CHAPTER 5
GROWTH AND FUNCTIONALIZATION OF GaN NANOTUBES FOR CATALYTIC AND GAS SENSING APPLICATION

5.1 Introduction:

Hollow nanostructures with tailored structural, optical, and surface properties, has received considerable interest in a wide range of applications pertaining to catalysis, chemical sensing, nanocapillary electrophoresis, nanofluidics, drug delivery, fillers, and nano-optoelectronics. Among different nanostructures, nanotubes (NTs) exhibit unique properties because of the unidirectional curvature and large surface areas. There is only a few published work on the growth of amorphous, polycrystalline, and single-crystalline GaN NTs, which are mostly realized by employing template, or using metal catalysts. However, incomplete removal of template material, partial inclusion of catalyst into the tube annulus and high porosity in as-grown samples were major blocks in the fabrication process of high pure GaN NTs. To date, contamination-free direct fabrication of a GaN tubular structure has been a technical challenge. In the present work, an effort has been made to synthesize catalyst-free growth of GaN NTs via a quasi-VS process elucidating the underlying growth mechanism.

While looking towards the device performance using NTs, the role played by various functional groups in interface with zero-dimensional nanocrystallities assumes enormous importance. Decoration of compound semiconductors with novel metal nanoclusters like Pd or Pt are of specific interest since these metals act as catalysts for numerous surface chemical reactions. An oxidation step is usually employed to specifically impart photocatalytic H2 generation capability, and to produce continuous hot electron flow in nanodiodes. In addition, such a step usually enhances electrochemical activity and H2 sensing response.
across wide range of temperatures.\textsuperscript{14,15} For example, there were several reports from Somorjai’s group on the generation of steady state chemicurrent using a novel planar nanodiode device which employs 5-8 nm sputtered thin film of Pt over thick GaN film, and also often using metal-oxide bases.\textsuperscript{11,12} They have achieved hot electron generation induced chemicurrent yield of \((3.5 \pm 0.8) \times 10^{-3}\) under catalytic reaction of \(\text{O}_2\) or \(\text{CO}\) gas. Above value is found to be one order of magnitude higher than that for Pt/Pd-TiO\textsubscript{2}.\textsuperscript{11} There are several reports on Pt catalyzed carbon materials, metal oxides and metal-oxynitrides used in large scale solar energy assisted \(\text{H}_2\) production from water.\textsuperscript{16} Pt-loaded metal nitride nanoclusters depict superior quantum yield than oxide counterpart with respect to solar energy assisted \(\text{H}_2\) production. However, studies on the metal-semiconductor interface structures, focusing morphology, crystallinity, and roughness and the local environments are important from several viewpoints as these aspects will ultimately control the efficiency of the end product generation process.

For some applications involving noble metals Pt or Au like hadron therapy,\textsuperscript{17} radiotherapy, photo-thermolysis of cancer\textsuperscript{18} and photocatalysis, it is often necessary to expose the materials to high levels of ionizing radiation such as laser light. This process is likely to induce secondary effects like phase transformation, melting or cleavage of materials. It is therefore, essential to know the thermal stability of the nanostructured materials in a catalytic environment. Recently, photo-assisted localized oxidation of group III- nitride thin films has been reported by Hwang et al. employing laser light onto water bridge between GaN thin film and Pt-coated atomic force microscopic (AFM) tip.\textsuperscript{19} Several groups have also reported oxidation of GaN thin film using AFM, UV light assisted photo-induced wet chemical oxidation, anodic treatment, and often by high power laser irradiation.\textsuperscript{20} Breakdown in single GaN NWs were reported by in-situ TEM characterizations.\textsuperscript{21,22} These studies revealed that the semiconductor NWs break at the mid-point by means of thermal heating under the
influence of high electric bias voltage (~35 V). Individual NW breaks at a maximum temperature of ~ 1000 K via thermal decomposition. However, the influences of catalysts on heat dissipation of GaN upon scaling down to lower dimensions and the effect on morphological evolution by laser power irradiation are not studied in detail.

