Nitriding molybdenum: Effects of duration and fill gas pressure when using 100-Hz pulse DC discharge technique

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Molybdenum is nitrided by a 100-Hz pulsed DC glow discharge technique for various time durations and fill gas pressures to study the effects on the surface properties of molybdenum. X-ray diffractometry (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) are used for the structural and morphological analysis of the nitrided layers. Vickers' microhardness tester is utilized to investigate surface microhardness. Phase analysis shows the formation of more molybdenum nitride molecules for longer nitriding durations at fill gas pressures of 2 mbar and 3 mbar (1 bar $= 10^5$ Pa). A considerable increase in surface microhardness (approximately by a factor of 2) is observed for longer duration (10 h) and 2-mbar pressure. Longer duration (10 h) and 2-mbar fill gas pressure favors the formation of homogeneous, smooth, hard layers by the incorporation of more nitrogen.

Keywords: pulsed DC glow discharge, scanning electron microscopy, atomic force microscopy, microhardness

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1. Introduction

Molybdenum nitride thin films exhibit fascinating properties that make them useful as both catalysts[1–5] and diffusion barriers.[6] These films also exhibit excellent tribological, wear, and superconducting[7–9] properties. Several crystalline nitrides exist including γ-Mo_2N, β-Mo_2N, and δ-MoN. Molybdenum nitride gamma phase is a face-centered cubic phase with random distribution of nitrogen in octahedral sites, whereas β-Mo_2N is a tetragonal phase and is believed to have ordered nitrogen sites, and δ-MoN is crystalline with a slightly distorted NiAs-type structure and is reported to be a thermodynamically stable phase with high nitrogen content.[10]

Molybdenum nitrides, like other transition metal nitrides (VI–B Group), are difficult to synthesize because of low reactivity with nitrogen. This makes them less chemically stable, which is less in the order Cr to Mo to W.[11–14]

In this study our aim is to nitride molybdenum. We synthesize MoN_x thin layers by low temperature ($< 500\ ^\circ$C) 100-Hz pulsed DC discharge. To the best of our knowledge, the effects of varied nitriding duration and fill gas pressures on phase constitution, morphology, and mechanical properties after plasma nitriding of molybdenum metal using a 100-Hz pulsed DC discharge technique are discussed here for the first time. Pulsed DC discharge has many advantages compared to simple DC discharge: it can operate at much higher peak voltages and peak currents for the same average power. This results in high instantaneous sputtering, ionization, and excitation and hence exhibits better discharge efficiencies[15] with shorter nitriding durations. It is also a cost-effective way to improve surface properties including the hardness, wear, and corrosion resistance.[16,17]

The present paper concentrates on the phase formation, surface morphology, kinetics of layer growth, and surface microhardness after plasma nitriding.

2. Experimental details

The glow discharge is produced in a cylindrical stainless steel vacuum chamber of 45-cm diameter and height by applying a potential difference between two parallel plate electrodes with a diameter of 9 cm, a thickness of 1 cm and interelectrode spacing of 3.0 cm. To avoid additional discharge, the side and back of the electrodes are enclosed with ceramic casing. Specimens of molybdenum metal are placed at the lower electrode which acts as the cathode of the glow discharge. The chamber is evacuated prior to introducing nitrogen and argon gases down to 10^{-2} mbar by using a rotary vane pump. The pressure inside the chamber is monitored by a capsule type vacuum gauge (0 mbar–25 mbar). The plasma generating system is illustrated in Fig. 1. A 50-Hz AC power is transmitted to the step-up transformer through a Variac (0 V–250 V). The AC

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voltage is converted into pulsed DC voltage by using a bridge rectifier circuit. The input voltage and current of discharge are monitored using a voltmeter and an ammeter.

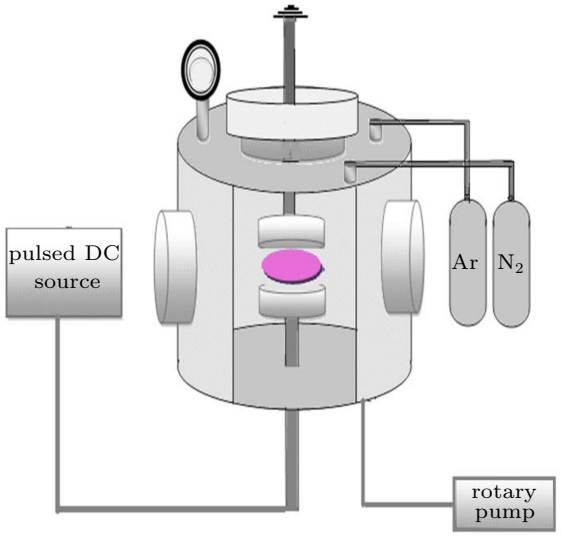


Fig. 1. Schematic diagram of plasma generating system.

