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Annealing temperature effect on the mechanical and tribological properties of molybdenum nitride thin films

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Abstract

Mo thin films with 100-nm thickness were deposited on silicon substrates using DC magnetron sputtering method. Mo thin films were subsequently annealed at different temperatures (400°C to 900°C) with flow of nitrogen. The crystallographic structure of the samples was obtained using X-ray diffraction method. Atomic force microscopy and scanning electron microscopy were used for surface morphology investigation. Nano-indentation and scratch tests were performed to obtain the surface hardness and friction coefficient of the samples, respectively. Results show that the γ-$Mo_2N(111)$ phase of molybdenum nitride with face-centered cubic structure and higher hardness, elastic modulus, and lower coefficient of friction and scratch volume is formed when the sample is annealed at 650°C, while the Mo_2N phase with tetragonal structure and lower hardness, elastic modulus, and higher scratch volume and friction coefficient is formed at higher temperatures of 775°C and 900°C. It is found that increasing the annealing temperature causes an increase of the grain size and film surface roughness. From the mechanical results, it may be deduced that 650°C is a critical temperature for variation of mechanical and tribological properties.

Keywords: Molybdenum nitride, Nanostructure, Hardness, Friction coefficient, Scratch volume

Background

Studies of the transition metal nitrides, especially in the form of thin films, have both scientific and technological significance. Molybdenum nitride is one of these materials that exhibit interesting properties. Molybdenum nitride thin films show high electrical conductivity and chemical stability and are promising candidates for use as Cu diffusion barrier and electrodes in microelectronics [1-4]. Furthermore, molybdenum nitrides have excellent hardness, catalytic ability, and superconductivity effects [5-9]. Hence, many researchers have produced molybdenum nitride thin films using different methods such as DC and RF magnetron sputtering, chemical vapor deposition, pulsed laser deposition, ion-assisted deposition, reactive magnetron sputtering, and heavy nitrogen ion-implantation and reported their characterization results [7-18].

In this work, we have prepared molybdenum nitride thin films using different techniques by post-annealing Mo/Si thin films with 100-nm thickness at different annealing temperatures (400°C–900°C) in the nitrogen constant flow and have investigated the influence of these variables on the nanostructure and mechanical and tribological properties of these films.

Experimental details

Film preparation

Molybdenum (99.998% purity) thin films of 100-nm thicknesses were deposited by means of a DC magnetron sputtering system using a circular sputtering target of 76-mm diameter and 1-mm thickness. The target-to-substrate distance was 10 cm. A DC power supply of 750 V and 125 mA was used as power source for sputtering. The film thickness and deposition rate were checked *in situ* by a quartz crystal monitor (6 MHz gold, Inficon Company, East Syracuse, NY, USA) positioned close to the substrate

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holder during the sputtering process. The molybdenum thin films were deposited at a deposition rate of 3 Å/s. The base pressure was 1×10^{-5} mbar, achieved with a diffusion pump coupled with a rotary pump that was changed to 3.2×10^{-2} mbar after the presence of Argon. The purity of argon gas in this work was 99.998% and controlled by a mass flow controller. The substrates for the deposition were 20×20 mm^2 of single crystal Si (400) and were ultrasonically cleaned in heated acetone then etalon. The substrates were not subjected to any heating treatment before and during the sputtering process. Post-annealing of Mo/Si films were performed at five different temperatures (400°C, 525°C, 650°C, 775°C, and 900°C) with a 200-sccm nitrogen flow. A 5°C/min temperature rise was used to reach the required annealing temperature, and the samples were kept at their annealing temperature for 120 min, then gradually cooled down to room temperature with flowing nitrogen gas.

