Organosilane functionalization of InN surface

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Abstract

Direct coupling of aminosilane molecules onto the plasma hydroxylated InN surface is demonstrated. By using synchrotron-radiation photoelectron spectroscopy, the authors have studied the surface chemical properties of (3-aminopropyl)trimethoxysilane coupled InN. They have also found that the positively charged amine terminal groups on the functionalized InN surface can be utilized to bind negatively charged Au colloids (10 nm diameter) in aqueous solution. Combining with the existing bioconjugation techniques for Au colloids, this approach opens up the possibility of nanoparticle-biomolecular hybrid systems for chemical and biosensing using electronic devices based on surface-functionalized InN. © 2006 American Institute of Physics.

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Organosilane functionalization of GaN, AlN, and AlGaN surfaces has received intense interest because of its potential applications in highly sensitive chemical and biosensors.1−3 The anticipation of group-III nitride materials for sensing applications is mainly due to their chemical stability and biological compatibility.2,3 In particular, it has recently been shown that wurtzite AlGaN/GaN heterostructure field effect transistors (FETs) can be used as ion-sensitive and biologically modified FETs for direct electronic detection of pH values as well as the presence of ions, gases, and biomolecules.2,4,6 In these schemes, the gate surfaces need to be functionalized for specific detection of chemical or biochemical interactions in gas, vapor, or aqueous solution environment.

At present, wurtzite-type InN is being considered as a promising III-nitride material for sensor applications.5,7 It has been found that wurtzite InN exhibits strong, intrinsic electron accumulation at its surface: very large surface charge of the order of 10^13 cm^-2 was first discovered by electrolyte capacitance-voltage measurement,8 and later confirmed by photoelectron spectroscopy9 (PES) and electron energy loss spectroscopy.10 The presence of surface electron accumulation can bring perspectives for designing high-sensitivity sensors. Furthermore, InN has the additional advantage as a chemically stable semiconductor. The InN surface naturally forms a thin native oxide layer under ambient conditions, which could facilitate the route toward surface functionalization for chemical and biosensor applications. In this letter, we demonstrate that the oxidized InN surface can be conveniently functionalized using the technique of organosilane surface coupling agents.

Direct coupling of organosilane agents on oxidized silicon,11 silica, and metal oxide surfaces (e.g., indium tin oxide, ITO) is a technique which has been widely used as the first step to functionalize the oxide surfaces. Recent results have indicated that this technique can also be applied to GaN, AlN, and AlGaN surfaces with a native or intentionally oxidized surface layer.2,3 By using the FET configurations, the organosilane functionalized gates can then be tailored for specific detection of chemical or biochemical interactions such as enzyme activity and DNA hybridization. Especially, the recent developments of micro-nanopatterning techniques and selective adsorption of ions and colloidal nanoparticles onto patterned organosilane surface templates have made this approach very appealing for sensor applications.12,13 Because that a wide range of bioconjugation techniques have already been developed for colloidal nanoparticles,14 nanoparticle-biomolecular hybrid systems are promising to be developed as III-nitride sensor building blocks with increased sensitivity and functionality.

In this study, we adopted an air-plasma technique15 to hydroxylate the oxidized InN surface for the formation of (3-aminopropyl)trimethoxysilane [H₂N(CH₂)₃Si(OCH₃)₃, APTMS] surface coupling layer. The reactive amine terminal groups on the APTMS-functionalized InN surface can be applied to immobilize molecular recognition receptors through either covalent coupling or electrostatic interactions. In particular, we demonstrate that the positively charged (protonated) amine groups on the functionalized InN can immobilize negatively charged Au colloidal nanoparticles in aqueous solution.

The wurtzite InN(0001) samples (1.35 μm thick) used in this study were grown on 3 in. Si(111) substrates by plasma-assisted molecular-beam epitaxy (PA-MBE). Details of the growth procedure can be found elsewhere.15,16 Figure 1 shows the schematic for the reported functionalization process of InN surface. Prior to the APTMS coupling, the InN surface was activated by air plasma (XEI Scientific) operated at 0.6 Torr and 10 W rf power for 10 min.13 After the plasma activation process, the InN surface was terminated by hydroxyl groups, indicated by a highly hydrophilic surface. The InN film was then immersed in liquid-phase APTMS (97%, Aldrich, No. 281778) for 30 min. For Au colloid adsorption, the InN film coupled with an APTMS layer was immersed into an aqueous Au colloidal solution (10 nm mean particle diameter, ~0.01%, Sigma, No. G1527) for 30 min. The PES measurements were performed at the scanning photoelectron microscope station by using monochromatic radiations provided from the U5 undulator beam in the National Synchrotron Radiation Center (NSRRC), Hsinchu, Taiwan. The take-off angle of collected photoelectrons is 57° relative to the surface normal.

