Influence of O2 – plasma ambience and growth temperature on the oxidation of Mo-metal and volatilization of oxides

Rabindar K. Sharma and G. B. Reddy

Influence of O$_2$ – plasma ambience and growth temperature on the oxidation of Mo-metal and volatilization of oxides

Rabindar K. Sharma[a] and G. B. Reddy

Thin film laboratory, Department of Physics, Indian Institute of Technology Delhi, New Delhi (India) – 110016, India

In this communication, we investigated role of the oxygen plasma on the oxidation of Mo strip surface (source of Mo) and volatilization of formed oxide species. Molybdenum oxide thin films are deposited on Si substrate simultaneously by using the volatilized oxide species as vapor source. A special setup is designed to create stable discharge oxygen plasma. Both the Mo strip surface and oxide films deposited on Si substrates at different temperatures are characterized independently. The presence of well indexed and intense peaks corresponding to MoO$_3$ and Mo$_8$O$_{23}$ oxide phases in x-ray diffraction (XRD) patterns of metals strips, heated at different temperatures in oxygen plasma ambience has been considered as proof of oxidation of Mo-strip surface. The reduction in peaks intensity with increase in metal strip temperature indicates high rate of oxidation and oxide volatilization. It is observed that film formation on silicon substrate could not take place without oxygen plasma even at 500°C. The scanning electron microscopy (SEM) studies of Mo strips as well as the films deposited on Si substrates, at different temperatures are showing the modifications in surface morphology and agreed with the XRD results. Both Raman and FTIR observations of Mo strip are also in consonance with the XRD and SEM findings. The occurrence of oxidation of Mo metal and volatilization of oxide species at this low temperature 300°C is reported for the first time. © *2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4821284]

I. INTRODUCTION

Molybdenum based alloys have numerous useful applications such as resistive furnaces, spacecraft applications and fusion devices because of their high melting point, excellent mechanical strength at high temperatures and good thermal conductivity.[1] Many investigations have been carried out to understand oxidation of molybdenum metal and the volatilization of the formed oxides as function of metal temperature in the range of 300–1700°C. Analytical techniques like thermogravimetry and mass spectrometer have been used to monitor the rate of oxidation and volatilization.[2] it is widely recognized that in the temperature up to 600°C, oxidation of molybdenum leads to a compact oxide film, which prevent reaction behind a specific time lapse. At high temperatures (>795°C, the melting point of molybdenum) though oxidation occurs the net presence of oxide on the metal surface is negligible due increased volatilization.[1] The temperature at which volatilization starts during oxidation depend on pressure, specimen size, gas flow and reaction system.[3] Gulbransen and Wysong[4] found very low thickness but adherent oxide films formed when the metal was oxidized below 400°C. Simnad and Spilners[5] found that the oxidation kinetics followed the parabolic (linear) rate law at 500°C (above 500°C) and demonstrated that the vaporization of MoO$_3$ occurred at 650°C in 1 atm, but catastrophic oxidation took place at 725°C. Li et.al[3] have also presented the oxidation kinetics for Mo with oxygen consumption and the mass gain measurements, drawn the kinetics

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[a]Corresponding Author: rkrksharma6@gmail.com
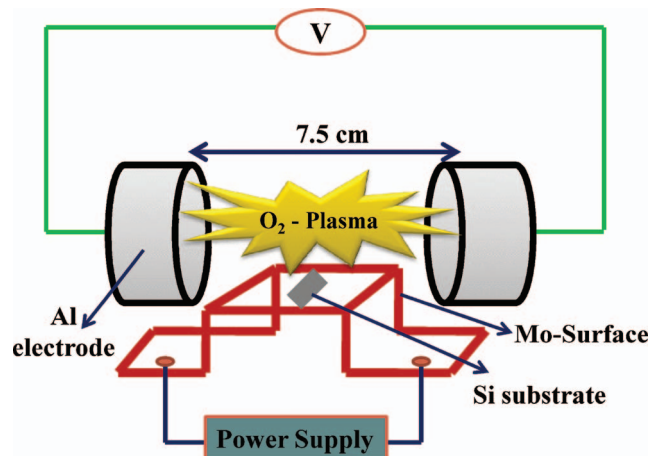
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FIG. 1. Schematic diagram of experimental setup with plasma arrangement.

