Investigation of growth, coverage and effectiveness of plasma assisted nano-films of fluorocarbon

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Received 26 January 2005; received in revised form 15 June 2005; accepted 20 July 2005
Available online 27 September 2005

Abstract

Plasma-assisted functional films have significant potential in various engineering applications. They can be tailored to impart desired properties by bonding specific molecular groups to the substrate surface. The aim of this investigation was to develop a fundamental understanding of the atomic level growth, coverage and functional effectiveness of plasma nano-films on flat surfaces and to explore their application-potential for complex and uneven shaped nano-materials. In this paper, results on plasma-assisted nano-scale fluorocarbon films, which are known for imparting inertness or hydrophobicity to the surface, will be discussed. The film deposition was studied as a function of time on flat single crystal surfaces of silicon, sapphire and graphite, using microwave plasma. X-ray photoelectron spectroscopy (XPS) was used for detailed study of composition and chemistry of the substrate and coating atoms, at all stages of deposition. Atomic force microscopy (AFM) was performed in parallel to study the coverage and growth morphology of these films at each stage. Combined XPS and AFM results indicated complete coverage of all the substrates at the nanometer scale. It was also shown that these films grew in a layer-by-layer fashion. The nano-films were also applied to complex and uneven shaped nano-structured and porous materials, such as microcellular porous foam and nano fibers. It was seen that these nano-films can be a viable approach for effective surface modification of complex or uneven shaped nano-materials.

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Keywords: Growth; Plasma; Nano-film

1. Introduction

Plasma thin film deposition techniques are very useful in many engineering applications. They are known for their capability of depositing conformal ultra thin films (several nm) as well as relatively thick...
films (several μm thick). Applications of plasma films include improved hydrophobicity, hydrophilicity, biocompatibility, printability, adhesion, and corrosion protection. It is agreed upon that plasma deposition techniques are highly system dependent and influenced by process parameters [1–8]. Optimization of these parameters and their impact on coating chemistry has been investigated by many researchers. Previous publications from this group show that plasma time and coating chemicals play a crucial role in the deposition processes [9,10].

Despite the earlier studies performed on thick films for conventional materials, the fundamental mechanisms that explain how functional groups in the plasma bond with the substrate atoms, begin to nucleate and eventually grow into complete films are not discussed. Systematic study of the nucleation and growth of these films is needed, to obtain an estimation of the minimum possible thickness of the coating; that still provides effective surface modification. This basic understanding could be extended to effective surface modification of complex shaped nano-structured materials.

The objective of our research is to characterize, initial states of nucleation, growth and coverage of plasma-assisted nano-films. This was accomplished by depositing these films as a function of total deposition time on flat surfaces and analyzing, ex situ, the change in chemical composition, morphology and coverage, at the nanometer scale. The aim of investigation is to discern weather these nano-films grow as individual islands (three-dimensional growth) or layers (two-dimensional nucleation growth). In this paper, the growth and characterization of inert fluorocarbon films are discussed.

Fluorocarbon films are known for making the surface inert and thereby make the surface hydrophobic or water repellent. This phenomenon is attributed to the presence of –CF₂₋₋CF₃ functional groups present in these films. The water contact angle value of such fluorocarbon coated surfaces is around 140–170° indicating super-hydrophobic surfaces [11–13]. A commercial Teflon (PTFE) surface has a water contact angle very close to these values. These films may have potential application in preventing aggregation of nanomaterials through surface modification [14].

2. Experiments

Plasma-assisted fluorocarbon film deposition was performed using a microwave plasma reactor (PlasmaTech Inc., Model No.V-15 G) with multimode microwave source. The aluminum vacuum chamber size is 250 mm × 250 mm × 250 mm (15.6 l), which uses a microwave generator magnetron of 850 W (electrodeless chamber) and the maximum power available is 600 W. Grade 4.0 octafluoropropane (C₃F₈) was used as the coating chemical. The gas flow rate inside the treatment chamber for all coating times was kept constant at 50 ml/s.

