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Influence of different pretreatments on the adhesion of nanodiamond composite films on Ti substrates via coaxial arc plasma deposition

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Abstract

In this study, we report on the novel growth of nanodiamond composite (NDC) films on titanium (Ti) substrates using the coaxial arc plasma deposition (CAPD) at room temperature, which offers several advantages over conventional growth techniques. CAPD employs a unique coaxial arc plasma gun structure that provides a supersaturated condition of highly energetic carbon ions (C^+) for ultrafast quenching on the substrate, promoting the growth of nanodiamond grains. This allows for NDC films' growth on diverse substrates without the need for initial seeding or substrate heating. However, the growth of NDC films on Ti substrates at room temperature is challenging due to the native oxide layer (TiO_2). Here, we grew NDC films on Ti substrates using three different pretreatments: (i) hydrofluoric acid (HF) etching, (ii) insertion of a titanium carbide (TiC) intermediate layer, and (iii) *in situ* Ar^+ plasma etching. The morphology and structure of the grown NDC films were examined by 3D laser, high-resolution scanning electron microscopies (HR-SEM), Raman, and x-ray photoelectron (XPS) spectroscopies. Our results demonstrate that *in situ* Ar^+ plasma etching is the most effective pretreatment method for completely removing the native TiO_2 layer compared to the other two *ex situ* pretreatments, in which re-oxidation is more likely to occur after these pretreatments. Furthermore, NDC films grown using the hybrid Ar^+ ion etching gun (IG) and CAPD exhibit the highest sp^3 content (63%) and adhesion strength (16 N).

1. Introduction

Titanium (Ti) is a widely used biomaterial for dental and orthopedic implants [1]. The desirable bio-properties of Ti are attributed to the formation of a native surface oxide layer (TiO_2) that is typically 3–7 nm thick [2] and develops spontaneously upon atmospheric exposure. However, its ability to resist corrosion is limited and tends to decrease over time [3]. Therefore, it is essential to search for an effective biocompatible, wear and corrosion resistant coating. A promising solution is the application of nanodiamond composite coatings to Ti implant surfaces.

Nanodiamond composite (NDC) coatings combine diamond crystallites (less than 10 nm in diameter) within an amorphous carbon phase. Owing to sp^3 hybridized carbon bonding of diamond crystallites, NDC films yield impressive physical properties [4–6], outstanding biocompatibility [7], and antibacterial properties [8]. Despite this, achieving good adhesion of NDC films to Ti substrates is a challenging mission. Conventional chemical vapor deposition (CVD) methods are commonly used to grow NDC films on Ti. These methods require elevated substrate temperatures ($\sim 1000^\circ C$) to overcome the TiO_2 layer and achieve good adhesion [9].

However, high substrate temperatures induce residual internal stress in the films, leading to exfoliation due to thermal expansion mismatch between diamond ($\alpha_{\text{dia.}} 1.0 \times 10^{-6} \text{ K}^{-1}$) and Ti ($\alpha_{\text{Ti}} 9.4 \times 10^{-6} \text{ K}^{-1}$).

Many attempts have been made to reduce the internal stress in NDC films through metallic doping or interlayer insertion. Carcione *et al* [10] grew Ti-doped diamond film on Ti substrates via hot filament CVD (HFCVD) at 750 °C to investigate osteoblast-like cell growth. In a separate study, Esquivel-Puentes *et al* [11] achieved adhesion of hydrogenated amorphous carbon (a-C:H) films on titanium alloys (Ti6Al4V) via microwave plasma CVD (MPCVD) by inserting a zirconia-doped with silicon interlayer via R.F. sputtering prior to (a-C:H) film deposition to study bias effects on wear and corrosion behavior. While these efforts improved the adhesion of NDC films to Ti substrates, metallic doping can cause graphitization of diamond films and reduce their hardness, especially at high deposition temperatures [12]. Additionally, not all interlayers are beneficial in boosting adhesion strength due to deficiencies in suppressing elemental diffusion from the substrate material.

In the same regard, other attempts have been made to enhance the adhesion strength between Ti and NDC films through CVD methods at moderate temperatures to reduce residual stress. Dekkar *et al* [13] deposited NDC film on a 3D Ti implant using a distributed antenna array (DAA) (MPCVD) reactor at a median temperature (400 °C). Although MPCVD has been observed as a convenient method to deposit NDC films at lower temperatures than HFCVD, it has been reported that the growth rate decreases with decreasing substrate temperature in CVD methods [14]. Moreover, contamination is more likely to happen from the filament materials, which is another drawback of HFCVD [15].

Divergent pathways, such as chemical etching [16] of Ti substrates, have been adapted to remove the oxide layer and reinforce adhesion instead of the aforementioned alternatives. However, the concentration, temperature, and duration of acid pretreatment must be optimized, otherwise extreme induced roughness will subsequently increase the film roughness and proportionally affect *in vitro* and *in vivo* cell adhesion [17]. Indeed, following these strategies can contribute to tailoring the impediments of adhesion bonding strength between diamond films and Ti substrates, but CVD methods still involve heat exhaustion and prolonged diamond growth operation.

Motivated by the above-mentioned interesting studies on the growth of NDC films on Ti substrates and our expertise in coaxial arc plasma deposition (CAPD) [4, 18], we propose the growth of NDC films on Ti at room temperature using CAPD after various substrate pretreatments. Among the different treatments, using Ar^+ plasma etching of Ti substrates in a hybrid configuration of ion etching gun (IG) and CAPD produced the best film adhesion and hardness strengths. *In-situ* Ar^+ dry etching of Ti was highly efficient in completely removing the native TiO_2 layer and all contaminants on the Ti substrates, while also providing further protection against oxidation prior to NDC film deposition via CAPD in the hybrid system. In addition, the generated surface roughness after the dry etching was favorable for creating the appropriate surface bonding area and mechanical interlocking between NDC films and Ti substrates, leading to reliable adhesion quality.

2. Experimental procedures

2.1. Growth of nanodiamond composite films in different conditions

Nanodiamond composite (NDC) films were grown on commercially supplied Ti substrates (grade 2) measuring $1 \times 10 \times 10 \text{ mm}$ using the CAPD method. Prior to film growth, the Ti substrates were cleaned ultrasonically in acetone, methanol, and deionized water (DI) for 5 min each using SND, US-1 ultrasonic cleaning machine. The sonication power and frequency used were 80 W and 38 kHz, respectively. For sample (1), the Ti substrate was additionally immersed in 1% diluted HF acid for 3 min (optimized) and then in DI to remove any residual HF acid. In contrast, for sample (2), a TiC intermediate layer was deposited directly from a TiC target onto an untreated Ti substrate using D.C. sputtering operated with 60 W and 600 V. The TiC target (Toshima Manufacturing Co., Ltd, Japan) [$\varphi 76.5 \times 5 \text{ t}$] was sputtered with Ar^+ ions for 15 min at a pressure of 10 Pa. To ensure the diffusion of carbon atoms into the Ti substrate and generate a chemical composition gradient, sample (2) was annealed using a rapid thermal annealing (RTA) machine (MILA-5000, Advance Riko, Inc., Japan) at 800 °C for 10 min.