curves and the observed results were same as reported earlier. All the results mentioned above show that oxidation and volatilization from molybdenum surface occurred at higher temperatures in simple oxygen ambient. Sarburi Tei et.al[6] have shown that oxygen plasma is sole cause of molybdenum oxide sublimation (volatilization) above 500°C (600°C). The oxidation mechanism of Mo metal in presence of oxygen plasma is not explored to that extent as compared to the simple oxygen ambience, because the oxidation reactions of molybdenum in oxygen plasma is complex and includes several types of oxidation processes. It is reported that the minimum temperature required for the oxidation of molybdenum metal in oxygen plasma ambient is 400°C.

In this communication, we have demonstrated the effect of oxygen plasma on the oxidation of Mo as well as oxide volatilization as function of temperature. Due to the presence of reactive oxygen plasma ambient the required minimum oxidation and volatilization temperature is reduced to 300°C. The aim of this work is to develop an optimized sublimation source for the synthesis of nanostructured thin films on large substrate area for device applications.

II. EXPERIMENTAL DETAILS

The specific electrode arrangement is used to investigate the role of oxygen plasma on the oxidation of Mo metal as well as the oxide volatilization as the function of Mo strip temperature and the schematic diagram is shown in Figure 1. A flat 80×30 mm^2 Mo metal strip is connected to a variable electrical power source and polished Si substrates of 5×5 mm^2 are mounted on the metal strip. The whole assembly is placed between the cup-shaped electrodes at such a position to expose both metal surface and Si substrates to uniform oxygen plasma. The optimum spacing between the electrodes is maintained 7.5 cm. The spacing is adjustable and could be varied from 4.5 to 10 cm. The chamber was first evacuated to create a base vacuum of 7.5×10^{-6} Torr and then 99% pure oxygen was leaked into the chamber through a needle valve to maintaining the vacuum level at 7.5×10^{-2} Torr. First, the plasma was created and stabilized by applying 2500V across electrodes. Metal strip temperature/growth temperature (referred as T_s) was increased gradually by suitably adjusting the voltage and it was measured with the thermocouple arrangement. Three identical experiments were carried keeping all parameters constant except the T_s value, which was kept constant at 300°C, 500°C, and 600°C, respectively. The heating duration was maintained constant as 30 min in all cases and then the samples allowed to cool naturally at room temperature. Both, the heated metal strip and the corresponding films deposited on silicon substrate were analyzed as separate samples. The metal strips oxidized keeping T_s at 300°C, 500°C, and 600°C are referred as S1, S2, and S3 respectively and the corresponding films deposited on Si substrates are denoted as F1, F2, and F3 in this paper. The silicon substrate kept at 500°C for 30 min in oxygen ambience without exciting plasma is concerned as F0. The surface microstructure of heated Mo surface and
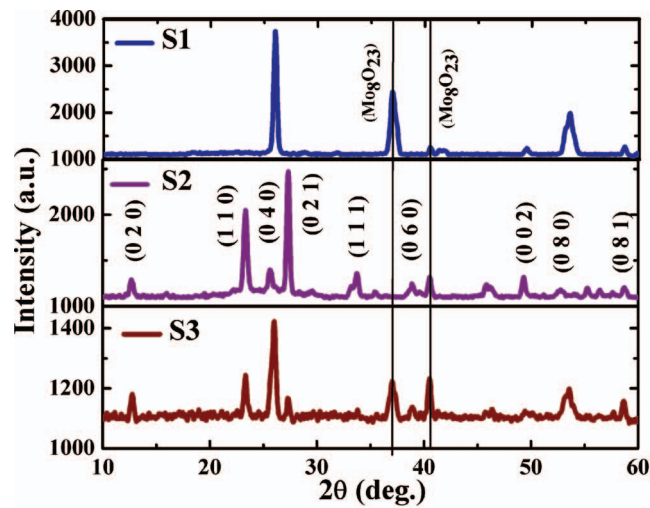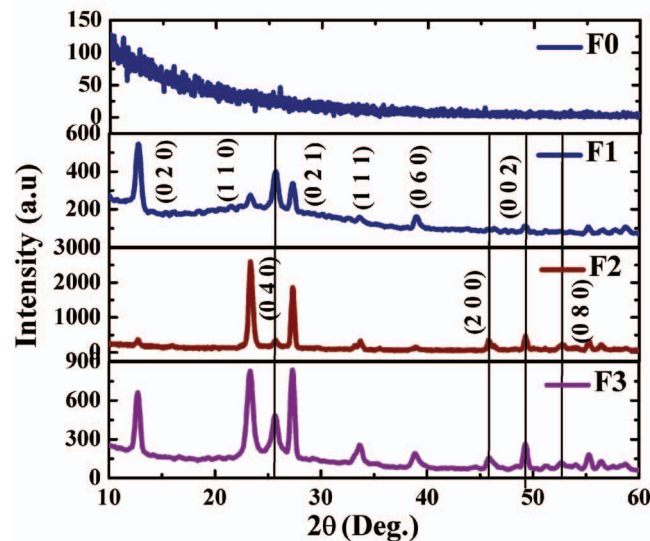
FIG. 2. (a). X-ray diffractrograms of Mo surfaces heated at different temperatures: 300°C (S1), 500°C (S2), and 600°C (S3). (b). X-ray diffractrogram of oxide films deposited on silicon substrate: without oxygen plasma (F0), 300°C (F1), 500°C (F2), and 600°C (F3).