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Direct coupling of the APTMS surface agent onto the plasma-activated InN surface was verified by the presence of Si 2p and amine-related N 1s emissions in the core-level PES measurements. For the APTMS silanization process, a clear Si 2p emission with a binding energy of 101.5 eV was recorded, implying the presence of Si–O bonds on the functionalized InN. In Fig. 2, we present the detailed spectra about N 1s emission spectra for dilute-HCl-etched, air-plasma-treated, and APTMS-coupled InN surfaces, respectively. In comparison with the HCl-etched InN surface (without the surface native oxide layer), the N 1s emission from the plasma-treated InN shows a broad shoulder peak next to the main InN-related peak. The origin of this N 1s shoulder peak might be due to the plasma-induced oxidation process of InN. On the other hand, the N 1s spectrum from the APTMS-coupled InN surface clearly shows three N 1s emission peaks at 396.7 eV (InN), 397.8 eV (NH₃), and 400.4 eV (NH₃⁺). The assignment of two amine-related N 1s peaks is in accordance with that for the APTMS-coupled Si surfaces. We have found that extensive x-ray irradiation while taking the PES spectra could significantly weaken the amine-related spectral features, implying the possibility of irradiation-induced modification of surface terminal groups. Therefore, during the PES measurement of N 1s emission for the APTMS/InN surface, we periodically moved the sample position with respect to the focused spot of x-ray radiation by using a piezoelectrically controlled sample stage. This procedure was found to be effective in obtaining a strong signal from amine-related N 1s emission. In the inset of Fig. 2, we show the O 1s core-level emissions from HCl-etched and plasma-treated InN surfaces. After the plasma treatment, in addition to an O 1s peak at 530.6 eV (InOₓ), a second strong O 1 s peak at 532.5 eV also appeared. This peak is assigned to the surface OH groups, which are known to have a higher binding energy. The appearance of the second O 1s peak at a larger binding energy is in good agreement with previous reports on hydroxylated metal oxides, especially hydroxylated ITO (In:Sn ≈ 12:1).

The plasma-treated and APTMS-coupled InN surfaces also exhibit very different spectral features in the valence-band (VB) PES spectra. Figure 3 shows that, although the In 4d core level remains largely unchanged, the VB spectral features change drastically after plasma treatment and APTMS coupling. Since the VB features detected by PES are very sensitive to the surface properties, this result indicates significant surface chemical changes upon these procedures. As a reference, we also show the VB-PES spectrum for a HCl-etched InN surface. The resolved spectral features and the energy separation between the InN 4d core level and the valence-band maximum (VBM) of InN (~17.0 eV) are in excellent agreement with the values reported earlier. On the Au-nanoparticle-adsorbed APTMS/InN surface, the Fermi edge of metallic nanoparticles is also evident in the VB-PES spectrum and the energy separation between the Au nanoparticle Fermi edge and the InN VBM can be determined to be about 1.8 eV. This value is considerably larger than that reported earlier for metal-covered InN surfaces.

FIG. 1. (Color online) Schematic diagram (no to scale) showing the organosilane functionalization process for the wurtzite InN surface. It should be noted that, in the actual situation, there is no one-to-one correspondence between charged amine groups and Au colloids. In addition, not all surface amine groups are charged, as shown in Fig. 2 (PES spectrum).
face after 30 min immersion in an aqueous solution of Au colloidal nanoparticles are immobilized on the APTMS/InN surface is 10 nm. The density of adsorbed nanoparticles on the APTMS/InN surface is \( \sim 950 \) nanoparticles/\( \mu \)m\(^2\).

The binding energy shift (both core levels and the Fermi edge) of adsorbed Au clusters on poorly conducting substrates has been reported earlier. This phenomenon was suggested to be related to the charging effect in Au clusters.\(^{19}\) In our case, a shift of the Fermi level of adsorbed Au clusters was suggested to be related to the charging effect in Au nanoparticles toward a lower binding energy indicates that the adsorbed nanoparticles are negatively charged.

In our previous work, we have shown that Au colloidal nanoparticles in an aqueous solution are negatively charged and can be used to perform controlled electrostatic adsorption of Au nanoparticles onto APTMS-covered Si surfaces with positively charged amine terminal groups.\(^{13}\) Figure 4 is a scanning electron microscopy image showing that Au colloidal nanoparticles are immobilized on the APTMS/InN surface after 30 min immersion in an aqueous solution of Au colloidal nanoparticles (10 nm average diameter). The adsorbed nanoparticle density on this APTMS/InN surface is estimated to be \( \sim 950 \) nanoparticles/\( \mu \)m\(^2\) (controllable by the nanoparticle concentration and ionic strength of the colloidal solution). In a control experiment, an untreated InN sample was immersed in the colloidal solution under the same conditions and only \( \sim 75 \) Au nanoparticles/\( \mu \)m\(^2\) adsorbed onto InN (not shown). We speculate that the unintentional adsorption of Au nanoparticles onto an untreated InN surface is likely due to the existence of charged defects and dislocations in the as-grown InN films. It should be noted that, since most biomolecules carry charges in aqueous solutions, the electrostatic adsorption scheme presented here can also be applied to surface functionalization using nanoparticle-biomolecular hybrid systems.

In conclusion, a method for organosilane functionalization of InN surface is demonstrated. Effects of air-plasma treatment and coupling of an APTMS layer onto the PA-MBE grown InN film have been studied by core-level photoelectron spectroscopy. The positively charged amine terminal groups on the APTMS-functionalized InN film are shown capable of immobilizing negatively charged Au colloidal nanoparticles in aqueous solutions.

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