Regarding the CAPD technique, an arc plasma gun (APS1, Advance Riko, Japan) equipped with a cathodic graphite target (Nilaco corp. Japan, purity 99.99%, $\varphi 10 \times 30 \text{ mm}$) located inside a coaxial cylindrical anode was used as a highly dense and energetic source of carbon ions (C^+) to deposit NDC films, as shown in figure 1(a). To avoid any residual internal stress due to the mismatch in the thermal expansion coefficients of NDC films and Ti substrates, NDC buffer layers were deposited on both sample (1) etched with HF acid and sample (2) with an inserted TiC intermediate layer, respectively, with 350 and 500 pulses at 550 °C by an external heater connected to the substrate holder. The arc discharge was operated at a frequency of 1 Hz and a discharge voltage of 100 V, paired with a 720 μF capacitor. Finally, the two samples were allowed to cool down to room temperature under vacuum before the final deposition of NDC top layer.

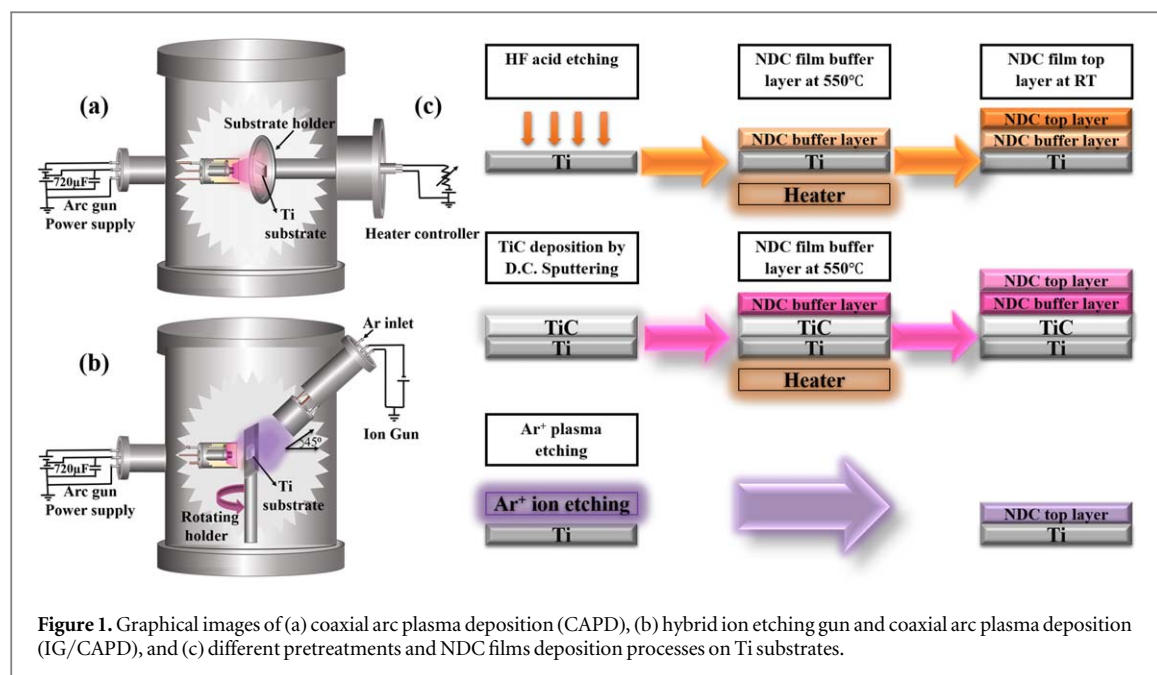


Figure 1. Graphical images of (a) coaxial arc plasma deposition (CAPD), (b) hybrid ion etching gun and coaxial arc plasma deposition (IG/CAPD), and (c) different pretreatments and NDC films deposition processes on Ti substrates.

Table 1. Preparation conditions of the deposited NDC films on different pretreated-Ti substrates.

Pretreatment nature		<i>Ex-situ</i>		<i>In-situ</i>
		Sample 1	Sample 2	Sample 3
Pretreatment method		HF acid etching	TiC D.C. sputtering	Ar ⁺ plasma etching
Etching	Time (min)	3	15	15
	Thickness (nm)	—	448	—
	Surface roughness (nm)	251.05	70.46	47.18
TiO ₂ elimination		Incomplete	Incomplete	Efficiently complete
NDC film buffer layer	Number of pulses	350	500	—
	Substrate temperature (°C)	550	550	—
	Thickness (nm)	200	300	—
NDC film top layer	Substrate temperature (°C)	Room temperature	Room temperature	Room temperature
	Thickness (nm)	746	900	3000

In a different manner, sample (3) was prepared via a hybrid configuration of ion gun (IG) and CAPD technique (IG/CAPD), as shown in figure 1(b). The IG was used *in situ* to etch the native TiO₂ layer and other impurities on the Ti substrate using Ar⁺ ions. The pressure during the etching process was maintained at 7×10^{-2} Pa, while the IG was operated at 1 kV to ignite Ar glow discharge under a gas flow of 3 sccm. To attract and accelerate the Ar⁺ ions towards the Ti substrate, the substrate holder was negatively biased with a D.C. voltage power supply of -500 V. The etching duration was optimized to last 15 min with a conformable etching rate of 44 nm min^{-1} before switching off the ion gun and the negative bias. Subsequently, the sample holder was rotated to face the *in situ* arc plasma gun, and NDC films were deposited at room temperature and at the same base pressure. More details on the sample preparation can be found in our previous work [19]. Figure 1(c) and table 1 summarize the conditions used to prepare all samples.

2.2. Characterizations of nanodiamond composite films

The surface roughness of bare- and pretreated-Ti substrates was observed using a 3D laser scanning microscope (Keyence VHX11nn). Following the deposition of NDC films, the thickness of the films on all pretreated Ti substrates was measured from cross-sectional images obtained by field emission scanning electron microscopy (FE-SEM) (JEOL/JSM-IT700HR). FE-SEM was also used to capture top-view images of the NDC films for morphology exploration. The depth profile of the films was determined by analyzing cross-sectional SEM images and energy-dispersive x-ray spectroscopy (EDX) for a survey and detailed chemical composition acquisition. For mechanical characterization, the adhesion strengths of the NDC films were evaluated using scratch tests with a Rockwell diamond indenter (N2-7269) with a tip radius of $200 \mu\text{m}$. The indenter loading gradually increased parallel to the film with a steady load rate of 100 N min^{-1} , stopping gently when the load

reached 50 N. The exfoliation points in the films within a groove length of 4.9 mm referred to the critical load value, which is a direct indication of adhesion strengths, and were confirmed by optical microscope images to emphasize side-by-side peeling fractions along the scratch track. Moreover, the hardness and elastic modulus of the NDC films were estimated by a nanoindentation test using a nanoindenter (Picodentor HM500) equipped with a Berkovich diamond indenter. The penetration depth of the nanoindenter did not exceed ten percent of the film thickness to prevent substrate impact on the measurement [20]. This was achieved by applying a load force of 5 mN/10 s.