5.2 Quasi Vapor-Solid Growth of GaN Nanotube:

5.2.1 Materials and Methodology:

NTs were synthesized using same CVD reactor used for the growth of GaN NWs. The only difference maintained here is that the 3 nm Au coated Si substrate was kept horizontally at a height of 10 mm from the Ga source, whereas, the substrates were usually kept vertically from the Ga source for the growth of NWs. In addition, a faster temperature ramping rate of ~ 40 °C per min was maintained while increasing the temperature from 500 °C to 900 °C at a base pressure of 1 mbar. After the chamber temperature reached at 900 °C, the base pressure was slowly increased to 1 atm pressure in 10 minutes by bleeding high purity NH₃ gas at a flow rate of 10 sccm. The reaction was terminated after duration of 2 h. The system was allowed to cool down slowly to room temperature in the same NH₃ ambient. A large quantity of light yellowish material was found to be uniformly coated throughout the Si substrate. To identify the growth mechanism of NTs, the role of the most decisive growth parameters, namely, growth rate, temperature, and NH₃ partial pressure was taken into consideration.

5.2.2 Morphological and Structural Properties:

Figures 5.1(a-c) show typical FESEM images of the NTs on Si substrate. A highly dense GaN layer of thickness ~40 µm is seen over the Si substrate, as revealed from the cross-sectional image [Fig. 5.1(a)]. A close view of the magnified image at middle region [Fig. 5.1(b)] reveals that NTs are homoepitaxially grown over a layer of GaN nanoclusters with overall thickness ~5 µm [Fig. 5.1(c)]. The underlying GaN nanoclusters layer may have
acted like a buffer layer, which has initiated the NT formation. On mechanical scratching, it is found that the as-grown GaN NT layer can be smoothly removed from the nanocluster interface region. This is observed while focusing the of top and bottom part of as-grown GaN NT sample through FESEM [Figs. 5.1(d,e)]. It is worthwhile mentioning that NTs can be isolated without being contaminated with nanocluster impurity. The surface layer, as observed from the side [Fig. 5.1(b)] reveals that the GaN NTs are homogeneously distributed throughout the surface. Most of the NTs exhibit nearly square shaped cross-section [Fig. 5.2(a)] with wall thickness of about $\sim$10-15 nm and average lateral dimensions of nearly $\sim$ 50 nm [Fig. 5.2(b)]. A typical length extends to several micrometers. These images are recorded from the Pt nanocluster functionalized GaN NT samples (detailed in subsequent sections).
Figure 5.2 FESEM images of the NTs with (a) and (b) square shaped (c) nearly square shaped facets.

Figure 5.3 shows the X-ray diffraction (GIXRD; Bruker D8 Discover) pattern of the as-synthesized GaN NTs. The peaks correspond to (100), (002), (101), (102), (110), (103) and (112) planes of hexagonal WZ-GaN phase with lattice parameter of $a = 0.318$ nm and $c = 0.518$ nm (JCPDS: 50-0792), while no cubic phase is found. All the peaks of the as-grown GaN NTs are relatively sharp and the value of the full width at half maximum (FWHM) has narrow peak width. The GIXRD analyses show that the GaN NTs possess well developed crystalline character. The structures of the individual GaN NT are further investigated by HRTEM analysis. The typical tube like contrast is observed [Fig. 5.4(a)]. The areas close to the edge are appearing darker than the central zone. The NTs exhibit uniform cross-section.
Fig. 5.4 (a) TEM images of a NT with visible side facets, (b) tube with open end, (c) lattice images of the NT shows presence of family of \textit{m}-planes and growth direction along \textit{[11\bar{2}0]}, (d) smooth transition between side facets and (e) corresponding lattice image; (f) SAED pattern of NTs shows WZ-GaN phase; Inset shows the region from which the pattern is generated.