Film characterization

The nanostructure and crystallographic orientation of the samples were obtained using a Philips XRD X'pert MPD diffractometer (Philips Analytical, Almelo, The Netherlands) (Cu Kα radiation) with a step size of 0.02° and a count time of 1 s per step. A Hysitron TriboScope® nanomechanical test instrument with 2D transducer (Hysitron Inc., Eden Prairie, MN, USA), complete software, and Berkovich diamond indenter were used for mechanical test and surface imaging. The AFM part was a NanoScope E from Digital Instruments (Santa Barbara, CA, USA). Over four indentation tests were performed on all samples, and the average of the obtained data is presented. The scan size and scan rate were 5×5 μm^2 and 1.001 Hz, respectively. Surface images, roughness parameters, nano hardness, elastic modulus, scratch volume, and friction coefficient are obtained from this analysis. A scanning electron microscope (Leo-440i, Leo Electron Microscopy Ltd., Cambridge, UK) was also used for the surface morphology study.

Results and discussion

Crystallographic structure

Figure 1 depicts the X-ray diffraction (XRD) pattern of Mo/Si as-deposited and annealed thin films with 100-nm thickness prepared in this work. In the XRD pattern of the as-deposited molybdenum thin film, two peaks (except the substrate peak) can be observed at 40.51° and 87.57° that can be related to Mo(110) and Mo(220) crystallographic orientations, respectively (with reference to JCPDS card no. 42–1120, 2θ = 40.516° and 2θ = 87.598°, system: cubic, and space group: 229). In the X-ray diffraction pattern of the annealed sample at a temperature of 400°C with flow of nitrogen, the intensity of the Mo peaks decreased, and a new peak appeared at 37.39° that can be attributed to the γ-Mo_2N(111) crystallographic orientation (with reference to JCPDS card no. 25–1366, 2θ =37.376°, system: cubic, and space group: 221). By increasing the annealing temperature to 525°C, the Mo peaks disappeared, and the intensity of the γ-Mo_2N(111) peak increased. In addition, a new peak of the γ-Mo_2N phase also appeared at 43.49°, which may be related to the γ-Mo_2N(200) crystallographic orientation (with reference to JCPDS card no. 25–1366,

