected to be very rapid. It is very difficult to classify metals into various groups on the basis of their interaction in oxidizing environment due to vast difference in terms of their oxidation mechanism, the type and thickness of scale or oxide film etc.¹ In general the simplest classification would be in terms of their oxidation resistance. Noble metals like platinum, gold, palladium etc. can be categorized in one group. They are most resistant to oxidation. Another group consists of transition metals, such as iron, nickel, cobalt, molybdenum, vanadium etc., these have moderate oxidation resistance but are the base elements for the important alloys used in high temperature applications.³⁻⁶ The study of oxidation kinetics of metals provides an important and reliable base to understand the oxidation behaviour of metals. The extent as well as the rate of oxidation reaction can be measured by the amount of metal consumed and the amount of oxygen consumed or the amount of oxide produced.

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The most general oxidation reaction between a metal (M) and oxygen (O₂) can be written as:



where, *M* is an oxidising metal, *a* and *b* are the number of atoms/molecules.

Thermodynamically, the oxide will form on the surface of metal, when the oxygen potential in the oxidizing environment is greater than the oxygen partial pressure in equilibrium with the oxide.¹ This indicates that the oxygen partial pressure plays crucial role in oxidation process. According to reported results, at 1 atm pressures, a thin adherent oxide layer is formed on metal at 200 °C when it oxidized in air, resulting in negligible oxidation rate is obtained at ≤ 200 °C. Whereas, in the temperature range from 300 to 450 °C oxidation rate of metal gets increased and also followed a slow parabolic rate. At ≥ 450 °C linear rate is generally occurs even at low oxygen partial pressures.⁸ Medium of oxidation and metal temperature are also played crucial roles in metal oxidation particularly at oxygen partial pressure (~ 10⁻² Torr), where the scaling is minimized.⁹ So far, many investigations have been done to understand the oxidation of metals and the volatilization of their resultant oxide films formed on it as a function of metal temperature in the range of 300-1700 °C.^{10,11} Numerous analytical techniques like thermogravimetry and mass spectrometer have been used to study and control the rate of oxidation and volatilization. According to these models the dissolution of oxygen in metals is also very important particularly of fifth group elements (i.e. vanadium, niobium etc.) in periodic table. These metals dissolve large amount of oxygen, which may affect their mechanical properties and also could limit their use at high temperatures. But the lesser resistance of oxidation of metals is favorable to deposit films on substrates using the oxide layer (which formed on metal surface) as a source of oxide. In this report, our discussions are mainly focused on the oxidation of vanadium metal. There are only few number of reports have been published, those include the study of oxidation behaviour of vanadium metal.^{12,13} Since, it is mentioned above that vanadium metal has very low oxidation resistance and offers a great possibility of oxidation at relatively lower temperature. In most of the reports, metals including vanadium have oxidized in different ambients (i.e. air and oxygen gas) under different experimental conditions like temperature, oxygen partial pressure, duration of oxidation etc.¹⁻⁷ But very limited reports were published on the oxidation of metals using oxygen plasma as an oxidizing medium. It has been reported that oxygen plasma comprises positive ions, negative ions, neutrals, and many excited metastable states of oxygen molecules. But most of the fraction of oxygen gas in plasma is present in ionic form. These energetic oxygen ionic species in plasma are relatively more reactive than naturals (those present in oxygen gas and air) to oxidize metals into their oxides. Because of that oxygen plasma is selected to oxidize vanadium metal in the present work. The complete details and the advantage of using oxygen plasma as an oxidizing medium has been reported in our previous work for Mo metal.⁹

In this communication, we have investigated the role of oxygen plasma on the oxidation of vanadium metal and the volatilization of its oxide formed, as a function of source temperature (*T_{s,s}*) and oxygen partial pressure (*P_{O₂}*). The oxidized vanadium strips and the respective films deposited on substrates are characterized separately to study the oxide volatilization. Structural, morphological, compositional and vibrational studies of all samples (i.e. oxidized metals strips and film deposited on substrates) have been carried out to study the oxidation behaviour of vanadium in oxygen plasma. The aim of this work is to obtain the appropriate growth conditions to deposit nanostructured films on substrates using the volatilized oxide species as a source of vapor. It has been reported earlier that oxygen plasma is the most effect medium to oxidized metal then the rest of other oxidizing medium. Because the presence of ionic oxygen species makes oxygen plasma as a more effective medium for oxidation of metals.

EXPERIMENTAL

The experimental setup used to oxidize V metal has been schematically shown earlier.¹⁴ The setup consists two cylindrical shaped Al-electrodes confronting to each other. Rectangular flat shaped vanadium metal strip (sublimation source) of area 9 × 2 cm² is connected to a variable electrical power source and bare glass/polished Si substrates of area 1.0 × 2.0 cm² are mounted over it. The source temperature (*T_{s,s}*) is increased with the rate of ~ 4 °C/sec by suitably passing

