Influence of Surface Hydroxylation on 3-Aminopropyltriethoxysilane Growth Mode during Chemical Functionalization of GaN Surfaces: An Angle-Resolved X-ray Photoelectron Spectroscopy Study

A. Arranz,[†] C. Palacio,[*,†] D. García-Fresnadillo,[‡] G. Orellana,[‡] A. Navarro,[§] and E. Muñoz[§]

Departamento de Física Aplicada, Facultad de Ciencias, C-XII, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain, Laboratory of Applied Photochemistry, Department of Organic Chemistry, Faculty of Chemistry, Universidad Complutense de Madrid, 28040 Madrid, Spain, and ISOM and Departamento de Ingeniería Electrónica, ETSI Telecomunicación, Universidad Politécnica de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain

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A comparative study of the chemical functionalization of undoped, n- and p-type GaN layers grown on sapphire substrates by metal−organic chemical vapor deposition was carried out. Both types of samples were chemically functionalized with 3-aminopropyltriethoxysilane (APTES) using a well-established silane-based approach for functionalizing hydroxylated surfaces. The untreated surfaces as well as those modified by hydroxylation and APTES deposition were analyzed using angle-resolved X-ray photoelectron spectroscopy. Strong differences were found between the APTES growth modes on n- and p-GaN surfaces that can be associated with the number of available hydroxyl groups on the GaN surface of each sample. Depending on the density of surface hydroxyl groups, different mechanisms of APTES attachment to the GaN surface take place in such a way that the APTES growth mode changes from a monolayer to a multilayer growth mode when the number of surface hydroxyl groups is decreased. Specifically, a monolayer growth mode with a surface coverage of ∼78% was found on p-GaN, whereas the formation of a dense film, ∼3 monolayers thick, was observed on n-GaN.

Introduction

During the last few years, there has been an increasing interest in combining microelectronics and biotechnology for integrated sensing applications, in such a way that several devices based on biologically modified semiconductors have been proposed in the literature.[1–13] Among semiconductor materials, gallium nitride thin films are especially attractive for biosensing applications because of their good optical and electrical properties and high chemical stability under physiological conditions, which make them biocompatible substrates for biomolecular covalent coupling.[7–14] Before the attachment of the biosensing molecules, the GaN surface must be functionalized with organosilanes having reactive groups that allow the subsequent immobilization of such biomolecules via covalent bonds. Therefore, a detailed characterization of the surface in this first step is of crucial importance since a poor initial surface functionalization will prevent an appropriate attachment of the biosensing molecules. Because of its high surface sensitivity, X-ray photoelectron spectroscopy (XPS) has been widely used to prove the attachment of organosilanes carrying reactive amino or thiol groups. However, little attention has been devoted to the morphology of such films.[1–5,10–15]

The purpose of this work was to carry out a comparative study of the chemical functionalization of n-type (nonintentionally doped) and p-type GaN surfaces. Both layers were chemically functionalized with 3-aminopropyltriethoxysilane (APTES) using a procedure described by Baur et al. for silane-based functionalization of hydroxylated surfaces.[10] The untreated surfaces, as well as those modified by the two steps of the functionalization procedure, namely, hydroxylation and APTES deposition, were analyzed using angle-resolved X-ray photoelectron spectroscopy (ARXPS). This not only demonstrates APTES attachment on the surface but also obtains the morphology of the deposited APTES films, that is, the growth mode. Strong differences have been found between the APTES growth mode on n- and p-GaN surfaces. A self-assembled monolayer (SAM) growth mode with a surface coverage of ∼78% was found for the p-GaN substrate, whereas for the n-type GaN substrate, APTES forms a dense film, ∼3 monolayer thick. This difference in the growth mode

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[*] Corresponding author. Fax: ++ 34 91 4974949; E-mail: carlos.palacio@uam.es.

[†] Universidad Autónoma de Madrid.

[‡] Universidad Complutense de Madrid.

[§] Universidad Politécnica de Madrid.

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of the APTES film is discussed according to the different behavior of n- and p-GaN substrates upon hydroxylation.

