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Influence of UV irradiation in low frictional performance of CN_x coatings

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ABSTRACT

The influence of ultraviolet (UV) irradiation on low frictional performance of CN_x coatings with 100 nm thickness having nitrogen contents of 9%, 14% and 19% deposited on Si(100) substrate by ion beam mixing was investigated in N_2 atmosphere environment. Three UV lights of 254, 312 and 365 nm were used to irradiate the surface of CN_x / Si(100) for 60 min. The changes of N / C ratio and atomic binding energy in the coating were analysed using Auger electron spectroscopy and X-ray photoelectron spectroscopy, respectively. The friction coefficient of Si_3N_4 ball sliding against CN_x was measured by a pin-on-disc tribometer, and wear tracks were analysed by the transmission electron microscope image. The results showed that UV irradiation on CN_x coating can decrease the critical frictional cycles for low friction coefficient and that the mechanism is due to the formation of graphite-like structure in the topmost CN_x coating.

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KEY WORDS: UV irradiation; CN_x; pin-on-disc; TEM; friction coefficient

INTRODUCTION

It is well known that the researches in the carbon nitride (CN_x) area originally focused on realising the super hard β-C_3N_4 compound predicted by Liu and Cohen.[1,2] Most of the techniques that were used to synthesise this material are based on vapour phase method where a thin film is condensed onto a substrate. The relationship between CN_x film structure and nitrogen concentration was investigated by Hellgren *et al.*,[3] who suggested that sputtered CN_x film shows amorphous structure when substrate temperature is below 150°C. Another topic on CN_x film is to realise the low or super low friction behaviour of the CN_x coatings.[4,5] Sanchez-Lopez *et al.*[4] studied the low friction behaviour of CN_x film by in situ method and found that the formation of transfer layer plays an important role for low friction.

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Quiros *et al*.[5] researched the environmental influence on low friction behaviour of ion beam deposited CN_x film, and their results showed that CN_x film could reach lower friction coefficient in dry nitrogen than in air. Our early research also reported that super low friction was obtained when CN_x coating sliding against Si_3N_4 ball in N_2 environment;[6,7] the mechanism about the dependence of super low friction on certain critical sliding cycles was proposed that during the friction in N_2 environment, nitrogen atoms desorbed from the topmost surface of CN_x coating by cyclic friction, which caused the structural reformation with low shearing strength at topmost surface, that led to CN_x coating's super low friction.[8,9] The thickness of the structural changed layer in range of 10–20 nm was obtained by depth measurement of Auger electron spectroscopy (AES).[10] Furthermore, the studies on the influence of gas flowing to the CN_x coating surface during the initial friction[11] and the carbon overcoat on CN_x coating on the friction properties[12] were carried out for the purpose of super low friction of CN_x coating.

However, the aforementioned studies showed that the surface fabrication by the cyclic friction or thin film deposition on CN_x coating is difficult to realise low or super low friction performance in the early stage of the sliding distance; thus, it is necessary to develop a new method to reach super low friction of CN_x at the initial sliding stage when we consider the super low friction surface to supply for lubrication industrial field. Therefore, this study focused on ultraviolet (UV) irradiation on the CN_x coating surface to obtain low frictional performance.

