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Elucidation of Different Steps Involved in Allylamine Functionalization of the Diamond Surface and Its Polymerization by Time-of-Flight Secondary Ion Mass Spectrometry

Hao Zhuang,[†] Vadali V. S. S. Srikanth,[†,∥] Xin Jiang,*[,†] I. Aronov,[‡] B. W. Wenclawiak,[‡] J. Luo,[§] and H. Ihmels[§]

[†]*Institute of Materials Engineering, University of Siegen, Paul-Bonatz-Str. 9-11, 57076 Siegen, Germany,* [‡]*Department of Analytical Chemistry, University of Siegen, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany, and* [§]*Department of Organic Chemistry, University of Siegen, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany.* [∥]*Currently at School of Engineering Sciences and Technology, University of Hyderabad, Hyderabad, India 500046, and also contributed a part of the work from the present address.*

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The H-terminated polycrystalline diamond thin film surface is photochemically functionalized using allylamine. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) aided by principal components analysis (PCA) is then employed to systematically elucidate (i) the photochemical grafting of trifluoroacetamide group protected allylamine (TFAAA) onto the diamond thin film surface and (ii) the deprotection of the amine group. PCA of the SIMS shows that the diamond surface is fully covered by TFAAA after 24 h of UV illumination. SIMS spectra (in the high mass range) show that TFAAA cross-polymerizes on the diamond surface before the whole surface is covered by TFAAA. PCA of the SIMS also shows that the deprotection reaction follows approximately an exponential law with a time constant of 1 h. Additionally, the unchanged CN^- intensity in the deprotection step shows that the allylamine linkage to diamond is stable. A shadow mask was employed during the photochemical grafting of allylamine, leaving the masked region unfunctionalized. The SIMS mapping shows high intensities and homogeneous distribution of CN^- in the region which is UV illuminated. On the basis of the overall SIMS analysis a modified chain reaction grafting model which illustrates a competition between TFAAA bonding and its cross-polymerization is discussed.

Introduction

It is now well understood that diamond possesses diverse sensing abilities.[1] Diamond received considerable attention in biosensoric applications[2−8] only after its surface (which was otherwise considered chemically inert) was chemically modified.[9] Among the chemical modification methods of the diamond surface, photochemical functionalization[2−8] is the widely used one, and among the several steps that are involved in a typical photochemical grafting procedure of biomolecules (such as DNA) onto the diamond surface, bonding the functional groups like $-NH_2$ (amine) or −COOH (carboxyl) is the most important one prior to the biomolecule attachment.[9] Previously, in the very important systematic studies, it was understood that the photochemical grafting gets initiated by the photoejection of electrons from the diamond surface into the liquid phase.[10−12] Subsequently, through the systematic studies based on atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), a chain reaction initiated at isolated carbon dangling bonds was proposed[13] to explain the grafting of 10-aminodec-1-ene protected with trifluoroacetamide (TFAAD) onto the diamond surface; it was explained that shorter grafting times result in the growth of well-organized 2D monomolecular amine layers, whereas longer grafting times result in 3D amine layer growth tendency due to cross-polymerization. However, AFM

*Corresponding author. Tel.: +49 271 7402966. Fax: + 49 271 740 2442. E-mail address: xin.jiang@uni-siegen.de.

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only delivers information of surface morphology and roughness while XPS delivers information of elements and binding energies but not the molecule structural information of the surface monolayer. The polymerization details, that is, its initiation time and mechanism based on the composition changes of surface monolayer as a function of grafting procedure (e.g., grafting time) have not yet been investigated. Such an investigation is imperative to the better understanding of the overall photochemical grafting mechanism, which in turn will aid controlled surface layer formation eventually imparting control on surface modification procedure for biosensoric applications.