controlled current across it, till the temperature reached at the desired level. The source and substrate temperatures are monitored and recorded using separate thermocouple arrangements. The optimum plasma parameters viz. plasma voltage, electrode separation, and oxygen pressure were kept constant at 2500 Volts, 7.5 cm, and 7.5×10^{-2} Torr, respectively. To investigate the effect of $T_{s,s}$, vanadium metal strips are oxidized at 200 °C, 300 °C, 500 °C, and 600 °C, named as V1, V2, V3, and V4, respectively and the respective oxide films deposited on substrates placed over source are referred as VF1, VF2, VF3, and VF4, respectively. The estimated error in $T_{s,s}$ is found to be ± 5 °C. Before oxidation vacuum chamber is evacuated till the base vacuum of 7.5×10^{-6} Torr. The deposition/oxidation duration is sustained for 30 minutes in all cases. Both the oxidized metal strips and the respective films deposited on glass/silicon substrates are analyzed as separate samples. In the present work, glass substrates are often used upto 500 °C and polished Si substrate is used for > 500 °C. The film deposited on glass substrate kept on V metal in oxygen gas without exciting plasma at 500 °C for 30 min is referred as VF0. In addition of that, vanadium metal strips are also oxidized at two different oxygen partial pressures other than its optimum value viz. 6.5×10^{-2} and 2.0×10^{-1} Torr to study effect of P_{O_2} on its oxidation. The surface morphologies of heated V metal strips and the films deposited on substrates are studied using scanning electron microscopy (SEM) ZEISS EVO series model EVO-50. Structural studies of all samples are carried out by Philips X-ray diffractometer with Cu- K_{α} radiation ($\lambda \sim 1.54$ Å) source by keeping glancing angle constant at 1° . The atomic vibrational studies in all samples are investigated using Micro-Raman spectroscopy of Renishaw inVia (excited with an Ar⁺ line at 514.5 nm) and Perkin Elmer (Spectrum BX) FTIR in the spectral range of 100-1000 cm^{-1} and 400-1800 cm^{-1} , respectively. The compositional analysis of all samples are performed using photoelectron spectroscopic studies of SPICS with anode Mg/Al 25 kV. The model number of the hemispherical analyzer is PHOIBOS HAS3500 150R6 [HW Type 30:14] MCD-9. Measurements are performed at 40 eV pass energy. The thickness of oxide layer formed on V-strips and the respective films deposited on substrates are determined by AMBIOS Technology (XP-2) Stylus profilometer.

RESULTS AND DISCUSSION

To study the structural properties, the X-ray diffractograms of oxide layers (V1-V4) and the respective film deposited on substrates (VF1-VF4) at different temperatures in oxygen plasma have been recorded and shown in Fig. 1 and 2. The XRD patterns of samples (V1-V4) confirm the formation of vanadium oxide with two different oxide phases. Most of the intense XRD peaks are correspond to stable orthorhombic (α) phase of vanadium pentoxide (JCPDS card No. 75-0457). However, single peak at 2θ value of 27.70° shows the presence of metastable monoclinic (β) VO_2 phase (JCPDS card No. 82-0661 with the space group $P21c$) on metal. It can easily be inferred that oxide layers formed on V metal strips have mixed oxide phases. The XRD pattern of sample V1 shows three less intense peaks, signifying that oxidation rate at 200 °C is very slow. As source temperature is increased to 300 °C (V2) the oxidation rate gets enhanced, which results the increase in peak intensities because most of the oxide content remains on the surface of V metal. Further decrease in peak intensities indicates the increase in oxide volatilization on increasing substrate temperature, as shown in Fig. 1 (V3 and V4). The thickness profile of oxide layers formed on V-metal strips (V2-V4) (as summarized in Table I) substantiate the different oxidation as well as volatilization rates from the surface of vanadium metal. The XRD patterns of films (VF1-VF4) deposited on glass/Si substrates placed on V metal are shown in Fig. 2. It is to be noted that in spite of different deposition temperature all deposited film have only orthorhombic phase of vanadium pentoxide, no other phase of vanadium oxide was found. The absence of monoclinic VO_2 phase in films can be attributed to higher melting point of β - VO_2 than α - V_2O_5 . Because of high melting point of VO_2 its volatilization rate would be lesser than V_2O_5 at the temperatures concerned. So, VO_2 required more energy as well as temperature to volatilize as compared to V_2O_5 . It has already observed in XRD analysis that the major phase on V metal is α - V_2O_5 and the minor phase is β - VO_2 , which also indicates that most of the volatilized oxide from V metal should be α - V_2O_5 . In case of sample VF1, the presence of two minor peaks corresponding to [200] and [010] crystal planes,

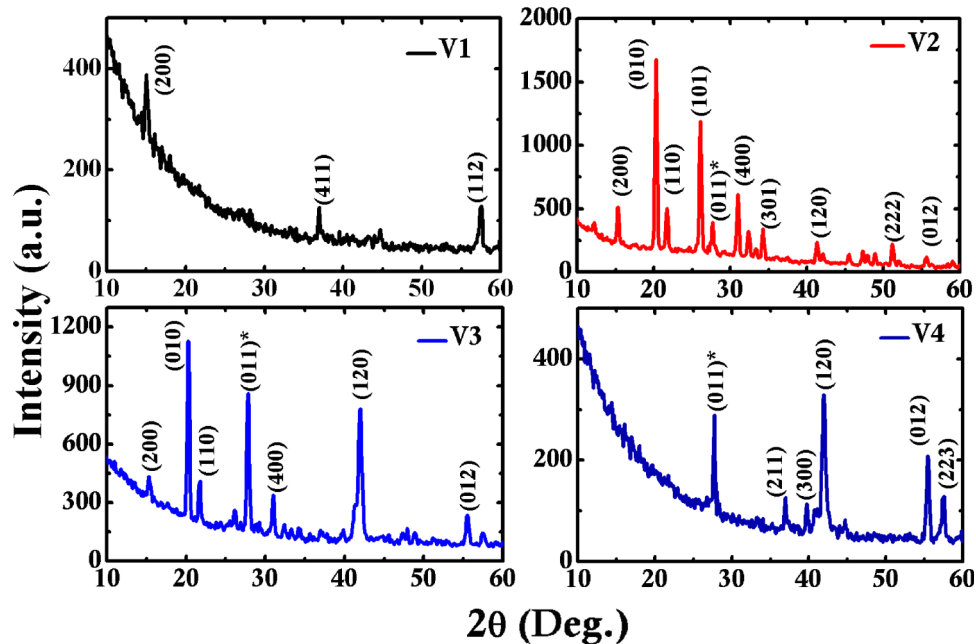


FIG. 1. X-ray diffractograms of vanadium metal strips oxidized at: 200 °C (V1), 300 °C (V2), 500 °C (V3), and 600 °C (V4).

indicates that oxide volatilization just getting starts from 200 °C. As the source temperature is further increased the intensity of XRD peaks get enhanced and become maximum for sample VF3.

