Nanomechanical properties evaluation of chromium nitride films by nanoindentation and nanowear techniques

Jyh-Wei Leea,*, Jenq-Gong Duhb

aDepartment of Mechanical Engineering, Tung Nan Institute of Technology, #152, Sec.3, Pei-Shen Road, Shen-Ken, Taipei, 222, Taiwan
bDepartment of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

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Abstract

Nanomechanical and nanotribological properties studies are needed to develop fundamental understanding of surface and interfacial phenomena on the nano scale. In this study, nanoindentation, nanoscratch and nanowear tests were employed to characterize the nanomechanical and nanotribological properties of both reactive r.f. magnetron sputtered and cathodic arc plasma deposited chromium nitride (CrN) thin films. Surface morphologies and roughness of CrN films on the nanoscale were explored. The nanohardness and elastic modulus of CrN films were evaluated using the nanoindentation method. Coefficient of friction of CrN films against a conical diamond tip was also calculated based on the nanoscratch data. Reciprocating nanowear tests on these two CrN films were conducted with 300, 400 and 500 μN normal loads. Residual wear depths of the two CrN films were examined by an atomic force microscope (AFM). The residual wear depths of two CrN films after reciprocating nanowear tests ranged from 4 to 7.5 nm under 300 to 500 μN loads, respectively. It was found that the r.f. sputtered CrN film exhibited higher nanohardness and better surface roughness value. The r.f. sputtered CrN film showed more nanowear resistance and lower coefficient of friction than the cathodic arc plasma deposited one.

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1. Introduction

Recently, nanotechnology has been promoted globally [1]. Since the surface-to-volume ratio of a material is a key point in nanotechnology, surface engineering has become more and more important nowadays. The combination of surface engineering and nanotechnology is currently a focus of research issue [1].

Nanomechanical and nanotribological properties studies are needed to develop a fundamental understanding of surface and interfacial phenomena on a small scale, such as the micro/nanostructures used in micro-electromechanical systems (MEMS), nano-electromechanical systems (NEMS), magnetic storage systems and other industrial applications [2]. Sundararajan and Bhushan [3,4], Bhushan [5,6], Liu et al. [7] and Prioli et al. [8] studied the micro/nanotribological properties of various thin films using atomic force/friction force microscopy (AFM/FFM) with successful results.

Chromium nitride films deposited by various PVD techniques exhibit potential tribological applications due to a lower coefficient of friction, better wear [9] and corrosion resistance [10] than those of titanium nitride films. The mechanical properties of CrN films deposited by d.c. magnetron sputtering were reported by Nam et al. [11], Gautier et al. [12]. Ichimura and Ishii [13], Gautier et al. [12] also studied the mechanical properties of arc-evaporated CrN coatings. Wei et al. [14] explored the nanotribological properties of Cr, Cr2N and CrN thin films using the nanoscratch technique and obtained promising results. In a previous study [15], the pin-on-disk, scratch and Daimler-Benz Rockwell-C (DB-HRC) adhesion test results revealed that the cathodic arc plasma deposited CrN thin film showed excellent tribological performance on the macro scale. However, detailed
comparative nanomechanical and nanotribological property evaluations of CrN thin films produced by different techniques, such as sputtering or arc plasma deposition process, have not been reported in the literature to the best knowledge of the authors. The objective of this study is to evaluate the influence of different preparation techniques on nanotribological properties of CrN thin films. A nanoindenter interfaced with an atomic force microscope (AFM) was employed to conduct the nanohardness, nanoscratch and nanowear tests of two types of CrN thin films deposited by different methods, reactive radio frequency (r.f.) magnetron sputtering and cathodic arc plasma deposition, respectively. The surface morphologies, surface roughness, nanohardness, elastic modulus, coefficient of friction and nanotribological performance of CrN coatings were also evaluated.

2. Experimental procedure

A laboratory made Fe–Mn–Al–C alloy cold rolled plate [15] was used as the substrate in this study. Specimens with 20\(\times\)20\(\times\)2.2 mm dimension were cut from the cold rolled plate, abraded with SiC paper and polished up to 1 \(\mu\)m \(\text{Al}_2\text{O}_3\) powder, washed in distilled water, ultrasonically degreased in acetone and rinsed in alcohol. The reactive r.f. magnetron sputtering process and cathodic arc plasma deposition method, respectively, were employed to deposit chromium nitride thin films on these specimen surfaces.