Raman spectroscopy (MicroRam-300ATG) was employed to investigate the crystalline structure of the nanodiamond crystallites embedded in the NDC films. Raman spectroscopy is a powerful and non-destructive technique to identify all members of the carbon family. The evaluation was performed using a confocal microscope (in Via, Renishaw) paired with an excitation laser beam of 532 nm, while a 5% laser filter was applied to reduce laser power and avoid thermal-induced graphitization or noise. The Raman scattering wavenumber axis was calibrated using a commercially-supplied standard single crystalline diamond sample (HPHT Ib, Sumitomo Electric Industries) grown under high pressure and high-temperature conditions of 5 GPa and 1300 °C or higher. This diamond sample exhibits a characteristic Raman peak at 1333 cm^{-1} which serves as a reference peak for calibration. It is worth noting that for single crystalline diamond, the shift is not more than $\pm 1.0\text{ cm}^{-1}$ from the diamond peak position of 1333 cm^{-1} [21]. To investigate the structural composition and chemical bonding in the NDC films, x-ray photoelectron spectroscopy (XPS) was employed. A survey scan of the XPS was collected using an incident photon energy of 1253.6 eV from a Mg K α line source. The C 1 s photoemission spectra were conducted at beamline 12 of Kyushu Synchrotron Light Research Center/Saga Light Source (SAGA-LS), using an incident photon energy of 350 eV. The parameters of the peaks associated with the sp^2 - and sp^3 -bonded carbon were calculated by fitting the experimental spectra of Raman and XPS with a Voigt function using OriginPro software (OriginLab Corporation, USA).

3. Results and discussion

A 3D laser scanning microscope was used to investigate the roughness of Ti substrates over an area of ($129 \times 130\text{ }\mu\text{m}^2$) before and after the pretreatments, as shown in figure 2. The bare Ti substrate had an estimated roughness of 42.76 nm, as indicated in figure 2(a). HF acid-etched Ti substrate (1) induced a significant increase in roughness, with a roughness value of 251.05 nm on the bare Ti substrate, as shown in figure 2(b). The TiC intermediate layer roughness on the bare Ti substrate (2) was 70.46 nm, as depicted in figure 2(c). However, a minor increase to 47.18 nm in the roughness value of the bare Ti substrate (3) was detected after Ar $^+$ plasma etching, as shown in figure 2(d). In order to explore the relationship between the outermost oxide layer and stimulated roughness after substrate pretreatment alteration, detailed EDX measurements of the instant pretreated-Ti substrates were performed.

The bare Ti substrate had an oxygen contribution of $2.78 \pm 0.03\%$, indicating the presence of the exterior TiO $_2$ phase, as shown in figure 2(e). On the other hand, the oxygen content of the HF acid-etched Ti substrate (1) decreased only slightly, to $2.06 \pm 0.04\%$, compared to the bare Ti substrate, as shown in figure 2(f). This can be explained by the drastic increase in roughness (251.05 nm) after HF acid-etching (confirmed by 3D laser scanning microscope) and the associated oxide topography in the roughened grooves [20]. The correlated increased surface contact area is anticipated to act as oxygen traps over time. In addition, the sputtered TiC intermediate layer on top of the Ti substrate (2) showed a carbon contribution of $2.53 \pm 0.01\%$, emphasizing the carbide phase, with much oxygen content of $8.37 \pm 0.06\%$, as shown in figure 2(g). The largest oxygen content in the substrate (2) with TiC intermediate layer among other pretreatments could be ascribed to double contribution of oxygen to the TiC intermediate layer through either incorporation into an amorphous TiO $_2$ phase or as substitutional oxygen in carbon positions in the TiC phase [22]. This happens even after the annealing process, which eliminates the oxide contribution but re-oxide during sample transfer from the annealing machine to the CAPD for NDC film deposition. Meanwhile, the oxygen content was significantly decreased to $0.48 \pm 0.02\%$ after Ar $^+$ plasma-etching of the Ti substrate (3), as shown in figure 2(h), indicating the absolute efficiency in completely removing the TiO $_2$ layer. Nonetheless, the hybrid (IG/CAPD) design provides adequate protection against further oxidation. We undoubtedly believe that the negligible amount of oxygen found might have been acquired during EDX processing.

At room temperature, an ordinary model of deposited NDC film on a bare Ti substrate using the CAPD technique delaminates due to the existence of the native TiO $_2$ layer on the substrate surface, as shown explicitly in figure 3(a). Nevertheless, SEM measurements confirm successful growth of NDC films for all samples investigated, as obvious in figure 3. Our previous report [23], demonstrated that an adhesive NDC buffer layer deposited at 550 °C on a Si substrate is indispensable for achieving thick NDC film adhesion at room temperature using CAPD to relieve the residual internal stress. Similarly, we deposited an adhesive NDC buffer