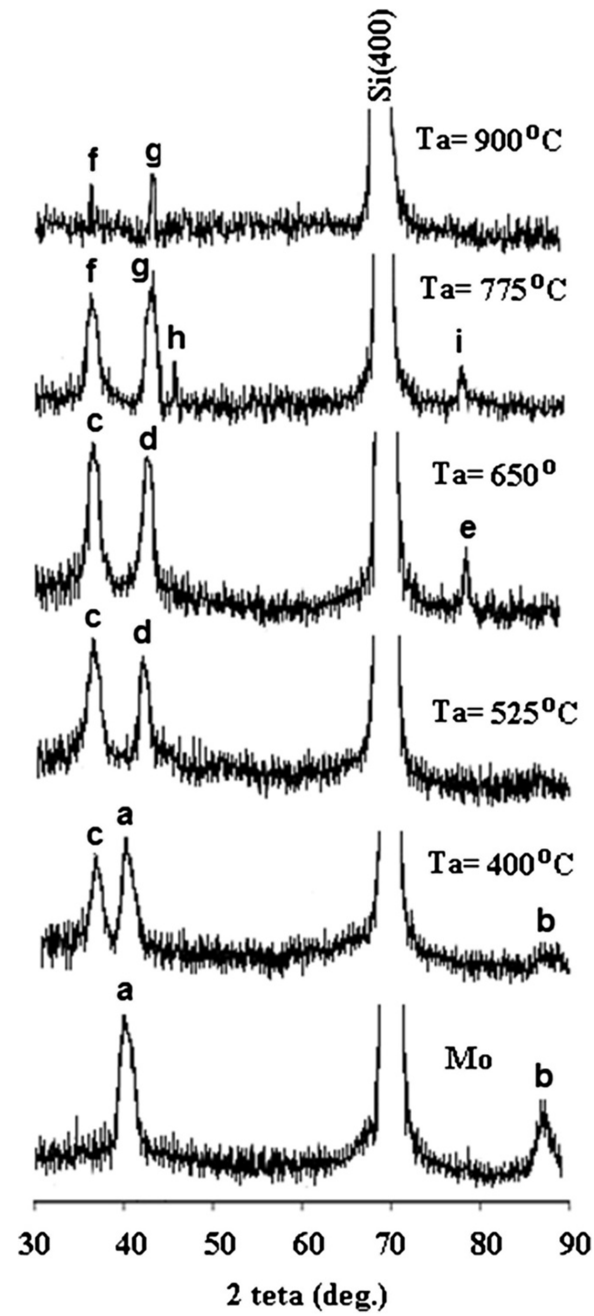

Figure 1 XRD of unheated and annealed Mo/Si thin films. (**a**) Mo(110), (**b**) Mo(220), (**c**) γ-Mo_2N(111), (**d**) γ-Mo_2N(200), (**e**) γ-Mo_2N(222), (**f**) Mo_2N(112), (**g**) Mo_2N(200), (**h**) Mo_2N(004), and (i) Mo_2N(116).

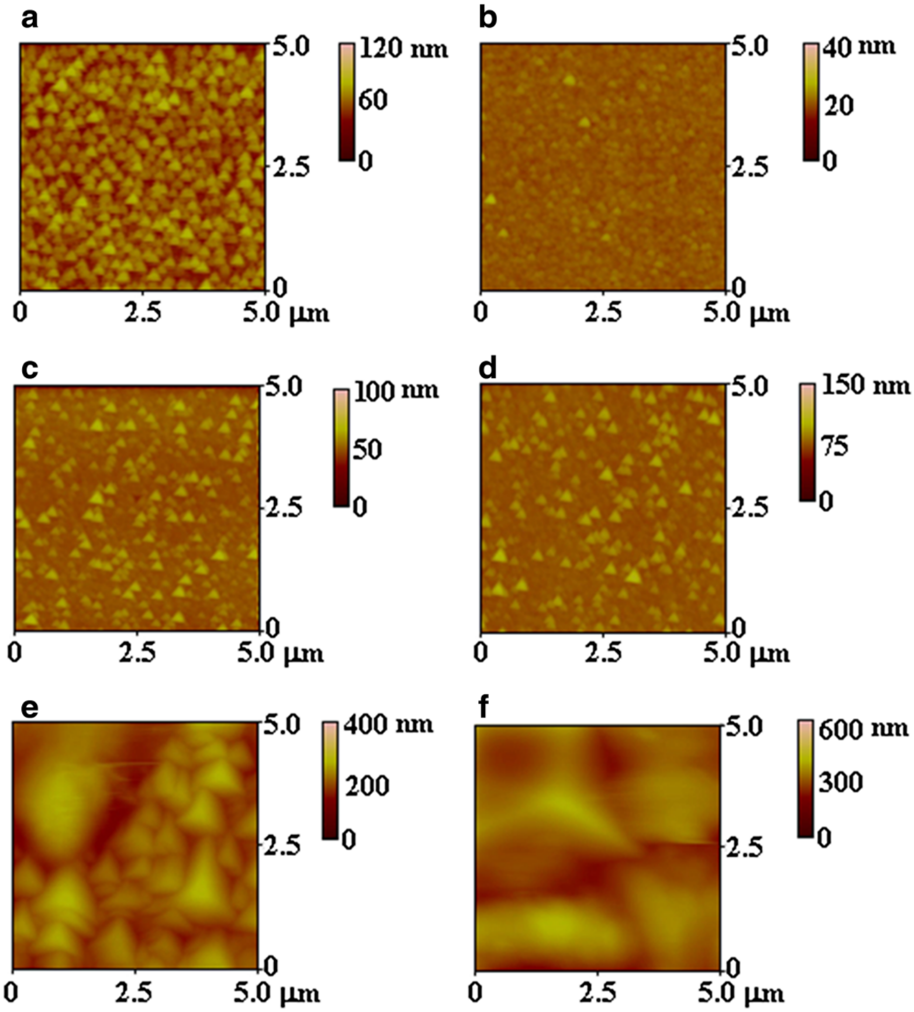

Figure 2 2D AFM images of Mo/Si thin films produced in this work. (**a**) Unheated (Mo) and annealed at (**b**) 400°C, (**c**) 525°C, (**d**) 650°C, (**e**) 775°C, and (**f**) 900°C.