and extend to several micrometers in length [inset Fig. 5.4(a)]. The external surface is relatively rough as seen from the HRTEM image [Fig. 5.4(b)]. The typical segment of the open end of a NT is shown in figure 5.4(c). Lattice pattern shows a family of \textit{m}-planes with growth direction along\textit{[11\bar{2}0]}. A smooth transition takes place between the side faces of the NT as indicated by the HRTEM image [Fig. 5.4(d)]. Further studies suggest that the tube surfaces are composed of \textit{(0001)} planes and the tube axis is subtended along \textit{[11\bar{2}0]} direction, which is normal to \textit{a} plane. The high resolution lattice image of the transition region, with the interface region at the corner over \textasciitilde2 nm, is shown in figure 5.4(e). The \textit{m} planes, orthogonal to \textit{c} plane are indicated in the high resolution image. A typical SAED pattern along one of the facets shows zone axes along \textit{(0001)} of WZ-GaN phase [Fig. 5.4(f)].
Faint spots close to the indexed diffraction spots in the SAED pattern indicate twin like features, which are essentially from the opposite facet of the NT having same crystalline orientation ([0001]) with a small tilt. The tilt is likely as the facets are not exactly parallel to each other. The observation, however, establishes the fact that all the facets are oriented along [0001] direction.

**5.2.3 Growth Mechanism:**

The growth mechanism of GaN NTs proceeds via a quasi-VS process. As depicted schematically in figure 5.5, it is postulated that the nucleation and further growth of the NTs might occur in following stages: 1) generation of ultra-small, nanosized GaN clusters on the substrate surface, 2) self-agglomeration and coalescence induced formation of facets, and 3) further oriented attachment of incoming vapor phase clusters to specific crystallographic facets. In the present study, experiments are conducted with faster ramping rates, initially, to provide enough population density of Ga followed by the atomic nitrogen flux to start the nucleation process aided by Au catalyst. Under this condition, unlike the VLS process the reaction occurs faster than the effective incubation time, stimulating the formation of agglomerated nanoclusters. A longer incubation time is anticipated in the VLS process and Au-Ga interfacial energy drives a directional growth. Upon increasing the

![Fig. 5.5 Schematic representation of NT growth mechanism via quasi vapor-solid process in the CVD technique.](image-url)
incoming Ga and N flux rate, the nanoclustes undergo further self-agglomeration process. The nucleation of facets leading to NT formation possibly stems from agglomeration of GaN clusters leading to coalescence process, which might form ring shaped nucleation front. Further, reactant species from the vapor phase is exposed continually over these nucleated facets leading to the formation of GaN NTs. The observed square or rectangular shape of NTs possibly results due to the differential adatom migration behavior among different crystallographic faces. Faceting of nucleated grains stems from the fact that certain crystal faces are energetically disfavored for co-ordination with adatoms thereby restricting growth directions. The calculated surface energy for polar (0001) and non-polar (11̅20) surfaces of GaN are 100 and 123 meV/Å, respectively. Although, the difference of surface energy between the non-polar and polar surface is relatively small, nevertheless, they do behave differently to incoming adatom species. As a matter of fact, polar surfaces prefer systematic adsorptions, whereas non-polar surfaces maintain their stoichiometry by systematic atomic diffusions. The interaction between adsorbate and surface is strongly dependent on the most decisive parameter such as incoming Ga or N flux ratio. In Ga rich condition, a nonstoichiometric surface having Ga-Ga dimers is stable. N-rich condition increases the nucleation rate of GaN due to the higher strength of the Ga-N bond and shorter diffusion length of Ga than that of Ga-Ga bond. It is thus apparent that, N-rich condition promotes stoichiometric growth of non-polar surface. The higher nucleation rate in the (11̅20) surface over (0001) surface is expected to stimulate the axial growth of the NTs along [11̅20]. On the other hand, relatively lower surface energy along (0001) planes than that of the (11̅20) plane promote formation of (0001) facets in the square symmetry, while the GaN system is in the hexagonal symmetry.
5.3 Functionalization of GaN Nanotube with Platinum Nanoclusters:

5.3.1 Materials and Methodology

For catalytic and sensor application, the as-grown NTs were functionalized with Pt nanoclusters using lysine \([\text{HO}_2 \text{CCH(NH}_2 \text{)(CH}_2)_4 \text{NH}_2]\) as a capping agent. Initially, GaN NTs were treated with 50% aqueous solution that contained a mixture of \(\text{H}_2\text{SO}_4\): \(\text{H}_2\text{O}_2\) (ratio 3:1) for a period of 5 min, and then washed with double distilled water followed by drying using \(\text{N}_2\) gas. This process was often used for cleaning nitride surfaces as well as to activate hydroxyl groups on the surface. The hydroxylated samples were further dipped inside 3 ml of \(\text{H}_2\text{O}\) solution containing 1mM of lysine followed by addition of another 3ml of \(\text{H}_2\text{O}\) containing 1mM of \(\text{HPtCl}_4\). The suspension was gently stirred for a period of 30 min, and then 3 ml of 0.1 M fresh \(\text{NaBH}_4\) (slightly in excess) solution was added to reduce \(\text{HPtCl}_4\) to metallic Pt. After stirring for further 30 min, the samples were washed with water and dried with flowing \(\text{N}_2\) gas. This reduction invariably results in nanocrystallites of Pt.

5.3.2 Morphological and Structural Properties:

Figures 5.6(a,b) shows the FESEM image of Pt nanocluster functionalized GaN NTs (Pt-GaN) from top view and side view, respectively. The typical high-resolution image reveals that the Pt nanoclusters are uniformly spread over the GaN NT with different

![Fig. 5.6 FESEM image of Pt nanocluster functionalized GaN NTs (a) from top and (b) side view.](image-url)
crystalline orientations [Fig. 5.7(a)]. The corresponding $d$-spacings are indexed to cubic Pt along with the presence of WZ-GaN calculated from the SAED pattern [Fig. 5.7(b)]. Figure 5.7(c) shows the bright field image of Pt decorated NTs and the corresponding dark field image is depicted in figure 5.7(d). These images are recorded by taking $<111>$ diffraction spot of the Pt nanoclusters. The Pt-GaN NT exhibit relatively rough external surface as compared to that for the pristine NTs, as shown in the inset of figure 5.7(c). By analyzing a number of samples, the average size distribution of Pt nanoclusters is found to be ~1.6 nm (Fig. 5.8). It is further inferred from EDX analysis that along with the depth of the bulk sample, the present method of Pt functionalization provides an excellent spatial distribution of Pt (~ 1.5 atomic percentage) across a depth extending to well over 10 µm from the surface layer [Figs. 5.9(a-c)].
Fig. 5.8 shows the average size distribution of Pt cluster decorated on the NTs wall.

Fig. 5.9 Cross-sectional FESEM images and the corresponding EDX analysis showing the distribution of Pt nanocluster in the (a) surface, (b) middle and (c) close to the substrate region of the GaN NTs.

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5.4 Optical Properties:

Figure 5.10(a) shows the typical micro-Raman spectra of control NTs at incident laser power of 2 mW using 514.5 nm laser line. The Raman spectra reveal three fundamental modes with frequencies around 541, 571 and 732 cm\(^{-1}\), which correspond to \(A_{1}(TO)\), \(E_{2}\)(high)
and $A_1$(LO) phonon modes of WZ-GaN phase, respectively. The spectra exhibit strong $E_2$(high) mode, blue shifted by 2 cm$^{-1}$ with a broad line width of $\sim$10 cm$^{-1}$. This may be attributed to small crystallite size. Similarly, LO mode is also blue shifted by 8 cm$^{-1}$ with line width $\sim$ 14 cm$^{-1}$. Additional peaks are attributed to ZB and SO phonons as described earlier. Low temperature micro-PL spectra of NTs show strong emission in the region of photon energy 3.0-3.6 eV [Fig. 5.10(b)]. The PL emission lines at 300 K (RT) possesses a broad and asymmetric line shape with weak band-edge-emission. Pt functionalization leads to a decrease of emission line by two orders of magnitude compared to the emission spectra of control NTs because of the quenching effect due to carrier transfer taking place between GaN and Pt nanoclusters. As temperature decreases to 80 K, the emission is dominated by a peak at 3.47 eV with a series of emission peaks centered at 3.24 and 3.30 eV. The peak at 3.47 eV corresponds to $I_2$ emission. The $I_2$ emission possesses broad line shape of $\sim$ 65 meV, which is blue shifted by 18 meV. This is attributed to the size effect in the NTs. The prominent

Fig. 5.10 (a) Raman spectra of GaN NTs at room temperature corresponding to WZ-GaN phase; (b) Low temperature micro-PL spectra of GaN NTs using 325 nm laser excitation. The spectra possess a strong $I_2$ line at low temperatures.
peaks observed at 3.3 and 3.24 eV have been assigned to zero phonon line and their phonon replica of the FB emission line, respectively.\textsuperscript{30}

5.5 Laser Assisted Catalysis

The Pt nanoparticles are known to act as catalyst for numerous applications. Here, the catalytic activities of Pt nanoclusters functionalized over GaN NTs are demonstrated by coupling with high laser power and appropriate local ambience. Understanding the mode of catalytic action induced by the laser power is important from many technical points of view and for advanced optoelectronic applications.

5.5.1 Laser Induced Localized Oxidation and Photofragmentation of GaN Nanotube:

Figure 5.11(a) shows the typical micro-Raman spectra of control NTs at different incident laser power (2 - 40 mW) using 514.5 nm laser line. At low laser power (2 mW), all the Raman modes are corresponding to WZ-GaN phase. Upon increasing the laser power from 2 to 40 mW, while maintaining the same exposure time, it is observed that all primary modes are red shifted and asymmetrically broadened on the low frequency side, as plotted in figure 5.11(b). The $E_{2}(\text{high})$ mode, recorded at 40 mW laser power, is red shifted by $\sim$4 cm$^{-1}$ and the corresponding intensity increases by a factor of 12. The observed red shift can be attributed to the laser heating effect of the NTs and that the asymmetric line shape is apparently originated from Fano resonance, which arises as a result of interference between scattering from the $k = 0$ optical phonon and electronic continuum scattering from photogenerated carriers in the conduction bands.\textsuperscript{31} However, there is no observation of structural evolution during the laser exposure. Notably, a peculiar scenario is observed on Pt-decorated NTs upon exposure with different laser power [Fig. 5.11(b)]. A structural change from WZ-GaN phase to monoclinic ($\beta$-) $\text{Ga}_2\text{O}_3$ phase occurs after irradiation with a threshold of laser power exposure above 4 mW [Figs. 5.11(c,d)]. The new peaks those evolved, upon 20-40
mW of laser power exposure, correspond to mode frequencies of 147, 168, 200, 347, 416, 476, 630, 653, 766 cm\(^{-1}\) of \(\beta\)-Ga\(_2\)O\(_3\) phase.\(^{32}\) The origin of such chemical-structural evolution is deliberated in forthcoming sections.

Fig. 5.11 Raman spectra recorded by varying the laser power from 2 to 40 mW of (a) control GaN NTs, (b) Pt decorated NTs; (c) laser power dependent change in the line width and Raman peak shift corresponding to \(E_2\text{(high)}\) mode of as-grown samples; (d) Raman intensity plots corresponding to \(\beta\)-Ga\(_2\)O\(_3\) and WZ-GaN phases showing the evolution of the latter over the former.