Pure Mo metal (purity 99.99%) is used for this study as a substrate material. Polishing is carried out using an abrasive SiC paper from coarse to fine grade (320–1000) on a polishing machine, following standard polishing measures. Finally, the samples are cleaned in ultrasonic bath and then cleaned with acetone.[18]

X-ray diffraction (XRD) patterns are obtained by an X'Pert PRO MPD θ–2θ X-ray diffractometer operated at a voltage of 40 kV and current of 40 mA and using CuK_α ($\lambda = 1.5406$) Å radiation. The surface morphology of the nitrided specimens are investigated with a (HITACHI S-3400 N) scanning electron microscope. Atomic force microscopy (Veeco CP-II) is also employed for surface morphology and surface roughness. Microindentation measurements are performed to test the surface hardness of the nitride layer using a Vickers microhardness tester.

3. Results and discussion

3.1. Crystallographic structure

The effects of various nitriding durations (4, 5, 6, 7, 8, 9, and 10 hours) on phase constitution in the Mo–N system are evaluated using X-ray diffraction analysis. The XRD spectrum for unexposed sample in Fig. 2 confirms the bcc Mo structure. The XRD spectra presented in Fig. 3 clearly show the presence of molybdenum nitride phases in all the nitrided samples For 4-h nitriding duration a weak peak of thermodynamically stable hexagonal MoN phase corresponding to $\delta\,(200)$ plane reflection is observed. For 5 h, a new peak corresponding to

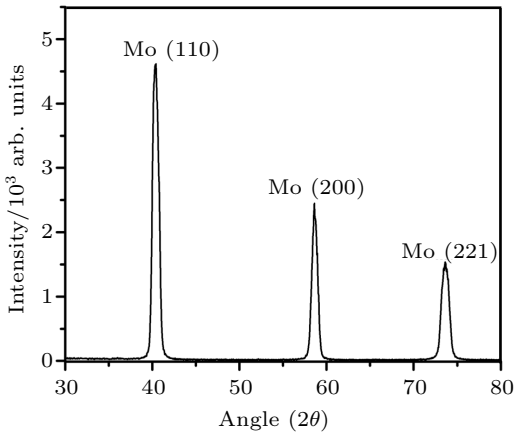


Fig. 2. X-ray diffraction pattern for unexposed specimen.

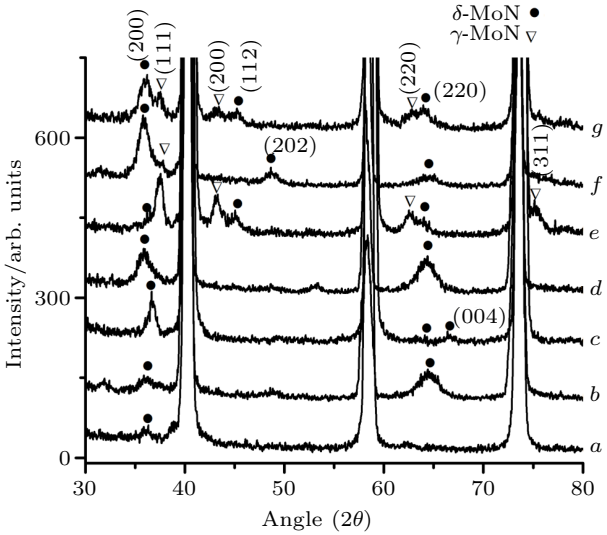


Fig. 3. X-ray diffraction patterns of samples nitrided for various nitriding durations. Curve *a*: 4 hours, curve *b*: 5 hours, curve *c*: 6 hours, curve *d*: 7 hours, curve *e*: 8 hours, curve *f*: 9 hours, and curve *g*: 10 hours.

(220) plane reflection of hexagonal MoN phase is evolved. For 6 h, the intensity of the $\delta\,(200)$ phase increases along with development of an MoN (004) peak. For 7 h the peak corresponding to the (004) plane disappears completely. This may be due to the growth of MoN (220) phase, which may hinder the growth of MoN (004) phase. For 8 h the development of $\gamma(111)$, $\gamma(200)$, $\delta\,(112)$, $\gamma(220)$, $\delta\,(220)$, and $\gamma(311)$ plane reflections for molybdenum nitrides takes place, which hinders the growth of $\delta\,(200)$ and $\delta\,(004)$ phases. Further increase in duration to 9 h results in the growth of (200) MoN phase significantly and $\gamma\,(111)$ Mo2N phase becomes very weak. Moreover, a new peak corresponding to the (202) plane reflection of δ-MoN evolves at the expense of previously present weak intensity peaks. For 10 h, the $\delta\,(200)$ phase grows significantly due to the greater supply of nitrogen. It is interesting to note that gamma molybdenum nitrides appear only for longer nitriding durations. It was reported by Kazmanli *et al.*[19] that a