EXPERIMENTAL

CN_x Coating Synthesis

CN_x coatings were deposited by ion beam mixing method to obtain 100 nm thickness coating on Si (100) substrate with 350 μm thickness and 50 mm diameter. The vacuum chamber was pumped to 1.0×10^{-4} Pa before introducing nitrogen gas up to 2.2×10^{-2} Pa. Prior to the deposition, the Si substrate was cleaned for 5 min by nitrogen ions sputtering with the energy of 1.0 keV. The deposition process of CN_x coating consisted of two essentials: one was the sputtering deposition of amorphous carbon on the substrate, and the other was an ion-mixing process of the coating by N ions. Therefore, CN_x coating was produced by a combination of both deposition and mixing processes. The target of the sputtering process was sintered graphite with 99.999% purity, which was bombarded by argon ions with the energy of 1 keV and current of 100 μA. N ions for the ion-mixing process had the energy of 0.5 keV and an ion current density of 30 $\mu A\,cm^{-2}$. The deposition temperature was maintained at 25 ± 5°C by 18°C circulating cooling water at the back side of the substrate. The deposition rate of CN_x coating was 0.9 $nm\,min^{-1}$, which was measured by quartz crystal microbalance (QCM). The QCM was calibrated by thickness results measured by a profilometer. We prepared three different nitrogen concentrations of CN_x as 9%, 14% and 19% by changing nitrogen ion beam current. The contaminant elements in CN_x films were not observed; only a small number of oxygen and water molecule attached on surface was detected.[13]

Prior to tribotesting, UV irradiation treatment on CN_x film was carried out using an equipment of BLX-312 (Cosmo Bio Co., Ltd, Tokyo, Japan). Three different types of discharge tubes are able to attach to the equipment, and these tubes can generate three different UV wavelengths. The CST-8A generates 254 nm, CST-8B 312 nm and CST-8 C 365 nm. The maximum UV irradiation energy is 99.99 J, irradiation area is 260 mm × 300 mm. The environment of UV irradiation equipment was ambient air, and the distance from the tubes to specimens was 160 mm.

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Raman, AES, XPS and TEM Analysis

The prepared CN_x coating was UV irradiated with 254, 312 and 365 nm wavelength for 60 min. The structural change of CN_x coatings was investigated by Raman spectroscopy (NRS-1000, Jasco International Co., Ltd, Tokyo, Japan, 530.3 nm wavelength, 10 mW beam power), AES (PHI-650, Perkin-Elmer, Waltham, MA, USA, acceleration voltage 5 kV, current 100 nA), X-ray photoelectron spectroscopy (XPS; ESCALAB 220i, Thermo Fisher Scientific, Waltham, MA, USA, X-ray Mg-Kα, 13.5 kV, 20 mA) and transmission electron microscope (TEM) as well as electron diffraction (ED; JEM-3010 microscope, JEOL Ltd, Akisima, Tokyo, Japan, acceleration voltage 300 kV, point resolution 0.19 nm; the images were captured by Gatan 894 CCD camera [Gatan, Inc., Pleasanton, CA, USA]).

Pin-on-disc Tribometer

The friction tests with the pin-on-disc tribometer were carried out in a vacuum chamber at the temperature of 23°C. The test conditions were fixed at a normal load of 0.1 N (400 MPa Hertzian pressure), sliding velocity of 0.04 m s^{-1} and counter material Si_3N_4 ball with 8 mm diameter. The peak to valley height of the ball and CN_x coating surface roughness were 30 nm and 1.0 nm, respectively, which were obtained by contact model atomic force microscopy measurement. The schematic image is shown in Figure 1. Before the friction test, the vacuum chamber was pumped to 0.1 Pa, and then N_2 gas was filled into the chamber at atmospheric pressure. Before the friction tests, Si_3N_4 balls were cleaned by ultrasonic cleaner in acetone for 15 min.

RESULTS

Influence of UV Irradiation on Nitrogen Content

The nitrogen content of CN_x was determined by AES. Figure 2a shows the AES spectra of each specimen. The ratios of N / C were approximately calculated from N KLL peak height divided by C KLL peak height

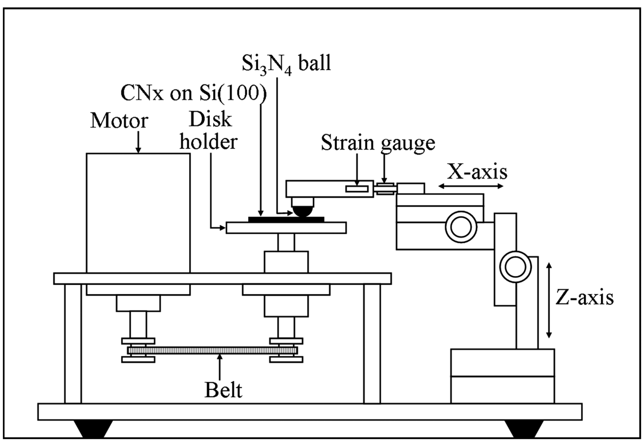

Figure 1. The schematics of pin-on-disc tribometer equipment.