Experimental Procedures

Nonintentionally doped n- and p-type (Mg doped) GaN layers, grown on c-face sapphire substrates by MOCVD were used throughout this work. Electron and hole concentrations were in the mid-10^{17} cm^{-3} range. Both layers have a surface roughness below 2 nm as measured by atomic force microscopy. The chemical functionalization of both samples was carried out with 3-aminopropyltriethoxysilane ($NH_2(CH_2)_3Si(OC_2H_5)_3$, APTES, Sigma-Aldrich) using the procedure described by Baur et al.[10] In the first step, GaN hydroxylated surfaces were prepared by cleaning the samples in piranha solution, H_2SO_4/H_2O_2 (3:1 v/v) since the formation of hydroxyl groups on the surface is required for the silanization process. The substrates were treated for 20 min with a fresh solution prepared in situ. Preparation of this solution is a strongly exothermal process (with heat and vapor evolution). Therefore, the process was not carried out at room temperature. After this treatment, the substrates were rinsed with deionized water (18 MΩ cm, Millipore) and dried under argon flux and finally under vacuum (0.1 Torr) overnight. After the cleaning procedure using the piranha solution, all samples displayed carbon contamination as detected by XPS. The origin of carbon contamination is attributed to the uptake of volatile carbon containing compounds during sample transport from the chemical preparation laboratory to the XPS analysis chamber. However, bulk carbon contamination was ruled out since GaN samples similar to those used in this work, which were sputter-cleaned in UHV conditions, displayed free carbon surfaces. In a second step, APTES attachment was carried out also following the procedure described by Baur et al.[10] The XPS analysis was performed in an UHV system at a base pressure below 6×10^{-10} Torr. XPS spectra were obtained using a hemispherical analyzer (SPECS Phoibos 100 MCD-5). The pass energy was 9 eV, giving a constant resolution of 0.9 eV. The Au $4f_{7/2}$, Ag $3d_{5/2}$, and Cu $2p_{3/2}$ lines of reference samples at 84.0, 368.3, and 932.7 eV, respectively, were used to calibrate binding energies. Although sample charging was observed due to the insulating character of the sapphire substrates, this effect was corrected, peaking the C 1s band at 285.0 eV and shifting accordingly all other core levels. A twin anode (Mg and Al) X-ray source was operated at a constant power of 300 W. All core level spectra were recorded using Mg Kα radiation. However, due to the strong overlapping of the C 1s photoemission peak with the Ga LMM Auger transition using Mg Kα radiation, the C 1s core level spectra also were recorded using Al Kα radiation. The samples were placed in a sample holder with four degrees of freedom in such a way that the takeoff angle of the electrons could be varied between 0 and 70° to perform angle-resolved measurements.

Results and Discussion

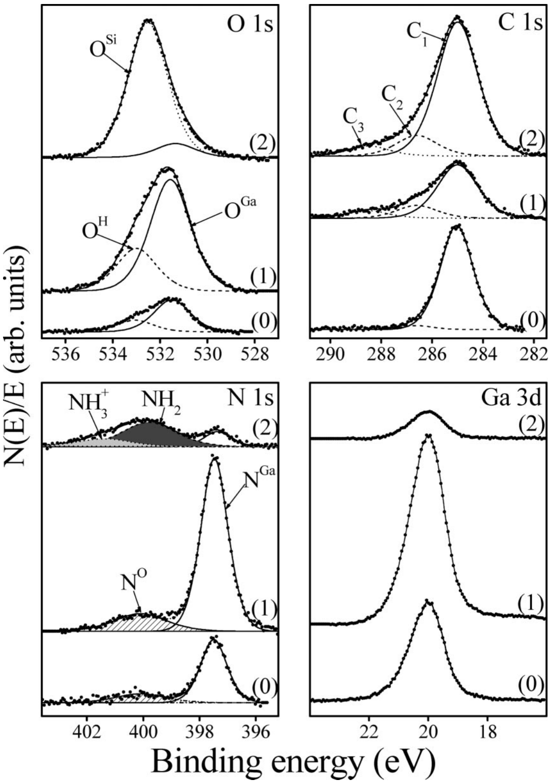

Figure 1. O 1s, C 1s, N 1s, and Ga 3d core level XPS spectra, measured with a takeoff angle φ of 70°, for untreated (0), hydroxylated (1), and APTES functionalized (2) n-type GaN. Deconvolution of spectra is explained in the text.