films on Si was studied with Scanning Electron Microscope (ZEISS EVO Series, Model EVO-50). Structural analysis was carried out using Philips X-Ray diffractometer using Cu-K$_\alpha$ radiation $\lambda \sim 1.54$ Å keeping the glancing angle as constant at 1°. Vibrational study of molybdenum oxide was carried out by 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 from 200–1000 cm^{-1} and 400–2500 cm^{-1} respectively. The thickness of oxide films deposited on Mo strip surface and silicon substrate is determined by AMBIOS Technology (XP-2) Stylus profilometer and it varies from 600 to 2000 nm.

III. RESULTS AND DISCUSSION

The x-ray diffractrograms of Mo surface (S1-S3) and those of the corresponding films deposited on silicon substrate (F0-F3) are shown in Figures 2(a) and 2(b), respectively. The diffractrogram

TABLE I. Comparison of oxide films thickness formed on Mo strip surface and silicon substrates.

Mo strip surface	Oxide film thickness (nm)	Silicon substrate	Deposited film thickness (nm)
S1	2000	F1	600
S2	1000	F2	1500
S3	800	F3	900

of metal strip samples (S1, S2 and S3) confirms the oxidation of molybdenum metal. The study of the observed highly intense diffraction peaks in all S1, S2, and S3 samples indicates the presence of orthorhombic phase MoO_3. But the additional peaks of relatively lesser intensity at 37.04 and 40.50 corresponding to 2θ values confirm the formation of molybdenum sub oxides (Mo_8O_{23}) phases. The obtained average value of lattice parameters were a = 3.962 Å, b = 13.849 Å and c = 3.691 Å, which is in good agreement with those given in the JCPDS (Ref. Code: 00-005-508) (a = 3.962 Å, b = 13.858 Å and c = 3.697 Å) for orthorhombic phase (α-MoO_3) and for monoclinic phase the average lattice parameters are a = 13.38 Å, b = 8.10 Å, c = 16.88 Å also well matched according to (JCPDS Ref. code 00-080-0990) (a = 13.39 Å, b = 8.062 Å and c = 16.82 Å). Further investigations reveal that the intensity of all peaks gets reduced with increasing T_s which is attributed to the enhanced volatilization of MoO_3 with increasing T_s. When the T_s was 600ºC almost instantaneous volatilization of MoO_3 occurred leads to minimum amount of oxides on metal surface. The absence of peaks in x-ray diffractogram of film (F0) deposited on silicon in oxygen ambience without exciting plasma at 500ºC clearly endorse that the MoO_3 vapor did not reached on the Si substrate. Though the Mo-metal gets oxidized in oxygen ambience without plasma but in the absence of oxygen plasma the formed MoO_3 molecules transportation could not take place from Mo-surface to substrate. The existence of intense electric field in plasma is directing the vaporized MoO_3 molecules on the entire substrate. In case of films deposited on silicon substrates more intense diffraction peaks were observed in F2 compared to F1 and F3 films. The observed XRD pattern could be explain in terms of the film thickness, Table I show that the F2 film is thicker than F1 and F3. Low thickness in case of F1 film is due to lesser volatilization of MoO_3 and the same in case of F3 is reasoned due to re-volatilization of MoO_3 from Si substrate. Thus, we can conclude that 500ºC is the optimum temperature to grow the nanostructures on large area substrate because of high rate of volatilization as well as less re-volatilization from substrate surface. X-ray diffractograms shown in Fig. 2(b) reveal the formation of single phase MoO_3 in case of films deposited on Si substrates irrespective of the T_s values. The absence of monoclinic phase in deposited films, though observed in case of Mo strip, can be stated that MoO_3 get volatized more rapidly compared to the sub-oxide species like MoO_2, Mo_8O_{23} etc. The average crystallite size is calculated for S1, S2, and S3 using the following Debye-Scherre equation.[7]

