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Assembly of titanosilicate ETS-10 crystals on organosilane-functionalized gallium nitride surfaces

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ABSTRACT

Integration of titanosilicate ETS-10 crystals with optoelectronic semiconductors is hypothesized to allow activation of these crystals for photocatalytic applications without direct exposure to light, and to more efficiently use the photons available. ETS-10 crystals were assembled on 3-aminopropyltrimethoxysilane (APTMS)-functionalized n-type GaN (0002) substrates. Strong attachment of crystals to the functionalized substrates was shown by minimal to no loss of crystals on the GaN surfaces as tested by 30 min substrate sonication in water. Successful substrate functionalization was confirmed by the appearance of the Si 2p peak at 102.2 eV in the XPS spectra. The observation of the N 1s photoelectron peak at 401.19 eV suggested the presence of amino groups protonated by the surface hydroxyl groups of the substrate. Angle resolved XPS analysis of the APTMS-functionalized GaN surfaces showed a decrease in the relative N:Si ratio upon decreasing the take-off angle from 90° to 30°. These results suggest Si–O terminal groups are preferentially located at the surface of the APTMS linker, while the protonated amino groups are likely located at the substrate-linker interface. Therefore, the strong ETS-10 crystal attachment to the functionalized GaN (0002) substrates can be hypothesized to be due to covalent bonding between the external ETS-10 surface hydroxyl groups and the Si–O terminal groups of the APTMS-functionalized GaN surfaces.

1. Introduction

Engelhard titanosilicate ETS-10 is a large-pore microporous zeotype material [1]. The framework structure of ETS-10 is comprised of corner-sharing SiO_4 tetrahedra and TiO_6 octahedra linked through the bridging of oxygen atoms forming 12-membered ring channels with pore openings of 4.9×7.6 Å. The well-defined monatomic semiconductor ...Ti–O–Ti–O–Ti... chains with a band gap energy (E_g) of 4.03 eV make this material a promising candidate for photocatalytic applications [2]. Only a wavelength with energy greater than or equal to the band gap energy of the photocatalyst is sufficient to initiate the photocatalytic reaction. Typically, photocatalytic experiments with wide band gap semiconductors (e.g., TiO_2) are performed using UV light sources equipped with appropriate cut-off filters to narrow the wide spectrum of wavelengths emitted (i.e., 200–2500 nm). The efficiency of photocatalytic devices can be improved by using optoelectronic semiconductor materials that produce photons in a narrow wavelength range (10–20 nm) around the band gap energy. This minimizes the production of unusable photons whose energy is either lower than or much greater than the band gap energy of the photocatalytic material, thus more efficiently converting the input energy to catalytic activity.

The III-nitrides have attracted much interest in areas such as optical devices in the visible short-wavelength and UV region (wavelengths ranging from the red to deep in the UV region). Gallium nitride (GaN) is one of the most promising optoelectronic semiconductors for such applications as blue/UV light emitting diodes (LEDs) due to its direct transition band structure and the ability to tune its band gap energy from the 3.39 eV energy of GaN [3] to 6.2 eV (E_g for AlN) [4] through the incorporation of Al. Thus, it is hypothesized that the integration of ETS-10 crystals onto AlGaN substrates will allow the direct use of the light emitted from these LEDs to efficiently activate the crystals for photocatalytic reactions in applications where sunlight is not available. Chen et al. [5] have shown promising results using UV LEDs as an external light source for photocatalysis using Degussa P25 TiO_2-coated optical fibers, even though the UV LED light optical power output of 16 mW (i.e., total optical power output of 16 LEDs used) was significantly lower than that of the black light source (300 mW) typically used in photocatalysis experiments.

