Photochemical Modification of Single Crystalline GaN Film Using $n$-Alkene with Different Carbon Chain Lengths as Biolinker

Chun Wang,† Hao Zhuang,‡ Nan Huang,† Steffen Heuser,‡ Christoph Schlemper,‡ Zhaofeng Zhai,† Baodan Liu,† Thorsten Staedler,‡ and Xin Jiang*†‡

†Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Wenhua Road 72, 110016 Shenyang, China
‡Institute of Materials Engineering, University of Siegen, Paul-Bonatz-Str. 9-11, 57076 Siegen, Germany

ABSTRACT: As a potential material for biosensing applications, gallium nitride (GaN) films have attracted remarkable attention. In order to construct GaN biosensors, a corresponding immobilization of biolinkers is of great importance in order to render a surface bioactive. In this work, two kinds of $n$-alkenes with different carbon chain lengths, namely allylamine protected with trifluoroacetamide (TFAA) and 10-aminodec-1-ene protected with trifluoroacetamide (TFAAD), were used to photochemically functionalize single crystalline GaN films. The successful linkage of both TFAAA and TFAAD to the GaN films is confirmed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurement. With increased UV illumination time, the intensity of the secondary ions corresponding to the linker molecules initially increases and subsequently decreases in both cases. Based on the SIMS measurements, the maximum coverage of TFAAA is achieved after 14 h of UV illumination, while only 2 h is required in the case of TFAAD to reach the situation of a fully covered GaN surface. This finding leads to the conclusion that the reaction rate of TFAAD is significantly higher compared to TFAAA. Measurements by atomic force microscopy (AFM) indicate that the coverage of GaN films by a TFAAA layer leads to an increased surface roughness. The atomic terraces, which are clearly observable for the pristine GaN films, disappear once the surface is fully covered by a TFAAA layer. Such TFAAA layers will feature a homogeneous surface topography even for reaction times of 24 h. In contrast to this, TFAAD shows strong cross-polymerization on the surface, this is confirmed by optical microscopy. These results demonstrate that TFAAA is a more suitable candidate as biolinker in context of the GaN surfaces due to its improved controllability.

INTRODUCTION

GaN, a wide band gap semiconductor, is a promising material for the fabrication of high electron mobility transistors, short-wavelength optoelectronics, and high-power electronics. At the same time, owing to its long-term chemical stability, non-toxicity, and excellent biocompatibility, GaN is also deemed to be a suitable material for biosensing applications. In order to utilize GaN as platform for biosensors, a stable linkage of biomolecules to its surface is a prerequisite. Since GaN is bioinert, some kind of functionalization is normally required to render its surface bioactive. One option to achieve this is a linkage of organic molecules with functional groups to the surface. In this context, several organic materials such as thiols combined with gold buffer layer coating, organosilane, and alkenes have been reported to successfully modify GaN films. Unfortunately, coating of GaN with gold layers would add an increased complexity to the fabrication process and reduce the sensitivity of the sensors. The functionalization with organosilane, on the other hand, would only be possible on oxidized GaN films. Such oxidized films, however, appear to encourage the concentration of hydroxyl groups on the surface, which potentially introduces challenges with respect to reproducibility. In addition, the degradation of the organosilane layer in a humid environment is also not conducive to the lifetime of the sensors. Moreover, due to their high reactivity, organosilane molecules easily form thick organic layers on the film, which deteriorate the performance of the corresponding sensors. As a result, GaN surface modifications based on alkenes, which feature the advantages of being simple and mild and which are realized by a photochemical method, received increased attention in recent years. Alkenes with different functional groups, both electron withdrawing and donating alkenes, have been intensively studied in the context of the functionalization of GaN surfaces. However, research on alkenes with different carbon chain length has not been carried out yet. Nevertheless, such kind of research is important and necessary since the length of the linker molecule is known to show significant influence on the sensitivity of the final biosensor. In this work, we studied the behavior of the photochemical reaction of $n$-alkenes featuring two different carbon-chain lengths on single crystalline GaN surfaces. TFAA (3-carbon chain) and TFAAD (10-carbon chain) were chosen as model linker molecules. ToF-SIMS and X-ray photoelectron spectroscopy (XPS) were carried out in order to...
study the differences in the linkage of both molecules to GaN surfaces. The experiments showed that TFAAA reacts with GaN at a much lower rate compared to TFAAD. Unfortunately, TFAAD demonstrated a significantly stronger cross-polymerization.