The increment peaks intensities on increasing temperature can also be related to oxide film thickness deposited on substrates (see in Table I). The thickness of film depends on the amount of volatilized oxide vapor emerge from V metal surface reaching substrate placed on the top of it. Table I represents the thickness profile of oxide layers formed on V metal as well as the films deposited on glass/Si substrates at different temperatures. It shows that the layer thickness formed on vanadium is recorded maximum for sample V2 and is minimum for V1. In sample VF1 a film of thickness ~ 200 nm it deposited on glass. The film deposited in sample VF3 is thicker (1800 nm) than the rest of samples. Low film thickness in samples VF1 and VF2 are the result of lesser oxide volatilization. However, for sample VF4 the same is due to prominent volatilization of already deposited V_2O_5 film from Si substrate. It can be noted that the variation in oxide layers/films thicknesses is not in the same trend. Because their thicknesses are mainly depend on the rate of oxide volatilization. As temperature increases from 300 to 600 °C the volatilization rate gets remarkably increased and is responsible for this observed thickness variation. X-ray diffractogram of sample VF0 reveals that no oxide film is deposited on substrate in oxygen gas without plasma due to the absence of any XRD peak. This clearly points out that oxide vapor cannot reached on substrate without plasma. So, it is concluded from XRD results that the presence of plasma is most essential for the transportation of oxide vapor from metal surface to substrate placed over it.

It has been well established that the presence of oxygen plasma and source temperature are very important parameters to control the oxidation rate of V metal and its oxide volatilization. Besides that, oxygen partial pressure (P_{O_2}) is also very crucial for oxidation of metal, because it directly affects the number of oxygen ions in plasma. In order to investigate the effect of oxygen partial pressure vanadium metal strips are oxidized at three different oxygen partial pressures 6.5×10^{-2} , 2.0×10^{-1} , and 7.5×10^{-2} Torr. Figure 3 depicts the X-ray diffractograms, recorded from V metal strips oxidized at 6.5×10^{-2} and 2.0×10^{-1} Torr. However, the results of V metal oxidized at 7.5×10^{-2} Torr has been discussed in earlier sections. The X-ray diffractograms of both samples endorse nearly the same peak pattern and confirm the presence of similar mixed oxide phases (orthorhombic and monoclinic phases) in both samples. Most of the peaks are associated with orthorhombic phase (i.e. V_2O_5) and a single peaks as marked by (*) confirms the presence monoclinic VO_2 as obtained previously. At high partial pressure (2.0×10^{-1} Torr.) the intense XRD

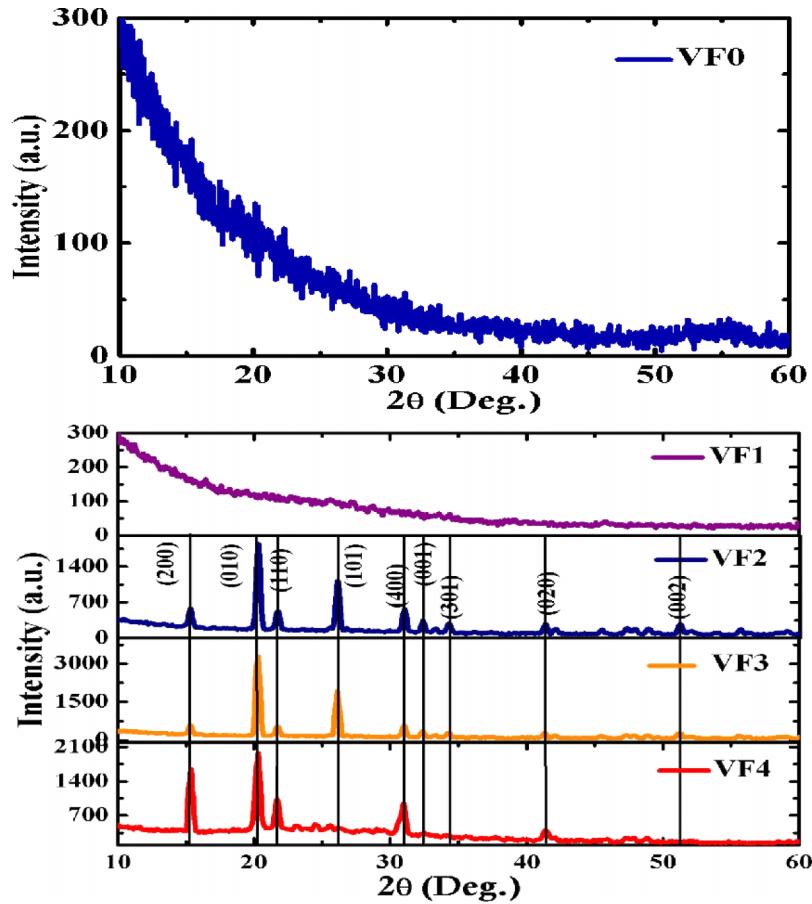


FIG. 2. X-ray diffractograms of vanadium oxide films deposited on glass/Si substrates: without oxygen plasma at 500 °C (VF0), 200 °C (VF1), 300 °C (VF2), 500 °C (VF3), and 600 °C (VF4).

peaks confirm the presence of thick oxide layer on V metal, whereas less intense XRD peaks are recorded, when it oxidized at low partial pressure, confirmed the presence of thin oxide layer on it. Since, at low pressure (6.5×10^{-2} Torr.) the mean free path of electrons get enhanced, which allows them to traverse a large distance without any collision. During that electrons will acquire more energy to ionize oxygen molecules, resulting in the generation of ions in plasma get enhanced and leads to high oxidation rate at low pressure. The reported density of oxygen ions in plasma at 10^{-2} Torr is nearly of the order of 10^{16} ions/cm³ and it decreases nearly one order lesser as pressure increases to 10^{-1} Torr in order.¹⁵ From XRD results, it is observed that low partial pressure not only increases oxidation rate but also enhances the oxide volatilization because it impose less ambient pressure on the oxide species formed on V metal surface. The presence of less intense XRD peaks from V metal oxidized at low P_{O_2} are mainly due to enhanced oxide volatilization, as shown in Fig. 3(a). In contrast, at high partial pressure the reduced mean free path of electrons diminished the

TABLE I. Comparison between oxide layer thicknesses formed on vanadium metal and films deposited on glass/silicon substrates for same T_{ss} .