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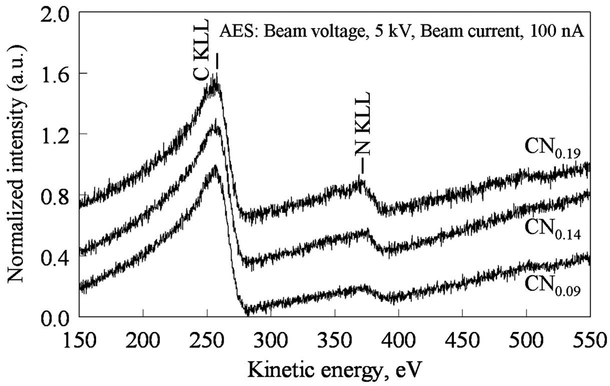
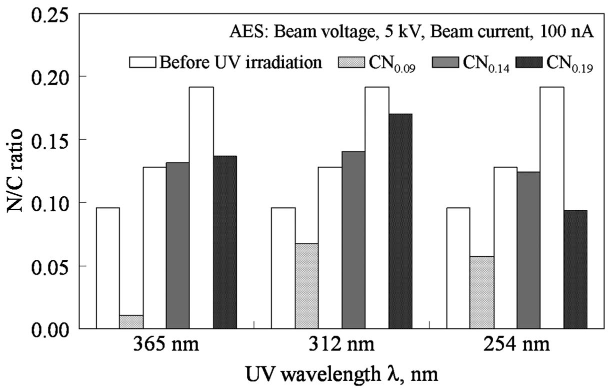


(a)



(b)

Figure 2. (a) The Auger electron spectroscopy (AES) spectra of CN_x without ultraviolet (UV) irradiation. (b) The influence of UV irradiation on N / C ratio change in CN_x coating.

based on elemental sensitivity factor method[14] for confirming the influence of the nitrogen relative content in CN_x coatings on friction behaviour after UV irradiation. The results were shown in Figure 2b. The N / C ratio of CN_x without UV irradiation showed 0.09, 0.14 and 0.19. The results in Figure 2b also show that the influence of UV irradiation on nitrogen content of $CN_{0.14}$ is smaller than that of the other two films.

The CN_x coating atomic structure was analysed by Raman spectroscopy, and the spectra with the broad peak were shown in Figure 3a. This spectrum we obtained differs from that reported by Ferrari *et al.*,[15] which is suggested to be caused by the difference in nitrogen content of CN_x films, the scanning wave number range and the laser wavelength that were used for Raman excitation. The spectrum was decomposed into I_D and I_G peaks; the G peak position and the I_D / I_G ratio were shown in Figure 3b. It can be seen in Figure 3a and 3b that the D peak intensity increased with N / C ratio, whereas the G peak position increased from 1550 to 1570 cm^{-1} when N / C ratio increased up to 0.19 and I_D / I_G ratio increased from 0.3 to 1.7 cm^{-1}. These results indicated that each CN_x coating includes sp^2 and sp^3 sites.[16] The atomic force microscopy measurement results also showed that surface roughness of all specimens did not change after UV irradiation, which was approximately 1.0 nm.