**EXPERIMENTAL SECTION**

**Materials.** Single crystalline GaN films were grown on c-plane sapphire substrates utilizing the hydrogen vapor phase epitaxy (HVPE) method. The phase and purity of as-grown GaN nanostructures were examined by a Rigaku RINT2000 X-ray powder diffractometer (XRD) with Cu Kα radiation. The functionalization procedure of the GaN surfaces was adapted from corresponding work reported in the context of functionalization of diamond surfaces. Prior to such a procedure, the GaN films were cleaned in acetone and alcohol. In a next step, they were then treated in piranha solution to remove any residual organic contaminations. Subsequently, it was dipped in 10% HCl solution to remove any potential oxide layer. Afterward, the films were washed three times with deionized water in an ultrasonic bath and, in turn, dried under nitrogen (N2) gas. TFAAA and TFAAD were dip-coated onto the GaN films. Details regarding the synthetic procedures of TFAAA and TFAAD are described in one of our previous publications as well as by Nebel et al. Finally, the samples were placed in a steel chamber sealed by a quartz window.

Prior to UV illumination, this chamber is evacuated (10\(^{-2}\) mbar) and filled with N2 to a pressure of 500 mbar. Subsequently, the samples were illuminated by UV light (\(\lambda = 254\) nm, Philips, TUV PL-L 35 W, 20 mW/cm\(^2\) at the sample surface) for different exposure times. Postfunctionalization, the samples were cleaned in acetone and alcohol to remove any unreacted reagents.

**Characterization.** ToF-SIMS measurements (ION-TOF GmbH, Germany) were carried out to acquire surface information after functionalization. In this context, a 25 keV Bi liquid metal ion gun was used at 1 \(\mu\)A emission current. Each measurement was carried out on a surface area of 500 \(\mu\)m \(\times\) 500 \(\mu\)m while the acquisition time was set to 30 s. For each spectrum, the mass scale was calibrated by utilization of the peaks of C\(^{-}\), C\(^{2-}\) and C\(^{3-}\). In order to compare the results of the various samples, the spectra initially have to be normalized. This normalization is based on the division of the absolute peak intensity by the corrected total intensity. Details of this procedure are described below. As a result of the low reproducibility of the H\(^-\) signal and the high secondary ion yield of F\(^-\), F\(^{+}\) ion intensity was normalized to the total intensity excluding the contribution of the H\(^-\) signal. All other ion signals were logically normalized to the total intensity minus the contribution of the H\(^-\) and F\(^+\) signals. XPS measurements were recorded on an ESCALAB250 (Thermo VG) using a monochromated Al Kα beam as X-ray source. The C (1s) sp\(^3\) carbon peak was calibrated at 284.6 eV, and all other XPS spectra were calibrated accordingly based on the position of their sp\(^2\) carbon peak. AFM

---

**Figure 1.** (a) XPS C (1s) spectrum of a GaN film after TFAAA modification and UV illumination for 14 h. (b) XPS F (1s) spectrum of a bare GaN film (black line) and the same film after TFAAA modification and UV illumination for 14 h (red line).

**Figure 2.** ToF-SIMS results of a GaN film before (i) and after (ii) TFAAA modification in combination with UV illumination for 14 h. The structure of TFAAA is shown in the inset.
surface images were acquired on a psia XE-100 instrument. The optical images were recorded on an Olympus BX51 microscope.

**RESULTS**

**Grafting of TFAAA to GaN.** Figure 1 shows the XPS spectra of GaN after functionalization with TFAAA. The C (1s) spectrum as illustrated in Figure 1a can be deconvoluted into several peaks associated with different specific chemical states. Among those, the sp$^3$ carbon peak is located at 284.6 eV (width = 1.43 eV) while the peak assigned to 285.4 eV (width = 2.27 eV) stems from the alkyl chain ($\text{C}_x-\text{C}_y-\text{H}_z$) of TFAAA.\textsuperscript{18} The peaks located at 288.3 eV (width = 1.86 eV) and 292.5 eV (width = 1.20 eV) are indication of carbonyl ($\text{C}==\text{O}$) and CF$_3$ groups, respectively.\textsuperscript{6} This carbonyl is related to the trifluoroacetamide (TFA) protecting group. Furthermore, after TFAAA modification, a peak at 687.8 eV can be observed in the F (1s) spectrum shown in Figure 1b. In summary, these findings signify a successful functionalization of a single crystalline GaN film with TFAAA.

