

Structure and Morphology of Diamond-like Carbon Coated on Nylon 66/Poly(phenylene ether) Alloy

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Abstract

In order to investigate the structure and morphology of diamond-like carbon (DLC) film coated on a polymer alloy prepared by a particular four-steps method in the plasma-based ion implantation and deposition (PBIID) process, studies were made on the structure and properties of the DLC film with special reference to its surface morphology by scanning (SEM) and transmission (TEM) electron microscopies. It is revealed from TEM microscopy that the amorphous structure of the DLC film consists of a silicon-implanted layer on the polymer substrate, a hard acetylene-implanted layer and a flexible acetylene/toluene-deposited layer. Some properties of the DLC film can be accounted for by the morphology examined in this study.

KEY WORDS diamond-like carbon / DLC / coating / plasma / implantation / polymer alloy / TEM / XPS

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Surface treatments of polymeric materials¹ are important methods for various industrial, medical and other applications. Plasma chemistry plays a role in surface treatment of polymers through use of low temperature glow discharge, ion beam bombardment and so on in gaseous state.^{2,3}

Since Aisenberg *et al.*⁴ applied ion beam to deposition of thin diamond-like carbon (DLC) film, a sort of network polymers mainly consisting of carbon and hydrogen, onto other materials, attentions have been paid to its hardness similar to diamond, tribological properties with low friction and wear, gas barrier properties, improved blood compatibility and so on.⁵ As is reviewed by Suzuki *et al.*⁶, many studies were made on the structures and properties, methods for preparation and applications of various kinds of coated DLC films.

Of these properties of DLC films, their tribological properties are of great interest because of their roles in improving the surface properties of metals, ceramics, polymers and composites by DLC coatings with special reference to their chemical structures, variable hardness, and low friction and wear.

Recently, studies on DLC coatings onto polymer surfaces have been increasingly focused on their friction and wear properties,⁷⁻¹⁷ a few on gas barrier enhancement^{14,15,18} and so on. In these studies, the tribological properties of DLC-coated polymers are mainly discussed in relation to the surface hardness and roughness, adhesive strength and surface morphology measured by optical and scanning electron microscopies. However, no detailed morphological study has been so far reported on the DLC films coated onto polymer surfaces by means of transmission electron microscopy (TEM) which may be a promising method for revealing the interface structure.

Of various DLC coating methods developed so far, ion beam deposition and ion beam assisted deposition methods are not preferred to complicated geometry of substrate specimens, and plasma-enhanced chemical vapor deposition and pulsed laser deposition methods usually need heating of specimens.¹⁹ On the other hand, a very recently developed method, i.e., a hybrid process of plasma-based ion implantation and deposition (PIIBD)²⁰ is promising for polymeric substrates because of prevention of temperature increase and residual compressive stress almost two orders less than that for

conventional methods for DLC films on quartz glass plate.²¹ In addition, PBIID can produce a mixing interface between a DLC film and a substrate and a uniform DLC film coating on three dimensional substrate.^{21,22} In this study, PIIBD method is applied to DLC coating onto a polymer alloy.

In this paper, we will mainly report on the structure and morphology of a DLC-coated polymer alloy, consisting of nylon 66 and poly(phenylene ether), prepared by the PBIID method and its properties will be also discussed. The present study will be of importance for investigation of the tribological properties of DLC-coated polymers by the PBIID method.

EXPERIMENTAL

Polymeric substrates

As for a polymeric substrate for DLC coating, Noryl GTX6601 of GE Plastics Co. was chosen, which is a polymer alloy consisting of nylon 66 matrix and modified poly(phenylene ether) (PPE) domains, having properties such as dimensional stability, low water absorption, heat resistance and chemical resistance..

The polymer specimen subjected to DLC coatings was injection-molded into disks with a diameter of 70 mm and a thickness of 5 mm.

DLC film coating

The DLC film coating onto the polymeric surface was carried out according to the PBIID method.^{20,22} A schematic diagram of PBIID system is shown in Fig. 1. In this system, RF pulse for plasma generation was supplied to the substrate together with a negative high voltage pulse for ion implantation through a single electrical feed-through using a matching circuit for both pulses. As the substrate itself was used as an RF antenna, uniform plasma was generated around the substrate. A four-steps procedure for DLC coating²⁰ was carried out in this experiment. The sequence for DLC film coating procedure is summarized in Table 1.

Prior to DLC film coating, the disk specimen surface was sputter-cleaned for 10 min in the first step using a 300 W RF plasma of mixed gas of Ar (50%) and CH₄ (50%) at a

pressure of 0.4 Pa with a negative medium-voltage pulse (voltage: -5 kV, duration: 5 s, repetition rate: 2 kHz) in a stainless steel reaction chamber,²⁰ which has a gas inlet with a pressure and flow control system and a connection to pump through an oil diffusion pump. Flow rate of each gas was $30\text{ cm}^3/\text{min}$.

In order to produce a mixing interface between the polymeric substrate and DLC film to be coated for their improved adhesion, silicon ion implantation with a high voltage pulse (voltage: -5 kV, duration: 5 s, repetition rate: 1 kHz) and RF output power of 300 W was performed through the single electrical feed-through in the second step, where were made a flow rate of $15\text{ cm}^3/\text{min}$ and a flow time of 15 min of a precursor gas hexamethyl disiloxane (HMDS) for silicon implantation.

The third step was carried out to further produce the second mixing interface and then to produce DLC film using acetylene (C_2H_2) plasma by the same method as applied to the silicon ion implantation except for a flow rate of $100\text{ cm}^3/\text{min}$ and a flow time of 30 min.

In the last fourth step, deposition of DLC film was made using a mixed gas of C_2H_2 (flow rate: $90\text{ cm}^3/\text{min}$) and toluene ($\text{C}_6\text{H}_5\text{CH}_3$, flow rate: $20\text{ cm}^3/\text{min}$) with a flow time of 240 min.

X-Ray photoelectron spectroscopy (XPS)

Chemical elements of the specimen surface were measured by XPS under a pressure of 1.33×10^{-6} Pa in an Axis-HS spectrometer of Kratos Analytical, Ltd., using monochromated X-ray emitted from Al anode at a power of 150 W. The pass energy for measuring survey and element spectra was 160 eV and 40 eV, respectively. A charge neutralizer was equipped with the spectrometer to prevent peak shifts in the XPS spectrum due to specimen charging induced by X-ray irradiation. An XPS spectrum was recorded for specimen obtained in each PBIID step.

Raman scattering spectroscopy

In order to analyze the structure of the resultant coated DLC film, Raman scattering spectroscopy was carried out using an Ar laser with a wavelength of 514.5 nm in a

Renishaw Ramanoscope spectrometer, recording spectra over a Raman shift range from 200 to 3600 cm^{-1} .

Coated DLC film thickness measurement

The resultant coated DLC film thickness was measured in a Mitsutoyo SV-9634 surface roughness measuring system. After the PBIID procedure was made onto the polymer specimen surface with a piece of an adhesive tape thereon, the tape was peeled off to obtain a part of the specimen surface without DLC film and then the step height was measured at the coated DLC film edge thus formed in the boundary of surfaces with and without DLC film.

Nanoindentation measurement

Surface hardness of the neat polymer alloy and the DLC film coated thereon was measured by nanoindentation in a JEOL JSPM-4210 Scanning Probe Microscope equipped with a Berkovich-type of diamond indenter (tip). According to a reported method,²³ experiments were made using a triangular load-time profile, such that the nanoindenter was first loaded to a peak load (300 N or 500 N) in 5 min and then unloaded in 5 min, recording load-displacement curves during a loading and unloading cycle. Hardness, defined as the pressure under the tip given by the ratio of force to the projected area of plastic deformation, was estimated from the load-displacement curve. The measurement was carried out at 10 different positions of each specimen surface.