Laser induced morphological transformation of NTs is clearly elucidated by analyzing the laser treated zone by FESEM [Fig. 5.12(a)] analysis. Pt-decorated GaN NTs, exposed to 20-40 mW laser irradiations, undergo immediate melting and fragmentation in ambient conditions. Hole burnt into the specimen is depicted in figure 5.12(a). A hole of diameter \(\sim\) 2 \(\mu\)m, which is nearly equal to the size of the laser beam gets engraved [Figs. 5.12(b,c)]. However, there was no noticeable mark of melting or damage corresponding to the exposure.
Fig. 5.12 (a) Laser induced photo-fragmentation of NTs with different laser power (4-40 mW), magnified image of the hole region at (b) 40 mW and (c) 20 mW laser power irradiation; (d) high resolution image of the photo-fragmented NTs and (e) along the close proximity of laser heated below 4 mW laser power. Magnified image within the hole regions [Fig. 5.12(b) at 40 mW, and Fig. 5.12(c) at 20 mW] reveal that the NTs cleave into fragments. These fragments are constituted by Ga$_2$O$_3$ phase. Interestingly, a similar effect has been observed in case of a
single Pt-decorated GaN NT dispersed over HOPG substrate [Fig. 5.13(a)]. Pt-decorated NT melts down in the vicinity of the laser exposed (40 mW) zone in less than 1 second duration, as indicated by the arrow in the microscopic images, recorded in a confocal mode [Figs. 5.13(a,b)]. Typical Raman spectra [Fig. 5.13(c)] of a single Pt-decorated GaN NT shows oxide phase formation within laser heated area. However, increase in laser power does not bring about any morphological changes for NTs [Fig. 5.13(d)]. As usual, no structural transformation was also observed (not shown in figure) without Pt decoration. From the aforementioned observations, a photocatalytically motivated local oxidation seems to have caused the crystallo-chemical transformation.

A photo-thermal process causing the enhanced rate of oxidation of the Pt-decorated surface is quite feasible. In order to further understand the synergistic effect of Pt catalyst and laser power dependent local oxidation, as well as melting of GaN NTs, the measurement temperature is varied from RT to 773 K while keeping the laser power below the threshold limit (4 mW) in air ambient (Fig. 5.14). The thermal heating process neither affects the oxidation nor induces any structural changes, as it is observed in the Raman spectra [Fig. 5.11(c)] for the case of RT laser exposure with power \( \geq 20 \) mW. Hence, the observed
oxidation and melting of GaN NTs is definitively not as a result of localized thermal heating effect. However, it is believed to be photocatalytic in origin. Figure 5.15(a) shows the low temperature Raman spectrum of Pt-decorated GaN NTs using 40 mW of 514.5 nm excitation acquired over 80- 473 K span under N₂ flow condition [Fig. 5.15(a)]. Remarkably, the oxidative process of transformation, presumably aided by catalytic process, is apparent even at 80 K. The spectra show two distinct phases, namely, β-Ga₂O₃ and WZ-GaN [Fig. 5.15(a)]. The relative intensities of the Ga₂O₃ phases are nearly similar over the full range of temperature [Fig. 5.15(b)]. It is to be noted that GaN phase is still observed in the N₂ ambient even after exposure with 40 mW laser power in the presence of Pt catalyst. Interestingly, any surface structural damage like melting and fragmentation of NTs is not noticed under aforementioned condition despite local oxidation. Hence, by suitably choosing the local ambience, catalyst and laser power, it is possible to oxidize localized pockets. This novel methodology, although simple, can find potential applications in nanoelectronics, namely, in CMOS devices and in-situ gate dielectrics.