Figure 2 shows results obtained in the negative mode of ToF-SIMS for a GaN film before and after TFAAA modification. Because of its sensitivity and feasibility in obtaining composition and chemical structure of a surface layer, ToF-SIMS has been previously employed to analyze the linkage of TFAAA to diamond and silicon carbide films.\textsuperscript{19,20} For the GaN film after acid treatment, the spectrum is dominated by strong peaks corresponding to O$^-$ (15.995) and OH$^-$ (17.003), signifying an oxygen termination of the GaN surface. The minor peaks corresponding to the hydrocarbon fragments, namely C$_x$H$_y$ (x = 1, 2, ...; y = 0, 1, ...) can be attributed to the contamination of the surface before exposing it to air prior to the actual SIMS measurement. Peaks related to Cl$^-$ and SO$_3^-$ can also be observed. These originate from residual acidic species formed during the surface cleaning process. Except for the peaks mentioned above, no characteristic peaks corresponding to TFAAA are observable. However, after a reaction of TFAAA under UV illumination for 14 h, the spectrum is dominated by peaks corresponding to TFAAA: F$^-$ (19.000), CN$^-$ (26.003), CNO$^-$ (42.001), and CF$_3^-$ (68.999). This finding indicates a successful linkage of TFAAA on GaN. Moreover, the intensity of the OH$^-$ signal acquired from the GaN surface decreases, indicating the coverage of the surface by the organic TFAAA layers. In addition, as illustrated in Figure S1a of the Supporting Information, peaks corresponding to NHCOCF$_3^-$ (111.998) and CHNHCOCF$_3^-$ (125.017) also appear in the mass range of 110–160 amu. The existence of these peaks implies the nondegradation of the TFAA protected amine group under UV illumination. Based on such a result, the amino groups can be deprotected following a simple chemical process in order to link biomolecules to a GaN surface.\textsuperscript{16,21} For comparison, the spectrum of a GaN film covered with TFAAA but without UV illumination is shown in Figure S2a. The whole spectrum is dominated by peaks corresponding to O$^-$ and OH$^-$. Even though the peak related to F$^-$ is observable, too, its intensity is very low. Its presence could be explained by nonspecifically adsorbed TFAA molecules on the surface. These results, which agree well with the XPS observation, strongly indicate that the single crystalline GaN film is successfully functionalized with TFAAA under UV illumination.

Figure 3 illustrates the normalized intensities of the F$^-$, CNO$^-$, CN$^-$, and CF$_3^-$ peaks after various UV illumination times. This information allows for the deduction of the surface coverage of TFAAA on GaN. With increasing UV illumination time, the intensity of all species initially increases; a maximum is reached at 14 h. For longer illumination times, a decrease in intensity is observed for all peaks. It is well-known that the SIMS ion intensity is related to the fractional concentration of the specific element in the analyzed volume \( \theta \) as well as its ionization probability \( \alpha \).\textsuperscript{22} In SIMS characterization of a surface monolayer, \( \alpha \) is typically assumed to be constant. Therefore, at the initial functionalization stage, which is associated with an incomplete coverage of the surface, the SIMS intensity is a direct function of this surface coverage. In this context, an increasing SIMS intensity of a characteristic peak corresponding to TFAAA signifies an increasing coverage of TFAAA on the GaN surface with increasing UV illumination time. However, once the surface layer becomes thicker than one monolayer, \( \alpha \) starts to decrease, which in turn leads to a decreasing intensity of the corresponding peaks.\textsuperscript{23} Moreover, the increased intermolecular forces present in a thicker film also result in a reduction of peak intensity.\textsuperscript{22} Since the maximum intensity is reached at 14 h of UV illumination for all peaks corresponding to TFAAA, it is possible to conclude that the maximum coverage of TFAAA on GaN is achieved at that time. Topographical AFM images of GaN films before and after the modification with TFAAA are shown in Figure 4. The result for the as grown single crystalline GaN film is presented in Figure 4a. Here, the atomic terraces are clearly observable, and the roughness is estimated to be 0.424 nm (\( R_q \)) on scale of 1 \( \mu \text{m} \times 1 \mu \text{m} \). Additionally, the morphology of a GaN surface after acid treatment, as received by AFM, is shown in Figure S3. The results reveal no obvious changes of GaN surface after acid treatments. However, after a reaction with TFAAA under UV illumination for 14 h, a high density of TFAAA islands is noticed on the GaN film surface. Consequently, the surface roughness increases to 2.237 nm. Moreover, the atomic terraces no longer observable, which hints at a complete coverage of surface by an organic layer. On the basis of the AFM results, we could draw the conclusion that the TFAAA film is thicker than a monolayer. The reason behind this might lie in the cross-polymerization between TFAAA molecules. In analogy to our findings in the context of TFAAA functionalization of diamond films, TFAAA molecules potentially react with both the film surface and themselves, leading to a 3D structure.\textsuperscript{15}
Grafting of TFAAD to GaN. Figure 5 shows the spectra of single crystalline GaN films before and after modification with the long-carbon-chain molecule, TFAAD, obtained in negative mode ToF-SIMS. After a functionalization for 2 h, the corresponding spectrum is dominated by peaks corresponding to TFAAD: F$^-$ (19.000), CN$^-$ (26.003), CNO$^-$ (42.001), and CF$_3^-$ (68.999). This finding indicates a successful linkage of TFAAD onto the GaN surface. In comparison to Figure 2, a higher intensity of the hydrocarbon species (C$^-$, CH$^-$, C$_2$H$^-$) is observed, which directly corresponds to the longer carbon-chain length of the TFAAD molecules. As illustrated in Figure S1b, peaks corresponding to (CH)$_2$(CH$_2$)$_n$NHCOCF$_3^-$ (222.181), (CH)$_2$NHCOCF$_3^-$ (238.167), etc., appear in the mass range of 120–250 amu. The existence of these peaks is further proof of the already mentioned finding that the TFAA protected amine group in TFAAD is not damaged under UV illumination. The SIMS spectrum of the sample, which has not been exposed to UV illumination after TFAAD modification, is shown in Figure S2b. Comparable to the case of TFAAA, only a small peak corresponding to F$^-$ is observed, indicating that TFAAA molecules do not react with the GaN surface without UV illumination.