Vanadium metal strips	Oxide layer thickness (nm)	Glass/silicon substrate	Film thickness (nm)
V1	300	VF1	200
V2	2200	VF2	800
V3	1200	VF3	1800
V4	400	VF4	600

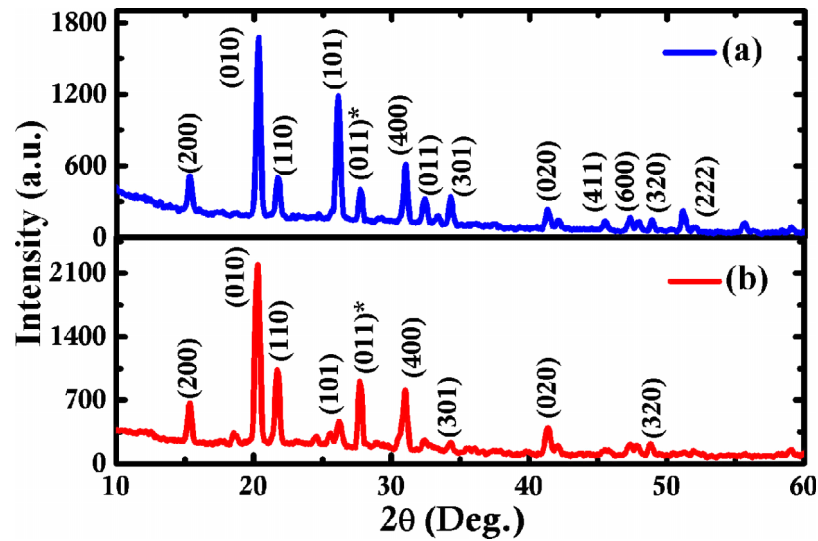


FIG. 3. X-ray diffractograms of oxide layers formed on vanadium at P_{O_2} (a) 6.5×10^{-2} Torr (b) 2.0×10^{-1} Torr (in oxygen plasma).

number of oxygen ions in plasma. But still sufficient number of oxygen ions are present in plasma to oxidize V surface. Simultaneously, the high P_{O_2} exerts excess pressure on the formed oxide molecular species and reduces the volatilization rate. Consequently, a relatively thicker oxide layer is formed on V surface and attributed to the intense XRD peaks, as shown in Fig. 3(b). Hence, from XRD results it is concluded that oxide volatilization from vanadium metal gets enhanced at low P_{O_2} or in other words it can be said that low P_{O_2} promotes oxide volatilization for a given temperature, and also favorable to deposit thick oxide film on substrate.

SURFACE MORPHOLOGICAL STUDIES

To study the surface morphology, SEM micrographs of samples (V1-V4) and the respective films (VF1-VF4) are recorded, as shown in Fig. 4 and 5, respectively. The results reveal that surface of vanadium metal foil oxidized at 200 °C (as confirmed by XRD) in oxygen plasma is rough. On observing, it is found that the color of V metal completely gets changed from bright silvery to brownish. However, no surface modification is recorded in SEM micrographs, which indicates that small oxidation, limited to the top most surface of metal is took place, as shown in Fig. 4(V1). At 300 °C, the SEM micrograph (V2, Fig. 4) shows the formation of pyramidal shaped islands like topography having non-uniform dimensions with well separated grains. The oxide layer formed in case of sample V2 has micro-cracks owing to temperature gradient between the interface of oxide layer and substrate, established after a given layer thickness or a certain time lapse during oxidation. The rate of oxide volatilization at 300 °C is recorded to be very small but it facilitates to generate micro-cracks on V surface. As T_{ss} increased at 500 °C, the dimensions of islands are reduced due to the enhanced oxide volatilization, as shown in Fig. 4(V3). The prolonged oxidation of metal is occurred continuously because the presence of fine micro-cracks or grains on oxide film, through cracks oxygen ions could penetrate deeper and reach at film and metal interface. The penetration/diffusion of oxygen ions can be explained by two different process either the diffusion of oxygen through lattice and second is the diffusion through grain boundaries formed on oxide layers. At low temperatures (≤ 500 °C) the diffusion of oxygen through grain boundaries is more probable.¹ Further increase in temperature again shows smooth vanadium surface, which is nearly same as obtained in case of lower temperatures. The SEM micrograph of sample VF0 (without plasma) in Fig. 5 depicts smooth substrate surface, which gives evidence that no oxide film is deposited over substrate in oxygen gas at 500 °C and the results remain consistent in absence of oxygen plasma even for the higher temperatures (> 500 °C) and completely support the XRD results. The SEM