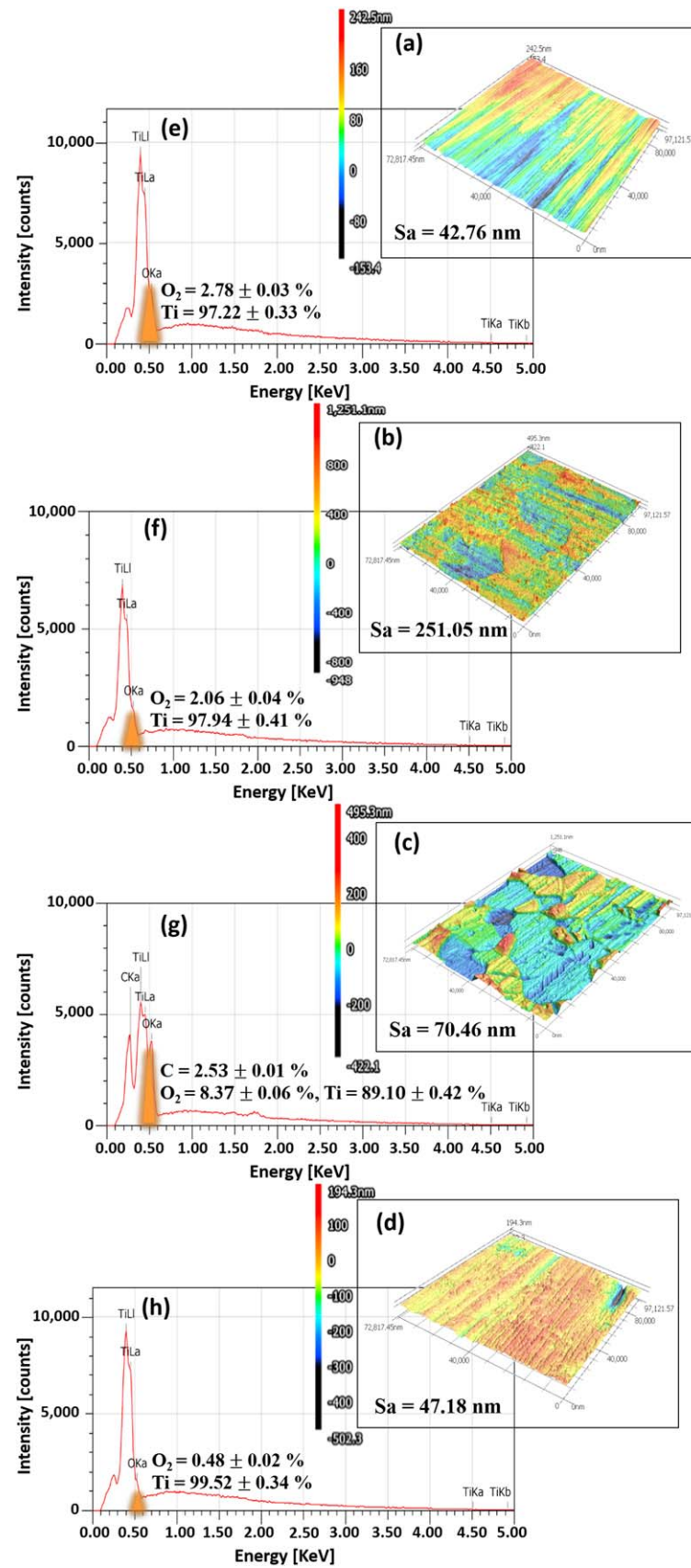


Figure 2. 3D Laser scanning microscope surface roughness measurement of (a) bare Ti substrate, (b) HF acid-etched Ti substrate (3 min), (c) TiC intermediate layer deposited on Ti substrate (15 min), and (d) Ar⁺ plasma-etched Ti substrate (15 min). EDX measurement of (e) bare Ti substrate, (f) HF acid-etched Ti substrate (3 min), (g) TiC intermediate layer deposited on Ti substrate (15 min), (h) Ar⁺ plasma-etched Ti substrate (15 min).

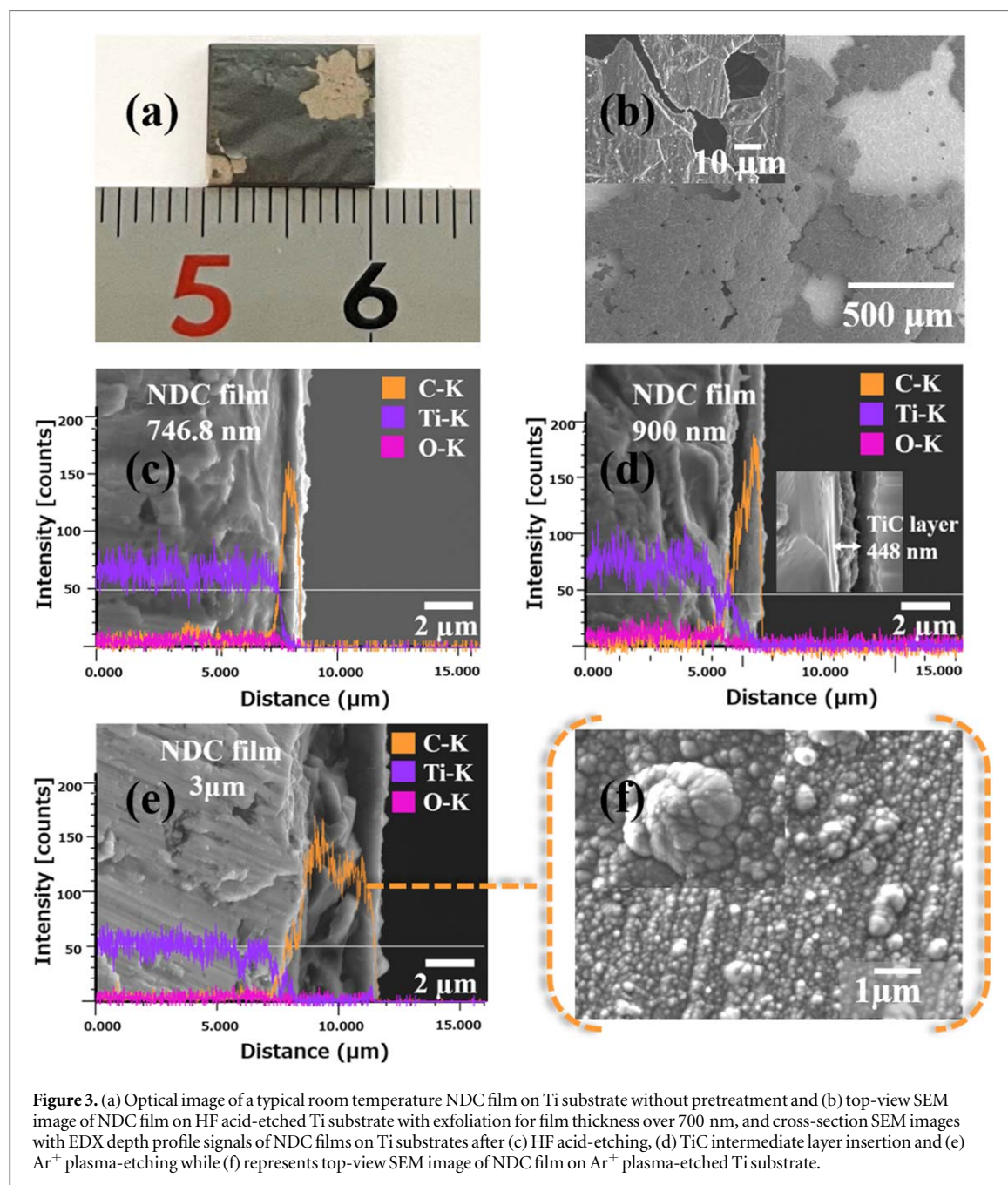


Figure 3. (a) Optical image of a typical room temperature NDC film on Ti substrate without pretreatment and (b) top-view SEM image of NDC film on HF acid-etched Ti substrate with exfoliation for film thickness over 700 nm, and cross-section SEM images with EDX depth profile signals of NDC films on Ti substrates after (c) HF acid-etching, (d) TiC intermediate layer insertion and (e) Ar^+ plasma-etching while (f) represents top-view SEM image of NDC film on Ar^+ plasma-etched Ti substrate.