mixed phase structure forms at higher temperatures (410 °C–510 °C) and hexagonal delta phase forms at low temperatures (300 °C–380 °C). Gamma MoN phase is a high temperature phase and is metastable at room temperature. This means that the substrate temperature has a critical effect on the phase formation and the effect increases with time, thereby enhancing the reaction kinetics. As the nitriding time increases, the nitrogen content and its density also increase, building a continuous MoN layer. The kinetic energy of the colliding ions and neutrals can increase the surface diffusion and chemical reaction by increasing the surface temperature locally, improving the surface layer,[19–21] forming more molybdenum nitride molecules.

The crystal structure of plasma-nitrided molybdenum samples for different pressures, i.e., 1, 2, 3, 4, and 5 mbar is investigated using XRD. All samples were nitrided in Ar + N_2 atmospheres for 4-hours processing time and 150-W power. XRD results (Fig. 4) for the treated specimens clearly indicate that the crystallographic structure of MoN_x films also depends on the process pressure in the plasma chamber. At relatively low pressure (1 mbar) the film is mainly bcc Mo structure with nitrogen incorporated into the lattice. A very low intensity peak corresponding to MoN (hexagonal) phase related to (200) reflections is present, which suggests low diffusion of nitrogen. At an intermediate pressure of 2 mbar, in addition to the previously observed peak, two new peaks, related to δ(103) and δ(220) reflections, appear. Moreover the intensity of the MoN (200) peak increases significantly, which shows crystal growth with nitrogen dosing. As the fill gas pressure increases to 3 mbar, new peaks of γ Mo_2N (200) and δ MoN (202) appear showing the presence of more molybdenum nitride. For 4 mbar, the XRD pattern shows only low-intensity broadened peaks corresponding to the (200) and (220) plane reflections of MoN. Further increase in pressure (5 mbar) shows a broader and weaker peak corresponding to the (220) plane reflection. The intensity and number of XRD peaks clearly increases with gas pressure up to 3 mbar and then decreases for higher fill gas pressures (4 mbar and 5 mbar). At intermediate fill gas pressures (2 mbar and 3 mbar), the electrons may have longer mean free paths and store higher energy before collisions with gas atoms/ions/molecules and may attain active ionizations by collision. It follows that many positive ions with relatively higher energies can strike the substrate and sputter more Mo atoms. This enhances the diffusion kinetics and reactivity of Mo to form more molybdenum nitrides and results in improved crystallinity. However, when the gas pressure is lower than 2 mbar, electrons have fewer opportunities to collide with gas atoms/ions and molecules. Moreover, molybdenum nitrides have low heat of formation, compared to group IV transition metal nitrides[22] and increasing the pressure to 2 mbar & 3 mbar supplies more nitrogen atoms,[19] resulting in the formation of more nitride, but at higher pressures (4 mbar & 5 mbar) the sputtered species suffers a number of collisions. As a result, the energy of ions impinging on the growing film is reduced, causing very low diffusion. Hence our XRD results reveal that in order to produce molybdenum nitride, it is necessary to have pressure greater than 1 mbar and less than 4 mbar inside the nitriding chamber.

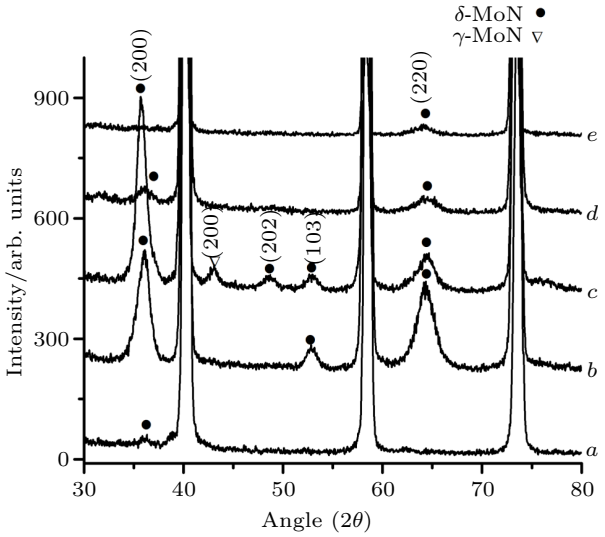


Fig. 4. X-ray diffraction patterns of samples nitrided at various pressures. Curve *a*: 1 mbar, curve *b*: 2 mbar, curve *c*: 3 mbar, curve *d*: 4 mbar, and curve *e*: 5 mbar.