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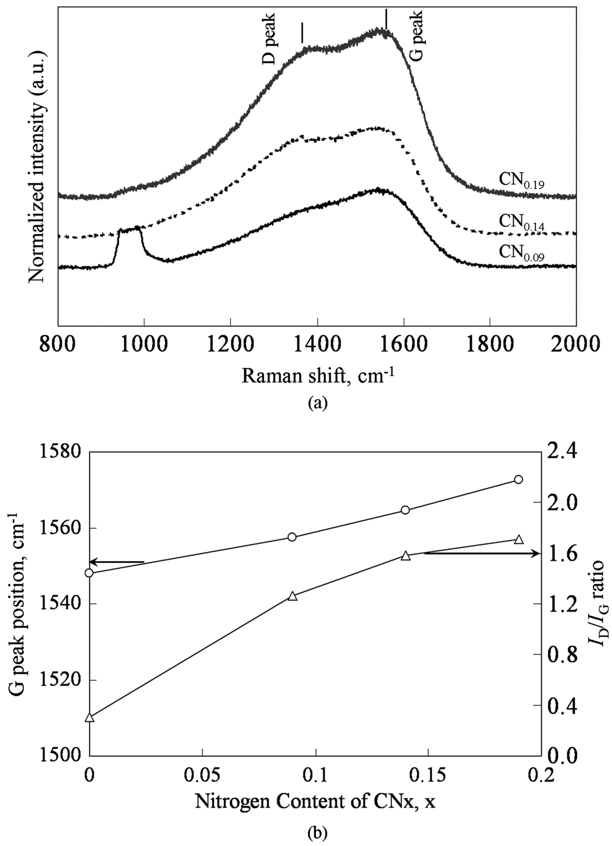

Figure 3. (a) The Raman spectra of CN_x without ultraviolet irradiation. (b) The relationships among G peak position, I_D/I_G ratio and nitrogen content in CN_x coating.

Influence of UV Irradiation on Frictional Properties

The influence of UV irradiation on the frictional properties of $CN_{0.09}$, $CN_{0.14}$ and $CN_{0.19}$ coating in N_2 has been characterised, and the results are shown in Figure 4a–4c. In the case of $CN_{0.09}$ (see Figure 4a), the critical cycles for stable average friction cycles were reduced by UV irradiation, and average friction coefficient (from 5000 to 10 000 cycles) also decreased after UV irradiation.

Figure 4b shows the frictional property of $CN_{0.14}$. The initial friction coefficient of $CN_{0.14}$ without UV irradiation fluctuate widely, and stable average friction coefficient is approximately 0.033. The 254 and 312 nm UV-irradiated $CN_{0.14}$ perform higher initial friction coefficient and wider fluctuation compared with those without UV irradiation. However, critical cycles for low friction and stable average friction coefficient are less compared with those without UV irradiation. It is notable that in the case of 365 nm UV irradiation, the initial friction coefficient is smallest and the critical cycles are the least among all specimens.

Figure 4c shows the influence of UV irradiation on frictional properties of $CN_{0.19}$. It can be seen that the fluctuation of initial friction coefficient is reduced remarkably by UV irradiation.