Figure 1 shows the O 1s, C 1s, N 1s, and Ga 3d core level XPS spectra, measured with a takeoff angle φ of 70°, for untreated, hydroxylated, and APTES functionalized n-GaN samples, labeled as (0), (1), and (2), respectively. The background was subtracted using a modified Shirley method.[16] Those core level spectra also were measured for different takeoff angles between 0 and 70° to allow further analysis of the APTES attachment mode. Similar measurements were carried out on the p-GaN sample. The spectra were analyzed as follows: The O 1s spectra of the untreated and hydroxylated surfaces were deconvoluted using two components, O^{H} and O^{Ga}, at 533.0 ± 0.1 and 531.5 ± 0.1 eV, which are attributed to O−H and O−Ga bonds, respectively.[17,18] For the APTES functionalized surface, a new component, O^{Si} at 532.4 ± 0.1 eV, was used. This component is attributed to O−Si bonds formed during attachment of the APTES molecules.[19–21] The C 1s spectra were deconvoluted using three components, C_1, C_2, and C_3, at 285.0 ± 0.1, 286.6 ± 0.1, and 288.5 ± 0.1 eV, which can be attributed to C−C+C−H, C−O, and C═O bonds, respectively, for the untreated and hydroxylated surfaces, whereas for the APTES functionalized surface, contributions from C−Si and C−N bonds also are expected in the C_1 and C_2 peaks, respectively.[11,15] The N 1s spectra of the untreated and hydroxylated surfaces were deconvoluted into two components, N^{Ga} and N^{O}, at 397.4 ± 0.1 and 400.0 ± 0.1 eV, which can be attributed to N−Ga and N−O bonds, respectively.[10,22] The high binding energy peak, N^{O}, of the untreated and hydroxylated surfaces suggests the formation of oxynitride species during hydroxylation of GaN samples as observed during the oxidation of transition metal nitrides.[23] For the APTES functionalized surface, the high binding energy side of the N 1s core level shows a more complex structure with components NH_2 (dark gray area) and NH_3^+ (light gray area), at 399.8 ± 0.1 and 401.4 ± 0.1 eV, which can be attributed to neutral (NH_2) and (NH_3^+) ω-amino end groups, respectively.[10,20,24] There is strong attenuation that shows the N^{Ga} signal after APTES attachment. Since a similar attenuation is expected for the N^{O} component characteristic of the untreated and hydroxylated surfaces, and

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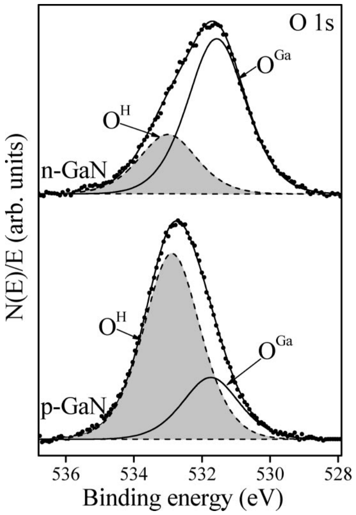

Figure 2. Comparison of O 1s XPS core level spectra measured with a takeoff angle φ of 70° for hydroxylated n- and p-type GaN layers.