$$D_{hkl} = \frac{0.9\lambda}{\beta(hkl).\cos(\theta_{hkl})}$$

Where λ is the x-ray wavelength ($\lambda_{Cu\,k\alpha}$ = 1.54 Å), θ_{hkl} is the Bragg diffraction angle and β (hkl) is the full width at half maximum in radians of the chosen peaks in XRD pattern. The estimated crystallite sizes in S1, S2, and S3 sample are 57.3 nm, 47.0 nm and 20.7 nm, respectively. The decrease in crystallite size with increase in T_s might be due to diminish in crystallinity and increase in the grain boundary discontinuities, which confirms the enhancement in volatilization with increase of T_s. But in case of films (F1-F3) the contradiction is observed, the crystallite size increases with increase in T_s. In sample F1 very less volatilization of oxide species from Mo- strip surface occurred in presence of oxygen plasma as a result the oxide film of very less thickness is observed on Si substrate. As the temperature increase (F2-F3) the MoO_3 vapor available for the films deposition become significant, consequently thicker films are formed than F1 with the increase in crystallite size. The calculated crystallite sizes by the same equation in case of films F1, F2, and F3 deposited on the Si substrates are 23.4, 42.8, and 54.6 nm respectively.
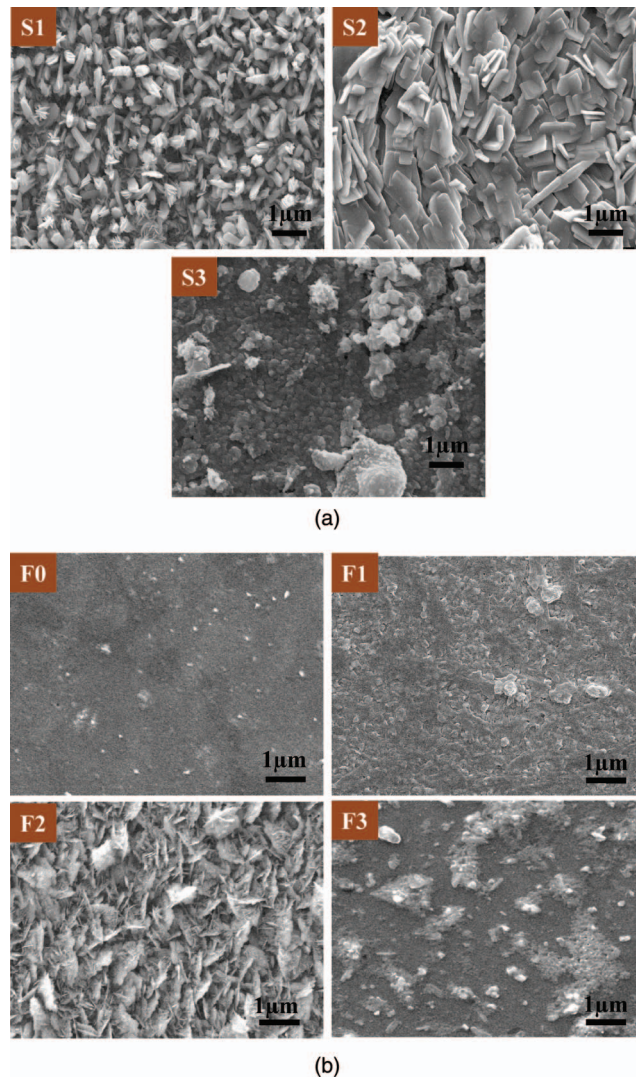
FIG. 3. (a). SEM micrograph of Mo surface kept at different temperature: 300ºC (S1), 500ºC (S2), and 600ºC (S3). (b). Surface micrograph of films deposited on silicon substrate: F0 (without plasma) 300ºC (F1), silicon substrate at 500ºC (F2), and silicon substrate at 600ºC (F3).