layer at 550 °C prior to NDC top layer deposition at room temperature on Ti substrate (1) that was etched with HF acid and substrate (2) with the inserted TiC intermediate layer. The NDC film's thickness on the HF acid-etched Ti substrate (1) was limited to 746 nm, as shown in figure 3(c). Subsequently, figure 3(b) reveals top view exfoliation of the NDC film out of the HF acid-etched Ti substrate with increased film thickness of more than 700 nm. Although, the introduced surface micro-pits after HF acid-etching of Ti substrates leads to the preferential enlarged specific surface area for better mechanical adhesion [24], exfoliation of the NDC films with elevated thicknesses may be due to the formation of multiple oxide needles, which are independent of the etching time and weaken the adhesion [25]. Alternatively, the additional TiC intermediate layer of 448 nm in thickness distinctly lies beneath 900 nm of NDC film on Ti substrate (2) as clearly shown in the cross-section image and inset SEM image in figure 3(d). The corresponding EDX signal depth-profile confirms the existence of the TiC phase, with small Ti (colored in purple) and C (colored in orange) peaks at the interface between the Ti substrate and the NDC film. Impressively, direct growth of the room temperature NDC film on the Ar^+ plasma-etched Ti substrate (3) is apparently approved, persistently protecting the entire substrate area without any porous or split morphology, as claimed by figure 3(f). The film thickness is 3 μm from SEM cross-section evaluation as shown in figure 3(e) and no peeling off was observed, even for increased thicknesses, without additional adhesive buffer layers.

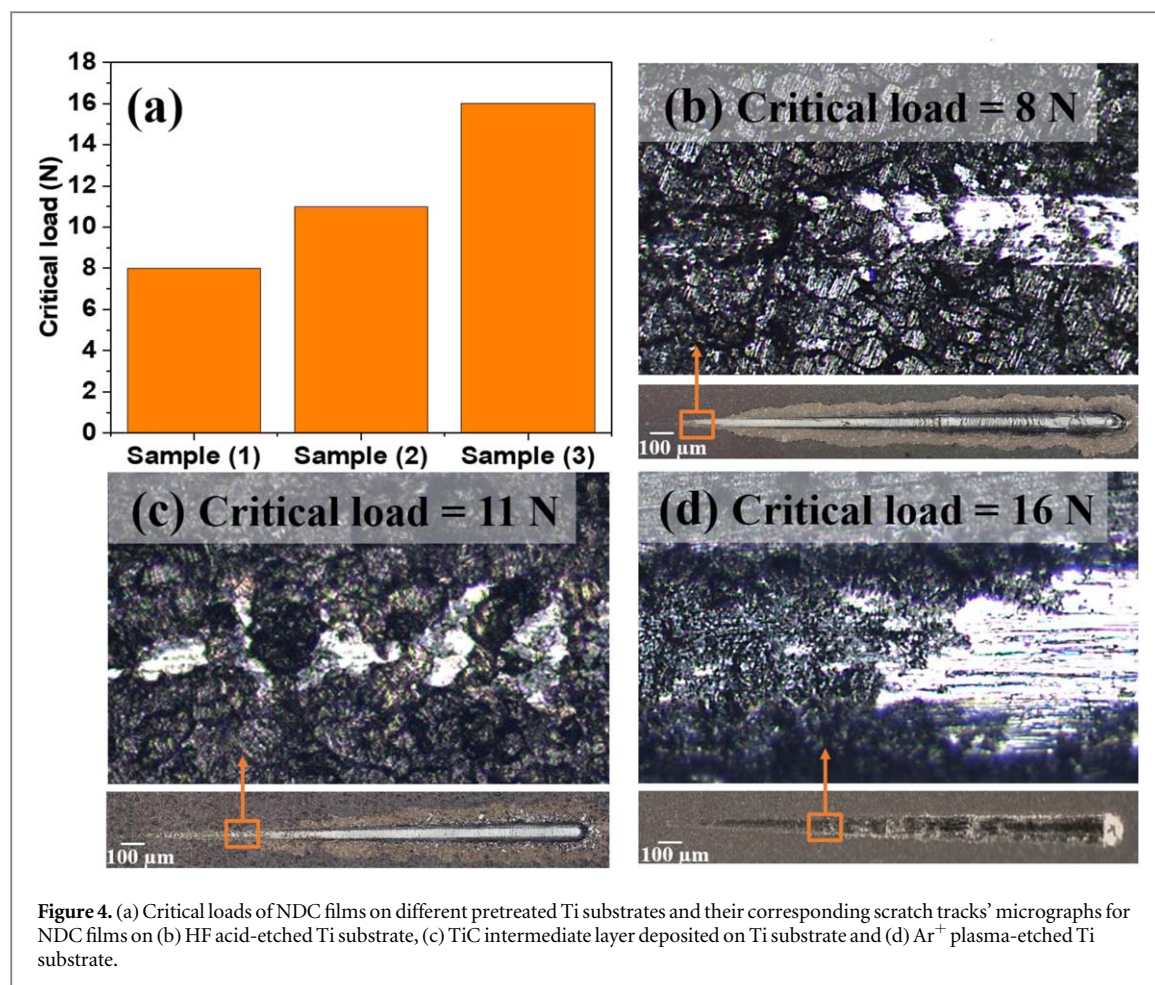
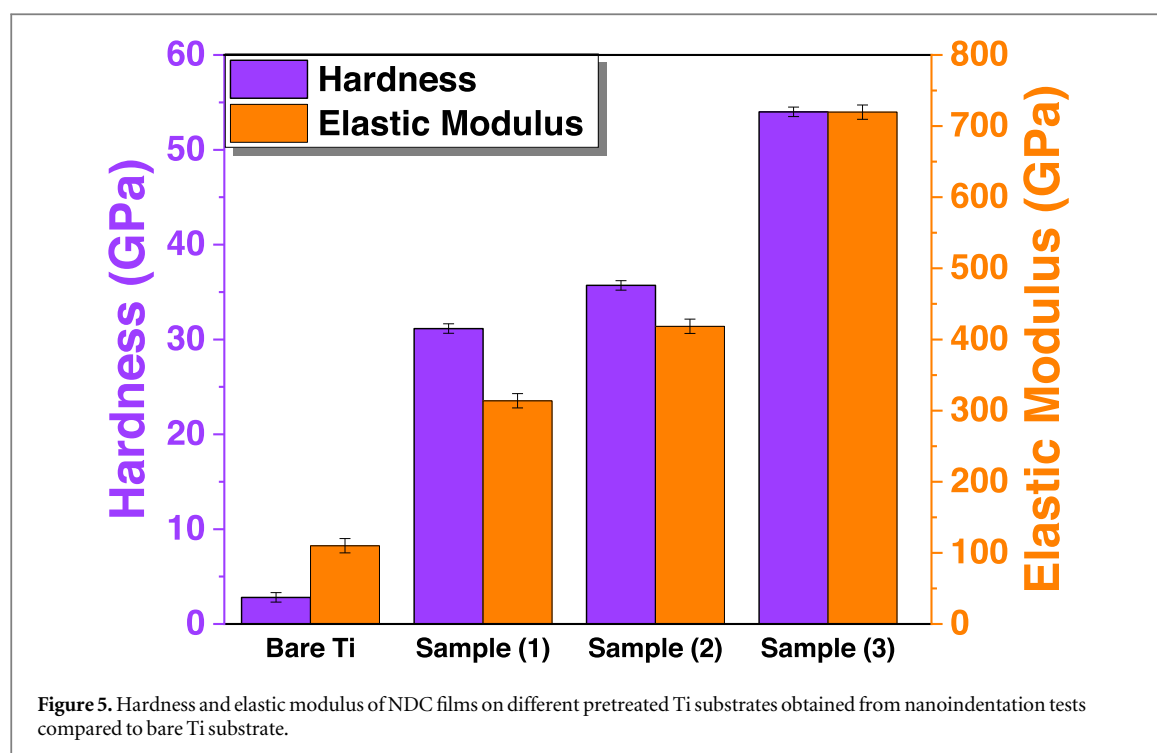