Flat single crystal substrates of silicon, sapphire and graphite were used as model surfaces for studying the chemistry and the morphology of films. Hydrophilic materials (initial water contact angle 0°), which include flat surfaces as well as inner layers of a multi-layered stack of porous materials with different permeation levels were also coated with these fluorocarbon nanolayers in a wide range of experimental conditions to study the effect on surface property change using water contact angle analysis. These results were then correlated with quantitative XPS data. Fig. 1 shows a typical set-up used for depositing fluorocarbon films on a batch of model surfaces. The coating time was varied from 15 s to 10 min in increments of 15 s. These films were also deposited on carbon foam, a three dimensional microcellular porous material that may have future use in lightweight aerospace composites [15–17]. This complex structure is known to contain layers, flakes, as well as nano-fibers of graphitic carbon [18].

![Microwave plasma chamber set-up showing how model surfaces are treated in a batch as a function of plasma time.](image-url)
X-ray photoelectron spectroscopy (XPS) (Kratos-Axis Ultra System) with monochromatized Al Kα photons (1486.6 eV) was used for identifying the chemical composition and bonding states of the top few atomic layers of the surface with 110 µm diameter aperture. The nano-scale surface morphology and coverage of films were monitored using atomic force microscopy (AFM) at each stage of deposition. Water contact angle measurement was used as a direct measure of effectiveness of the film. Contact angle results were used in conjunction with XPS to investigate how thick a film we need in order to provide the effective hydrophobicity (contact angle > 90°).

3. Results and discussion

Fig. 2A shows how the carbon XPS peak changes for graphite as the fluorocarbon film grows on it. It was evident that the untreated graphite has a single component carbon peak occurring at a binding energy (BE) of 284.5 eV, also known as the graphitic carbon peak. This peak started diminishing as the fluorocarbon film deposited on graphite and an additional peak due to film started showing up at higher BE of 290.3 eV, identified as CF₂ component. As the coating time (and therefore thickness) increased, the graphitic carbon peak diminished and eventually disappeared whereas the CF₂ component intensity increased. The CF₂ functional group is responsible for providing inertness/hydrophobicity to the substrate surface. The increase in the CF₂ component and concomitant decrease in the graphitic carbon peak can be correlated with the increase in the fluorine on the graphite surface (Fig. 2B). Similar trends of substrate peak attenuation and coating peak growth was observed for the sapphire and silicon substrates (Fig. 3). The attenuation of the substrate XPS peaks and growth of the coating peaks as the fluorocarbon film grows on model surfaces can be explained further as follows.

In XPS, electrons emitted from atoms below the outer-most layer undergo elastic and inelastic collisions with the outer layer electrons. A decrease in intensity of as well as energy of electrons occurs because of these collisions. These lower energy electrons, also called secondary electrons, form the background of the XPS spectrum. The sharp peaks come only from the electrons in the top few layers of the material that escaped without experiencing any inelastic collisions. As the coating forms on the surface, the substrate electrons experience resistance from the coating material in form of increased inelastic collisions. As a result the intensity and energy of the substrate electron decreases. As the film thickness increases this resistance to the substrate...
electrons increases, which is the main reason for the attenuation of the substrate signal.

This attenuated substrate signal I can be expressed as [19]:

\[ I = I_0 e^{-x/\lambda} \]  

(1)

\( I \) is the intensity of the substrate signal in the absence of the film, \( \lambda \) the inelastic mean free path of substrate electrons and \( x \) is the average thickness of the deposited layer with same units as \( \lambda \). When the coating thickness (\( x \)) becomes several times greater (2–3\( \lambda \)) than the escape depth of the substrate electrons, the substrate signal falls below detection level. This equation can be used to estimate the over-layer thickness (\( x \)) of the fluorocarbon film if the XPS intensity of...
a substrate peak (that is absent in the film) is measured before and after the film deposition.