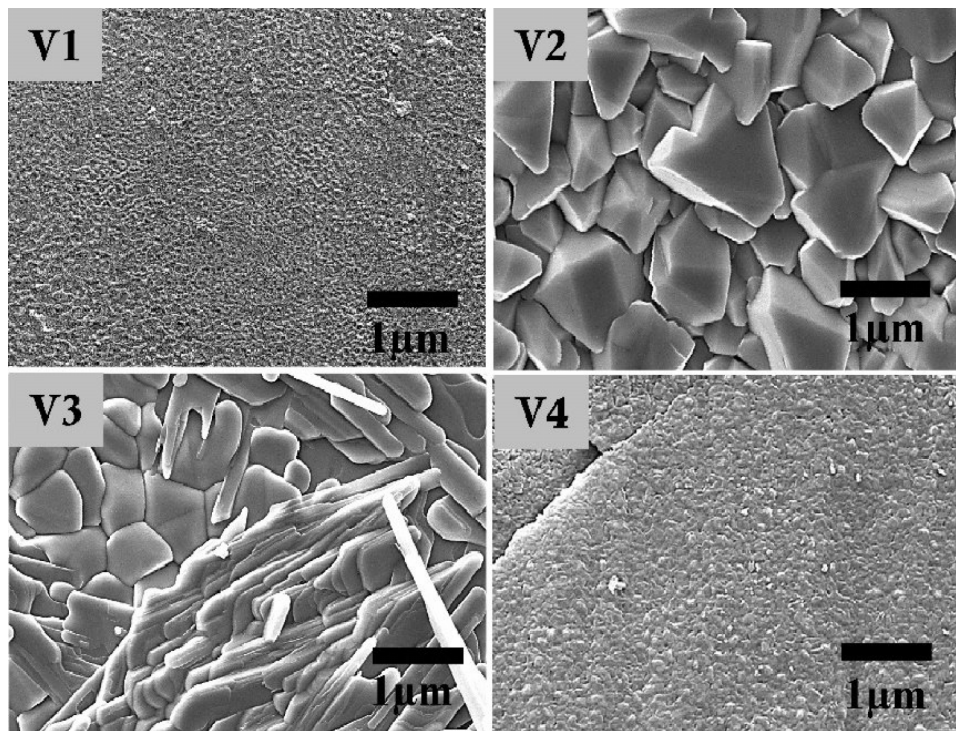


FIG. 4. SEM micrographs of vanadium metal strips oxidized at: 200 °C (V1), 300 °C (V2), 500 °C (V3), and 600 °C (V4).

image of sample VF1 shows some surface modification on glass substrate at 200 °C, which can be considered as a proof of oxide film deposition on glass substrate. The onset of oxide volatilization at very low temperature is because of the presence of reactive ionic oxygen species in plasma. It has been reported that more than 80% oxygen molecules/atoms in plasma occur in the form of ions and the rest (< 20%) are neutrals.^{15,16} Oxygen ions are likely to be considered more reactive than neutrals and also play a crucial role to stimulate the oxidation process. The measured film thickness on sample VF1 is found to be 200 nm. This result completely justifies XRD outcomes. In case of sample VF2, oxide film of thickness ~ 800 nm is deposited on substrate, which can be attributed to higher availability of oxide species at 300 °C, as shown in Fig. 5(VF2). On further increasing T_{ss} to 500 °C, oxide film becomes rougher with increased thickness (~ 1800 nm). This change in film thickness is due to the high temperature, which promotes oxide volatilization, resulting in more oxide vapor reaching onto glass substrate. Since, the substrate is kept on sublimation source, so the substrate temperature would be nearly same as source temperature. At 500 °C the impinging oxide molecules easily get the minimum energy configuration sites on substrate, once the preferential nucleation site is attained, the incoming molecules continuously incorporated in a specific direction, result in nanowire like morphology is grown uniformly on entire substrate, as shown in Fig. 5(VF3). Further on increasing temperature to 600 °C, (sample VF4) a nearly smooth oxide film is deposited due to prominent volatilization of oxide film deposited already on substrate at high temperature.

To study the effect of P_{O_2} on surface morphology, SEM micrographs of vanadium metal strips oxidized at 6.5×10^{-2} and 2.0×10^{-1} Torr and the simultaneously deposited films on glass substrate are recorded, as shown in Fig. 6. The SEM image of oxide layer formed at 6.5×10^{-2} Torr shows nearly rectangular shape particles. All particles are well-separated with fine grain boundaries or cracks, as shown in Fig. 6(a). Whereas, at 2.0×10^{-1} Torr, a continuous oxide layer is formed on vanadium surface with small number of cracks or grains, due to the slow rate of oxide volatilization from vanadium metal surface. So, most of the oxide layer content formed on vanadium metal remains on its surface at high partial pressure. The corresponding SEM images of the respective oxide films deposited on glass substrates are shown in Fig. 6(c)-6(d). Both micrographs depict nearly same nanobelts like microstructures but the number density of nanobelts at high partial pressure is found to be more to