SEM micrographs in Figure 3(a) and 3(b) show the variety of the surface microstructures of Mo strip surface (S1-S3) and the film deposited on silicon substrate (F1 to F3) at the different temperatures in oxygen plasma respectively. The SEM microstructure of F0 is distinctly different from that of other films and it shows smooth surface (see F0 in Fig. 3(b)). The x-ray diffractogram of F0 also shows no diffraction peaks. From both the experimental results it is obvious that no oxide film deposition take place without oxygen plasma at 500ºC. On oxidization in plasma ambience the surface undergo the remarkable changes. In case of 300ºC the SEM micrograph (S1 in Fig. 3(a)) shows uniform distribution of particles with arbitrary shape having approximate dimension of 400 nm. When metal heated at 500ºC, formation of rectangular shaped plate like morphology parallel to strip surface are observed (S2 in Fig. 3(a)) and the enhancement in the surface roughness indicates the generation of microcrackes. Through these crack openings, oxygen could penetrate deeper reaching the metal-metal oxide interface, which lead to the prolonged oxidation process. The surface structure of S3 shows enhanced roughness compared to other cases. This is due to the instant volatilization of oxide species, leading to the formation of craters. The SEM microstructure of F0 is distinctly different from that of other films and it shows smooth surface (see F0 in Fig. 3(b)). The
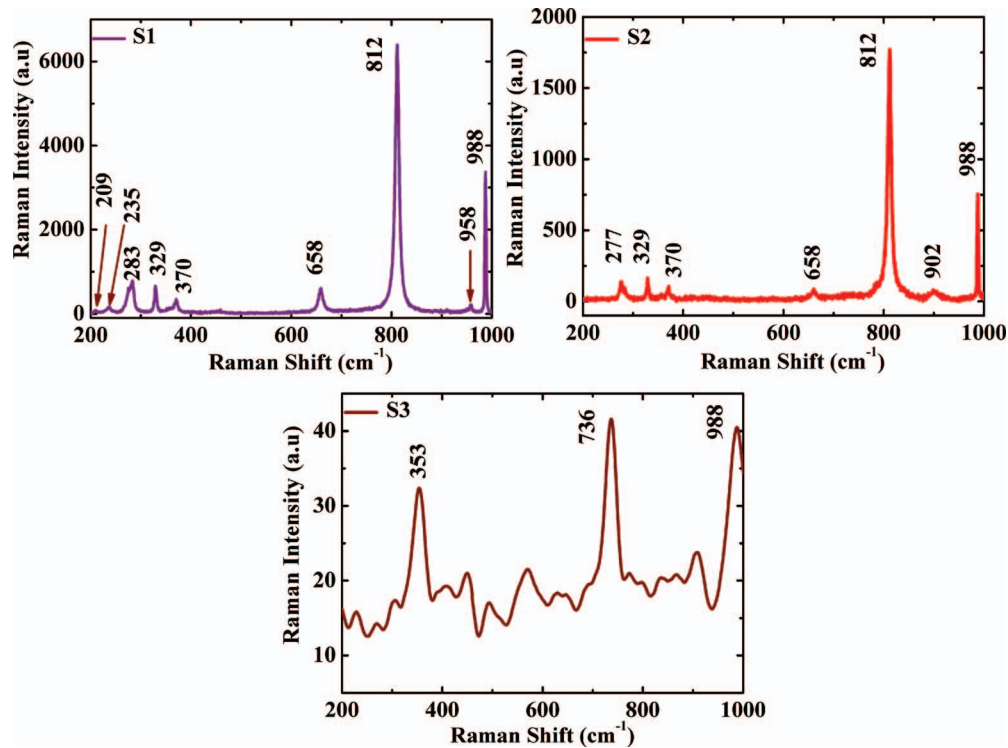
FIG. 4. Raman spectra of molybdenum surface: 300°C (S1), 500°C (S2), and 600°C (S3).