Adhesive strength measurement

Adhesive strength of coated DLC film and polymeric substrate was measured as a tensile strength to break using a Rheotech Rheometer RT-2020J-CW. The DLC-coated surface was first plasma etched to enhance an adhesion with a glue. A 5 mm x 5mm square part of the DLC-coated specimen surface was cut by a stainless knife, deep into the polymer substrate just beneath the interface layer. A nylon fiber was then adhered onto the square part using an instantaneously polymerizable cyanoacrylate resin as a glue. After complete adhesion, the specimen thus obtained was subjected to tensile

measurement in the rheometer by drawing normal to the specimen surface at a drawing speed of 6 cm/min.

Scanning electron microscopy (SEM)

Surface morphology of the DLC-coated polymer alloy prepared in each step was examined by a JEOL JSM-6700F field-emission scanning electron microscope after the specimen was coated by Pt with a thickness of 5 nm using a JEOL Auto-Fine Coater JFC-1600.

Transmission electron microscopy (TEM)

Embedding of the DLC-coated samples in an epoxy resin was chosen for preparation of TEM specimen. The sample, which had been cut into a small block suitable for further preparation, was subjected to a treatment by low temperature air plasma generated at 13.56 MHz under a pressure of ca. 13.3 Pa in a Samco Plasma Deposition System Model BP-1 to make the sample surface hydrophilic for a better adhesion to epoxy resin to be embedded therein. The plasma-treated specimen was embedded in an Oken epoxy resin consisting of 2.6 g Epok 812, 1.5 g DDSA, 1.2 g MNA and a few drops of DMP-30, and then cured overnight at 60°C. OsO₄-staining was made at 60°C for 3 h in the vapor phase of solid OsO₄ in order to make the polymeric substrate hard for easy ultrathin sectioning at room temperature. Ultrathin sectioning was made using a diamond knife in a Reichert-Jung Ultracut microtome. The ultrathin sections with thickness of 50 - 60 nm of the OsO₄-stained specimens were collected on copper grids. TEM observation was made at an accelerating voltage of 80 kV in a JEOL 1200EX transmission electron microscope equipped with a LaB₆ filament.

RESULTS AND DISCUSSION

Changes in surface structure in the PBIID process

In order to investigate the changes of surface structure of the polymer alloy Noryl GTX6601 consisting of nylon 66 and PPE in the PBIID process, XPS experiment was

made on the surface of specimen obtained in each PBIID step. Fig. 2 shows XPS spectra of surfaces of neat polymer alloy (a), Ar sputter-etched polymer alloy (b) obtained in the first step, Ar sputter-etched and then silicon ion-implanted polymer alloy (c) obtained in the second step, Ar sputter-etched, silicon ion-implanted and then C₂H₂-implanted polymer alloy (d) obtained in the third step, and Ar sputter-etched, silicon ion-implanted, C₂H₂-implanted and then C₂H₂/C₆H₅CH₃-deposited polymer alloy (e) obtained in the fourth step.

From the chemical structures of nylon 66 (-NH(CH₂)₆NHCO(CH₂)₄CO-) and PPE (-C₆H₄(CH₃)₂-O-), an elemental ratio C:N:O is estimated as 6:1:1 and 8:0:1, respectively. The alloy contains nearly equal amounts of nylon 66 and PPE according to our NMR study.²⁴ Thus, this polymer alloy should contain a large amount of carbon, the least amount of nitrogen and a small amount of oxygen. An XPS spectrum shown in Fig. 2 (a) indicates that the intensity is stronger for oxygen than for carbon. In addition, weak peaks for Si 2s and Si 2p are measured in the spectrum, though the polymer alloy contains no silicon compounds. This result indicates that the strong O1s peak and Si2s and Si2p peaks are due to contaminants such as silica deposited on the specimen. A very weak peak appearing at 400 eV can be assigned to N1s of nylon 66.

As shown in Fig. 2 (b), a strong C1s peak, medium strong O1s peak and no Si2s and Si2p peaks indicate that the polymer alloy surface was completely cleaned by Ar sputtering in the first step of the PBIID process. Fig. 2 (c) shows that silicon was implanted into the cleaned polymer alloy surface as is evident from medium strong Si2s and Si2p peaks. The intensity of O1s peak stronger than that of C1s one may be due to implanted oxygen together with silicon because HMDS was used as a precursor. This result suggests that oxygen tends to be implanted more than carbon, although HMDS contains 6 carbon atoms and 1 oxygen atom in the molecule. It is also noted that the intensity of N1s peak decreased down to a noise level, indicating that silicon was homogeneously implanted over the whole range of the polymer alloy surface.

Fig. 2 (d) shows an XPS spectrum of the C₂H₂-implanted surface obtained in the third step. This spectrum clearly indicates a drastic change in the surface structure such that Si2s and Si2p peaks completely disappeared and the O1s intensity is weak as

compared with that of C1s. In addition, N1s peak also disappeared. This result suggests that C₂H₂-implantation was successfully made onto the silicon-implanted polymer alloy surface.

An XPS spectrum shown in Fig. 2 (e), which was measured for the C₂H₂/C₆H₅CH₃-deposited polymer alloy obtained in the last step, is very similar to that of Fig. 2 (d), except for a little increase in O1s intensity probably due to somewhat an effect of the ambient air because a noise level N1s peak also appears in the spectrum. Taking into consideration that the XPS measurement was done for the specimen once exposed to air for a certain time after the PBIID process, the appearance of oxygen peak does not always indicate oxygen implantation in the PBIID process. The content of oxygen is estimated to be much lower in the coated DLC film than that measured by the XPS experiment, though the existence of oxygen in the coated DLC film can not be denied.

Structure of coated DLC film

As is reviewed in literatures,^{6,15,25,26} the structure of DLC is amorphous, consisting of both sp³ and sp² bondings, while diamond and graphite, which are both crystalline, are composed of sp³ and sp² bondings, respectively. Namely, DLC has both diamond structure with sp³ bondings and graphite structure with sp² bondings. Additional sp³ C-H bondings give rise to a long-range disordered structure of DLC.²⁶ Raman scattering spectroscopy is useful for characterizing DLC structure such that broad Raman bands centered at ca.1350 cm⁻¹ (D-band) and 1580 cm⁻¹ (G-band) are assigned to the disordered and graphite structure, respectively.^{6,25} In Fig. 3 is shown a Raman spectrum of the DLC film coated onto the polymer alloy obtained in the fourth step of the PBIID process. The spectrum has two distinctive peaks at ca. 1360 cm⁻¹ and ca. 1580 cm⁻¹, typical of DLC film. This result clearly indicates that the DLC film was coated on the silicon- and C₂H₂-implanted interface which had been formed on the polymer alloy surface, as is evident from the XPS results mentioned above.

Thickness of coated DLC film

Thickness of the DLC film coated on the polymer alloy was estimated as ca. 1 μm by measuring its step height as was mentioned in experimental. Taking into consideration that the third and fourth steps for 30 min and 240 min, respectively at similar gas flow rates, in the DLC coating process contribute to the resultant film thickness, an average rate of DLC film thickening can be estimated as ca. 3.7 nm/min.