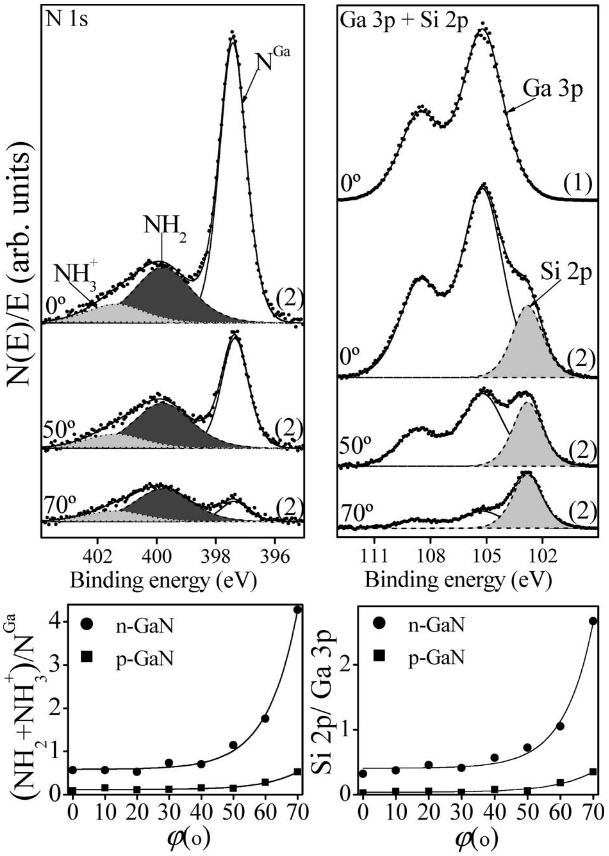

Figure 3. N 1s (upper left side) and overlapping Ga 3p + Si 2p (upper right side) core level spectra of APTES functionalized (2) n-GaN sample for several takeoff angles and $NH_2 + NH_3^+/N^{Ga}$ and Si 2p/Ga 3p peak area ratios for n- and p-GaN, as a function of the takeoff angle (lower side). The Ga 3p core level spectrum of the hydroxylated surface (1) measured for a takeoff angle φ of 0° also is shown as a reference. Deconvolution of spectra is explained in the text.

considering the severe overlapping between N^{O} and NH_2 components, no attempt to use the N^{O} component was carried out for spectral deconvolution of APTES functionalized surfaces. However, a small contribution of the N^{O} component within the band associated with NH_2 of Figure 1 cannot be completely ruled out. The Ga 3d core level shows a slightly asymmetric shape at high binding energies that can be attributed to Ga−O species. Those bands are only representative of the GaN sample, and therefore, no attempt to deconvolute them was carried out.

ARXPS measurements for the C 1s band show a strong increase of carbon concentration with increasing takeoff angle, indicating that carbon contamination is located on the outer surface. The carbon concentration measured after piranha treatment for n-GaN was 5.6 and 22.8% for takeoff angles of 0 and 70°, respectively. For p-GaN, the carbon concentration was 4.0 and 14.5% (0 and 70°, respectively). As observed in Figure 1, for n-GaN, the highly oxidative treatment for hydroxylation of the surface (step 1) strongly decreases the carbon contamination leading to an increase of GaN signals, Ga 3d and N^{Ga}. In addition to that, the surface chemical treatment carried out to create surface hydroxyl groups[10] leads to an overall increase of the O 1s signal due to the formation of a thin oxide layer. Considering that the inelastic mean free path (IMFP) for Ga 3d is $\lambda_{Ga} = 29.9$ Å and also that the takeoff angle used for XPS measurements was 70°, an upper limit for the oxide thickness of $3\lambda_{Ga}\cos(70°) \sim 30$ Å can be estimated. Although hydroxyl (-OH) groups already are present in the native oxide of the untreated surface, the observed decrease of hydrocarbon contamination makes the surface hydroxyl groups more accessible to APTES molecules, therefore promoting their attachment to the surface. In Figure 2, the O 1s XPS core level spectra measured with a 70° takeoff angle for hydroxylated n- and p-GaN layers are compared. Figure 2 clearly shows that the oxide film formed on the GaN surface after the hydroxylation step strongly depends on the semiconductor type as a consequence of the different reactivity of n- and p-GaN surfaces. Similar spectra to those shown in Figure 2 can be found in the literature for the n- and p-GaN native oxides, respectively.[17,18] The O^{H}/O^{Ga} peak area ratios are 0.4 and 3.0 for n- and p-GaN surfaces, respectively, indicating that the oxide films formed after hydroxylation are mainly gallium oxide for n-type GaN samples or gallium hydroxide-like for p-type GaN samples. Moreover, the intensity of the N^{O} component for the p-GaN sample is half of that shown in Figure 1 for n-GaN as a consequence of the different type of oxide formed on the GaN surfaces upon hydroxylation. The H_2SO_4/H_2O_2 mixture used for oxidative treatment generates hydroxyl radicals ($HO^\bullet$) that turn into hydroxy anions (HO^-) upon oxidation. The highly nucleophilic HO^- reacts at a faster rate with the electron-deficient p-type semiconductor surface than with the electron-balanced n-GaN. Therefore, the p-GaN surface is richer in OH groups for the attachment of the APTES molecules, and this difference, as we will see later, leads to differences in the APTES growth mode.