x-ray diffractogram of F0 also shows no diffraction peaks. From both the experimental results it is obvious that no oxide film deposition take place on Si substrate without oxygen plasma at 500°C. The observed SEM micrographs of deposited films on Si substrates show the variation in surface roughness. In case of F1 film of very low thickness is formed because of less incoming oxide vapor at 300°C (see F1 in Fig. 3(b)). At the initial stage the oxidation of Mo strip surface is relatively fast but after few minutes the process of oxidation becomes slow owing to the formation of oxide layer on the Mo strip at 300°C, this layer prevent the further oxidation of Mo. The film become very rough with increased thickness when the T_s value is 500°C (F2 in Fig. 3(b)), which is due to the high rate of oxide volatilization as a result prominent oxide content reaching on Si substrate. The substrate is itself on higher temperature, which facilitates to get the proper nucleation site to the incoming MoO_3 molecules. This leads to the formation of flakes like morphology at $T_s = 500$°C with increased thickness. F3 shows the discontinuous film because of the re-volatilization of oxide from film surface at high temperature 600°C (see F3 in Fig. 3(b)).

Further analysis of oxidation as well as oxide volatilization on Mo strip surface at different temperatures is carried out by using Raman and FTIR spectroscopy.

Figure 4 shows the micro Raman spectra of S1, S2, and S3 samples in the spectral range of 200–1000 cm^{-1}. The intensity of the absorption peaks reduced with increasing T_s, may be because of the difference in surface roughness and the grain boundary discontinuities in the grown structures of films formed on Mo-metal surface. This phenomenon is attributed to the reduced thickness of the oxide films with increased T_s. The most intense peaks observed at 209, 235, 283, 329, 370, 658, 812 and 988 cm^{-1} for S1 and at 283, 329, 658, 812 and 988 cm^{-1} for S2 in the measured spectra are corresponding to absorption associated with Mo=O and different modes of Mo-O-Mo bonds in MoO_3 (see in Table II). Therefore Raman spectra of Mo strip surface also confirm the formation of MoO_3.[8] The two additional low intensity peak observed in the Raman spectrum of S1 at 958 cm^{-1} and in the spectrum of S2 at 902 cm^{-1}, is indexed due to the presence of monoclinic Mo_8O_{23}.[9] Raman spectrum of the S3 shows a broad absorption peaks, supporting the XRD finding of less crystalline nature of films but at the lesser Mo strip temperature, the peaks are sharper, indicating

TABLE II. The observed Raman peaks of the samples (Mo strip surfaces) at different temperatures.