2θ = 43.450°, system: cubic, and space group: 221). When the annealing temperature increased to 650°C, the intensities of the γ-Mo_2N(111) and (200) peaks increased relative to the lower annealing temperature, while a weak γ-Mo_2N(222) diffraction line at 79.73° also appeared in the XRD pattern (with reference to JCPDS card no. 25–1366, 2θ = 79.708°, system: cubic, and space group: 221).

Table 1 Results of AFM analysis

Sample no.	T_a(°C) ±5	Grain diameter (μm) ±0.02	Roughness	
			rms (nm)	R_a
K-1	as-deposited	0.19	8.02	6.48
K-2	400	0.05	1.64	1.22
K-3	525	0.07	5.14	3.78
K-4	650	0.09	6.48	4.80
K-5	775	0.70	54.7	44.1
K-6	900	1.25	78.5	64.1

At an annealing temperature of 775°C, the diffraction lines belonging to the γ-Mo_2N phase of molybdenum nitride with cubic structure disappeared, and a new phase of molybdenum nitride as a tetragonal structure is formed with the following crystallographic orientations: Mo_2N(112), Mo_2N(200), Mo_2N(004), and Mo_2N(116) at 2θ = 37.69°, 2θ = 43.19°, 2θ = 45.05°, and 2θ = 78.19°, respectively (with reference to JCPDS card no. 25–1368; 2θ = 37.685°, 43.166°, 45.020°, and 78.151° system: tetragonal; and space group: 141). At the highest annealing temperature of 900°C, the XRD pattern of the sample shows that the intensity of the molybdenum nitride peaks decreased, so the Mo_2N(004) and Mo_2N(116) peaks almost disappeared. This observation may indicate that at high temperature, reaction between nitrogen atoms/molecules and molybdenum is not favored. The tendency to grow in the γ-Mo_2N(111) crystallographic orientation at temperatures below 700°C is due to the (111) planes which are closest

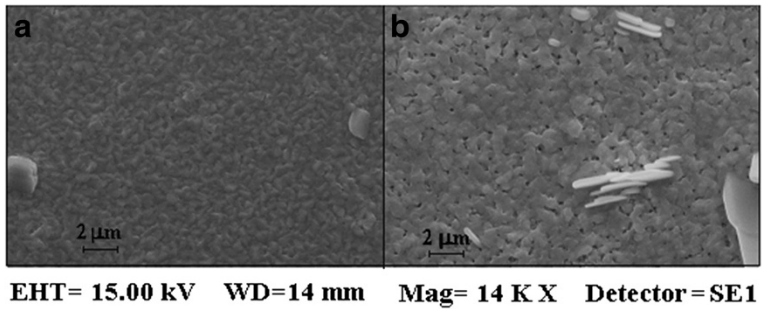

Figure 3 SEM images of annealed Mo/Si thin films at (a) 775°C and (b) 900°C.

packed in the face-centered cubic (FCC) molybdenum nitride structure with the lowest surface energy, and is consistent with the results of Shen for sputtered molybdenum nitride thin films [19]. In summary, the results show a mixed structure of Mo and molybdenum nitride for the annealed sample at 400°C, a polycrystal of γ-Mo_2N with FCC structure for annealed samples at 525°C and 650°C, and a Mo_2N phase of molybdenum nitride for samples which were annealed at 775°C and 900°C.