In the present work, different steps involved in photochemical functionalization (including the overall surface chemistry) of the diamond thin film surface have been elucidated by using time-of-flight secondary ion mass spectrometry (ToF-SIMS). The monolayer composition on the diamond surface as a function of grafting procedure leading to the elucidation of the trifluoroacetamide group protected allylamine (TFAAA) polymerization on the diamond surface was also studied; it was revealed that TFAAA polymerization starts already before the surface is fully covered by TFAAA, which is different from the previous report of TFAAD polymerization.[13]

It is well-known that high surface sensitivity and chemical specificity[14] of ToF-SIMS makes it quite suitable to obtain the compositional information of the surface monolayers; in our previous work it was used to characterize the linkage of amine group onto the diamond surface.[15] But, SIMS data overloading (data analysis) is a main drawback. To overcome the drawback, principal components analysis (PCA) was employed as an aid to the original data in this study. By employing PCA,[16−18] the complicated SIMS data sets can be reduced to a lower dimension (loadings and scores) to obtain explicit trivial data (see the Supporting Information). In this work, the optimal surface reaction times for different functionalization steps as derived from the PCA of the SIMS data will also be discussed; based on the overall SIMS analysis (including surface mapping), a modified chain reaction grafting model will also be proposed and discussed. Prior to the discussion, it is important to mention here (to understand the grafting model) that PCA of the ToF-SIMS data reiterates not only the successful TFAAA grafting[15] onto the diamond surface but also the optimal time (24 h) of UV illumination needed to obtain complete TFAAA surface coverage on diamond.

Experimental Section

Three micrometer thick polycrystalline diamond thin films grown on p-type Si(100) were used for the functionalization. The photochemical grafting of TFAAA on the diamond surface was discussed in our previous work[15] (see the Supporting Information).

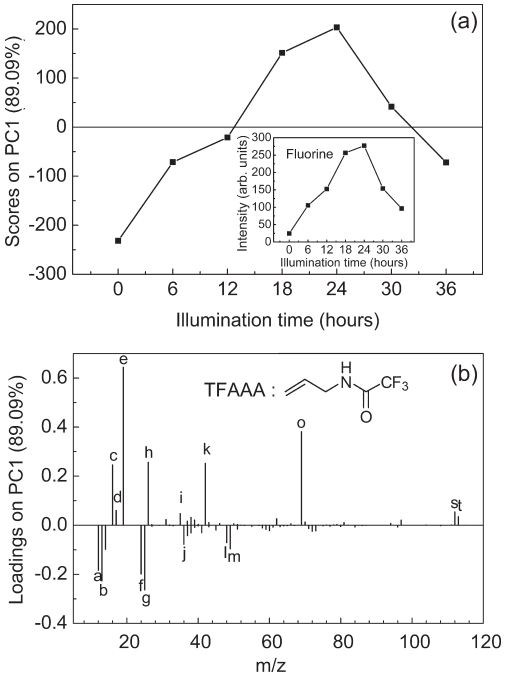

Figure 1. PCA of the ToF-SIMS data. PC1 (I) scores and (II) loadings from PCA of the negative ion spectra for different illumination times. a-t representations are given in Table 1. The structure of the TFAAA molecule is shown in the inset.

For SIMS measurement, a ToF-SIMS IV instrument (ION-TOF GmbH, Germany) was used to acquire the static data. The 25 keV Bi liquid metal ion gun was used at 1 μA emission current. Negative secondary ion mass spectra were acquired over the mass range from $m/z = 0$ to 800 using Bi^+ ions (target current $\sim$ 1.0 pA). The analysis area for each spectrum was 500 μm $\times$ 500 μm, and the acquisition time was set to 30 s. Each sample was measured at different places at least three times. The mass scale was calibrated using peak sets C^-, C_2^-, C_3^-, and CF_3^- and the errors were kept below 10 ppm. Images contained 256 $\times$ 256 pixels. All data were collected using an ion dose below the static SIMS limit of 1×10^{12} ions/cm^2. The mass resolution ($m/\Delta m$) of the negative secondary ion spectra was typically between 6000 and 7500 for $m/z = 26$ peak.

For each spectrum considered, all the peaks in the mass range 0−120 amu which are three times higher than the background were selected for PCA. Each raw spectrum was normalized by dividing the absolute peak intensity with the corrected total intensities discussed below. As a result of the low reproducibility of H^- and the high secondary ion yield of F^-, F^- ion intensity was normalized to the total intensity minus H^- intensity; the other ions are logically normalized to the total intensity minus the H^- and F^- intensities. All the spectra were put in an $n \times m$ matrix where the rows are samples (spectra) and the columns are variables (peaks). Before PCA, the data was mean-centered, which subtracts column means from each of the data points in the column.