Figure 4. (a) Critical loads of NDC films on different pretreated Ti substrates and their corresponding scratch tracks' micrographs for NDC films on (b) HF acid-etched Ti substrate, (c) TiC intermediate layer deposited on Ti substrate and (d) Ar⁺ plasma-etched Ti substrate.

The failure of NDC films to adhere to Ti upon contact with biological media can lead to serious consequences. This is why the adhesion strength of NDC films to Ti is an irreplaceable standard for applications in implants and artificial joints. In this study, we estimated the adhesion strengths of NDC films on Ti substrates that had been pretreated in different ways using Rockwell scratch test. Typically, the scratch test includes four critical load values (L_c): the initial cracking due to film cohesive failure (L_{c1}), the start of spallation and extensive cracking due to film adhesive failure (L_{c2}), film full spallation (L_{c3}), and the ending load of the test (L_{c4}) [26]. Therefore, the (L_{c2}) value is a relevant measure of the film's adhesion strength to the substrate [27].

We successfully performed the scratch test for all the deposited NDC films on the different pretreated Ti substrates. The corresponding critical load values were depicted in figure 4(a) while the scratch groove of the films were represented by optical micro-shots as shown in figures 4(b)–(d). The critical load value (L_{c2}) for sample (1) [NDC film deposited on HF acid-etched Ti substrate] was 8 N as shown in figure 4(b) while, (L_{c2}) value for sample (2) [NDC film over the deposited TiC intermediate layer] was 11 N as clear in figure 4(c). The feeble adhesion strength for sample (1) compared to sample (2) can be attributed to the trapped oxygen content in the roughened surface area after HF acid-etching of the Ti substrate. On the other hand, the improved adhesion strength for sample (2) can be ascribed to two main reasons: firstly, the annealing of the sputtered TiC intermediate layer at 800 °C ensures the thermal interdiffusion of C atoms into the Ti substrate at the interface [28]. Secondly, the deposition of the NDC interlayer at 550 °C affirms the extension of the TiC phase with an intermediate thermal expansion coefficient ($\alpha_{TiC} 7.4 \times 10^{-6} K^{-1}$) and forms overall chemical composition gradient into the top NDC layer at room temperature. Both adhesion strengths are comparable with the adhesion strengths of nitrogenated-DLC films on Ti substrate with Ti/TiC arc intermediate layer (8.1 N) synthesized by plasma enhanced CVD technique [29] and DLC films on laser textured and carburized Ti6Al4V alloy (~12 N) by D.C. pulsed magnetron sputtering system [30].

Furthermore, the adhesion strength of the NDC film is significantly enhanced to 16 N for sample (3) after the Ar⁺ plasma-etching of Ti substrate as displayed in figure 4(d). This result emphasizes the potential of Ar⁺ plasma in external cleaning of the substrate from impurities and total removal of the TiO₂ layer, stimulating mechanical interlinking, and enlarging active bonding surface sites between Ti substrate and NDC film through the induced nano-grooves [31]. The posterior growth of the NDC film with the arc plasma gun in the hybrid design without further exposure to the ambient atmospheric oxygen during the process is also reliable.



Alves *et al* [32] reported that plasma etching yields better coating adhesion to the substrate than chemical etching, which is consistent with our findings. Besides, the lower adhesion strength of sample (2) with the inserted TiC intermediate layer compared to sample (3) with Ar^+ plasma-etching can be assigned to the presence of residual oxide traces at the interface between the Ti substrate and TiC intermediate layer (as no oxide removal process was carried out), as well as contamination or exposure to atmospheric oxygen during the relocation of the sample for NDC film deposition (as supported by the high oxygen content observed in the EDX measurement, as shown in figure 2(g)). Despite these factors, we were able to achieve well-adherent NDC films on Ti substrates under both conditions using the CAPD technique at room temperature.

The mechanical properties of the deposited NDC films was investigated through the load-displacement curves obtained from nanoindentation tests using the Oliver-Pharr model [33]. Prior to conducting the tests, NDC films on the different pretreated Ti substrates were polished to a mirror-like finish to prevent the influence of surface adsorbed oxygen functional groups (C=O) and (C-O/C-O-C) resulting from atmospheric exposure on the accuracy of hardness measurements. Figure 5 depicts the hardness and elastic modulus of the films on different pretreated Ti substrates compared to the bare substrate. The hardness and elastic modulus values of the bare Ti substrate were 2.1 and 110 GPa, respectively [34, 35]. Remarkably, these values experienced a significant improvement upon deposition of NDC films on the Ti substrate, regardless of the pretreatment method employed. The NDC films exhibited hardness values of 31.15, 35.7, and 54 GPa, along with corresponding elastic modulus values of 313.8, 418.53, and 719.61 GPa, for HF acid-etched, TiC intermediate layer-inserted, and Ar^+ plasma-etched Ti substrates, respectively. This emphasizes the exceptional potential of NDC films in providing significantly enhanced hardness, surpassing the magnitude of the bare Ti substrate by at least fifteen times. As shown, the NDC film on the Ar^+ plasma-etched Ti substrate (3) exhibited the highest hardness and elastic modulus values, while the NDC film on the HF acid-etched Ti substrate (1) had the lowest values. The low hardness value of the NDC film on the HF acid-etched substrate (1) is likely due to the accumulation of oxide needles on the highly roughened surface after HF acid-etching, which may facilitate the formation of undesired sp^2 (C=O) or sp^3 (C-O/C-O-C) chemical bonds responsible for film softening [36]. Nonetheless, the unprecedented film hardness (54 GPa) and elastic modulus (719.61 GPa) values obtained after the Ar^+ plasma-etching of Ti demonstrate the exceptional effectiveness in eliminating sp^2 chemical bonding (due to oxygen or contaminant presence) and promoting sp^3 (C-C) bonding responsible for film hardening [37].