The inelastic mean free path (IMFP) used in above equation is approximated from the following equation:

\[ \lambda = kE^m \]

where, \( k \) and \( m \) are materials parameters proposed by Wagner, Davis and Riggs [20]. This equation is widely accepted as the closest estimate for a standard solid. The escape depth values used in this work for the core electrons of model substrates (Si 2p, Al 2p and C 1s) are taken from literature [21,22] and are 2.5, 2.0 and 2.7 nm, respectively.

Using the Eq. (1), the “average” film thickness was estimated, which was averaged over an analysis area of 110 \( \mu \)m diameter in XPS. The coating thickness (\( \gamma \)) at which complete attenuation of substrate signals is occurring is in the range of 6–9 nm. Starting from the initial stages of deposition to all the way to thick over-layer, deposited film was characterized. AFM was used to observe the morphology of the film and XPS was used to estimate the “average” over-layer thickness.

Fig. 4 shows a graphical representation of fluorocarbon over-layer thickness as a function of coating time up to 1 min. A fairly constant rate of film growth could be seen for each of the model surfaces. Estimated over layer thickness for 1 minute deposition time it was about 4, 7 and 8 \( \AA \) for sapphire, silicon and graphite respectively. Though all surfaces were coated simultaneously (together as a batch in plasma chamber) for specific coating time, the growth rate was distinctly different. This could be due to various reasons, such as difference in surface activity and roughness. These treated surfaces were observed in AFM for morphology and coverage characterization.

Phase imaging capability of AFM was used to investigate the growth of deposited fluorocarbon films. The cantilever of the AFM is driven by a piezoelectric...
device at resonance frequency and phase. Upon interaction with the surface, this phase tends to change. The resulting electric phase lag or phase shift of the cantilever oscillation relative to driving signal is dependent on the materials properties [23,24]. Plotting this would provide contrast between dissimilar materials (substrate and coating), which can be used to observe the growth morphology. Fig. 5 shows an example of AFM phase image obtained on a silicon surface coated with fluorocarbon coating for 40 s. Fig. 6 shows similar images on silicon surface for 30 s to 1 min coating time. It was evident that the films were patchy with detectable phase change in the cantilever vibration over the film when compared to the substrate. They indicate sub-monolayer coverage at these deposition times. It was noticed that the film had formed different size clusters of several hundred nanometers (lateral dimension). The average height of these clusters was found to be in the range of 2–3 nm as indicated by the line profiles taken on the surface (Figs. 6 and 7). These clusters, which are randomly dispersed on the substrate surface, tend to grow in lateral direction at a faster pace than in the vertical direction. It should be noted that as the coating time increases from 30 s to 1 min, the substrate coverage had increased significantly in lateral direction with almost same vertical height (Figs. 6 and 7 combined). These individual islands (average height of ~3 nm) eventually merged into a complete layer between 2 and 3 min of deposition time, as shown below.

Fig. 8 shows a comparison between AFM phase images (2 μm x 2 μm area) of 2 and 3 min fluorocarbon coated silicon surfaces. For the coating time of 2 min, very small patches of the substrate surface was still exposed, whereas for a 3 min coating time, complete coverage of the underlying surface was seen with no detectable phase change (constant phase). This means that within 2–3 min of deposition time, fluorocarbon film completely covered the underlying surface. Fig. 9 shows AFM topographic images of silicon surface treated for 3 and 5 min with their phase images, indicating layer-by-layer growth of fluorocarbon film at nano-scale with no evident phase change. AFM data taken on sapphire surface revealed similar trend as that of silicon (Fig. 10).

XPS results obtained on fluorocarbon treated samples were evaluated in relation with relevant AFM images. Fig. 11 show a comparison of the
Fig. 8. (A) AFM phase image for 2 min indicating patchy coating with evident phase change. (B) AFM phase image for 3 min indicating complete coverage with no phase change.

Fig. 9. AFM topographic and phase images for 3 and 5 min indicating layer-by-layer growth with complete coverage for fluorocarbon coating on silicon surface.
attenuated substrate signals (silicon 2p in this case) for coating times between 1 and 5 min.