Surface physical morphology

Surface morphology of as-deposited and annealed samples was studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Figure 2 depicts the two-dimensional (2D) AFM images of these samples, while Figure 3a,b shows SEM images of the annealed samples at 775°C and 900°C. The grain diameter (calculated from 2D AFM pictures using the Jmicrovision code) and surface roughness parameters are also given in Table 1. The results show that the grain size and surface roughness decreased by annealing at 400°C. This reduction in grain size and surface roughness can be related to the reaction of Mo surface atoms with nitrogen atoms. An increase in annealing temperature to a higher temperature (>400°C) has an inverse effect, so increasing the annealing temperature causes an increase of the grain size and film surface roughness. The increase of the grain size and surface roughness is due to the increased surface diffusion (mobility) which causes the coalescence of the grains which in turn produces larger and deeper valleys between these newly formed grains; hence, larger grains and higher surface roughness are obtained.

Mechanical properties

Figures 4 and 5 illustrate the variation of hardness and elastic modulus of all samples as a function of annealing temperature, respectively, while Figure 6a shows the 2D AFM image of the selected sample after nano-indentation test. The results show that both these quantities increase by increasing the annealing temperature up to 650°C, and then decrease. These observations can be explained as in the following paragraphs.

Film hardness and mechanical properties can be affected by different parameters such as grain size, crystallographic orientations, film density, lattice parameters, and stoichiometry [20-23]. On the other hand, the close-packed structures and small grains (with more grain boundaries) result in higher hardness. Grain boundaries

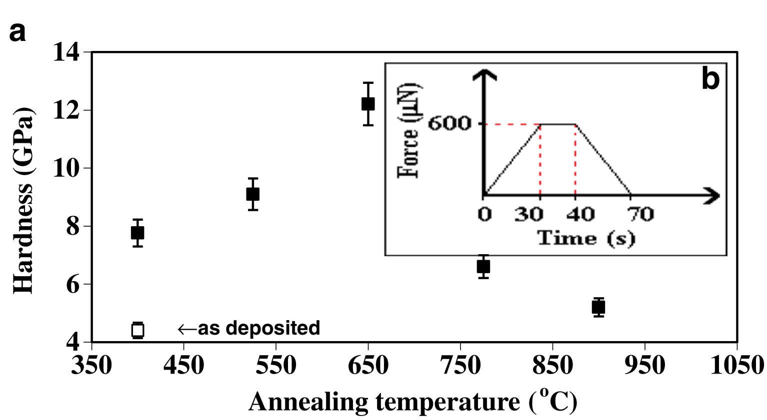

Figure 4 Variation of hardness and loading force. (**a**) Variation of hardness of as-deposited and annealed Mo/Si samples as a function of annealing temperature and (**b**) variation of loading force as a function of time at nano-indentation test.

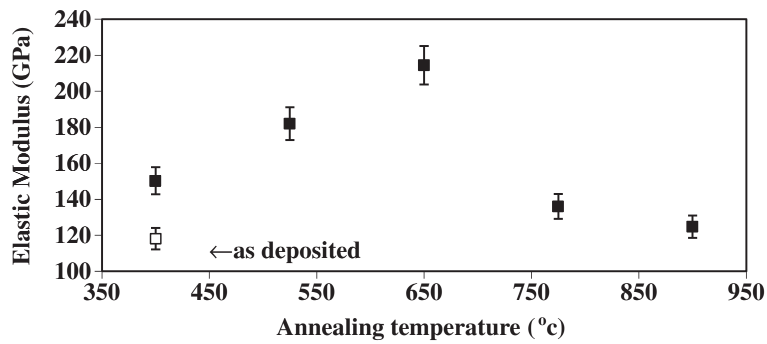

Figure 5 Variation of elastic modulus of as-deposited and annealed samples as a function of annealing temperature.

in polycrystal act as an impediment to the dislocation motion for the following two reasons: (1) dislocation must change its direction of motion due to the different orientations of grains; (2) discontinuity of slip planes from one grain to another [23].