The obtained NDC film's hardness at room temperature after the Ar^+ etching is two orders of magnitude higher than the hardness of Si-DLC coating with Cr sublayer on negatively biased Ti-29Nb-13Ta-4.6Zr (TNTZ) alloys (27.2 GPa) deposited using magnetron sputtering [38]. Furthermore, this hardness value is comparable to the hardness of nanocrystalline diamond (NCD) films prepared by microwave plasma CVD on Ti6Al4V alloys at substrate temperatures of around 750 °C [39]. Additionally, these findings are consistent with our previous reports on NDC/WC (51 GPa) [18] and NDC/Si (55 GPa) [23] using the CAPD technique at room temperature.

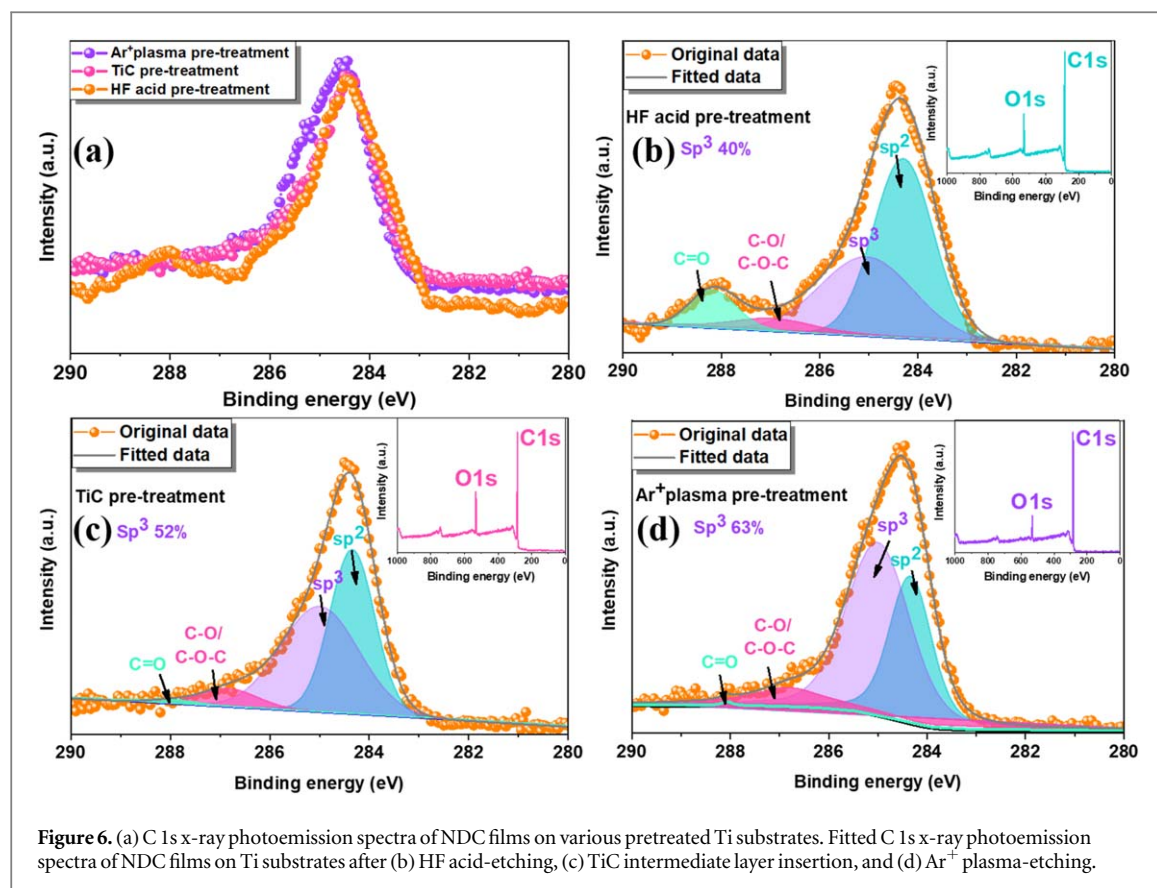


Figure 6. (a) C 1s x-ray photoemission spectra of NDC films on various pretreated Ti substrates. Fitted C 1s x-ray photoemission spectra of NDC films on Ti substrates after (b) HF acid-etching, (c) TiC intermediate layer insertion, and (d) Ar⁺ plasma-etching.

Table 2. Mechanical properties of NDC films on different pretreated Ti substrates' conditions.

Pretreatment method	Sample 1 HF acid etching	Sample 2 TiC D.C. sputtering	Sample 3 Ar ⁺ plasma etching
NDC film's adhesion strength (N)	8	11	16
NDC film's hardness (GPa)	31.15	35.7	54
NDC film's elastic modulus (GPa)	313.8	418.53	719.61
NDC film's sp^3 content (%)	40	52	63

C 1s x-ray photoemission spectra of NDC films were obtained from core levels of NDC films after various pretreatments of Ti substrates using synchrotron radiation to reveal the film's chemical bonding configurations. A detailed analysis of the C 1s x-ray photoemission spectra of the NDC films for the different Ti substrate pretreatments is shown in figure 6(a) which reveals a matching behavior except for a slight broadening towards higher binding energies. This broadening is relevant to the expansion in sp^3 hybridized carbon content in the films and the decrement into sp^2 hybridization content [40]. The spectrum from NDC film on HF acid-etched Ti substrate (1) exhibits the slightest tendency to broaden towards higher binding energies, which means the lowest sp^3 content and corresponding lowest film hardness (31.15 GPa) [41]. The spectrum from the film on the inserted TiC intermediate layer on Ti substrate (2) has an averaged broadening (averaged sp^3 content) with intermediate film hardness (35.7 GPa) among the three samples. Moreover, the spectrum from the film on the Ar⁺ plasma-etched Ti substrate (3) has the largest broadening towards the higher binding energies, which explains why it has the highest film hardness (54 GPa) as an indication of the largest sp^3 content in comparison [37].

To gain a deeper understanding of the sp^3 contents in NDC films, the detailed C 1s x-ray photoemission spectra were fitted into their component peaks. Voigt function was used to fit the spectra into sp^2 (C=C), sp^3 (C-C), and atmospheric oxygen related component peaks C-O/C-O-C and C=O at 284.3, 284.9, 286.7, and 288 eV [42] respectively, after Shirley's background abstraction. The associated sp^3 content in NDC films can be calculated from the $sp^3/(sp^3+sp^2)$ ratio deduced from the areas below the fitted sp^3 and sp^2 peaks [43]. Based on that, sp^3 contents in NDC films are 40, 52, and 63% for sample (1) with HF acid-etching as shown in figure 6(b), sample (2) with TiC intermediate layer insertion as in figure 6(c) and sample (3) with Ar⁺ plasma-etching as in figure 6(d) which are consistent with their corresponding hardness strengths as tabulated in table 2.