Results and Discussion

Figure 1 shows the principal component (PC) 1 (a) scores versus illumination time and (b) loadings versus the peak

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Table 1. Significant Peaks of the Negative Ion ToF-SIMS Spectra of Diamond

negative mode peaks	12.000: C^- (a); 13.008: CH^- (b); 15.995: O^- (c); 17.003: OH^- (d); 18.998: F^- (e); 24.000: C_2^- (f); 25.008: C_2H^- (g); 26.003: CN^- (h); 34.969: Cl^- (i); 36.000: C_3^- (j); 41.998: CNO^- (k); 48.000: C_4^- (l); 49.008: C_4H^- (m); 63.944: S_2^- (n); 68.995: CF_3^- (o); 79.957: SO_3^- (p); 95.952: SO_4^- (q); 96.960: HSO_4^- (r); 112.001: $NHCOCF_3^-$ (s); 112.985: CF_3COO^- (t)

mass. The structure of the TFAAA molecule has been shown in the inset of Figure 1b. The peaks with significant loadings on PC1 are listed in Table 1. PC1 captured 89.09% of the total variance, suggesting that the major differences among the considered samples have been captured. The observed score trends suggest that different illumination times result in different surface structures. In PCA, the variables with higher positive loadings will, in general, have higher relative intensities in the spectra obtained from samples which have high positive scores on the same PC axis.[16] The sample without functionalization has the highest negative score implying that the carbon and carbon−hydrogen peaks dominate the whole spectrum which in turn shows the successful H-termination of the diamond surface. The sample with 24 h of UV illumination has the highest positive score implying that the characteristic peaks (e:F^-, h:CN^-, k:CNO^-, and o:CF_3^-) corresponding to TFAAA dominate the whole spectrum which in turn shows the successful grafting of TFAAA onto the diamond surface. For comparison, the samples with TFAAA but without UV illumination and without TFAAA but with UV illumination were also prepared to confirm the photochemical linkage of TFAAA onto the diamond surface (see the Supporting Information). The strong presence of the $NHCOCF_3^-$(s) peak implies that the protected group has not been dissociated during the photochemical reaction. Furthermore, peaks corresponding to $CHNHCOCF_3^-$ and $C_2H_2NHCOCF_3^-$ were also present (see the Supporting Information).

With the increasing illumination time (from 0 to 36 h), the PC1 scores at first increase, reach a maximum value at 24 h, and then drop. The score trend therefore describes the change in the peak intensities corresponding to TFAAA; to justify this, the normalized intensity of F^- obtained from samples with different illumination times has been shown in the inset of Figure 1a, which has exactly the same trend as that of the PC1 scores plot. In SIMS characterization of a surface monolayer, the ionization probability α is assumed to be a constant, and therefore the peak intensity (related to α) is a direct function of the surface coverage.[14] The initial increase in the PC1 scores (peak intensities) is related to the increase of the TFAAA coverage. With illumination time more than 24 h, the TFAAA layer grows thicker on the diamond surface, which results in the reduction of α,[14] which in turn results in the reduction of PC1 scores (peak intensities). This phenomenon and trend agree well with van Leyen et al.'s work.[19] According to the previous X-ray photoelectron spectroscopy (XPS) investigations that involved grafting of 10-aminodec-1-ene protected with trifluoroacetamide (TFAAD) onto a diamond surface, the