Reports to date regarding ETS-10 film preparation are limited. ETS-10 membranes were prepared on porous α-alumina and stainless steel substrates utilizing secondary growth of ETS-10 crystals deposited by either dip coating [6] or by evaporating droplets of ETS-10 suspensions deposited on the substrates [7]. Direct in situ

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crystallization on these substrates resulted in the formation of titanosilicate AM-1 crystallites, with no evidence of ETS-10 as indicated by the X-ray powder diffraction (XRD) patterns [6]. Preparation of ETS-10 films was also reported on fused silica optical fibers. The fibers were initially treated using tetraethyl orthosilicate (TEOS), followed by ETS-10 crystal deposition via dip coating, then secondary growth [8]. Exposure of the TEOS-treated fibers and attached crystals to flowing water for 24 h with little to no crystal loss was hypothesized to be due to covalent bonds between the crystals and the treated surfaces of the fibers [8]. Attachment of ETS-10 was also reported on butyrate functionalized glass substrates; in this work the crystals were functionalized with trimethylpropylammonium iodide [9]. Organosilanes, such as 3-chloropropyltrimethoxysilane (CPTMS), have been used to functionalize glass substrates for covalent attachment of ZSM-5 and zeolite A crystals [10], as well as functionalize α-alumina substrates for the deposition of MCM-22 crystals [11]. The binding of the zeolites was proposed to occur via a direct substitution of the terminal halide groups on the functionalized glass substrates and the surface hydroxyl groups on the crystals [10]. In all cases where molecular linkers (such as these) were used to modify the substrates, it has been hypothesized that attachment of the crystals occurs via covalent bonds between the linkers and the hydroxyl groups on the crystal surfaces.

Similar organosilanes, such as mercaptopropyltrimethoxysilane (MPTMS) [12], octadecyltrimethoxysilane (ODTMS), aminopropyltriethoxysilane (APTES) [13], and aminopropyltrimethoxysilane (APTMS) [14], were used to functionalize the GaN surfaces for applications such as immobilization of biomolecules [12,13] and functionalization of DNA [14]. However, the functionalization of GaN with organosilanes for zeotype applications has not been reported to date. Here, the functionalization of n-type GaN (0002) substrates using APTMS, and the attachment of ETS-10 crystals on the functionalized substrates is reported. This investigation was undertaken to explore the feasibility of integrating an ETS-10 photocatalyst with optoelectronic semiconductor to facilitate a more effective use of energy needed to activate the photocatalyst.