For the reactive r.f. magnetron sputtering process, a 76.2-mm diameter and 99.95 wt.% purity Cr target was used. The target-to-substrate distance was 60 mm. After loading of the substrate and target, the vacuum chamber was pumped down to 2.7 \(\times\) 10\(^{-3}\) Pa, followed by the inlet of argon and nitrogen. The ratio of argon to nitrogen was kept to 1:1. The working pressure was 0.4 Pa for the deposition. During sputtering, the r.f. power for the target was fixed at 200 W. The deposition time was 3 h and the temperature of the substrate was maintained at 300 °C. The thickness of the r.f. sputtered CrN film (denoted as RF-CrN) is 1.0 \(\mu\)m. The working parameter of the cathodic arc plasma deposited CrN film (denoted as CAPD-CrN) was reported elsewhere [15], except the thickness of the CAPD-CrN film is 1.7 \(\mu\)m in this study. Phases in thin films were identified with a grazing incidence X-ray diffractometer (PANalytical X’Pert PRO-MRD, Holland) equipped with a Cu X-ray source. The incident angle was 2°. The working condition was 45 kV and 40 mA. Grain sizes of two CrN films were measured by Scherrer equation. Residual stress analysis was performed by means of XRD. Detailed experimental method has been explained by Ma et al. [16].

The nanomechanical and nanotribological tests were performed by means of a nanoindenter (TriboScope, Hysitron, USA) interfaced with an atomic force microscope (AFM, Nanoscope E, Digital Instrument, USA). For the nanohardness and elastic modulus measurements, a Berkovich diamond probe tip was used under 3000 and 5000 \(\mu\)N loads. The nanohardness and elastic modulus of each indent were determined on the basis of the Oliver and Pharr method [17]. To eliminate the directional geometry difference, a conical shaped diamond probe was employed to conduct the nanoscratch and nanowear tests. The radius of curvature of the tip is less than 1 \(\mu\)m.

Coefficients of friction of CrN films were measured along with the nanoscratch tests. The normal load of the scratch test was ramped from 0 to 2000 \(\mu\)N. The scratch length was set to be 8 \(\mu\)m. The normal force, lateral force, normal displacement and lateral displacement during scratch tests were recorded with respect to time. The lateral force was divided by the normal force to calculate the coefficient of friction of CrN films. Five scratch tests were conducted on each CrN coating.

Reciprocating nanowear tests under 300, 400 and 500 \(\mu\)N normal loads were executed on CrN films to explore the nanotribological properties. Wear tests consisted of generating scratches in a reciprocatory mode at a given load for 19 cycles over a scan length (stroke length) of 4 \(\mu\)m at 0.4 \(\mu\)m/s. Similarly, forces and displacements in the normal and lateral directions were monitored as a function of number of cycles.

AFM impressions of indents, nanoscratch and nanowear tracks were taken with the identical diamond tip. The nanoscale surface morphologies and roughness of coatings were also analyzed by atomic force microscopy with the Berkovich diamond tip. The total scan area was 600 \(\mu\)m\(^2\).

3. Results and discussion

3.1. Phase, surface roughness and morphologies of CrN thin films

The CrN single phase has been identified by X-ray diffraction, as shown in Fig. 1. A sharp diffraction peak corresponding to a (200) preferred orientation is observed in the RF-CrN thin film, whereas a (111) preferred orientation is found in the CAPD-CrN thin film. The grain sizes of the RF-CrN and CAPD-CrN films are calculated to be 19.0 and 14.6 nm, respectively.