Mo_2N has two different types of cubic phase: γ-Mo_2N and NaCl-type B1-cubic MoN. γ-Mo_2N is an interstitial transition metal nitride with a Hagg's structure. Hagg's structure is a face-centered cubic or hexagonal close-packed lattice of metal atoms, with nonmetal atoms located at the centers of octahedral interstitial sites of the metallic lattice.[23] Thus, they have the same X-ray patterns but can be distinguished by calculating their lattice parameters.[24,25] It is reported by Perry *et al.*[26] that B_1-cubic MoN phase has a larger lattice parameter ($a = 4.190$ Å–4.270 Å) than the γ-Mo_2N ($a = 4.163$ Å–4.230 Å). This difference in lattice constants makes it possible to distinguish the cubic phases. Our calculated lattice parameters are in the range of 4.153 Å–4.181 Å, which clearly indicates the growth of γ-Mo_2N ($a = 4.163$ Å–4.230 Å) as described by Perry. The phase identification is also in accordance with the inorganic crystal structure data base (ICSD).

3.2. Surface physical morphology

3.2.1. SEM analysis

Figure 5(a) shows the morphology of untreated Mo metal, having a highly polished smooth surface with a few scratches on it, which might be induced by polishing. SEM is used to study the morphology of the surface of the nitride layer as well, and the results are presented in Figs. 5(b)–5(e), where

it can be seen that varying the nitriding duration has significant influence upon the morphology of the nitrided molybdenum. The exposed samples reveal morphologies that are entirely different from one another. For 4 h (1 mbar), a non-uniform distribution of small particles of different sizes on the surface of the specimen is observed. Morphology shows a less dense microstructure, which may be due to the presence of low-nitrogen active species. The specimen nitrided for 6 h has reduced grain size and increased packing density, reducing its porosity. However one can clearly observe a few voids remaining in the nitrided layer. The specimen nitrided for 8 h shows an interesting change in surface morphology: an irregular structure can be observed on the subsurface of the previously formed layer. This irregular layer does not cover the previous layer, forming a rough surface, which is also evident from AFM analysis. Nitriding for 10 h results in the formation of a desired smooth, homogeneous and pore-free surface. This is due to the increased diffusion and redeposition of Mo after nitride formation on the Mo specimen. Nitriding for longer durations supplies more nitrogen and results in the formation of more molybdenum nitride and hence denser layers, resulting in enhanced packing density.[27] Hence it is concluded that the nitrogen supply to the modified surface layer of molybdenum is enhanced with increased nitriding time, due to which molybdenum nitride concentration at the surface is enhanced, resulting in the formation of more compact pore-free films for longer nitriding (10 h) duration.