As can be observed in Figure 1, APTES attachment is characterized by an increase of the carbon signal and a decrease of the Ga 3d and N^{Ga} signals, characteristic of the GaN layer, along with changes in the O 1s core level associated with the formation of Si−O bonds. As indicated previously, component C_3 of Figure 1 is associated with the oxidation of carbon (C=O). The concentration for this component calculated using sensitivity factors provided by the manufacturer is 2.3% for the hydroxylated n-GaN surface and increases slightly up to 2.9% for the APTES deposited surface for a takeoff angle of 70° as shown in Figure 1, therefore suggesting that either the remaining carbon contamination or some carbon atoms of the APTES molecule are further oxidized during transference of the samples from the chemical laboratory to the XPS vacuum chamber. Likewise, Si and amino species, characteristic of the APTES molecule, are observed on top of the GaN layer as discussed next. Figure 3 shows the N 1s (upper left side) and overlapped Ga 3p + Si 2p (upper right side) core level spectra of the APTES functionalized n-GaN sample for different takeoff angles. The Ga 3p core level spectrum of the hydroxylated surface (step 1) measured for φ

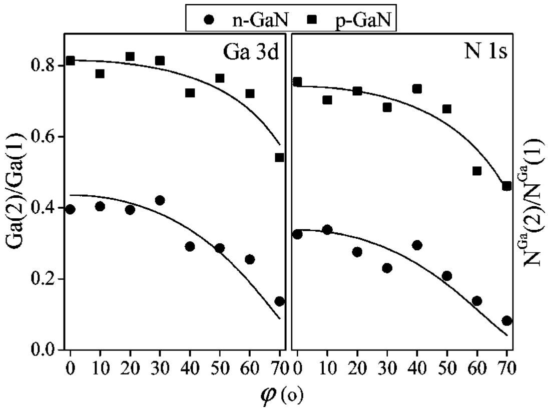

Figure 4. Ga(2)/Ga(1) and $N^{Ga}(2)/N^{Ga}(1)$ peak area ratios as a function of the takeoff angle (symbols) for n- and p-GaN. The best-fit to models proposed by eqs 1 and 2, for n-GaN and p-GaN, respectively, as explained in the text are shown by solid lines.

= 0° also is shown as a reference. The deconvolution of the N 1s spectra using N^{Ga}, NH_2, and NH_3^+, as previously discussed, also is shown. The Ga 3p + Si 2p spectra were deconvoluted using a component at 102.9 ± 0.1 eV for the Si 2p band and a double peak for the Ga 3p doublet. For this doublet, a Ga $3p_{3/2}$ main peak at 105.2 ± 0.1 eV, a spin−orbit splitting of 3.4−3.5 eV, and a theoretical Ga $3p_{3/2}/3p_{1/2}$ area ratio of 2 were used. In Figure 3, N^{Ga} and Ga 3p components are characteristic of the GaN layer, whereas $NH_2 + NH_3^+$ and Si 2p components are associated with APTES molecules. Evolution of the $NH_2 + NH_3^+/N^{Ga}$ and Si 2p/Ga 3p peak area ratios for n- and p-GaN samples, as a function of the takeoff angle, are shown at the bottom of Figure 3. These ratios increase with increasing takeoff angle, indicating that the APTES attachment takes place on top of the GaN surface.[25] The peak area ratios for p-GaN are always below those of n-GaN (Figure 3), and their variation with the takeoff angle is lower, suggesting that the thickness of the deposited APTES layer is smaller for p-GaN. This qualitative conclusion is in agreement with observed differences between carbon incorporation in p-GaN and carbon incorporation in n-GaN after APTES deposition.