Adhesive strength

Adhesive strength as an average tensile strength to break for the DLC-coated polymer alloy was estimated as 2.4 MPa. It is noted that the tensile break of the specimen took place at the glue resin. The true adhesive strength of the DLC-coated polymer alloy may be, therefore, higher than 2.4 MPa.

The above-obtained adhesive strength with magnitude of a few MPa is comparable to reported values of 1.1 – 3.0 and 2.0 – 3.7 MPa for DLC-coated polyethylene and silicone, respectively.⁸

Surface hardness of coated DLC film

It is of interest to estimate a difference in surface hardness of the polymer alloy and the coated DLC film. A measured hardness depends on the size of indenter because of easy deformation of polymer surface with a very thin DLC film coated thereon. Thus, the hardness was measured by nanoindentation. The measured surface hardness was 0.10 – 0.14 GPa and 2.14 – 3.54 GPa for the polymer alloy with and without DLC-coating, respectively. Fig. 4 shows a large difference in hardness between the polymer alloy surface (average hardness: ca. 0.12 GPa) and the coated DLC film (average hardness: ca. 2.96 GPa), indicating a hardness of the DLC film ca. 25 times that of the polymer surface. The large difference in hardness between the specimens suggests almost no deformation of the polymer substrate during measuring hardness of the DLC film.

Surface morphology of coated DLC film

Fig. 5 shows SEM micrographs of the polymer alloy surface obtained in each step of the PBIID process. Fig. 5 (a) shows a surface morphology of the neat polymer with as-mold surface roughness. The surface turned rather smooth after Ar sputter-etching (Fig. 5 (b)). Fig. 5 (c) shows the Ar sputter-etched and then silicon ion-implanted polymer surface, whose morphology seems to be similar to that shown in Fig. 5 (b) except for formation of ca. 0.2 μm -thick particles and a little ill-shaped rough edges on the surface.

A drastic change in surface morphology was found in Fig. 5 (d) by the C_2H_2 -implantation, where both smooth part and rough edges shown in Fig. 5 (c) were covered with nearly round particles with sizes less than ca. 2 μm . Coagulated particles with sizes of a few micrometers are also seen. It is of interest that the former smooth part still remained, while the latter rough edges were covered with large particles. This may indicate a heterogeneity in rate of implantation or deposition of DLC such that the rate is higher at rough edges than at smooth part of the surface.

Fig. 5 (e) shows a TEM micrograph of the surface after the $\text{C}_2\text{H}_2/\text{C}_6\text{H}_5\text{CH}_3$ -deposition, which is similar to the morphology shown in Fig. 5 (d). It is likely, however, that the morphology is somewhat smoother for the $\text{C}_2\text{H}_2/\text{C}_6\text{H}_5\text{CH}_3$ -deposited surface than for the C_2H_2 -deposited one. In addition, the fraction of large coagulated particles decreased and the size of most particles is less than ca. 1 μm . It may be said that the deposition of DLC onto rough edges of the surface was suppressed in case of $\text{C}_2\text{H}_2/\text{C}_6\text{H}_5\text{CH}_3$ -deposition.

The surface roughness of the resultant DLC film deposited in the last fourth step is anyhow not smooth as is evident from Fig. 5 (e), indicating a heterogeneity in DLC film thickness. The various surface hardnesses of 2.14 – 3.54 GPa may be accounted for by the heterogeneity of DLC film thickness, which is partly due to the original surface roughness of the polymer specimen itself.

Morphology of the interface

In order to examine the detailed morphology of the DLC-coated polymer alloy,

TEM observation was made on ultrathin sections prepared from specimen obtained in each step of the PBIID process. Fig. 6 (a) shows a TEM micrograph of a cross-section of the surface of Ar/CH₄-etched polymer alloy, where the etched surface is the boundary, indicated by an arrow, between the upper part (embedding epoxy resin) and the lower part (the polymer alloy). It is also seen from the micrograph that the polymer alloy, Noryl GTX6601, consists of a phase-separated structure with nylon 66 matrix and somewhat round PPE domain phases, the latter containing fine elastomer particles stained dark by OsO₄.

Fig. 6 (b) shows a TEM micrograph of a cross-section of the Si-implanted surface of the polymer alloy formed using HMDS in the second step, where dark layers, indicated by an arrow, with thickness of ca. 95 nm are seen on the polymer alloy surface, i.e., at the boundary between the polymer alloy surface and embedding epoxy resin. Taking into consideration the existence of Si2s and Si2p peaks in the XPS spectrum (Fig. 2 (b)), the dark layer on the polymer alloy can be assigned to the implanted Si. It can be also said that the discrete Si layer in the cross-section is due to roughness of the Si-implanted surface (Fig. 5 (c)).

Fig. 6 (c) shows a TEM micrograph of a cross-section of the C₂H₂-implanted polymer alloy surface, where the implanted layer texture was heavily deteriorated by sectioning. This may suggest that the C₂H₂-implanted layer was so brittle to be broken by sectioning into fractured thin particles with their narrow ends, indicated by arrow A. In the micrograph are also seen dark thin fractures with thickness of ca. 50 nm, indicated by arrows B, just on the polymer alloy surface, i.e., at the boundary between the brittle C₂H₂-implanted layer and the alloy surface. These dark thin fractures seem to be assigned to Si-implanted layer, taking into consideration their thickness, darkness and positions localized on the polymer surface. It is of interest to note that a single layer of fractured thin particles with their thin ends is also seen, as indicated by arrow C, strongly adhered to the embedding epoxy resin interface. A TEM micrograph inserted in Fig. 6 (d) reveals that the thickness of almost intact C₂H₂-implanted layer is estimated as ca. 580 nm.

Fig. 6 (d) shows a TEM micrograph of a cross-section of the DLC-coated polymer

alloy obtained in the last step of the PBIID process. Compared with the morphology shown in Fig. 6 (c), a very dark layered texture, indicated by an arrow A, with thickness of ca. 320 nm is seen in the interface between the polymer alloy and the embedding epoxy resin. Therefore, this dark layered texture highly stained by OsO₄ should be formed in the C₂H₂/C₆H₅CH₃-deposition step.

The interface in the cross-section at A consists of three layers: the Si-implanted layer (shown by arrow B), the intermediate C₂H₂-implanted layer (arrow C) and the C₂H₂/C₆H₅CH₃-deposited layer (arrow A), with thickness of ca. 50 nm, ca. 240 nm and 320 nm, respectively. Another part of the cross-section at D consists of apparent two layers: ca. 400 nm-thick C₂H₂-implanted layer and ca. 250 nm-thick C₂H₂/C₆H₅CH₃-deposited layer, the Si-implanted layer being likely obscure.

The total thickness of the DLC film coated on the polymer alloy is estimated as ca. 660 nm and 650 nm at position A and D, respectively, which are somewhat less than the value of ca. 1 μm estimated by a surface roughness measuring system.

Closer looking at these TEM micrographs of the OsO₄-stained ultrathin cross-sections, it is of great interest that the C₂H₂/C₆H₅CH₃-deposited layer is darkest of all, Si-implanted one intermediately dark and the C₂H₂-implanted one is rather bright. Taking into consideration the chemical composition of carbon and hydrogen in these layers except for Si-implanted one, darkness depends on the reactivity with OsO₄. It is thought that the lower the density (or the higher the mobility) of materials is, the higher the reactivity of OsO₄. That is to say, low density materials are so stained by OsO₄ to be seen dark in TEM observation. As this DLC is amorphous, the density of the C₂H₂/C₆H₅CH₃-deposited layer can be estimated to be lower than that of the C₂H₂-implanted one and the molecular mobility of the DLC prepared by C₂H₂/C₆H₅CH₃-deposition is high.