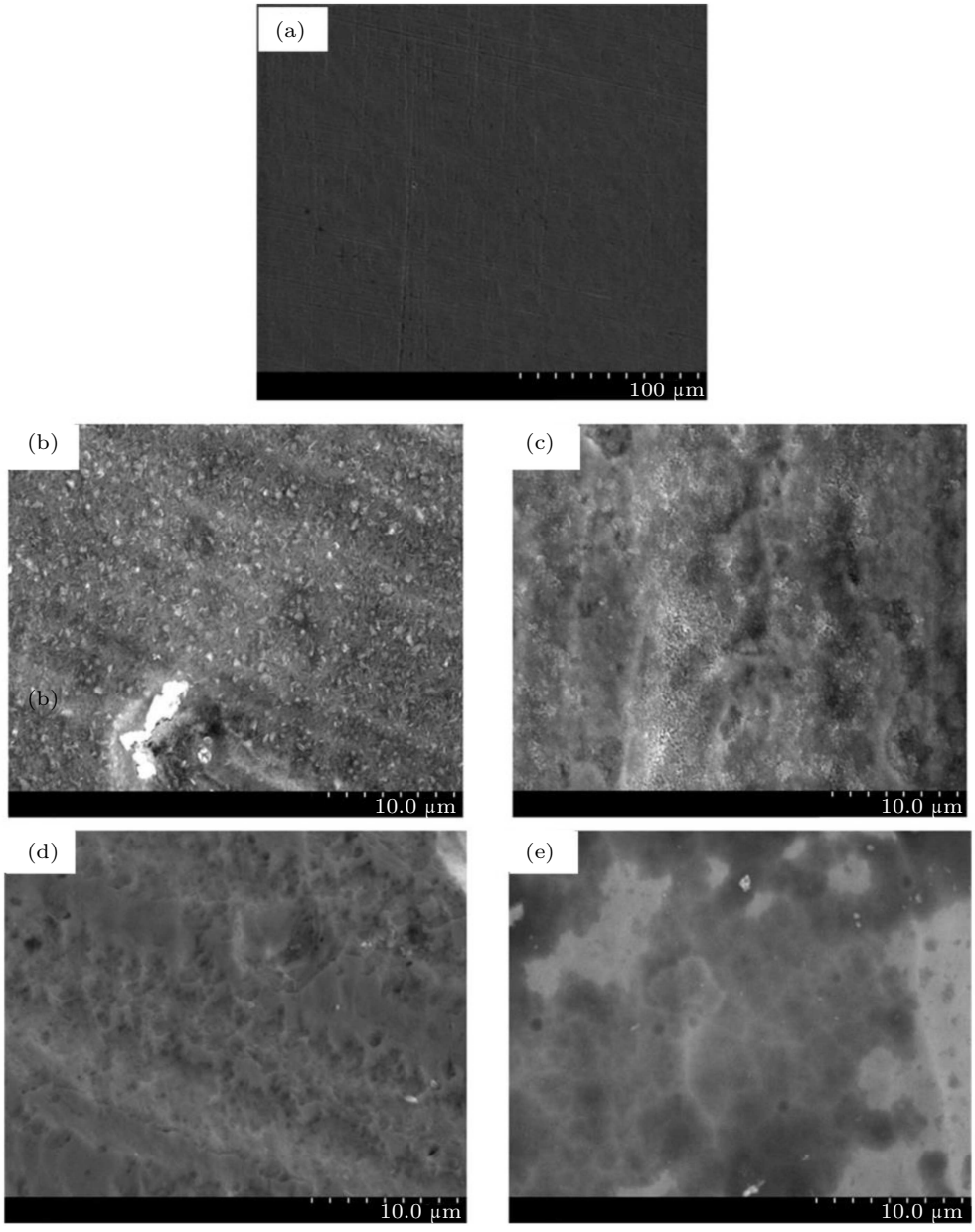


Fig. 5. SEM micrographs of nitrided samples at various nitriding durations: (a) untreated, (b) 4 hours, (c) 6 hours, (d) 8 hours, (e) 10 hours.

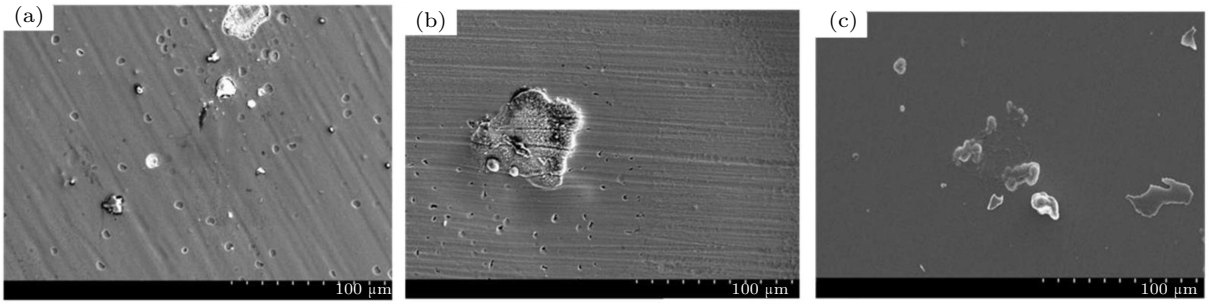


Fig. 6. SEM micrographs at higher magnification: (a) 2 mbar, (b) 3 mbar, and (c) 4 mbar.