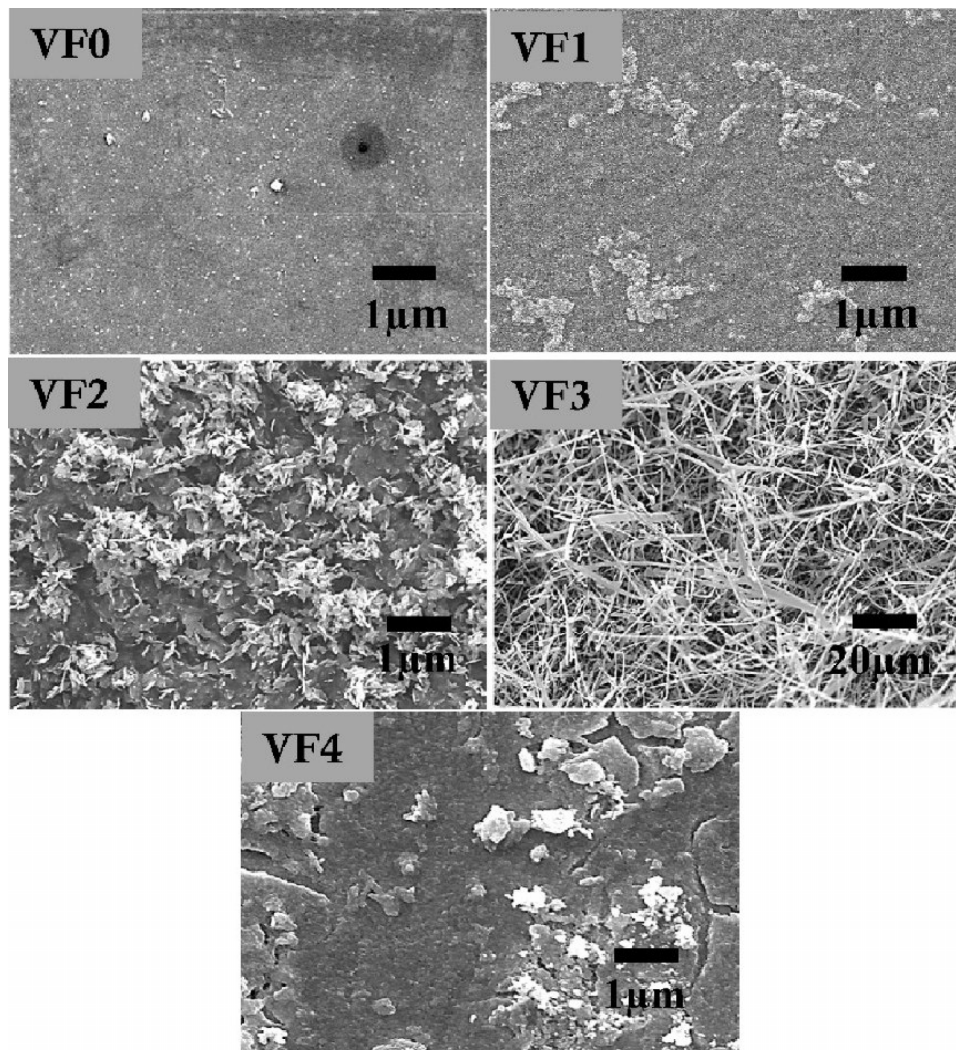


FIG. 5. SEM micrographs of vanadium pentoxide films deposited on glass/Si: (VF0) in O_2 -plasma 200 °C (VF1), 300 °C (VF2), 500 °C (VF3), and 600 °C (VF4).

that obtained at low partial pressure. It is again evidenced that at low P_{O_2} more oxide content reaches onto substrate from vanadium. Further to verify the effect of P_{O_2} on oxide volatilization, thickness measurements of oxide layers formed on vanadium and the films deposited on glass substrates are performed. At low partial pressure the measured oxide layer thickness on vanadium is found to be 1.5 μm and the corresponding film thickness deposited on glass substrate is 1.4 μm . Whereas, at high pressure a thicker oxide layer $\sim 2 \mu\text{m}$ is deposited on V metal and on glass substrate nearly the same film thickness is recorded as found at low pressure. This again experimentally confirms that the volatilization rate of oxide is increased at low P_{O_2} , whereas the thicker oxide layer is formed on vanadium metal at high pressure. It is worth noted that as P_{O_2} reduces below than 6.5×10^{-2} Torr, the intensity of oxygen plasma suddenly decreases and finally it gets disappeared. The same is also true at high partial pressure, as P_{O_2} increases till the order of Torr, the intensity of plasma again reduces abruptly and get vanished due to the lack of oxygen ions at such high pressure.

RAMAN AND FTIR ANALYSIS

In the further sections the oxidation behavior of only V metal strips at different temperatures are described. Raman spectra of samples (V1-V4) have been recorded in the spectral range of

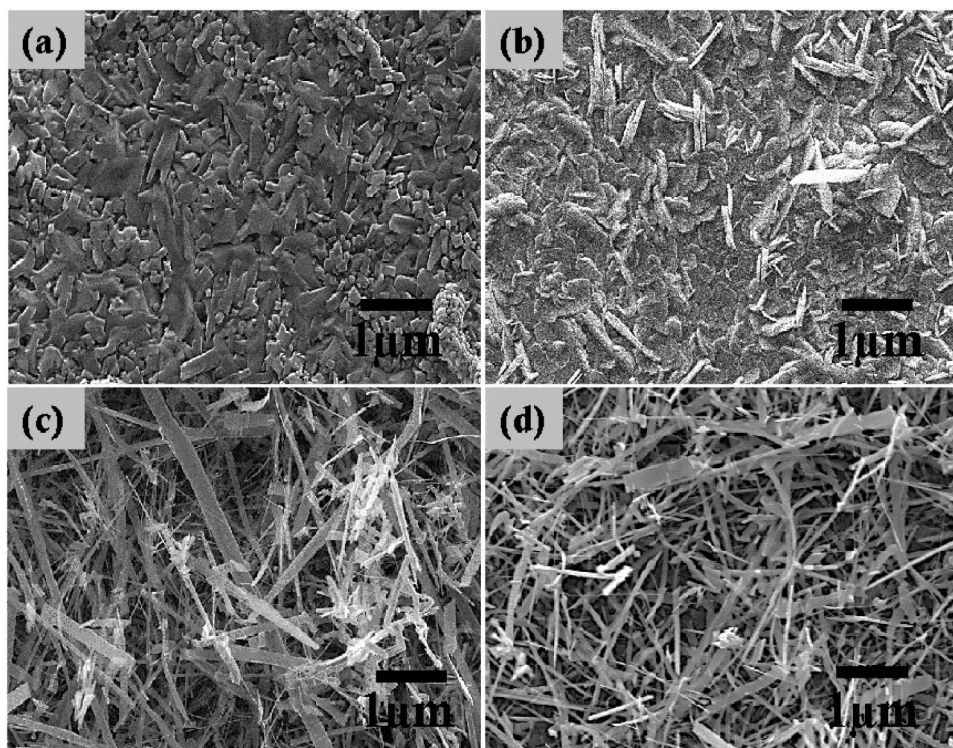


FIG. 6. SEM micrographs of vanadium metal foils oxidized at: (a) 6.5×10^{-2} Torr (b) 2.0×10^{-1} Torr, (c)-(d) the respective films deposited on glass at corresponding P_{O_2} (all in oxygen plasma).