The surface morphologies of CrN films analyzed by AFM are shown in Fig. 2(a and b). Based on the AFM analysis of the RF-CrN and CAPD-CrN films, the mean surface roughness \(R_a\) and maximum peak-to-valley highest \(R_{\text{max}}\) values are 2.4, 38.6 and 12.7, 283.0 nm, respectively. Nodular grains with diameter ranging from 80 to 120 nm are observed on the RF-CrN film surface. Almost no surface defects, such as macroparticles and pinholes, are found in Fig. 2(a). However, a rather rough morphology, with some macroparticles and pinholes around 1 to 2 \(\mu\)m in diameter on the film surface, is observed in
elastic modulus of the RF-CrN and CAPD-CrN thin films are 216 and 211 GPa, respectively, using $\nu=0.2$, $E_i=1141$ GPa, and $\nu_i=0.07$ under 3000 µN load. The maximum depth of the indent made by Berkovich, a 142.3° diamond probe tip, is only 71.6 nm under 3000 µN load, which is less than 1/10 of CrN films thickness. The substrate effect may thus be neglected. In this study, the hardness and elastic modulus of CrN films measured by nanoindentation are smaller than those reported by Ichimura and Ishii [13] and Cunha et al. [21], but comparable to that revealed by Sue et al. [22], Wei et al. [23] and Cunha et al. [24].
Based on the following equation \[16\], the residual stress \( \sigma \) can be obtained by determining the slope of the linear fitting between the fractional change in lattice spacing, \( \frac{d_{200} - d_0}{d_0} \), and the term \( \cos^2 \alpha \sin^2 \psi \).

\[
\frac{d_{200} - d_0}{d_0} = \frac{1 + v}{E} \sigma \cos^2 \alpha \sin^2 \psi + \frac{1 + v}{E} \sigma \sin^2 \alpha - \frac{2v}{E} \sigma
\]

(3)

whereas \( d_0 \) is the initial lattice spacing when tilt angle \( \psi \) is 0°, \( d_{200} \) is the lattice spacing when tilt angle \( \psi \) ranges from ±23° to ±50°, angle \( \alpha \) is a referenced Bragg angle of the observed plane (220) at \( \psi = 0^\circ \), \( \theta_0 \), minus the grazing angle \( \gamma \), i.e. \( \alpha = \theta_0 - \gamma \).

For the RF-CrN and CAPD-CrN thin films, the slopes of the linear fit are −0.00951 and −0.02989 with \( R \)-values of −0.985 and −0.996, respectively. The residual stresses of the RF-CrN and CAPD-CrN are calculated to be −1.71 and −5.25 GPa, individually. The magnitude of the residual stress of CrN films is comparable to that reported in the literature \[21\]. Gautier and Machet \[25\] reported that the mechanical properties of the vacuum are deposited CrN films were correlated to the microstructure of the films. The vacuum arc deposition parameters including the substrate bias voltage, the substrate temperature, nitrogen and argon partial pressure had direct effects on the texture and structures of the CrN films \[25\]. However, the two CrN films were prepared by two different deposition systems, i.e. r.f. sputtering and cathodic arc deposition, with different working parameters in this study. Therefore, the effect of residual stress and preferred orientation on the hardness and elastic modulus of two CrN thin films is not comparable directly.

3.3. Nanoscratch and nanowear tests

AFM surface morphologies of nanoscratch tracks on the RF-CrN and CAPD-CrN thin films, from 0 to 2000 \( \mu \)N (indicated by arrows), can be found in Fig. 4(a and b), respectively. Straight lines are shown on CrN thin films, which are plastically deformed by the conical diamond tip. Small pile-ups are observed along the two nanoscratch tracks. The width and depth of the scratch tracks increase with normal loading force. As compared with the smooth scratch track in Fig. 4(a), the nanoscratch track on the CAPD-CrN film is relatively rough as shown in Fig. 4(b). Apparently, a macroparticle on the CAPD-CrN thin film was also scratched over by the conical diamond tip. Note that no debris is found on the sides of the scratch tracks on the two CrN thin films. Obviously, CrN thin films are very hard and yet not too brittle to form any crack or delamination on the surfaces after nanoscratch tests. The normal and lateral forces with respect to scratch time on the RF-CrN thin film are shown in Fig. 5(a). The in-situ displacement in normal direction and the coefficient of friction against scratch time on the RF-CrN thin film are also indicated in Fig. 5(b). The scratch depth increases linearly with the normal load. It is noticeable that the in-situ displacement includes the elastic and plastic deformation produced during nanoscratch test. The in-situ displacement in normal direction against scratch time on the CAPD-CrN thin film also shows a similar trend, but more fluctuation is observed. Typical friction coefficients of CrN thin films with respect to scratch time are presented in Fig. 5(c).