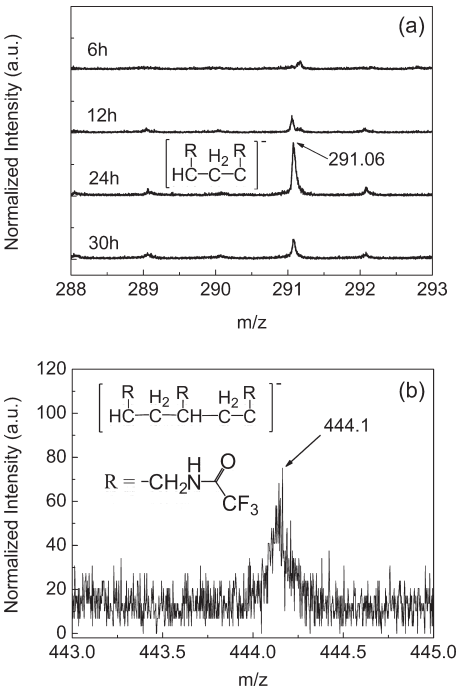

Figure 2. (a) Negative-mode ToF-SIMS spectra obtained in the mass range (a) 288−293 amu from the samples illuminated for different times; (b) 443−445 amu from the sample illuminated for 30 h.

coverage of the TFAAD layer versus time followed an exponential law: $R_{FC} = A[1 - \exp(-t/\tau)]$.[7,13] R_{FC} is the ratio of the F(1s) XPS signal to that of the C(1s) signal, A is the saturation R_{FC} observed after a long illumination time, t is the illumination time, and τ is the characteristic time constant. In the case of the single crystalline diamond surface (with spin coating of the TFAAD) the τ was 1.7 h,[13] while in the case of nanocrystalline diamond (without spin coating) it was 3 h.[7] Yang et al. investigated the growth of the TFAAD layer with different illumination times on single crystalline diamond by using atomic force microscopy (AFM) and proposed a chain reaction growth model; it was concluded that the highest TFAAD coverage needs 12 h of illumination, and with time greater than 12 h, 3D growth of the layer starts because of the cross-polymerization of TFAAD.[13] In the present study, the diamond surface microstructure and the method (dip coating) used in putting TFAAA onto the diamond surface (see the Supporting Information) are closer to the above-mentioned nanocrystalline diamond case; the higher τ value will result in a longer illumination time (for the surface to be covered by TFAAA monolayer), which is nearly 21 h according to the calculation. The measured value, which is 24 h (from SIMS data), agrees well with that of the calculated one.

As discussed above, long illumination time will lead to the cross-polymerization of TFAAA. Now the aim is to see if the same can be elucidated by SIMS. The negative mode SIMS spectra in the high mass range is shown in Figure 2. The peak at 291.06 corresponds to the species

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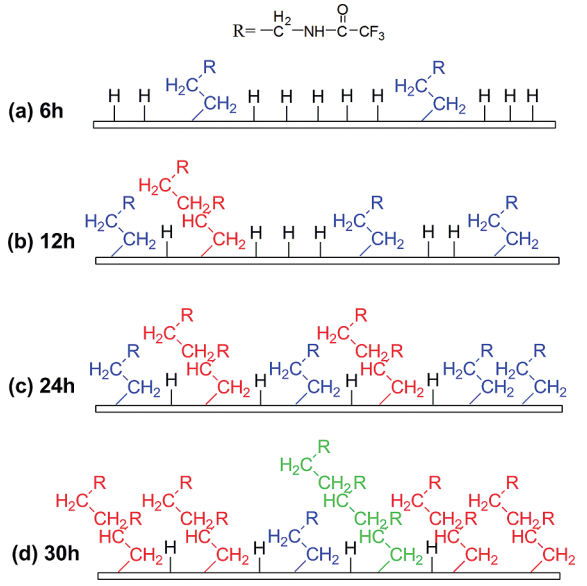

Figure 3. Illustration of TFAAA grafting on diamond with different illumination times. (a) 6 h; (b) 12 h; (c) 24 h; (d) 30 h. Meaning of different colors: black, original H-terminated diamond surface; blue, TFAAA; red, cross-polymerization of two TFAAA; green, cross-polymerization of three TFAAA. The representation for the group "R" is also shown in the figure.