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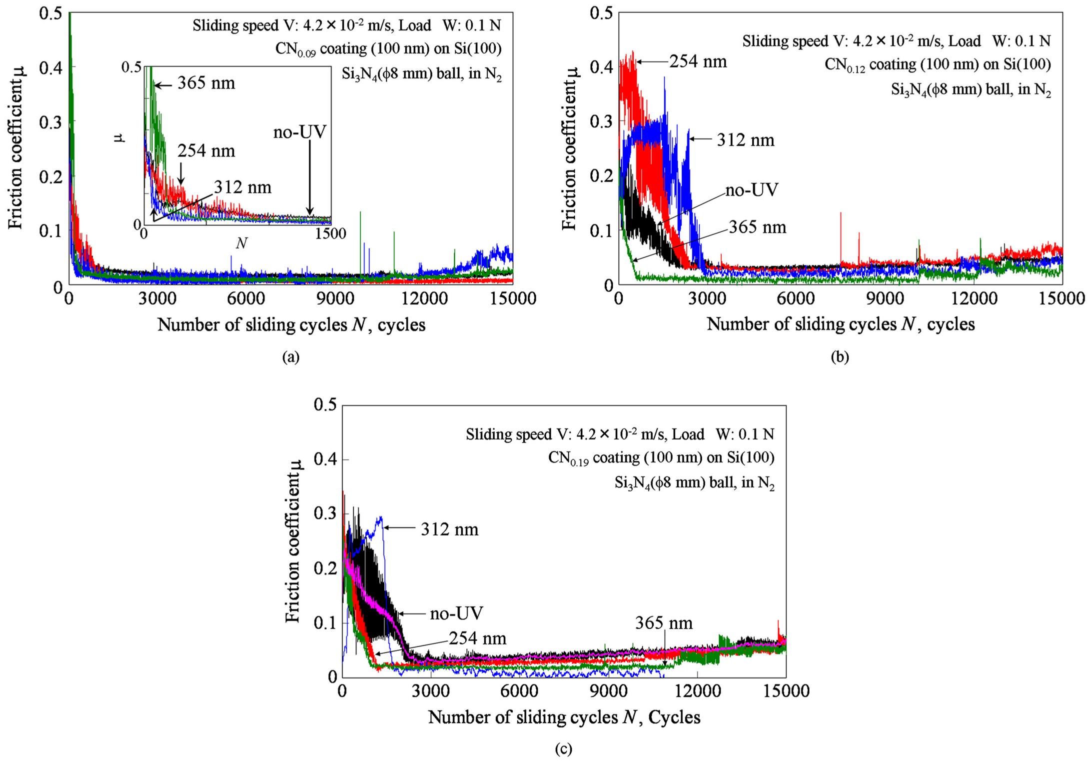

Figure 4. The influence of ultraviolet (UV) irradiation on friction coefficient of (a) $CN_{0.09}$, (b) $CN_{0.14}$ and (c) $CN_{0.19}$ coatings.

The relationship between the friction coefficient and the number of sliding cycles was summarised in Figure 5. It is clear that the critical cycle for stable low friction depends on the nitrogen content in CN_x. The influence of UV irradiation at different UV wavelength on critical cycles for low friction and the stable average friction coefficient are summarised in Figures 6 and 7, respectively. It is clear that UV irradiation reduced critical cycles for low friction and the value of stable average friction coefficient.

Influence of UV Irradiation on Structural Characteristics

The UV irradiation strongly influences the frictional properties of CN_x coating, which means that UV irradiation can influence the surface structure of CN_x coatings. Therefore, the change of binding configuration by UV irradiation was clarified by XPS analysis. One sort of the typical results is shown in Figure 8a and 8b. The N1s spectrum of with and without UV irradiation shows that N—C single bond reduction was induced by UV irradiation and N═C double bond increased. The N—C bonds, which appeared around 398.46 eV, was the bond in three-dimensional structures as fullerene.[17] On the other hand, the N═C bonds that appeared around 400.17 eV indicate nitrogen atoms switching position with carbon atoms in graphite-like structure, and those that appeared around 402.88 eV are N—N or N—O bond when N1s peak is

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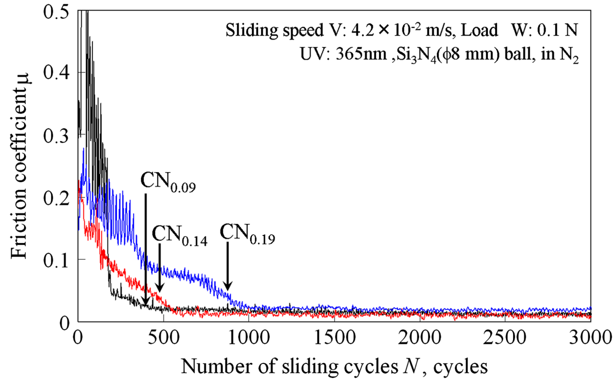

Figure 5. The influence of nitrogen content in CN_x coatings on friction coefficient. UV, ultraviolet.