The increasing film hardness before 650°C can be attributed to the change of the BCC structure of molybdenum to the FCC structure of γ-Mo_2N and small grains. However, an increase in annealing temperature to higher temperatures (i.e., 775°C and 900°C) has an inverse effect. This reduction is related to change of the γ-Mo_2N phase with FCC structure to the Mo_2N phase with tetragonal structure and larger size of the grains which form in higher temperature. Variation for elastic modulus in the samples is due to the ceramic nature of molybdenum nitride and larger elasticity of γ-Mo_2N relative to Mo_2N.

Tribological properties

Variations of the coefficient of friction obtained from the scratch test are plotted in Figure 7, while the 2D AFM image of the selected sample surface after the scratch test is shown in Figure 6b. The variation of (lateral force/normal force) of the selected sample as a function of time for obtaining the coefficient of friction is also shown in Figure 8. As can be seen, the friction coefficient of the molybdenum thin film decreases by annealing at the presence of nitrogen flow and increasing the annealing temperature up to 650°C. However, an increase in annealing temperature to higher temperatures (i.e., 775°C and 900°C) decreases the coefficient of friction. In the steady-state phase, the friction coefficient of the films depended mainly on their microstructure and had no direct relation to their surface topography [24]. On the other hand, the denser microstructure, namely, the smaller grain size and harder films, results in a lower friction coefficient. The variation of scratch volume of all samples as a function of annealing temperature is shown in Figure 9. As can be seen, the scratch volume decreases by increasing the annealing temperature up to 650°C, and then increases. This behavior of scratch volume is similar to the variation of friction coefficient and depends on the film microstructure. In fact, denser or harder microstructures have lower scratch volume. In summary, the results showed that an annealing temperature of 650°C is a critical temperature for mechanical and tribological properties that are due to transition of the FCC structure to the tetragonal structure and increase of the grain size which formed at a higher temperature.

Conclusions

Molybdenum nitride thin films prepared by post-annealing of MO thin films with 100-nm thickness at

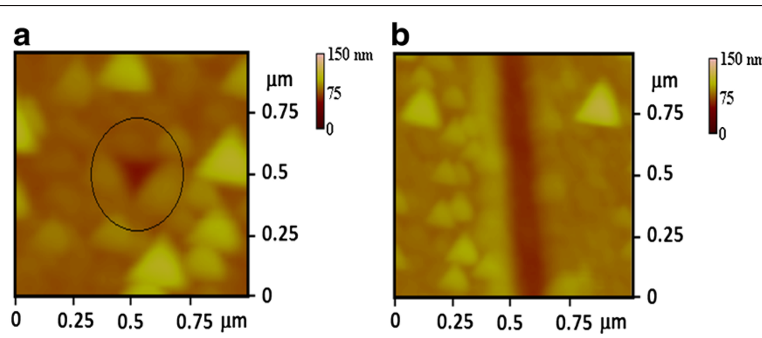

Figure 6 2D AFM pictures of a selected sample (with 100-nm thickness and annealed at 650°C). (**a**) After nano-indentation and (**b**) after scratch tests.