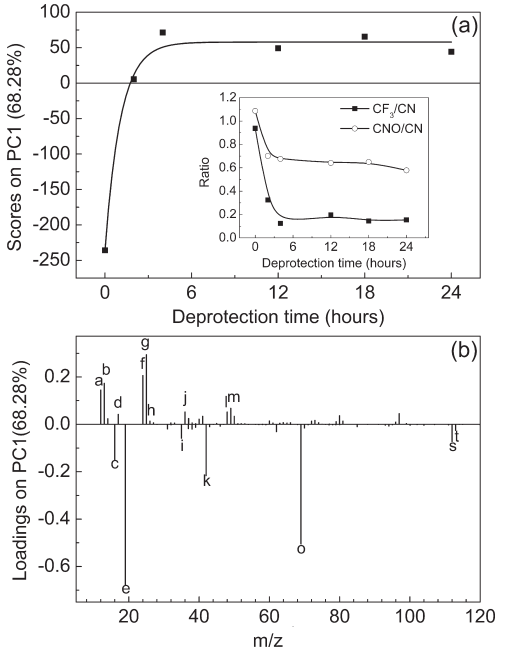

Figure 4. PCA of the ToF-SIMS data. PC1 (I) scores and (II) loadings from PCA of the negative ion spectra for different deprotection times. a-t representations are given in Table 1.

which has resulted from the cross-polymerization of two TFAAA molecules. By comparing different spectra (Figure 2), certain inferences can be easily made. The appearance of the 291.06 peak for 12 h of illumination implies that the polymerization has already started; this peak has the highest intensity for 24 h of illumination, but its intensity drops for 30 h which implies that the cross-polymerization has started even before the whole surface was covered by TFAAA. This result is different from Yang et al.'s result wherein the polymerization has started only after the whole surface was covered by the TFAAD.[13] However, allylamine in which the double bond of the allyl group is partially conjugated to the amine group (due to its resonance structure) may have a different reactivity from TFAAD which in turn may affect the overall reactivity of the molecule compared with TFAAD. Study on such an intricate aspect forms the scope of our future work. Herein we therefore propose a modified chain reaction growth model for TFAAA immobilization onto the diamond surface shown in Figure 3 which supplements Yang et al.'s work. With short UV illumination time (< 6 h), the immobilized TFAAA density on the diamond surface is not high, and as a result the chemical reacts with the diamond surface and forms a bond with it. With the illumination time greater than 12 h, the surface density of immobilized TFAAA molecules becomes higher, and some of the chemical starts to make covalent bonds with the already immobilized TFAAA. This discussion leads to the conclusion that there is a competition between TFAAA bonding to the diamond surface and its cross-polymerization. When the illumination time increases to 24 h, the surface is fully covered by TFAAA and has a higher coverage of TFAAA cross-polymerization, which in turn results in the observed high 291.06 peak intensity in the corresponding SIMS spectrum. With illumination time greater than 24 h, the chemicals can only link to the immobilized TFAAA, so that only cross-polymerization takes place during this period. Noticeably, the cross-polymerization of three TFAAA molecules can also be observed in the sample with 30 h of illumination (see Figure 2b). It is also interesting to see that the 291.06 peak intensity decreases with 30 h of illumination time (see Figure 2a). As illustrated in Figure 3c,d, compared with 24 h of illumination, the 30 h of illumination has more densely packed polymerized TFAAA. The increased coverage of such polymerized TFAAA will result in a long carbon chain array which will reduce the SIMS peak intensity corresponding to the large fragments due to the clipping mechanism that has been suggested by molecular dynamic simulations[20] and subsequently proven by Graham and Ratner's investigation.[21]

Subsequent to the photochemical attachment of TFAAA, the TFA protected amine group should be deprotected to necessitate the reaction between the primary amine and various biomolecules. PCA was also applied to analyze the SIMS data obtained from the deprotection procedure with different deprotection times. Figure 4 shows the PC1 (a) scores versus illumination time and (b) loadings versus the peak mass. PC1 captured 68.28% of the total variance. From Figure 4a, it can be observed that the time dependence of scores also follows approximately an exponential law, Score = $A[1 - \exp(-t/\tau)]$ with a time constant of τ of 1.0 h; the saturation of the score is achieved after about 4 h, which implies the deprotection is nearly completed after 4 h. From the loading plot, it can be observed that peak intensities of F^-, CNO^-, and CF_3^-