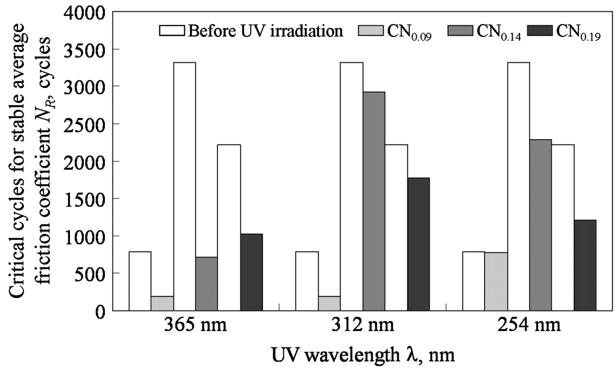

Figure 6. The relationship between critical cycles for stable average friction coefficient. UV, ultraviolet.

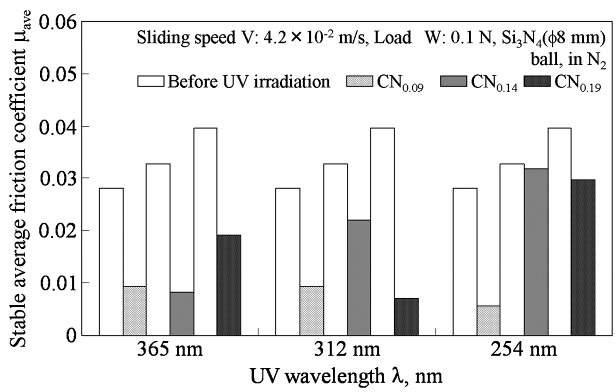

Figure 7. The relationship between stable average friction coefficient and ultraviolet (UV).

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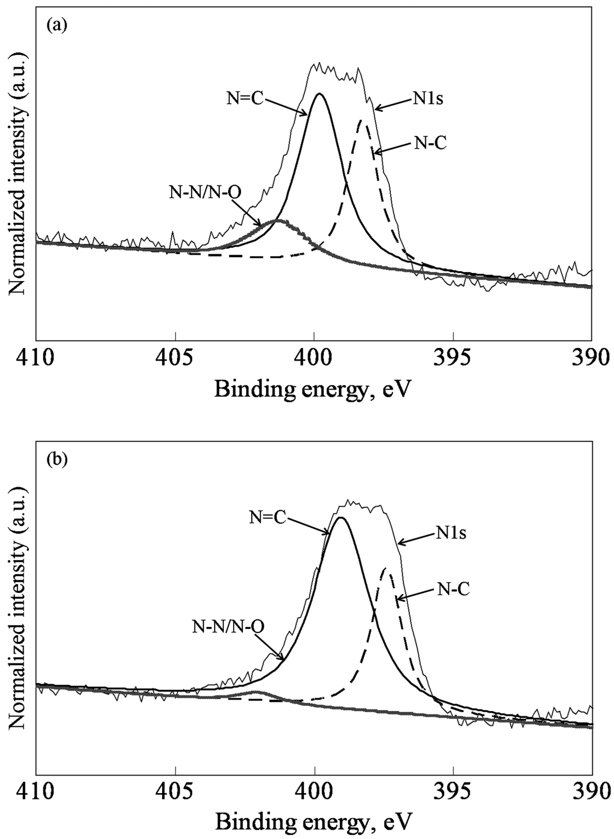

Figure 8. The N 1s XPS spectra of $CN_{0.14}$(a) without ultraviolet (UV) irradiation and (b) with 365 UV irradiation.

deconvoluted.[3] The UV irradiation on the CN_x coating surface caused N-C bonds reduction, and a graphite-like structure was left on the topmost layer of CN_x (see the following TEM observation). These structural changes influence on critical cycles and stable average friction coefficient.