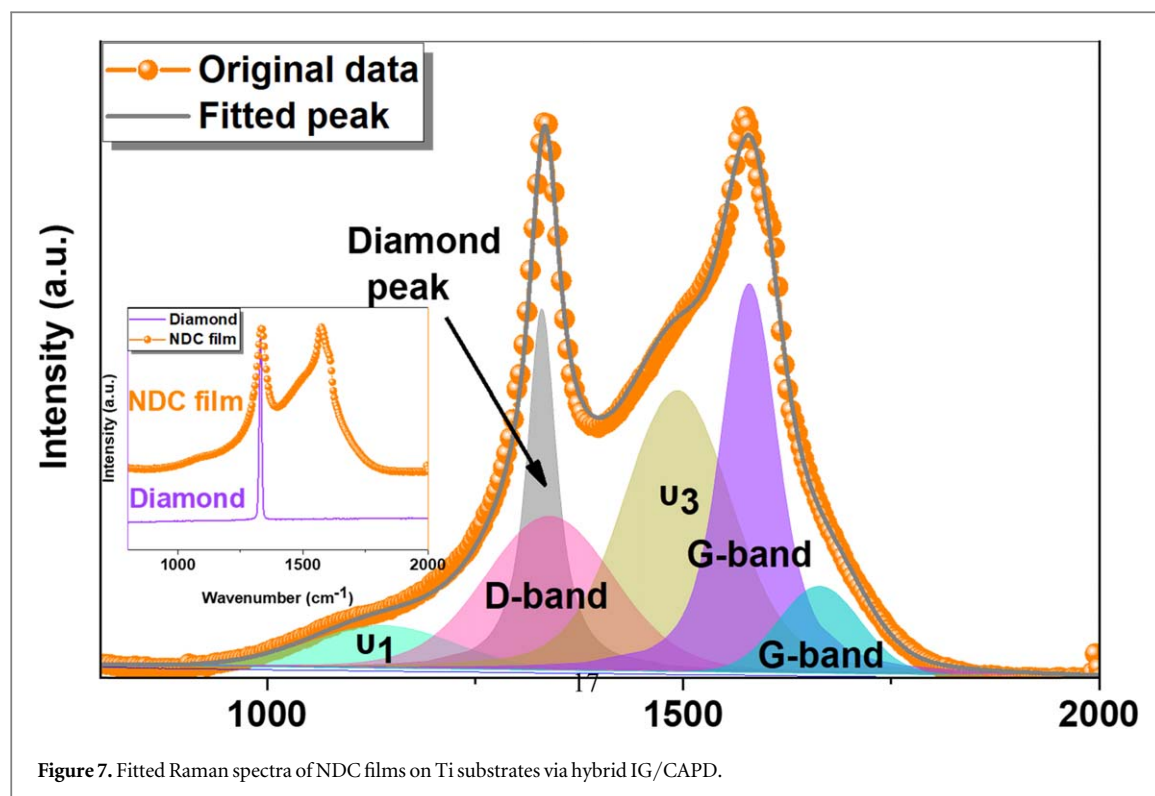


Figure 7. Fitted Raman spectra of NDC films on Ti substrates via hybrid IG/CAPD.

The diversity in the sp^3 content in the films strongly credited to the abundant participation of doubly carbon-oxygen bonding that adds up to sp^2 bonding hybridization. The raised surface roughness and the large accompanied surface area (oxygen traps) after the HF acid-etching of substrate (1), as revealed by EDX and 3D laser scanning microscope data, are thought-provoking for the highest doubly carbon-oxygen bonding responsible for the lowest film hardness of 31.15 GPa. Survey spectra for NDC films with changeable substrate pretreatments were carried out using the $MgK\alpha$ line, as shown in the insets of figures 6(b)–(d). The spectra only disclose binding energy peaks at 284.5 and 532.5 eV correlated to C1s of NDC films and O1s of the atmospheric oxygen contribution to the films' surface after deposition. In the case of HF acid-etched Ti substrate (1), it has an unprotected transfer process prior to NDC deposition via CAPD in addition to the related considerable roughened surface area that contains plentiful oxide needles. Similarly, the TiC intermediate layer on the Ti substrate (2) is vulnerable to atmospheric oxidation during transfer to the NDC film deposition chamber (CAPD), even after the annealing process that removes oxygen. However, the hybrid configuration of the Ar^+ ion gun and CAPD clearly demonstrates the ability to deposit NDC films without oxide layer inclusion, resulting in the highest sp^3 content and greatest hardness.

To confirm the presence of diamond phase in the NDC films fabricated on Ar^+ plasma-etched Ti substrates, visible Raman spectrum was obtained with a laser excitation line of 532 nm, as shown in figure 7. The spectrum was decomposed into six component peaks located at wavenumber positions 1141, 1333, 1343, 1496, 1583 and 1668 cm^{-1} , using a Voigt function. The reliable signature of the nanodiamond phase in the films was verified by the presence of two correlated humps ($\bar{\nu}_1$) and ($\bar{\nu}_3$) appearing at 1141 and 1496 cm^{-1} respectively, which are associated with the (C=C) chain stretching and (C-H) wagging modes of trans-polyacetylene (t-PA) segments at the grain boundaries of NDC films [44]. A diamond peak was clearly observed at 1333 cm^{-1} [45] which confirms the presence of first-order sp^3 (C–C) diamond bonding. In the visible Raman spectra, the diamond peak is hybridized with the D-band located at 1343 cm^{-1} . This D-band originates from the disordered sp^2 hybridized carbon atoms, indicating the presence of an amorphous or graphitic carbon phase at the grain boundaries [46]. Moreover, multiple G-band phonons are Raman allowed (up to six) with two dominant peaks observed at 1583 and 1668 cm^{-1} , respectively, which are linked to the doubly degenerate zone center E_{2g} mode of graphite due to sp^2 (C=C) hybridized carbon atoms [47].

4. Conclusions

In this study, we thoroughly investigated the impact of Ti substrate pretreatment on the mechanical and structural properties of NDC films by CAPD. We found that *ex situ* pretreatment of Ti substrates using HF

acid-etching partially removed the native TiO₂ layer. In addition, the insertion of the TiC intermediate layer further enhanced the adhesion of NDC films on Ti substrates. However, the residue atmospheric oxygen at the interfaces limited the adhesion strength of the NDC films on Ti after both *ex situ* pretreatments. In contrast, *in situ* Ar⁺ ion etching was advantageous in completely removing the hindering TiO₂ layer and initiating beneficial roughness for dynamic adhesion. The innovative hybrid configuration of Ar⁺ IG and CAPD facilitated adhesion of thick NDC films (>3 μm) on Ti substrates at room temperature with high hardness (54 GPa) and adhesion (16 N) strengths. These results are remarkable given the challenges of producing NDC films on Ti substrates at room temperature and competes with similar diamond films grown by CVD and PVD facilities. Moreover, the IG/CAPD technique is a powerful tool for inexpensive, eco-friendly, and fast NDC film mass production.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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