It can be, therefore, concluded that the present DLC-film coated on the polymer alloy consists of a C₂H₂/C₆H₅CH₃-deposited layer with a high flexibility and hard Si- and C₂H₂-implanted intermediate layers. This result is also consistent with the formation of a smooth surface by C₂H₂/C₆H₅CH₃-deposition (Fig. 5 (d)). It is worthy of note that a low structural strain²¹ of the PBIID-processed DLC film was first verified in this

morphological study.

It is also of interest to investigate tribology of the DLC-coated polymer alloy with a moderate hardness and flexibility because this sort of DLC film with particular structure and properties is said to give a low friction and wear under mild friction conditions. A tribological study of this polymer alloy will be reported elsewhere.

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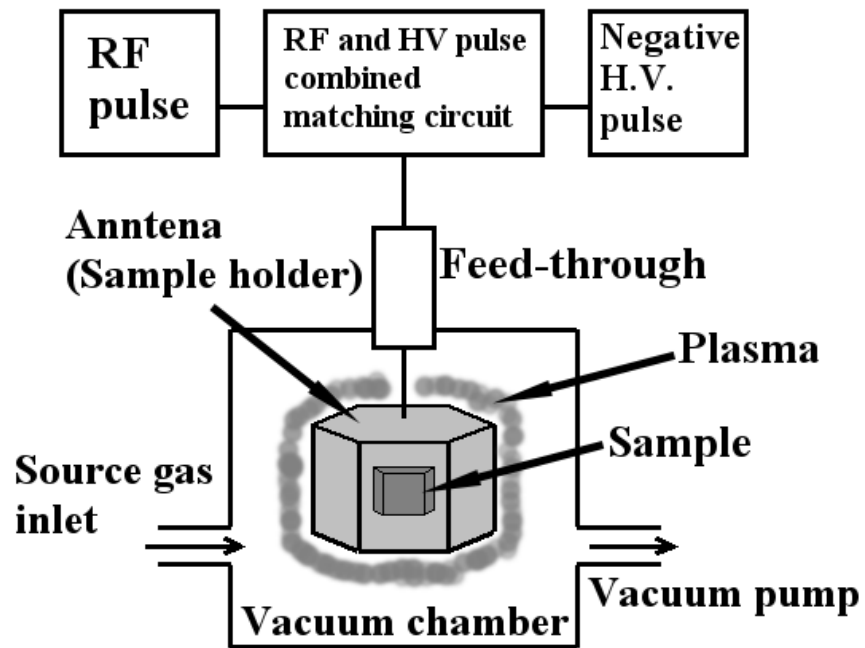
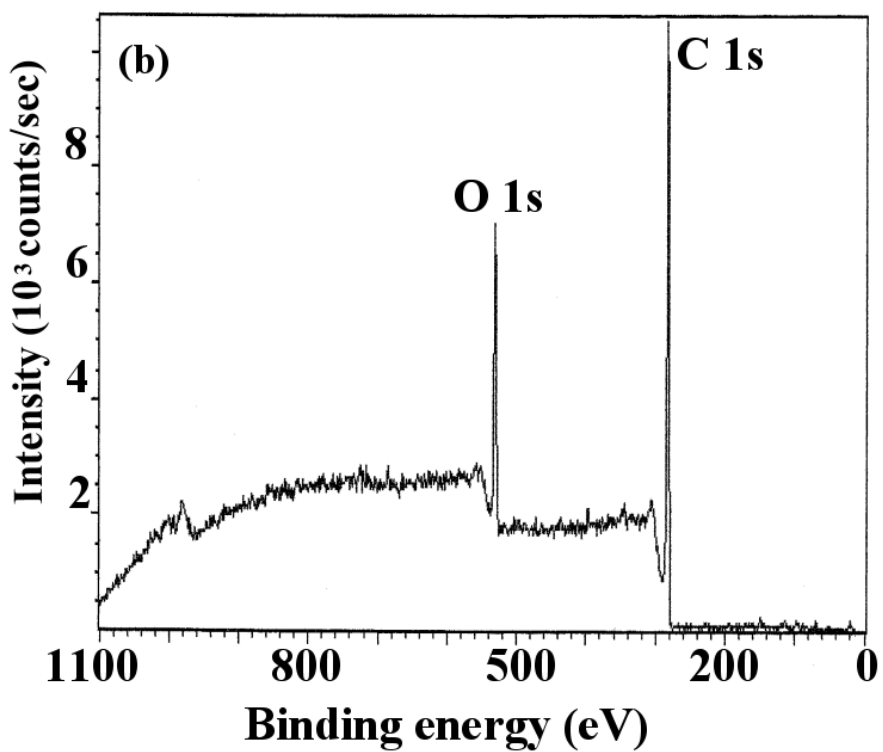
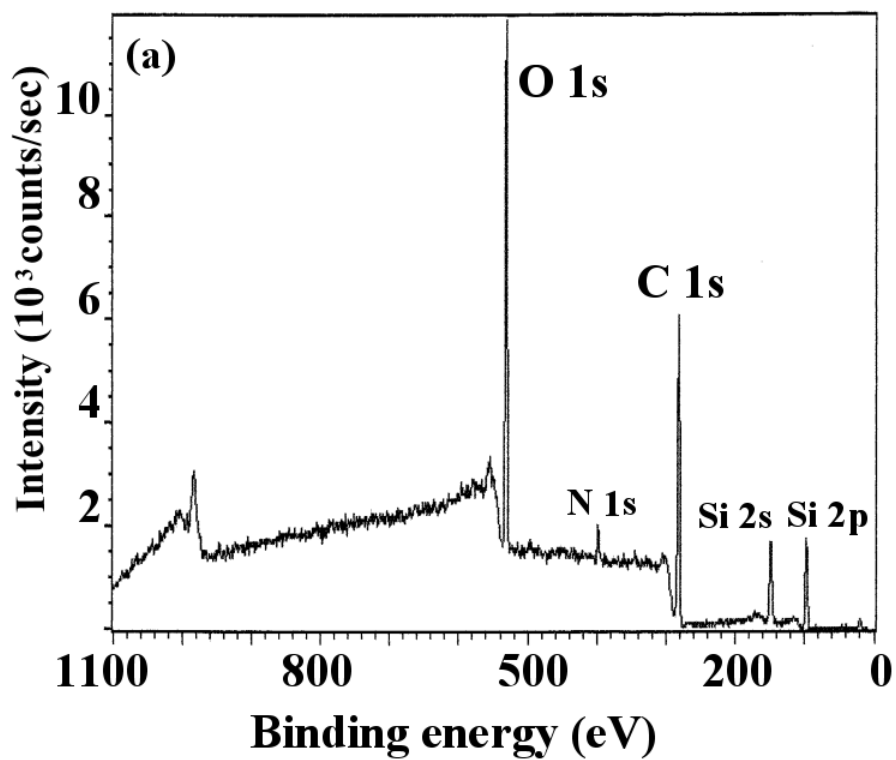
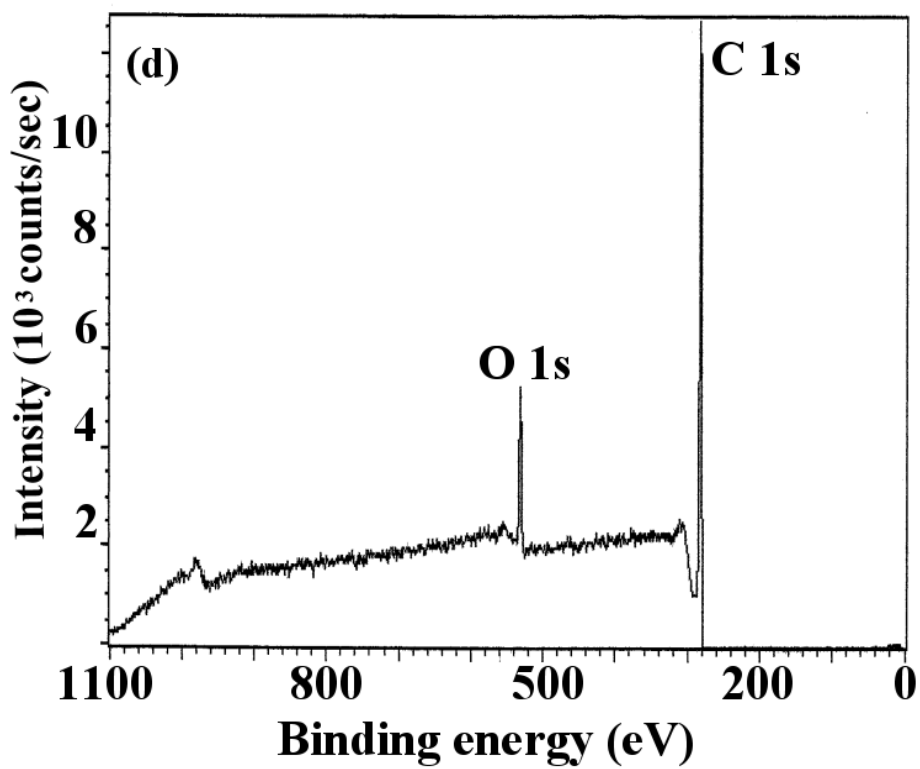
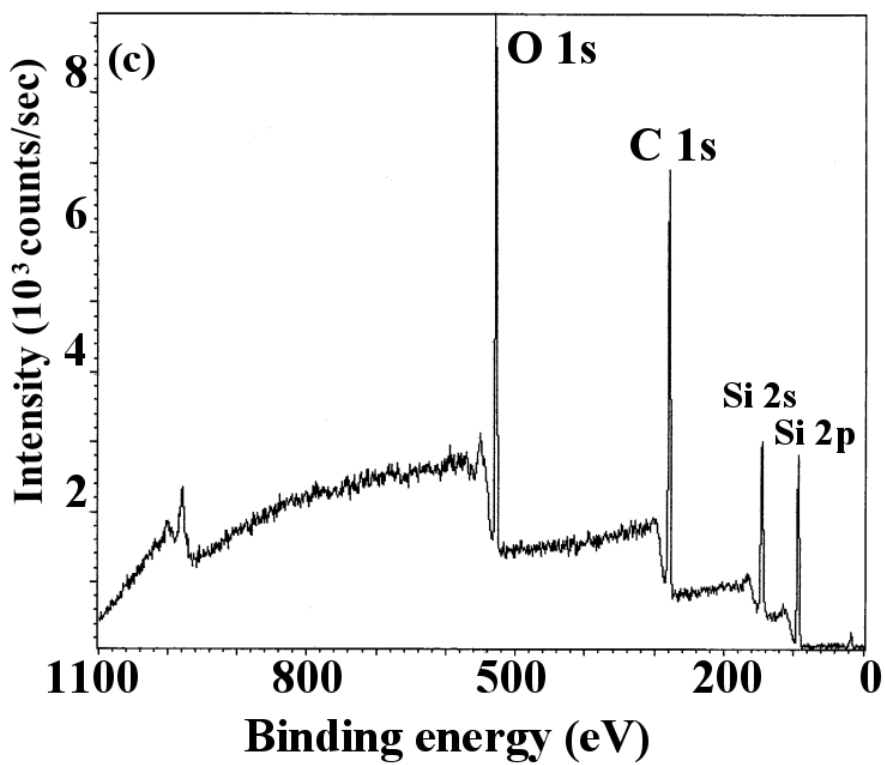