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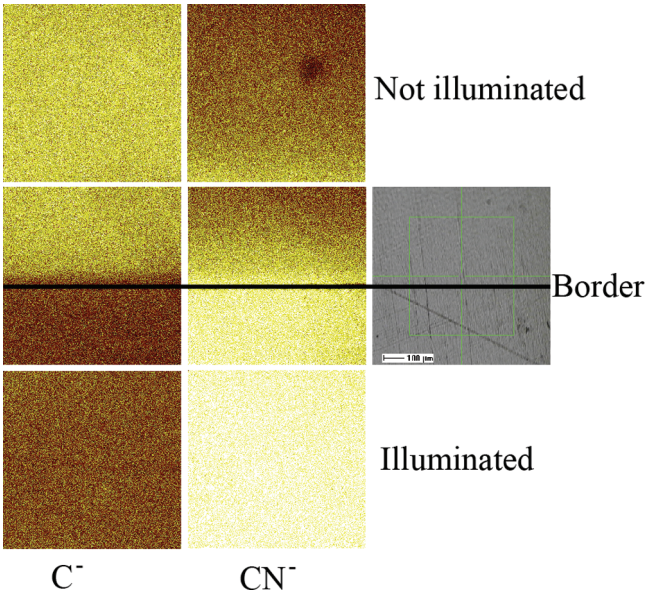

Figure 5. SIMS surface mapping image (corresponding to C^- and CN^-) of diamond sample with covalently attaced NH_2 group after employing a Cu shadow mask during the photochemical modification. The image area is 500 μm × 500 μm.

decreased a lot (with negative loadings) in the deprotected samples, while the peak intensity of CN^- remains nearly unchanged (see also Table S3 in the Supporting Information). This can be easily explained as follows: the deprotection procedure removes the TFA group which gives the characteristic F^-, CNO^-, and CF_3^- SIMS peaks and leaves the primary $-NH_2$ groups on the surface. The number of C−N bonds do not change in the deprotection procedure, which results in the constant intensity of CN^-. This phenomenon also implies that the linkage between allylamine and diamond is stable even under 24 h of refluxing in acidic conditions. The ratios of the intensities of CNO^- and CF_3^- to that of CN^- as a function of illumination time are also illustrated in the inset of Figure 4a, which have nearly the same trend as that of the scores.

To justify the success of the photochemical grafting and the uniformity of the amine group distribution on the diamond surface, a Cu mask with a 2 × 8 mm slit in the center (to allow the UV passage) was employed to cover the diamond surface during the photochemical functionalization. The masked sample was then illuminated for 24 h, and the patterned diamond was then reluxed in HCl in methanol for 4 h to deprotect the amine group. The SIMS surface mapping of the patterned sample is shown in Figure 5. A clear diffence can be observed between the illuminated area and the masked area. A high C^- intensity and low CN^- intensity can be observed in the masked area; however, in the illuminated area, the CN^- intensity is quite high. SIMS mapping in the illuminated area thus shows the uniform distribution of the amine group on the diamond surface, which implies the photochemical modification is quite suitable for the diamond surface functionalization. The successful surface patterning also proves that the photochemical funcationalization is a very useful way to array the sensor surface in the framework of high-throughput biosensor developments.

Conclusion

In conclusion, ToF-SIMS was used to reveal different steps involved in TFAAA functionalization of the diamond surface. It was understood that TFAAA cross-polymerizes on the diamond surface before the surface gets fully covered with TFAAA during a photochemical surface modification procedure. SIMS aided with PCA was used to systematically characterize the photochemical grafting of trifluoroacetamide group protected allylamine (TFAAA) onto the diamond thin film surface and the deprotection of the amine group. PCA of the SIMS data was also used to derive the optimal illumination time, which is 24 h, and deprotection time, which is 4 h. A modified chain reaction growth model to describe the photochemical grafting of TFAAA onto diamond was discussed in which there is a competition between TFAAA grafting and its cross-polymerization.

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Supporting Information Available: Details of the surface functionalization procedure and SIMS spectra of samples (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.