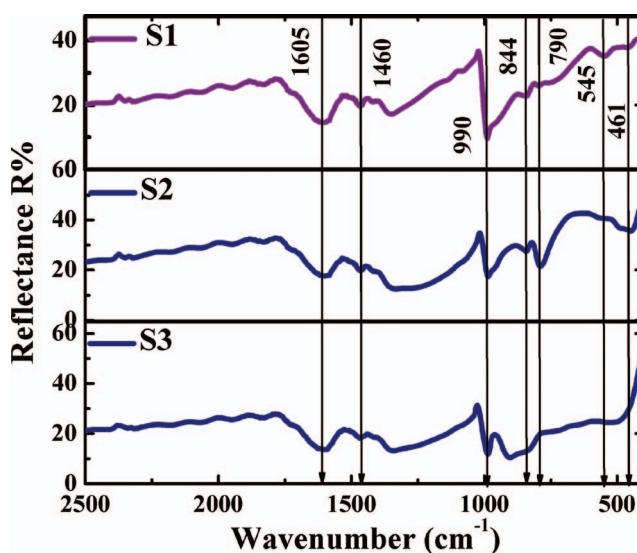| Mo strip surface (S1) Raman peaks position (cm^{-1})	Mo strip surface (S2) Raman peaks position (cm^{-1})	Mo strip surface (S3) Raman peaks position (cm^{-1})
209	283	353
235	329	736 (MoO_2)
283	658	988
329	812	
370	902 (Mo_8O_{23})	
658	988	
812		
988		
958 (Mo_8O_{23})		

FIG. 5. FTIR spectra of Mo-surface: 300ºC (S1), 500ºC (S2), and 600ºC (S3).

the high degree of crystallinity. The sample S3 also depicts the less intense Raman peak positioned at 736 cm^{-1} which is corresponding to MoO_2, formed at higher temperature. This observation is in agreement with the results reported in literature.[10]

FTIR studies of all samples were carried out in the spectral range from 400–2500 cm^{-1}. Measured IR reflectance spectra of S1, S2 and S3 are shown in Figure 5. The presence of absorption peaks at 990, 844, 790, 545 and at 461 cm^{-1} is evident the formation of α-MoO_3, and Mo_8O_{23}.[11, 12] According to reported results,[13] the resonance absorption peak of Mo=O the stretching modes of vibration lie at between 966 and 998 cm^{-1}. The absorption peak observed at 990 cm^{-1} in all samples confirms the presence of terminal double bonds, a basic characteristic of layered structure of MoO_3 and particularly in S1 its enhanced peak height points out the presence of thick oxide layer due to less volatilization at 300ºC. The intensity of the same peak reduced with increasing surface temperature due to high rate of volatilization in S2 and S3. Two resonance absorption peaks corresponding to asymmetric Mo–O bond are reported at 876 and 818 cm^{-1} in literature.[14] But the same absorption peaks are found at 844 cm^{-1} and 790 cm^{-1} in our samples which attributed to asymmetric Mo–O bond lengths on both sides of O in Mo–O–Mo bond. The absorption due to bending mode of vibration of Mo–O–Mo entity is reported to occur between 664 and 468 cm^{-1}. In our case the absorption peak due to this vibration is recorded around 550–450 cm^{-1} in S1 and S2 but absent in S3.[14] The presence of all these absorption peaks in samples and the variation in peaks height with Mo surface temperature confirmed the formation of MoO_3 as well as its volatilization and verifying the results

observed previous. There are two additional peaks at 1605 and 1460 cm^{-1} in all samples, confirm the presence of adsorbed water vapor on the Mo surface meanwhile the sample taking out of the chamber.[12] The observations inferred from XRD measurement, SEM analysis, Raman and IR studies are in the full agreement.

IV. CONCLUSION

It is experimentally concluded that the efficiency of oxidation of Mo surface as well as volatilization of the MoO_3 strongly depend on presence of oxygen plasma. With the help of oxygen plasma the Mo surface oxidized with oxide volatilization at much lower temperature 300°C compared to the earlier reported value of 400°C with oxygen plasma. The SEM and XRD results reveal that in absence of oxygen plasma no oxide film formed on the Si substrate even though the surface temperature kept at 500°C, while in oxygen plasma ambience Mo surface get oxidized at 300°C. As Mo strip temperature raised from 300°C to 600°C the volatilization rate of MoO_3 correspondingly enhanced, which directly indicate that oxygen plasma plays very crucial role not only in the oxidation of Mo metal but also in volatilization of formed oxide species. The generated energetic ionic species of oxygen in the plasma is considered to work as the reactive oxidizing regent for the high conversion rate of molybdenum metal to MoO_3 and other oxide species. Excellent correlation among the experimental results obtained from SEM, XRD, Raman spectroscopy and IR studies is established.

ACKNOWLEDGMENTS

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