Further information on the thickness and growth mode of the APTES film can be obtained analyzing the attenuation of Ga and N^{Ga} signals, characteristic of the GaN film, as a consequence of APTES attachment to the surface. Figure 4 shows the evolution of the Ga(2)/Ga(1) and $N^{Ga}(2)/N^{Ga}(1)$ peak area ratios as a function of takeoff angle for n- and p-GaN, where (2) and (1) stand for signals corresponding to the APTES functionalized and hydroxylated surfaces, respectively. To obtain the APTES layer thickness, the experimental data of Figure 4 were fitted to a model involving the formation of a dense uniform layer of thickness, *d*, given by eq 1

$$\frac{I(2)}{I(1)} = \exp\left(\frac{-d}{\lambda_X \cos \varphi}\right) \qquad (1)$$

where $I(2)/I(1)$ is the Ga(2)/Ga(1) or $N^{Ga}(2)/N^{Ga}(1)$ ratio, and λ_X is the IMFP of Ga 3d or N 1s photoelectrons. The thickness, *d*, is used as a fitting parameter. IMFP values of $\lambda_{Ga} = 29.9$ Å and $\lambda_N = 22.8$ Å, tabulated for an organic layer of density ~1.5 g/cm^3, were used.[26] The theoretical APTES chain length (i.e., the monolayer (ML) APTES thickness) is $D^{APTES} = 8.5$ Å.[10,24] The best-fit *d* values obtained were 24.8 ± 1.2 and 24.6 ± 1.2 Å for the Ga(2)/Ga(1) and $N^{Ga}(2)/N^{Ga}(1)$ ratios of n-GaN, respectively. The good agreement between *d* values obtained from both ratios shown in Figure 4 indicates that APTES forms a dense film ~3 ML thick on n-GaN. The use of the uniform layer model for APTES growth on p-GaN surfaces leads to meaningless *d* values around 6 Å. Such values below the APTES chain length suggest that the uniform layer model is not valid; therefore, a model involving the formation of an APTES self-assembled monolayer (SAM), given by eq 2, was used to fit the experimental data of p-GaN

$$\frac{I(2)}{I(1)} = (1-\theta) + \theta \exp\left(\frac{-D^{APTES}}{\lambda_X \cos \varphi}\right) \qquad (2)$$

The only fitting parameter in eq 2 is the surface coverage, θ, ranging from 0 for an uncovered surface to 1 for a fully covered surface. The best-fit θ values deduced for Ga(2)/Ga(1) and $N^{Ga}(2)/N^{Ga}(1)$ ratios are 0.75 ± 0.03 and 0.82 ± 0.04, respectively, so that on average, only ~78% of the surface is covered by an APTES SAM. The best-fit to the models described by eqs 1 and 2 are shown in Figure 4 by solid lines.

For electrochemical biosensor applications, an efficient electron transfer between the semiconductor layer and the immobilized biomolecules is required. Therefore, a well-controlled, ultrathin, and stable organic/inorganic linker interface must be fabricated.[6,13,27] For this reason, the formation of an APTES monolayer is preferred since the formation of thick films constitutes a barrier for electron transfer. However, thick APTES films are frequently reported in the literature.[12,20,28] The mechanism of APTES attachment to the surface involves the nucleophilic displacement of up to three ethoxy groups ($-OCH_2-CH_3$) of every APTES molecule by surface -OH groups (Ga-OH) with a loss of ethanol.[20,28] If the number of available hydroxyl groups on the surface is high enough, all three ethoxy groups of APTES can react with them to yield a good silane monolayer (see Figure 5a). On the contrary, if the density of surface hydroxyl groups is not enough to allow a three-legged attachment of the APTES molecules, some groups can react with silanol groups of other silane molecules to form siloxane bonds (Si−O−Si) with a loss of water (see Figure 5b).[20,28] Silanol groups can be formed by partial hydrolysis of APTES molecules in the presence of residual water during the silanization process. This alternative mechanism can lead to the formation of a multilayer or polymerized siloxane network attached to the semiconductor surface by less chemical bonds than the monolayer way, as shown in Figure 5b. Other mechamisms such as the formation of hydrogen bonds between adjacent amino groups or between amino and residual silanol groups also were proposed to explain the formation of three-dimensional APTES networks.[21,28]