100-1000 cm^{-1} to further confirm mixed oxide phases, as shown in Fig. 7. The Raman spectrum of sample V1 has only two less intense Raman peaks positioned at 139 and 995 cm^{-1} , which confirm the presence of only $\alpha\text{-V}_2\text{O}_5$ on V metal after oxidation.¹⁷ The less intense peaks in sample V1 insures that a very thin oxide layer is formed on V metal at 200 °C. At higher temperature ≥ 200 °C, strong absorption peaks are recorded at 139, 190, 285, 305, 389*, 590*, 695, 826*, and 995 cm^{-1} .¹⁸ The presence of these peaks reveals that the samples (V2-V4) have two different phases one is orthorhombic V_2O_5 and another is monoclinic VO_2 (marked by * in Fig. 7).¹⁷⁻¹⁹ The most intense Raman peaks in sample V2 are attributed to the maximum thickness of oxide film. The pattern and number of absorption peaks in sample V3 are exactly same as found in sample V2, but peak intensities in sample V3 are relatively smaller than sample V2 in accordance to the enhanced oxide volatilization. On further increasing temperature, the intensity of absorption peaks decreases owing to less oxide film thickness on V metal, as shown in Fig. 7(V4). As for sample V4 the same absorption peaks are recorded except for peaks at 305 and 590* cm^{-1} , which again supports the XRD investigations promoting the presence of mixed phases of vanadium oxide. The decrease in peak intensities with increase in temperature is attributed to the decrease in film thickness due to high rate of oxide volatilization at 600 °C.

FTIR analysis represents the study of vibrational bonds in the formed vanadium oxide layers on vanadium metal foils (V1-V4). Figure 8 shows IR spectra of V metals (V1-V4) in the spectral range from 400-1800 cm^{-1} . Prominent peaks positioned at 1625, 1460, 1008, 761, 640 cm^{-1} are found in all samples irrespective of temperature for oxidation. The absorption peaks positioned at 1008 and 761 cm^{-1} confirm the formation of $\alpha\text{-V}_2\text{O}_5$ during oxidation. The absorption peak placed at 1008 cm^{-1} shows the V = O stretching mode of vibration in all samples under investigation, confirms the presence of terminal double bonds, which is the characteristic of layered structure in $\alpha\text{-V}_2\text{O}_5$.²⁰ The intensity of peak at 1008 cm^{-1} considerably changes with increase in temperature, as shown in Fig. 8. Other absorption peak located at 761 cm^{-1} also characterize the presence of V_2O_5 on vanadium metal foils and relate to the asymmetric bending vibration of V-O-V bond.¹⁸ In sample

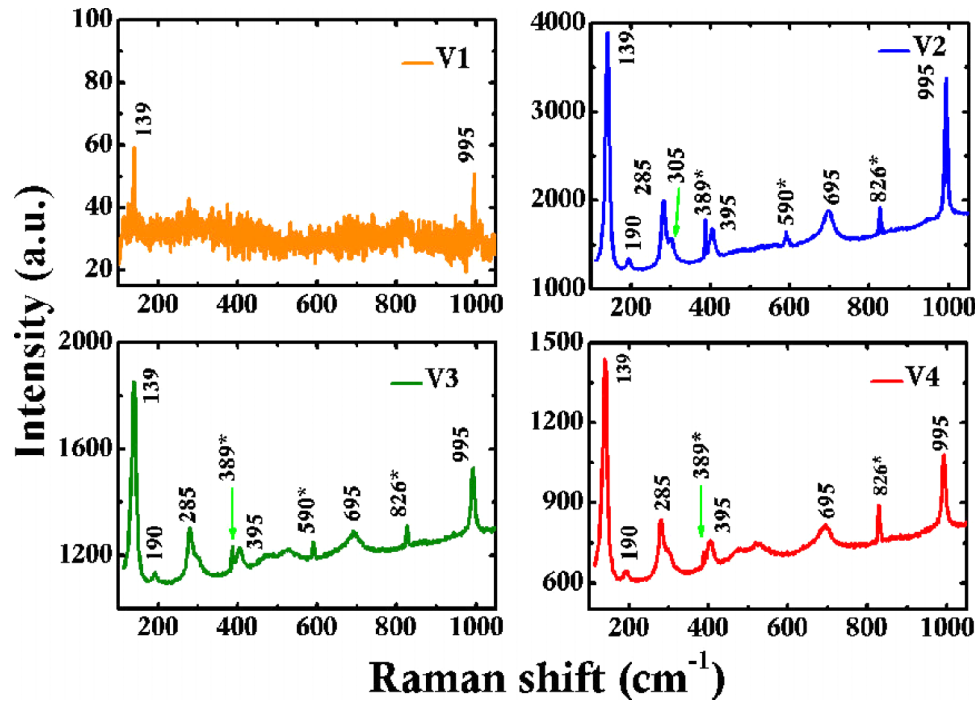


FIG. 7. Raman spectra of vanadium metal surfaces oxidized at: 200 °C (V1), 300 °C (V2), 500 °C (V3), and 600 °C (V4).

V2 the intense IR peaks indicate the presence of thick oxide layer on the surface of vanadium at 300 °C (see sample V2). As source temperature is increased the intensity of peaks gets decreased due to the reduction in film thickness. In addition, the peak observed at 640 cm^{-1} in samples V2-V4 (marked by * in Fig. 8), shows the presence of monoclinic phase of VO_2 on vanadium metal.²¹ The IR spectrum of sample V1 shows that all IR peaks are very less intense and the peak positioned particularly at 640 cm^{-1} corresponds to VO_2 phase is absent, which shows the presence of single orthorhombic phase with lesser oxidation. There are two additional peaks at 1625 and 1460 cm^{-1} in all samples, confirmed the presence of water molecules on the V surface corresponding to the bending mode of hydroxyl group (-OH).^{20,22} All the observed IR results are in consonance with the Raman and XRD analysis.