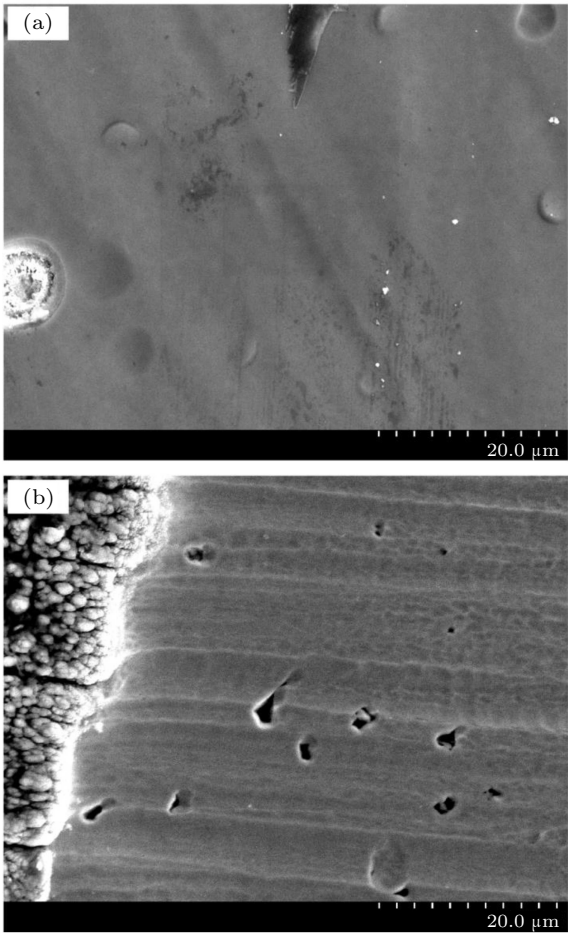


Fig. 7. SEM micrographs at higher magnification: (a) 2 mbar and (b) 3 mbar.

Figures 6(a)–6(c) show the surface morphology of the plasma-nitrided specimens for 2 mbar and 3 mbar fill gas pressures. For a pressure of 2 mbar, few small clusters of nitride can be observed on the subsurface of the previously formed layer. The SEM micrograph (Fig. 6(b) for the sample nitrided at 3 mbar pressure shows a columnar microstructure along with a significant number of voids in the subsurface. The columnar morphology develops due to the presence of voids in the film, which tends to shrink the films due to the high surface tension of the inner surface of the voids.[28] In summary, at relatively high pressure (3 mbar) multiple gas-phase collisions reduce the energy of the sputtered atoms and the angle at which the incident species impacts the substrate becomes more oblique. The resulting microstructure is characterized by a columnar structure with significant voids. The development of this void network structure and columns is evidence for the presence of tensile stresses in the film. Figure 6(c) shows the surface morphology of a sample treated under 4 mbar, which exhibits only a few small molybdenum nitride particles owing to very low nitridation. Figures 7(a) and 7(b) show a clearer view of the morphology of the specimens' nitride content at 2-mbar and 3-mbar pressures.

3.2.2. AFM analysis

Figure 8 presents three-dimensional (3D) AFM micrographs of the plasma-nitrided surfaces for various time durations, with a scan area of 4 μm × 4 μm. There is clear evidence of granular morphology in the AFM images. The sample nitrided for 8 h exhibits totally different morphology: a wavy shape can be observed, and the surface has become quite rough due to the formation of an irregular structure. This irregular structure can also be observed in Fig. 5(d). For 10-h duration, the surface is covered with smooth molybdenum nitride layers.

Using the 3D profiler, we also measured the root-mean-square (rms) roughness of all specimens. The surface roughness of the 4 h-nitrided specimen is found to be about 65 nm. But it is reduced to 36 nm by the 6th hour of exposure. Moreover, the surface roughness increases to about 48 nm for 8 h of treatment. As can be observed from Figs. 5(d) and Fig. 8(c), there is no homogeneous structure on the plasma-nitrided Mo surfaces after 8 hours of nitriding, and the surface becomes rougher. The plasma-nitrided specimen of longer nitriding (10 hours) shows a smooth surface with complete coverage of the substrate surface. The longer duration improves the surface finish by reducing the peak-to-valley height.[29] The smooth surface is also partly attributable to increased deposition rate, along with diffusion and redeposition of Mo atoms/ions after nitride formation. The smoother films are also harder. Moreover, longer nitriding duration may enhance the surface temperature locally, which in turn enhances the mobility of Mo atoms on the growing film surface, which also results in smoother film.[30]

Figure 9 presents 3D AFM micrographs of the plasma-nitrided surfaces for 2-mbar and 3-mbar pressures with a scan area of 4 μm × 4μm. The rms roughness for 1, 2, 3, and 4 mbar

fill gas pressures are found to be about 65, 28, 34, and 32 nm respectively. Maximum surface roughness is observed for a pressure of 1 mbar. At relatively low gas pressure (1 mbar), the sputtering rate is low, which forms low density film[31] with a high, rough surface. At 3 mbar and 4 mbar, rms roughness is higher than that in the 2 mbar case. At 3 mbar, collisions are more frequent, which reduces the energy of the ions. This in turn produces a slightly rougher surface.