The normalized intensities of the characteristic SIMS peaks, namely F$^-$, CNO$^-$, CN$^-$, and CF$_3^-$ groups, which correspond to the TFAAD coverage, are shown in Figure 6 with respect to various UV illumination times. As in the case of TFAAA, the intensity of all peaks initially increases. Here, however, the maxima are reached after 2 h of illumination time and subsequently decrease. Based on our discussion in the previous section, the maximum coverage of TFAAD on the GaN film surface is thus achieved after 2 h of UV illumination.

Optical Morphologies of TFAAA and TFAAD on GaN. The optical images of samples modified by TFAAA and TFAAD are shown in Figure S4. Two representative images of the corresponding samples have been selected and are shown in Figure 7. GaN films subject to a TFAAA or TFAAD treatment left in darkness for 48 h do not show any significant differences in comparison to a blank GaN film sample. However, once the surface is modified with TFAAD and illuminated by UV for only 2 h, a strong inhomogeneity of the surface can be observed (see Figure 7a). This finding can potentially be explained by
cross-polymerization of the TFAAD on the GaN film surface, which occurs even after a relative short UV illumination time. Even though it appears more convincing to compare the morphology of the GaN films functionalized with TFAAA and TFAAD by AFM, such small scale measurements sometimes struggle to be a good representation of a larger area. In case of the TFAAD cross-polymerizing into a thin polymeric film on the surface, as shown in the Figure 7 and Figure S4, for example, local detachment of this polymeric film can be observed. In latter case any individual AFM measurement would most likely fail to show the overall cross-polymerization of the TFAAD layer on the surface. Nevertheless, the corresponding optical surface image of GaN modified with TFAAA remains nearly unchanged even for the case of an increased UV illumination time. The latter indicates a homogeneous reaction of TFAAA with the GaN surface. It is noteworthy that the maximum coverage of TFAAA on GaN is only achieved after 14 h of UV illumination time, which is significantly longer compared to the time required in the case of a TFAAD treatment. Consequently, the reaction rate of TFAAD with GaN appears to be higher than that of TFAAA. Unfortunately, optical microscopy signifies a severe cross-polymerization in the TFAAD case, rendering it difficult to achieve an organic monolayer on GaN corresponding with the one found for the TFAAA case.