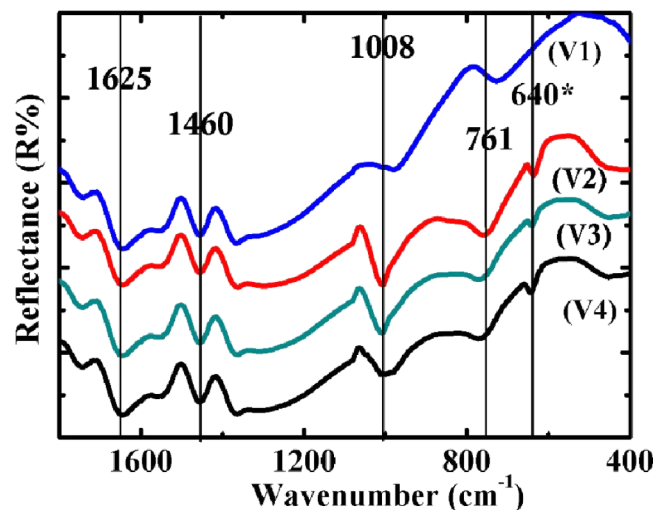


FIG. 8. FTIR spectra of V metal foils oxidized in oxygen plasma at: 200 °C (V1), 300 °C (V2), 500 °C (V3), and 600 °C (V4).

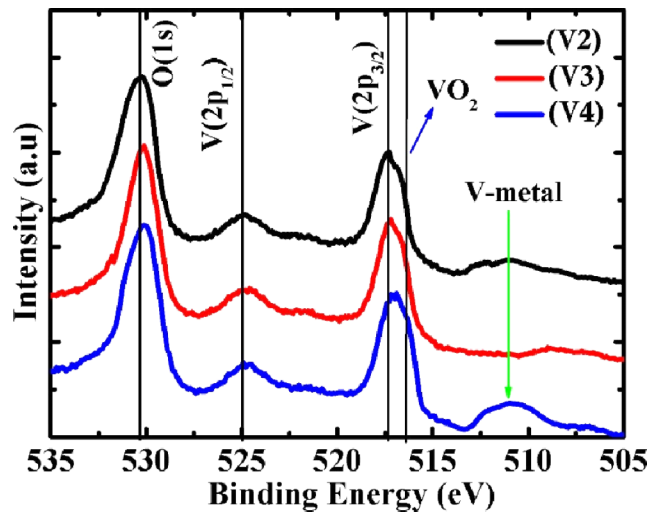


FIG. 9. XPS spectra of vanadium metal surfaces at: 300 °C (V2), 500 °C (V3), and 600 °C (V4).

COMPOSITIONAL ANALYSIS

Samples (V2-V4) have been characterized for the analysis of their compositions in terms of oxidation states present in samples under observation. For this study samples V2-V4 have been chosen for XPS analysis because of prominent oxidation of V metal is obtained at greater than 300 °C. The XPS spectra of oxide layers formed on V metal are recorded in the range of 505 to 535 eV, as shown in Fig. 9. The binding energy of all peaks are calibrated by at carbon peak recorded at 284.5 eV. The spectra have three peaks corresponding to O (1s), doublet relating to V (2p), and of pure vanadium metal, which confirm that all the samples are free from any other elemental impurity. The peaks correspond to O (1s) is positioned at 530.6 eV, which is shifted towards lower B.E. ~ 0.6 eV from the reported value.²³ The binding energies of the separated doublet peaks of vanadium in sample V2 are found to be at 524.6 eV and 517.3 eV corresponding to V(2p_{1/2}) and V(2p_{3/2}), respectively. The doublet peaks separation is found to be 7.3 eV, which shows a binding energy shift of ~ 0.3 eV to the reported value of pure V₂O₅.²⁴ This shift is attributed to the presence of reduced oxidation state (V⁴⁺) of vanadium in sample V2. As temperature increases, the doublet peaks are shifted towards the lower binding energy. It can also be seen that V(3p_{3/2}) peak is not completely symmetric but has a shoulder towards lower binding energy at the peak position 516.2 eV. This confirms the presence of monoclinic VO₂ phase on the surface of samples V3 and V4, as shown in Fig. 9. In addition, a broad peak located at 511.2 eV corresponds to pure vanadium metal is observed, particularly in case of sample V4, because of high oxide volatilization rate.²⁵ In other samples (i.e. V2 and V3), the peak of vanadium metal does not appear, because entire V metal is covered with the thick oxide film upto 500 °C. Thus, XPS analysis further concluded that two vanadium oxide phases are present on V metal when they oxidized at different temperatures.

CONCLUSIONS

The effect of oxygen plasma, source temperature, and oxygen partial pressure have been discussed on the oxidation (volatilization) of V (their oxide). The results indicate that oxygen plasma is the most effective oxidizing medium than others. The sublimation/volatilization temperature in O₂-plasma for V is recorded to be 200 °C, which is relatively smaller than the reported values so far. Oxygen plasma not only reducing $T_{s,s}$ but also helps in transporting of oxide species from metal to substrates. The structural and vibrational results endorse the existence of mixed oxide phases (major is orthorhombic V₂O₅ and minor is monoclinic VO₂) on the surface of V after oxidation, while the irrespective oxide films deposited on glass/Si substrates exhibit only orthorhombic phase. The compositional study of oxide layers formed on V metal surfaces, confirms their pureness and

also assured about the presence of mixed oxide phases on oxidized V surfaces. The SEM analysis of V metal surfaces shows the surface modifications at different T_{ss} . At low temperature ($\leq 400^\circ\text{C}$) most of the oxide film remains on V metal due to slow oxide volatilization, resulting in less thick oxide films are deposited on glass substrates. Thickness measurements reveal that the thickness of film on substrates increases up to 500°C , beyond that thickness starts to decrease again owing to volatilization of already deposited oxide film on substrate. The recorded optimum T_{ss} to deposit thick oxide film is 500°C particularly at 7.5×10^{-2} Torr. The role of oxygen partial pressure on the oxidation of vanadium has also been discussed in this paper.

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