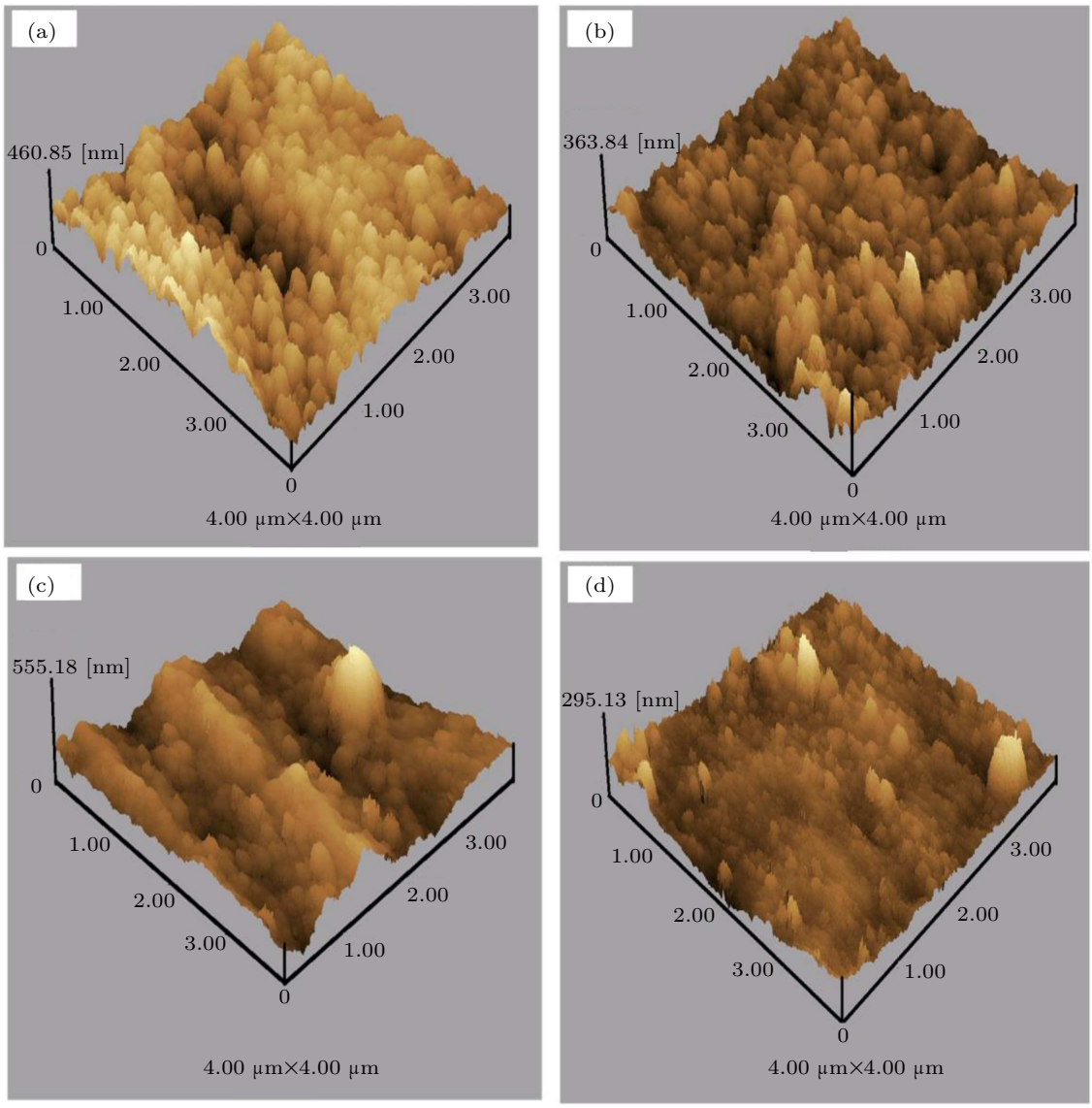


Fig. 8. (color online) The AFM micrographs of nitrided samples at various nitriding durations: (a) 4 hours, (b) 6 hours, (c) 8 hours, and (d) 10 hours.

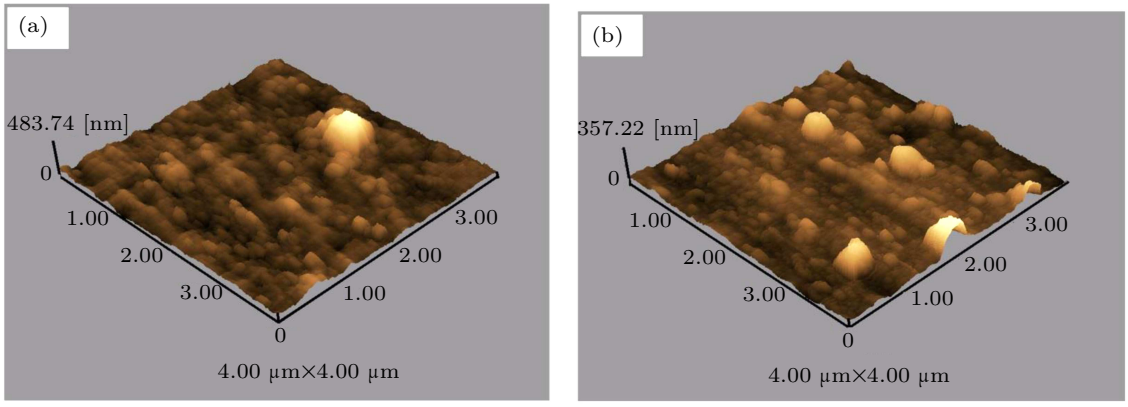


Fig. 9. (color online) The AFM micrographs of nitrided samples at (a) 2 mbar and (b) 3 mbar.