2. Experimental

n-Type GaN (0002) films with a surface roughness estimated to be ∼2.0 nm root mean square (rms), grown on sapphire substrates (0001) via metalorganic vapor phase epitaxy (MOVEP) [15], were degreased in heated (80 °C) solvents of trichloroethylene (99.5%, Fisher), acetone (99.5%, Fisher), and methanol (99.8%, Fisher) to remove surface contaminants. Hydroxylation of the degreased GaN surfaces was performed by treating the substrates (∼0.5 mm × 0.5 mm) in a freshly prepared piranha solution (3:1 H_2SO_4 (96.5%, Fisher): 30 wt.% H_2O_2 (Sigma) at 80 °C for 50 min [14]. The hydroxylated substrates were then rinsed thoroughly with deionized water (resistivity > 18 MΩ cm) and dried with argon (high purity, MedTech). The hydroxylated surfaces were then functionalized, using a modified technique adapted from Choi et al. [11], in a 10 vol.% of 3-aminopropyltrimethoxysilane (APTMS, 97%, Aldrich) in anhydrous toluene (99.8%, Acros) heated at 110 °C for 3 h in sealed 10 mL Teflon-lined autoclaves. The APTMS-functionalized GaN substrates were then rinsed with toluene (99.9%, Fisher) and dried with argon. ETS-10 crystals were synthesized in Teflon-lined stainless steel autoclaves for 2 days at 230 °C from a mixture with the composition $5.2Na_2O:0.5K_2O:TiO_2:5.5SiO_2:113H_2O$. The synthesis was carried out according to a procedure [16] utilizing anatase (99.0%, Aldrich), N-Brand sodium silicate (28.59% SiO_2, 8.88% Na_2O, PQ), sodium chloride (99.0%, Sigma), potassium chloride (99.0%, Fisher), and deionized water. In the crystal attachment step, the functionalized substrates were ultrasonicated for 2 min [11] in a 5 wt.% suspension of ETS-10 crystals in toluene, then rinsed with toluene and dried with argon. The stability of crystal attachment to the substrates was tested by means of successive sonication (Branson 2200, 50–60 Hz, 117 V, 1.0 amp) in deionized water for a cumulative time of 30 min. Six different locations on the substrates were selected for observation with their coordinates stored in the stage memory of the scanning electron microscope. These locations were imaged after each predetermined sonication time. Characterization of chemical bonding was performed by X-ray photoelectron spectroscopy (XPS) using a PHI model 04-548 Mg/Al dual anode non-monochromatic Mg Kα ($h\upsilon$ = 1253.6 eV) X-ray source and a PHI model 10-360 hemispherical analyzer. Sample rotation capability enabled angle resolved XPS. XPS peak deconvolution was performed using a minimum full-width-at-half-maximum of 1.20 eV and an 80/20 Gaussian/Lorenzian peak shape, as determined from a clean Au 4 *f*7 photoelectron peak. Identity of ETS-10 crystals was determined by X-ray powder diffraction (XRD). The XRD data was collected using Cu Kα radiation (40 kV, 30 mA) on a Bruker D5005 θ:2θ Bragg–Brentano diffractometer equipped with a curved graphite crystal diffracted beam monochromator and a NaI scintillation detector. The crystals were ground before the XRD measurements in order to minimize the effect of preferred orientation on the XRD pattern. Particle size distribution (PSD) analysis of ETS-10 crystals was carried out using an API Aerosizer LD equipped with an API Aero-Disperser dry powder dispersion system (TSI Inc., Particle Instruments/Amherst). The density of ETS-10 crystals used in these measurements was 1750 kg/m^3 [17]. Field emission scanning electron microscopy (FE–SEM) was used to observe the morphology of ETS-10 crystals and the coverage of substrates with crystals. The FE–SEM images were acquired for uncoated crystals using a Hitachi S-4700 FE–SEM (accelerating voltage 2 kV, beam current 10 μA) in the secondary electron imaging mode.

3. Results and discussion

3.1. XPS analysis of APTMS functionalized GaN surfaces

The presence of surface hydroxyl groups has been shown to be essential for successful silanization of various substrates, such as Si [18,19], AlN [13], and GaN [13,14]. XPS analysis of the hydroxylated GaN (0002) surfaces indicated two photoelectron peaks of the N 1s spectrum (Fig. 1a). The primary N 1s peak at a binding energy (BE) of 396.97 eV was assigned to bulk N–Ga, while the secondary peak at BE = 398.46 eV was attributed to either N–O_x or

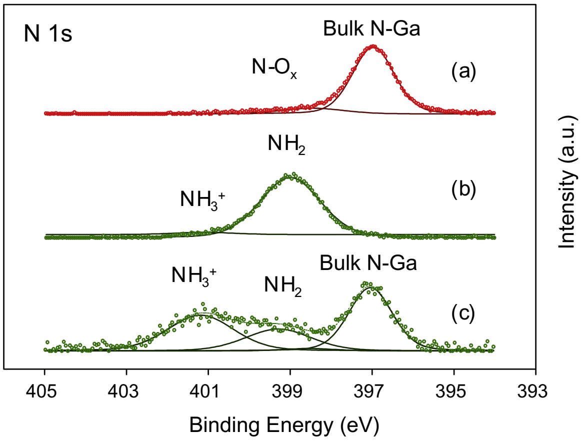

Fig. 1. XPS spectra of N 1s for: hydroxylated GaN (00 0v2) surfaces (a); “thick” APTMS film-functionalized GaN (0002) surfaces (b); “thin” APTMS film-functionalized GaN (0002) surfaces (c).