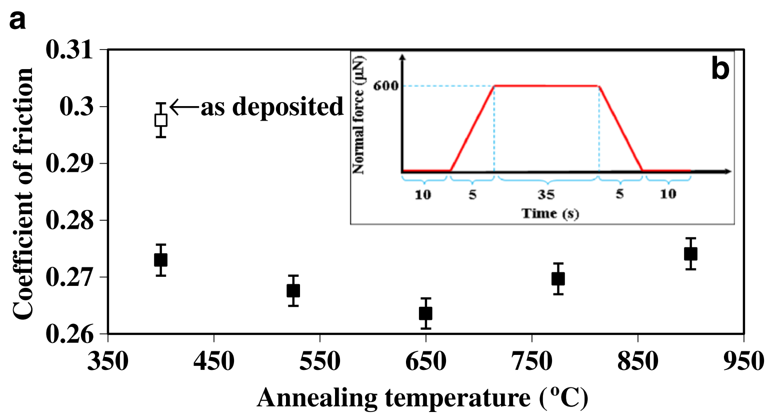

Figure 7 Variation of friction and normal force. (**a**) Variation of friction coefficient of as-deposited and annealed Mo/Si samples as a function of annealing temperature and (**b**) variation of normal force as a function of time at scratch test.

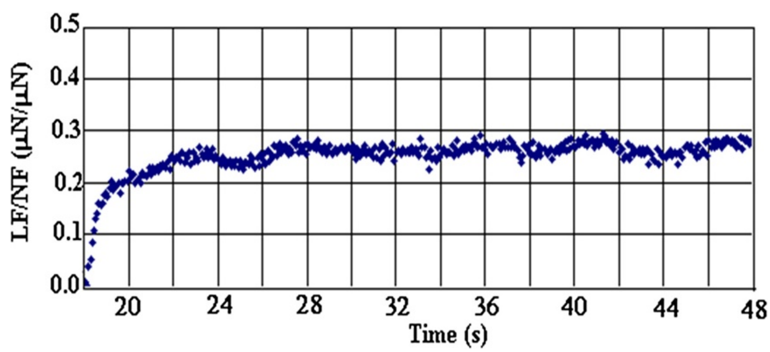

Figure 8 Variation of lateral force/normal force as a function of time of the selected sample. With 100-nm thickness and an annealing temperature of 650°C (K-4) in scratch test.

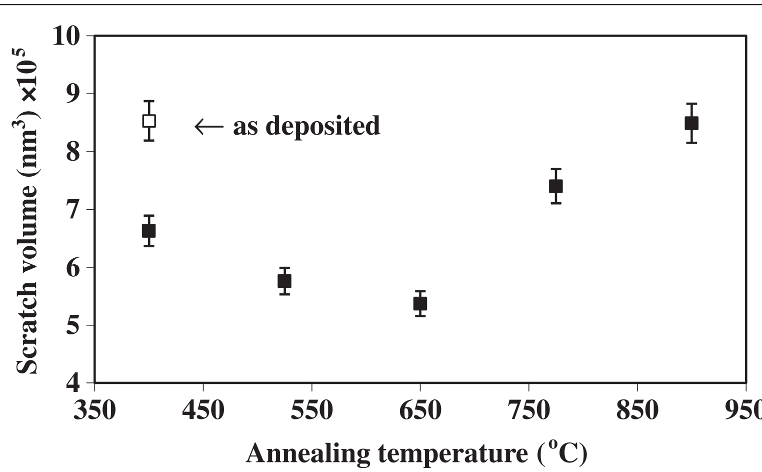

Figure 9 Variation of scratch volume of as-deposited and annealed Mo/Si samples as a function of annealing temperature.

different annealing temperatures in the range of 400°C to 900°C were studied. XRD, AFM, and SEM were employed for the study of the nanostructure and surface morphology. The mechanical and tribological properties of these layers were also considered using nano-indentation and scratch tests. The results showed that an annealing temperature of 650°C was a critical temperature for structural, mechanical, and tribological properties. The annealed sample at a lower temperature of 650°C had a γ-Mo_2N phase with FCC structure, smaller grains, and better mechanical properties, and the annealed sample at 775°C and 900°C had a Mo_2N phase with tetragonal structure and larger grains. The scratch test results also showed that scratch volume and friction of coefficient decreased by increasing the annealing temperature up to 650°C, and then increased.

Competing interests
The authors declare that they have no competing interest.

Authors' contributions
All authors provided the same contributions in this article. All authors read and approved the final manuscript.

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