3.3. Hardness of nitrided specimens

Surface microhardness as a function of nitriding duration is plotted in Fig. 10, measured for a dwell time of 15 seconds by means of a Vickers microhardness tester. All the nitrided samples are hardened by the formation of molybdenum nitride layers. The improvement in hardness after nitriding is caused by the increased nitrogen concentration and the development of new phases on the surface of the exposed material. Minimum surface hardness (253 HV) is achieved with the shortest duration (4 hours) for a constant pressure of 1 mbar. This suggests that a thin hard layer is formed without significant diffusion of nitrogen at shorter durations; whereas maximum surface hardness is about 378 HV for the longest nitriding duration (10 hours), which is about twice the hardness of the unexposed specimen. Moreover, microhardness decreases for 7-h and 8-h nitriding, compared to 6 hours. This unusual behavior may be related to the increased surface roughness at that stage of treatment. A more detailed study might well show that smoother surfaces with increased packing density may be harder than rough surfaces.[32]

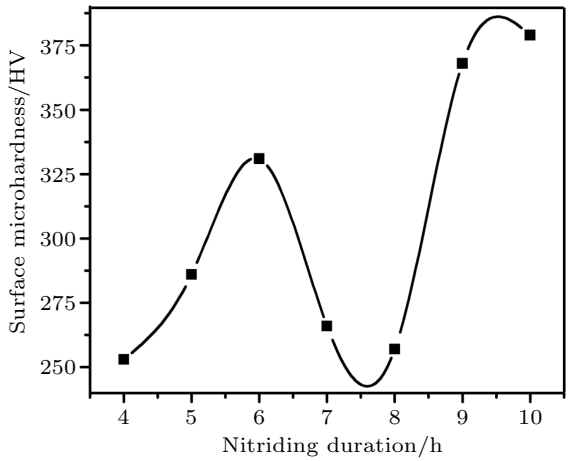


Fig. 10. Variation of surface microhardness as a function of duration.

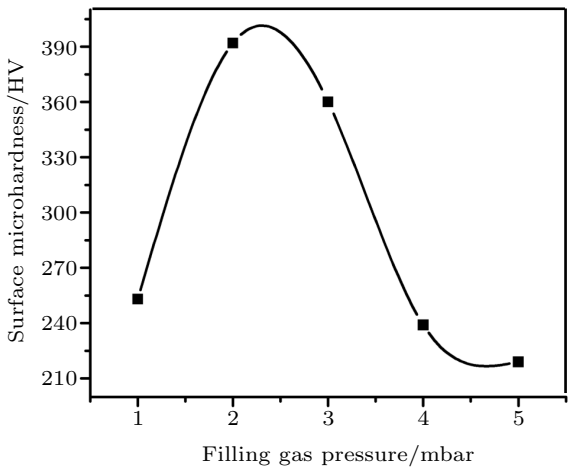


Fig. 11. Variation of surface microhardness as a function of fill gas pressure.

Figure 11 plots hardness variation for different treatment pressures. The graph indicates greater hardness at all pressures compared to the untreated specimen. The increase in microhardness after nitriding treatment is due to the diffusion of nitrogen content in the molybdenum surface. Hardness increases up to the treatment pressure of 2 mbar attaining a maximum value of 392 HV. This shows that 2 mbar is among the optimal pressures for achieving maximum hardness. The decreased hardness at 3 mbar compared to 2 mbar is due to tensile stress developing because of the presence of voids. Higher pressures (4 mbar, 5 mbar) provide a poor nitrogen environment that may result in less active nitrogen content and thin nitrided layers reducing the surface hardness.

4. Conclusions

Nitriding time and fill gas pressures significantly change the structural, morphological, and mechanical properties of nitrided molybdenum metal. XRD analysis confirms that the film is mixed phase for longer nitriding durations (8 hours and 10 hours) and higher pressures (3 mbar). Still higher pressures (4 mbar, 5 mbar) produce no significant changes, and hence are not suitable for the formation of molybdenum nitrides. The surface morphology, roughness, and hardness analysis found homogeneous smooth and hard nitrided layers are achieved by more nitrogen for longer nitriding duration (10 hours) at a pressure of 2 mbar, using 100-Hz pulsed DC discharge.

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