The average friction coefficients of the RF-CrN and CAPD-CrN films against conical diamond tip are calculated to be 0.189±0.030 and 0.223±0.074, respectively. These values are an average of coefficients measured from five
different regions on the CrN film surfaces. These values are comparable with the data obtained by nanoscratch tests on CrN thin film by Wei et al. [14]. It is observed that the friction coefficient of the CAPD-CrN film decreases slightly as the load increases. It should be noted that there is data scattering in the friction coefficient for CAPD-CrN film, while the coefficient of friction of the RF-CrN film shows constant results. It has been reported that the coefficient of friction is influenced by the nanoscale topography and surface structures in the low normal load [14]. Obviously, the higher \( R_a \) and \( R_{\text{max}} \) surface roughness values as well as macroparticle defects on the surface are responsible for the more scattering and higher friction coefficient of the CAPD-CrN thin film on the nanoscale.

As compared to the nanoscratch tests conducted by Wei et al. [14], the coefficient of friction of the RF-CrN thin film is independent of normal load in this study. Even in the low load regime (<1000 \( \mu \)N), the coefficient of friction of RF-CrN thin film still remains around 0.19 in magnitude. It is argued that the rather smooth surface morphologies and relatively low \( R_a \) and \( R_{\text{max}} \) roughness values of the RF-CrN thin film account for the better result in this study. Noticeably, Wei et al. [14] employed a Berkovich indenter
to conduct the nanoscratch test. It is believed that the geometry difference between the pyramided tip and the conical tip can make the results different. It is possible that the experimental data of nanoscratch and nanowear are more reliable when conducted with the non-directional geometry conical tip.

Fig. 6(a and b) illustrates AFM surface morphologies of CrN coatings after reciprocating nanowear tests under 300, 400 and 500 μN loads. The close-up of each nanowear track of the FR-CrN thin film is shown in Fig. 6(c–e). Note that the reciprocating nanowear tracks in Fig. 6(b) are not obvious since the surface roughness of the CAPD-CrN thin film is much greater than that of the nanowear track produced in this study. Nevertheless, it is still obvious that no any debris or crack is found in these images. Apparently, the accumulated

Fig. 6. AFM surface morphologies of (a) RF-CrN and (b) CAPD-CrN thin films and detailed 3-D residual wear tracks images under (c) 300 μN, (d) 400 μN and (e) 500 μN normal loads of the RF-CrN thin film after reciprocating wear tests.
Reciprocating wear loads are not high enough to produce any crack or delamination on surfaces of CrN thin films. The average residual wear depths analyzed by AFM on thin films plotted with respect to the normal loads are presented in Fig. 7. The average of the entire cross-sectional profiles of wear scar perpendicular to the reference line in the AFM images is calculated to ensure the accuracy of residual wear depths measurements. It is found that the residual wear depth increases linearly with the normal force. The residual wear depth of the harder and lower residual stressed RF-CrN film is lower than that of the softer and higher residual stressed CAPD-CrN film under the same loading. Based on the residual wear depth and the lower coefficient of friction, the RF-CrN thin film shows better nanowear resistance.

4. Conclusions

A comparison of surface morphology, nanohardness, nanoscratch and nanowear properties of CrN thin films produced by reactive r.f. sputtering and cathodic arc plasma deposition techniques using a nanoindenter interfaced with the atomic force microscope was performed in this study. It is observed that the reactive r.f. sputtered CrN thin film exhibits higher hardness, lower $R_a$ and $R_{\text{max}}$ roughness values, a lower coefficient of friction and wear rate than the cathodic arc plasma deposited CrN film. On the other hand, macroparticles and pinholes on the surface of the CrN film produced by cathodic arc plasma deposition lead to a rough surface topography and to a more scattered, higher coefficient of friction. It can be concluded that the nanotribological performance of the reactive r.f. sputtered CrN thin film is better than the cathodic arc plasma deposited one, in terms of nanowear resistance and coefficient of friction.

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