Figure 1
Schematic illustration of DLC-coating equipment for PBIID process.





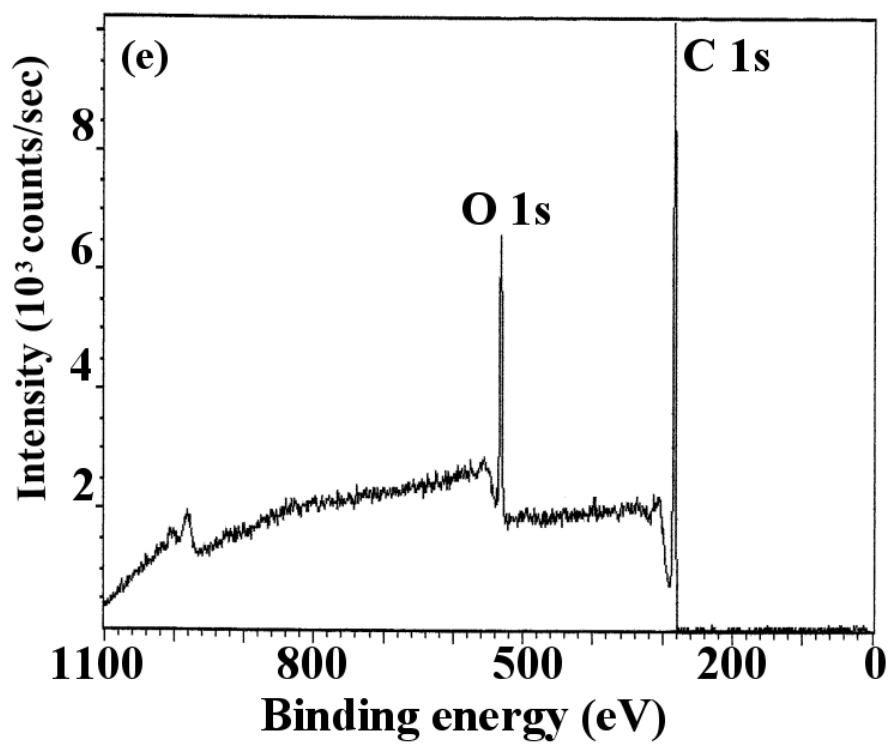


Figure 2.

XPS spectra of as-mold polymer surface (a), Ar/CH₄-cleaned surface (b), HMSD-implanted surface (c), C₂H₂-implanted surface (d) and C₂H₂/C₆H₅CH₃-deposited surface (e).