The structural details of CN_x coatings under different conditions were investigated by TEM images and ED patterns, and the results are summarised in Figure 9, which consist of three images named from (a) to (c), representing the structure of as-deposited CN_x coating, low friction stage CN_x coating and 312 nm UV-irradiated CN_x coating, respectively.

In Figure 9a, the TEM image of the as-deposited CN_x coating shows an amorphous structure, and the ED pattern contains no diffraction ring, indicating no crystallite in the coating. In Figure 9b, the TEM image of the low friction stage CN_x shows a short-range ordering structure with nanoclustering atoms, which can be clearly seen in the local magnified image where the nanoclusters are marked in white circle. The ED pattern shows two strong rings. From the diameter of the rings, two crystal-plan distances can be obtained as 0.1676 and 0.0893 nm, which are close to the known interplanar spacing of (001) graphite and (001) diamond as 0.1674 and 0.0890 nm, respectively. The structural difference indicated by Figure 9a and 9b suggests that CN_x coating having local nanoclustering carbon atoms (graphitised structure) can perform a low friction property. This viewpoint is similar to that reported

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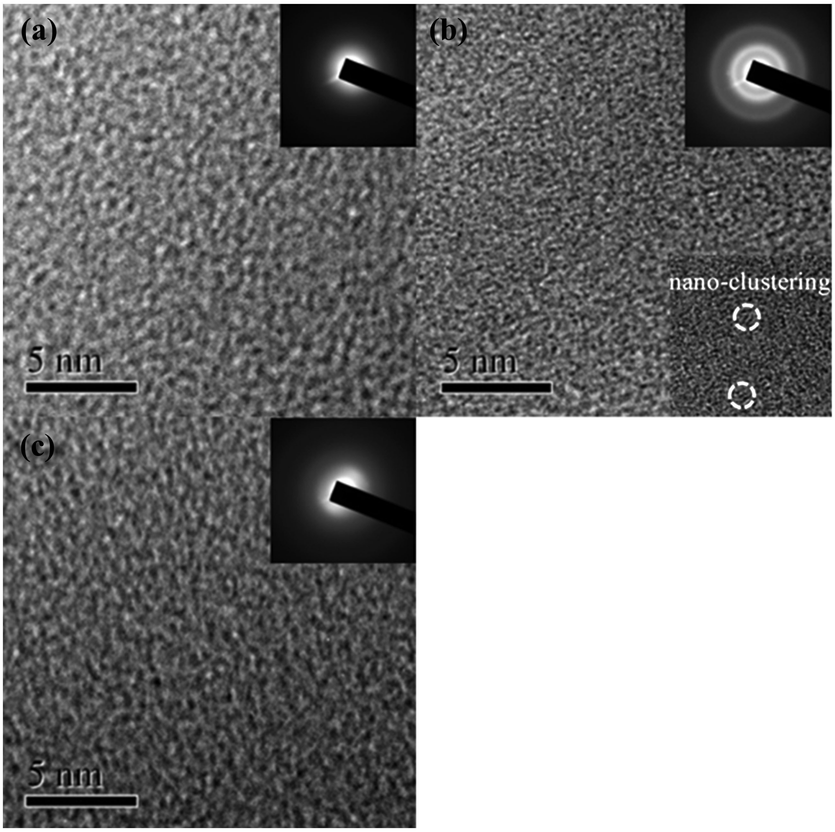

Figure 9. Transmission electron microscope images and electron diffraction patterns of CN_x coatings under different treatment: (a) as-deposited, (b) after low friction occurred and (c) 312 nm irradiated.

by A. Erdemir's group,[18] where they found that graphite-like structure was formed when diamond-like carbon performed a low frictional property in dry nitrogen environment. In Figure 9c, the ED patterns also show a diffuse ring, and a pair of diffraction spots responding to orienting distributed graphite can be seen. Comparing with image (a), the ED patterns of UV-irradiated CN_x coatings clearly imply that the structures of CN_x coatings after UV irradiation have slightly changed from amorphous to nanocrystallised, possibly consisting of short-range ordering carbon atoms. This is suggested to explain the reduction of critical cycles of CN_x coatings before low friction occurs: by UV irradiation, graphite-like nanocluster are induced to form in the amorphous CN_x matrix; thus, the CN_x coating can change into a nanocrystallised structure that is suitable for low friction through less sliding cycles.