Following observations were made from comparison of Fig. 11 with phase images obtained for 1, 2, 3 and 5 min of deposition time (refer earlier phase images). (1) Percentage coverage of substrate surface increased as the deposition time increased from 1 to 2 min (Figs. 6D, 8A and 11), but distinct phase change indicated that some percentage of silicon surface was still uncovered. The substrate peak in XPS (Si 2p) was attenuating in accordance with this coverage. (2) No phase change (constant phase) in AFM image of silicon coated for 3 min (Figs. 8B and 11) indicated complete coverage of silicon surface by fluorocarbon coating. Presence of substrate peak in XPS for this case indicated that the thickness of deposited layer was lower or comparable to the escape depth of the substrate electrons (λ = 2.5 nm for silicon). (3) Phase image of silicon surface coated with 5 minutes (Figs. 9D and 11), showed surface coverage by more...
than one thin layer of fluorocarbons. A weak substrate peak presence in XPS indicated the average film thickness is still comparable to the escape depth (within 2–3Å range, i.e. few nanometers).

It can be seen from the above discussion that the fluorocarbon film, even when less than 3 nm in thickness (3 min of coating time), is still completely covering the substrate, and growing in layer-by-layer fashion. Fig. 12 shows qualitative comparison of the XPS survey scans obtained on the model surfaces treated with fluorocarbon for few minutes in microwave plasma and commercial Teflon. It can be seen

![Fluorocarbon treated graphite](image1)

![Fluorocarbon treated silicon](image2)

![Fluorocarbon treated sapphire](image3)

![Fluorocarbon treated Teflon](image4)

Fig. 12. XPS survey scans obtained on model surfaces treated for few minutes with fluorocarbon coating show identical chemistry as that of commercial Teflon surface.
Fig. 13. Contact angle vs. deposition time for one substrate.

Fig. 14. Contact angle vs. $F/C$ ratio of a variety of substrates.

Fig. 15. Effective surface modification of micro-cellular carbon foam surface with nanoscale plasma-assisted fluorocarbon film. (A) SEM and TEM image of a micro-cellular carbon foam indicating complex surface; (B) water contact angle (77°) on untreated carbon foam surface; (C) water contact angle on fluorocarbon treated carbon foam surface indicating hydrophobicity.
that all surfaces look identical in chemical composition, indicating that deposited fluorocarbon film was similar in composition to commercial Teflon, but it was very thin and strongly bonded to the substrate surface.

Fig. 13 shows the variation of contact angle with the coating time on hydrophilic materials. As indicated earlier, these include flat surfaces as well as multilayered stack of porous materials. The contact angle value (measure of hydrophobicity in this particular case) increased very fast initially and then reached a steady state after few minutes of deposition. In XPS, an increase of about 20% in the surface fluorine to underlying carbon ratio was found (Fig. 14), at which contact angle value reached its saturation. This supports our argument that only few nanometers thick film is all we need in order to provide effective surface modification to any surface.

Fig. 15A shows the microstructure of the microcellular porous carbon foam material. Fig. 15 B and C show, the water contact angle measured on the surface of microcellular porous foam before and after the fluorocarbon film deposition. It was observed that untreated foam had water contact around 77°, whereas, fluorocarbon coated foam had become hydrophobic with 140° water contact angle value. These results are encouraging and indicate that effective surface modification of complex shaped nanostructured materials is possible.

4. Conclusion

Atomic level growth of plasma-assisted fluorocarbon films on various surfaces had been investigated. It was shown that these films were growing in layer-by-layer fashion and completely covered the underlying surface even at nano-scale. Combination of XPS, AFM and water contact angle results showed that even a few nanometer thin film of fluorocarbon film could provide effective surface modification to the surface. Therefore, this type of coating technique could be very useful in surface modification of complex and uneven shaped nanostructured solids such as nano fibers, and near net shape cellular foam structures.

References