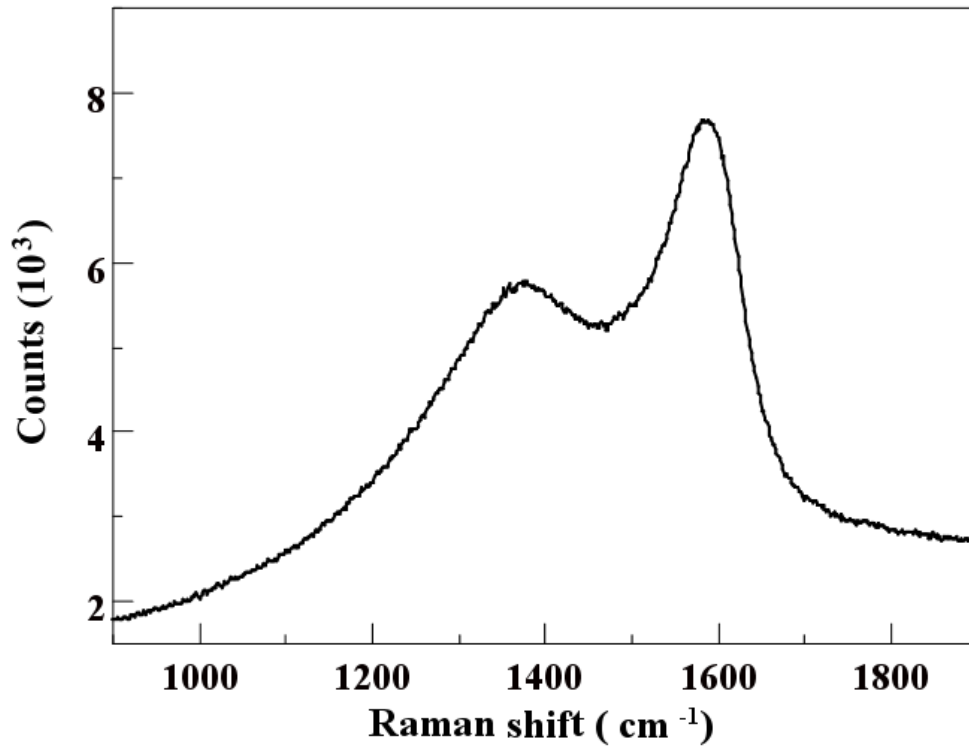


Figure 3. Raman scattering spectrum of DLC film coated onto the polymer.

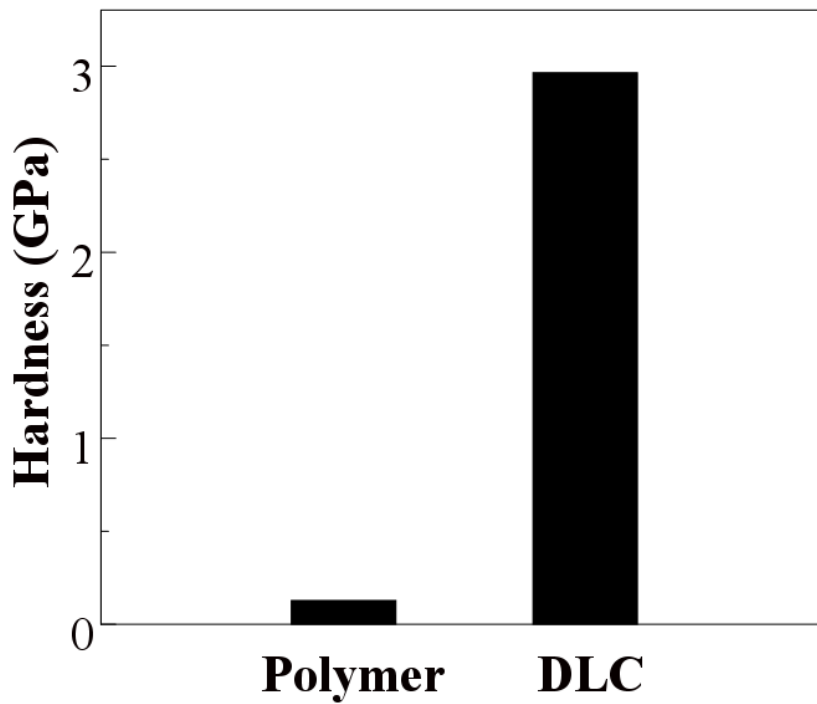
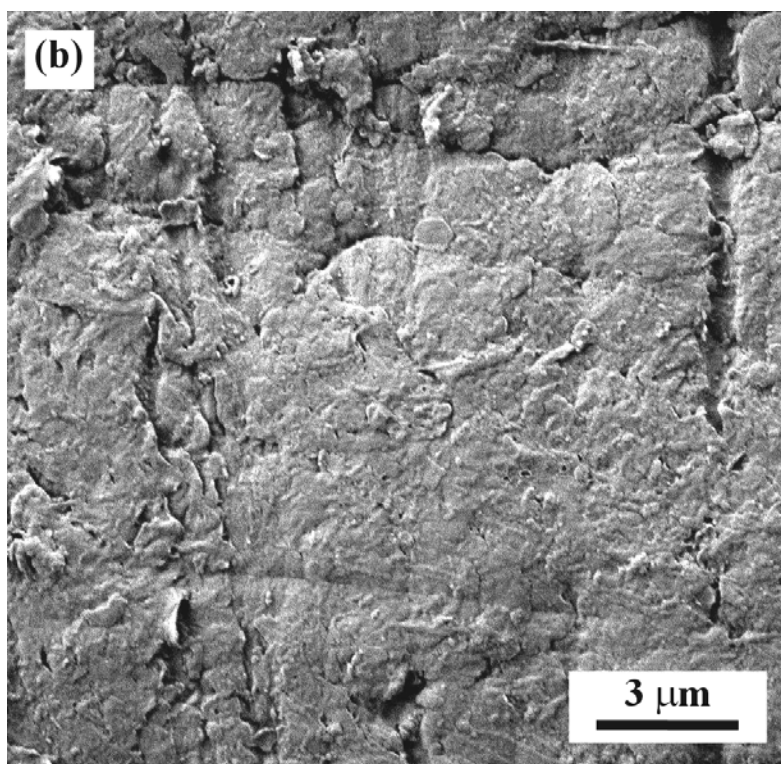
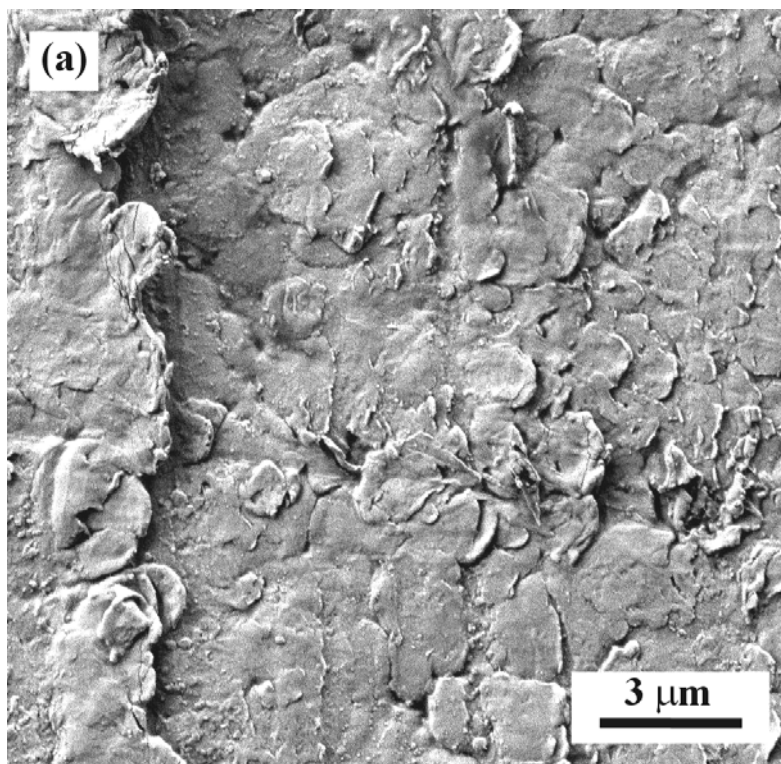
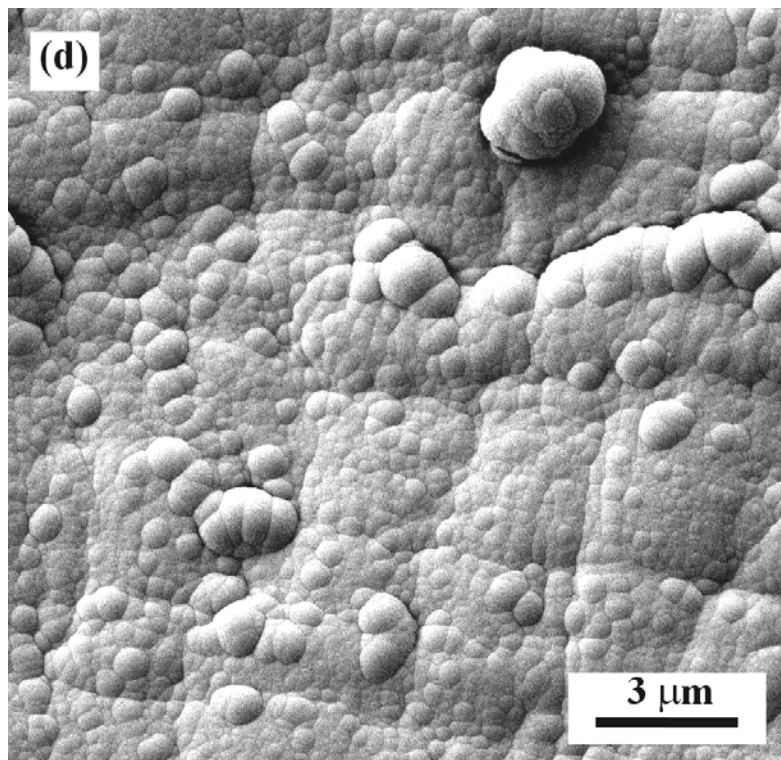
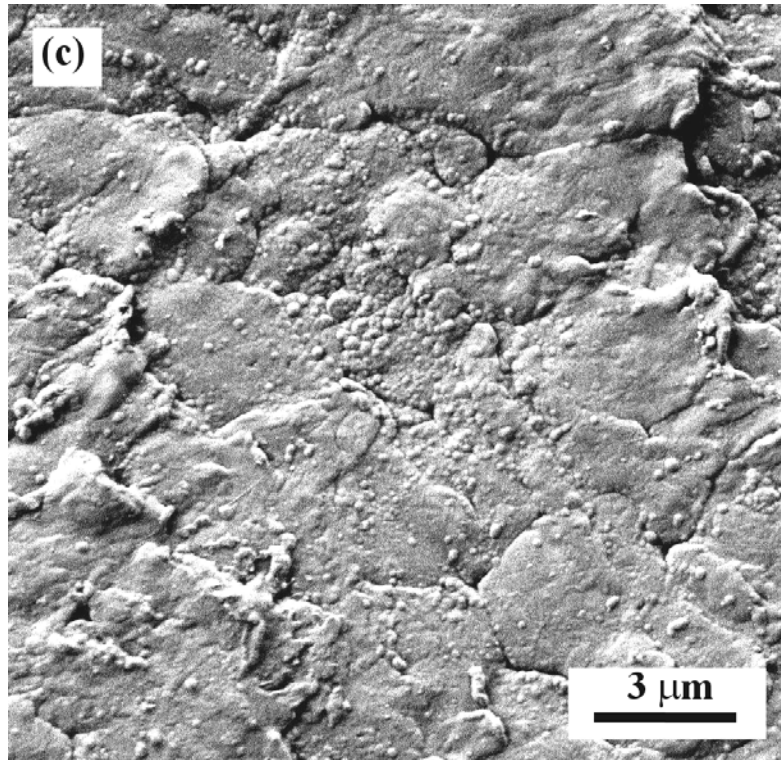