DISCUSSION

To find a tool to realise the low friction at the initial sliding stage, we studied the UV irradiation method in case of CN_x coatings sliding against Si_3N_4 ball. The results showed the possibility of the method for

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Table I. Bond energies of carbon and nitrogen atoms.

Bond	Bond energy, kJ mol^{-1}	Bond	Bond energy, kJ mol^{-1}
C—C	348	C=N	613
C—N	305	C=C	612

the purpose of super low friction of CN_x coating. However, it should be noted that the mechanism for the generation of low friction coefficient of CN_x coatings with UV irradiation needs to be discussed. During the friction of CN_x coatings in N_2 environment, we think that the several bonds between carbon atoms and nitrogen atoms included in CN_x coating may cut and generate another bonds such as C=C, which may cause the nitrogen atoms desorption at the topmost surface[8] more easily and in where a restructuring process affected the low frictional behaviour. For confirming the ideas, we made a simple calculation from the viewpoint of light energy. It was known that the photon energy of 1 mol can describe as the following formula: $E = h\,(c\,/\,\lambda){*}N_A$;[19] here, h is Planck's constant, c is light speed, λ is wavelength of the light and N_A is Avogadro's number. The UV wavelengths are calculated to be 469 (254 nm), 382 (312 nm) and 327 (365 nm) kJ mol^{-1}. Table I shows the single and double bond energies of carbon and nitrogen atoms. All UV wavelengths exceed C—N single bond energy. Thus, the UV irradiation is able to have influence on structural reformation.

The influencing depth of UV irradiation in CN_x coating is also an important knowledge for industrial application. Generally, the optical penetration depth into the surface depends on the material extinction coefficient. The extinction coefficient of $CN_{0.19}$ was measured by laser ellipsometer (MARY-102, Five Lab Co., Ltd, Kanagawa, Japan, spot size 20 µm, 632.8 nm wavelength, 10 times measurements) and the average extinction coefficient k was approximately 0.598. From the optical penetration formula $d_p = 1\,/\,\alpha$ $(\alpha = 4\pi k\,/\,\lambda)$,[20] here d_p is light penetration depth, α is absorption coefficient and λ is wavelength of irradiation light. From these formulas, the influencing depth of UV irradiation at 254 and 365 nm wavelengths at CN_x coating surface can be calculated approximately to be 33.8 and 48.6 nm, respectively. These results indicated that topmost surface of CN_x is able to be changed into the low friction structure through UV irradiation.

From the aforementioned discussion, we believe that the mechanism of lower critical cycles for the low friction is due to the formation of graphite-like structure in the topmost CN_x coating and that the UV irradiation technique to reduce the critical cycle for low friction is better than CN_x coating rubbing in N_2 environment[8] or several nanometre carbon overcoat method.[12]

CONCLUSIONS

The influence of UV light irradiation on low frictional performance of CN_x coating was investigated. Three wavelengths UV of 254, 312 and 365 nm were used for irradiation. The changes of N / C ratio and atomic binding energy in the coating were analysed. The friction coefficient of Si_3N_4 ball sliding against CN_x was measured, and wear tracks were analysed by the TEM image. The main conclusions are summarised in the following:

- The critical cycles for low friction coefficient can be reduced by the UV irradiation.
- The critical cycles for stable average friction coefficient depend strongly on UV wavelength and nitrogen content in CN_x coating.

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- The mechanism of low critical cycles for low friction coefficient is due to the formation of graphite-like structure in the topmost CN_x coating.

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