**DISCUSSION**

In analogy to other semiconducting materials, the mechanism of photochemical modification of GaN with alkenes follows a two-step process: photoelectron emission followed by a nucleophilic reaction. During the photoemission step, electrons from the surface will move to the corresponding electron-acceptor levels of the alkenes. Subsequently, surface holes, which have been created in the initial step, play an important role in the nucleophilic attack of other alkene molecules. Although electron–hole pairs in a GaN film ($E_g = 3.37$ eV) could be created by UV illumination (here, $\lambda = 254$ nm, with a corresponding photon energy of 4.88 eV), the dominant source of electrons remains photoelectron emission. In our present process, the rate-limiting step is attributed to the differences of the chemicals used for the functionalization process, which, in turn, leads to different nucleophilic reaction rates. It is well-known that the electron-withdrawing groups of the alkene molecules are able to decelerate the nucleophilic addition reaction on the C=C groups while electron-donating groups accelerate it. Since the TFA group is a strong electron-withdrawing group, its presence in the molecules can slow down the reaction rate of the alkenes with the surface, even though it captures the surface photoemitted electrons and initiates the photochemical reaction. On the other hand, the –(CH$_2$)$_n$– groups are considered as electron-donating groups. In this context, the influence of the TFA groups on the process of electron withdrawing is screened for the case of a long carbon chain. A longer carbon chain also decreases the space hindrance of the TFA groups. Furthermore, the angle formed between the molecules and the surface potentially also has an influence on the reaction rate of the molecules. TFAAD moieties with a long alky chain could be introduced with a tilt with respect to the surface of GaN, while TFAAA will align vertically on the GaN surface. As a result, TFAAD shows a higher reaction rate compared to TFAAA during the photochemical modification. In addition, during modification, small amounts of water and oxygen may still exist in the chamber and would also affect the reaction behavior of organic layers, which needs further research in the future.

The functionalization of GaN films is a crucial step in utilizing GaN for biosensor applications. To guarantee a good performance of the biosensors, the bonds between the biomolecules and the GaN surface need to be stable enough. Moreover, control over the formation of the organic layers is required to achieve a high sensitivity. The results shown here indicate that TFAAA is superior to TFAAD in functionalizing of a GaN surface. This result can be explained by the higher reactivity of TFAAD compared to TFAAA. This higher reactivity results in the formation of a thicker TFAAD layer, which, additionally, features severe surface cross-polymerization, as illustrated in Figure 7 and Figure S4. Moreover, based on theoretical calculations, the organic linker molecule should be as short as possible to achieve the highest sensor sensitivity. In this context, it has been reported that glucose biosensor modified by biolinkers with longer carbon chains showed higher electron transfer resistance, while the biosensor modified with a shorter carbon chain gave rise to higher detection sensitivity.
CONCLUSION

In this work, two kinds of n-alkenes with different carbon chain lengths, TFAA and TFAAD, are used to functionalize single-crystalline GaN films. SIMS, XPS, and AFM measurements are carried out to characterize the corresponding functional surface layers. Similar phenomena are observed for both cases: the SIMS peak intensity of $F^-$, $CNO^-$, $CN^-$, and $CF_2^-$ groups initially increases and subsequently decreases with increasing UV illumination time. This behavior is explained by a decreased ionization probability $\alpha$ after a full coverage of the GaN surface with the organic layer is reached. The surface morphology after TFAA modification is recorded using AFM. With increasing UV illumination time, the GaN film is fully covered by a TFAA layer. TFAA shows a higher reactivity. In this case, a full coverage is already reached after 2 h. However, in the case of TFAAD, optical imaging indicates a significantly stronger tendency for cross-polymerization on the GaN surface. The latter finding illustrates the difficulty to control the formation of a monolayer by means of TFAAD. On the other hand, GaN films functionalized with TFAAD show no visible cross-polymerization even after a UV illumination for 24 h; in summary, all the findings presented here are a clear indication that TFAA is more suitable to be used as biolinker for single-crystalline GaN films. Nevertheless, the evaluation of the actual biosensing properties of the functionalized surfaces is beyond the scope of this paper. Consequently, the study of the sensing behavior of GaN films functionalized by TFAA will be part of our current research goals and work is in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b00837.

Figures S1–S4 (PDF)

AUTHOR INFORMATION

*E-mail: xjiang@imr.ac.cn (X.J.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We sincerely acknowledge financial support from the National Natural Science Foundation of China (Grant No. 51202257). B. D. Liu also thanks the Chinese Scholarship Council (Grant No. 201400260067) for the support of this work. T. Staedler also thanks the DAAD for the financial support of this work under Grant No. 57054770.

REFERENCES