Figure 4. Surface hardness of the as-mold polymer and DLC film coated thereon.





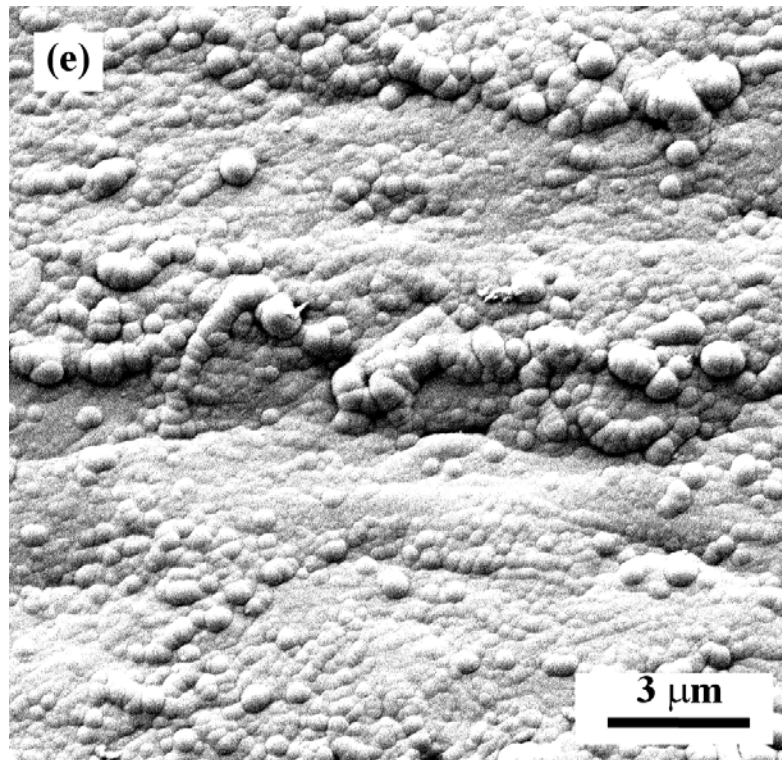
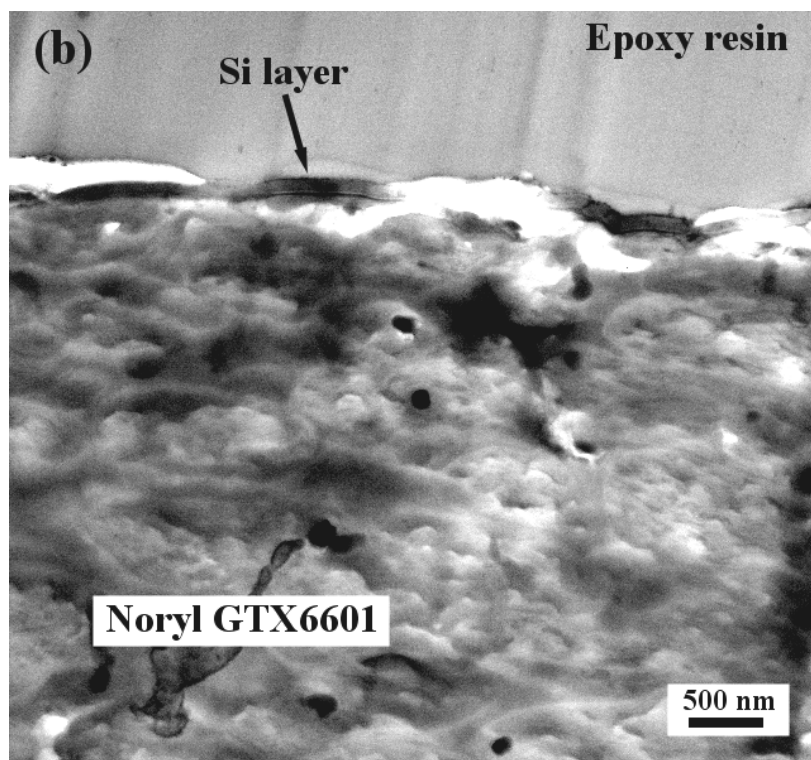
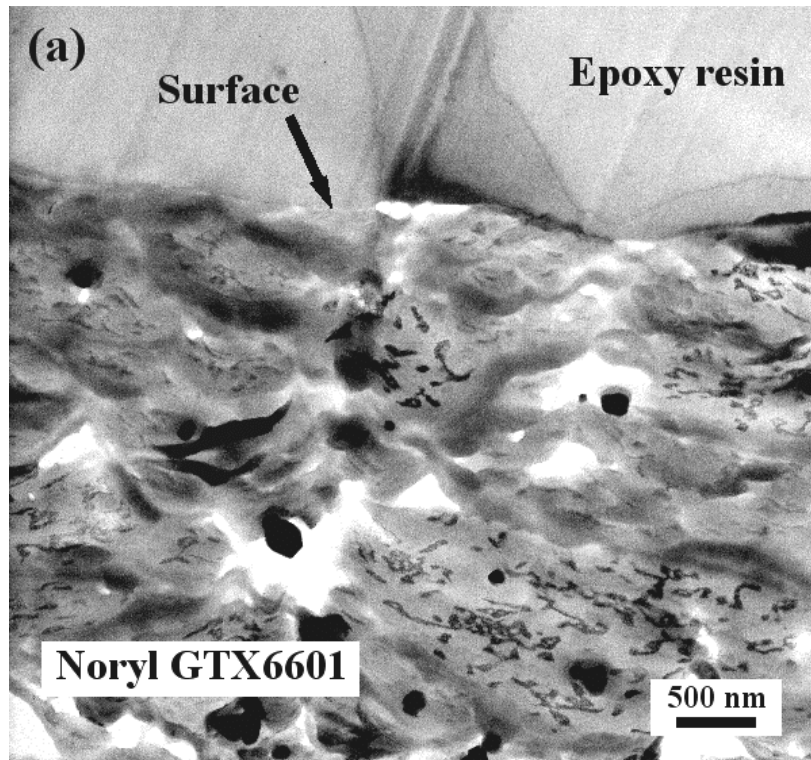