According to the previously mentioned mechanisms, the APTES growth mode should depend on the number of hydroxyl groups available on the surface. As shown in Figure 2 and discussed previously, the n- and p-GaN surfaces have a rather different behavior toward hydroxylation, in such a way that APTES monolayer growth mode is expected for p-GaN, while a multilayer growth mode is to be expected for n-GaN, supporting results obtained from the data of Figure 4. The formation of a multilayer film on n-GaN is not only supported by data of Figures 3 and 4 but by the fact that the intensity of the O^{Si} component, associated with the formation of O−Si bonds after APTES attachment, is ca. twice as large in n-GaN than in p-GaN as a

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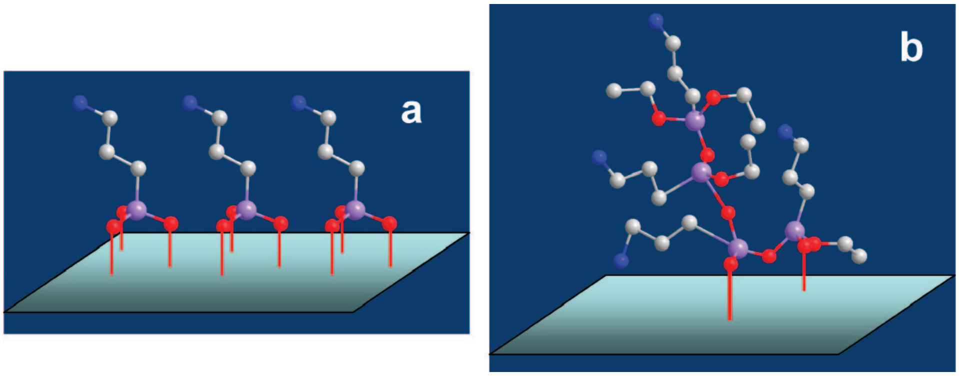

Figure 5. Schematic model of APTES attachment on (a) p-GaN and (b) n-GaN hydroxylated surfaces, respectively, as proposed in the text. Red, blue, purple, and gray spheres depict O, N, Si, and C atoms, respectively. Additional H atoms of the APTES molecule have not been plotted for clarity.

consequence of higher oxygen incorporation in the multilayer film in the form of siloxane structures.

Therefore, the strong difference in the APTES growth mode on n- and p-GaN surfaces can be associated with different behavior to hydroxylation of both surfaces (i.e., with the number of available hydroxyl groups). To summarize, if an APTES self-assembled monolayer is required as a linker between the GaN layer and a biosensing molecule, special care should be taken to achieve an appropiate hydroxylation of the GaN semiconductor surfaces leading to the desired APTES growth mode.

Conclusion

The influence of surface hydroxylation on the chemical functionalization of GaN surfaces was studied by angle-resolved X-ray photoelectron spectroscopy. The n- and p-GaN surfaces were chemically functionalized with APTES following a silane-based approach for functionalizing hydroxylated surfaces. Strong differences were found between the APTES growth mode on n- and p-GaN layers that can be associated with different behavior to chemical hydroxylation that leads to a dramatically different density of hydroxyl groups on the GaN surface. Depending on the density of surface hydroxyl groups, different mechanisms of APTES attachment to the GaN surface were found, in such a way that the APTES growth mode can be changed from a monolayer to a multilayer-like growth mode when the number of surface hydroxyl groups decreases. A high density of surface hydroxyl groups leads to the formation of a monolayer that covers ~78% of the p-GaN surface. However, the formation of a dense, ~3 monolayer thick film was observed on the n-GaN hydroxylated surface due to its lower density of surface hydroxyl groups.

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