Figure.5.

SEM micrographs of as-mold polymer surface (a), Ar/CH₄-cleaned surface (b), HMSD-implanted surface (c), C₂H₂-implanted surface (d) and C₂H₂/C₆H₅CH₃-deposited surface (e).



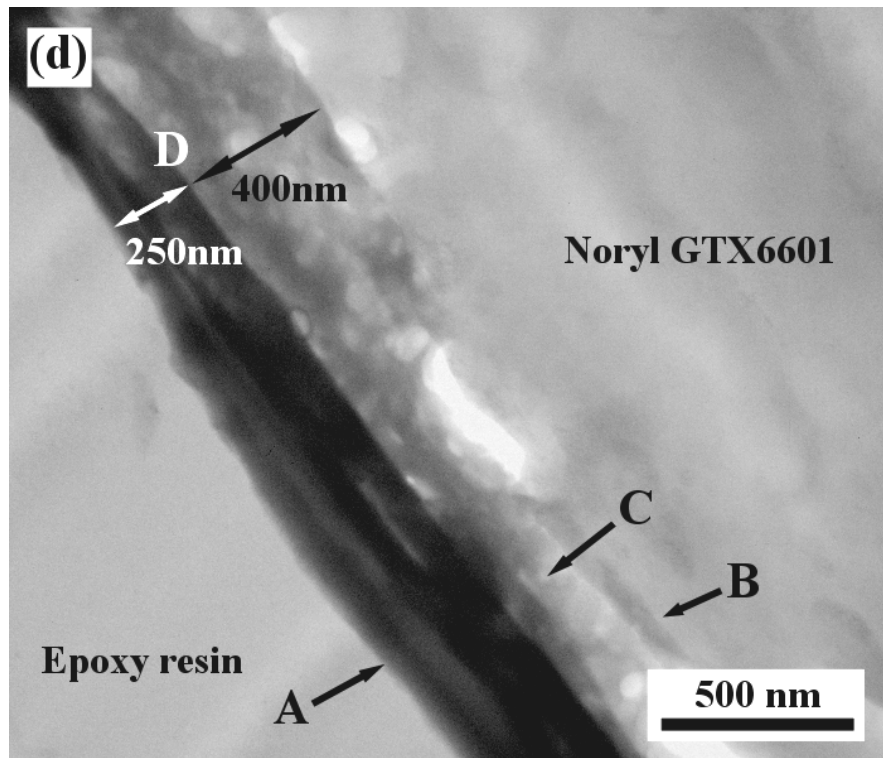
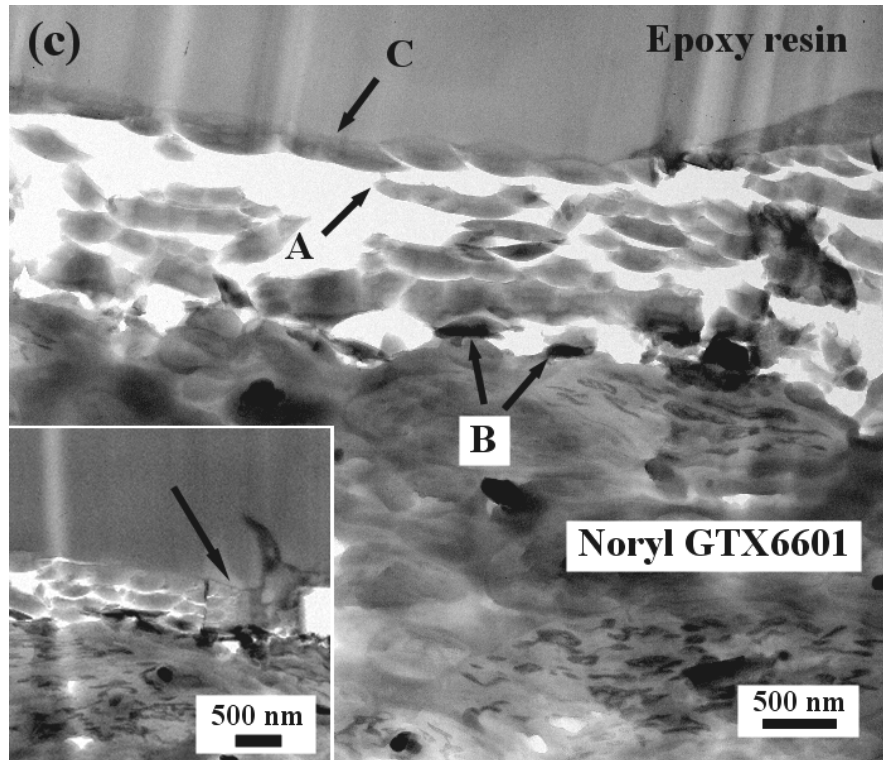


Figure 6. TEM micrographs of OsO₄-stained ultrathin cross-section of polymer surface subjected to Ar/CH₄-cleaned surface (a), HMSD-implantation (b), C₂H₂-implantation (c) and C₂H₂/C₆H₅CH₃-deposition (d).

Table 1 DLC deposition parameters

Process	Gas	Flow rate (cc/min)	Time (min)
1: Cleaning	Ar + CH₄	30 + 30	10
2: Ion implantation	HMDS	15	15
3: DLC deposition	C₂H₂	100	30
4: DLC deposition	C₂H₂ + Toluene	90 + 20	240