Fig. 5.15 (a) Raman spectra of Pt-decorated GaN NTs recorded from 80 K to 473 K with 40 mW laser irradiation in N₂ flow condition. All the spectra are indexed to two distinct phases, WZ-GaN and β-Ga₂O₃ (*); (b) The Raman intensity of 200 cm⁻¹ peak corresponds to β-Ga₂O₃ phase with varying temperature.
5.5.2 Mechanism of Photocatalyzed Oxidation in Pt-GaN Nanotube:

The quantitative data obtained here is used to gain further insight into the mechanism of photocatalyzed oxidation of GaN NTs. There is a change in mode of catalytic action induced by the laser power in the presence of different local ambient; O₂ or N₂. It was shown by Baker et al. that Pt nanocluster with diameter less than 25 nm could catalytically oxidize graphite in dry O₂ at temperature above 600 °C. It was found that Pt nanoclusters initiated formation of pits followed by channel propagation, usually along <11̄20> direction, making 60 or 120 degree angle between them. Photo-thermal-catalytic processes initiated by laser incidence appear to preponderate over thermally activated process. Since the coverage of Pt nanocluster is uniform over the NTs, and the NTs possess a large number of dangling bonds and relatively small wall thickness (~10 nm), it is expected that the rate of oxidation is more appreciable. The process may form pits and channels, which may have initiated the rapid breakdown of specimens. The rate of channel propagation indeed depends on catalyst particle size. Smaller the particle size higher is the rate of channel formation due to an additional increase in the mobility, as observed in our case for Pt nanoclusters with diameter ~1.6 nm. The mode of action of the Pt nanocluster is further enlightened from the phenomenological view point of laser matter interaction. A photo-catalytic oxidative pathway appears mechanistically feasible. Recent studies reveal that high power laser irradiation raises local temperature of the metal nanocluster surface above the melting point leading to shape deformation. In addition, there is a high probability of generation of multiple ionization states in noble metal nanoclusters as a result of high plasmon resonance absorption, during laser irradiation. For ultra short laser pulse, the high production of multiphoton ionization state leads to the Coulomb explosion and subsequent photo-fragmentation of the material. Generation of multiple ionization states, mediated wide thermionic emission during laser irradiation, raises the temperature of metal nanoclusters higher than that of the surrounding
medium. Meanwhile, the available native O$_2$ species may be oxidized and emits the hot electron that flows at the interface between nanocluster and NTs. The catalytically activated exothermic process can cause partial melting of GaN NT surface, which ballistically combines with ionized/radical O$_2$ to result in topographic transformation of a surface containing channels and pits.

Two distinct mechanisms are involved in bringing about the photo-fragmentation process. The exothermic step generates thermal energy that fails to get dissipated quickly in the GaN NT matrix due to poor thermal conduction. This eventually causes surface cracks and fragmentation which reveal a multitude of surface dangling bonds. These bonds ballistically combine with available photo-generated O$_2$ ionic / radical species, represented schematically in figure 5.16, to yield chemisorbed oxide layer of Ga$_2$O$_3$. Control of local ambience (flow of N$_2$ gas) by reducing the number of reactive O$_2$ species can reduce the rate of photocatalytic activity, which can modulate the photo-fragmentation process. Only a few literature are available on melting behavior of GaN NTs using molecular dynamic simulation.$^{36,37}$ The results reveal that NTs begin to melt at the surface, and then the melting rapidly extends to the interior of the NTs with increase in temperature. The anomalies in the melting behavior were reported by Wang et al., which showed that NT with [10$ar{1}$0] oriented lateral facets was having higher propensity towards melting than that for [11$ar{2}$0] oriented
lateral facets for a given wall thickness. Furthermore, surface roughness and phonon confinement can also contribute significantly to the reduction of the lattice thermal conduction, and the latter is more prominent at low temperatures. All the above phenomena significantly cause energy imbalance, which results in photo-fragmentation as a consequent dissipative pathway.

5.6 Hydrogen Sensing Properties of GaN Nanotube

There has been significant recent interest in the development of nanomaterial based gas and chemical sensor for the benefits of health, safety, and environments. In particular, H₂ sensors are of increasing importance in connection with its uses in fuel cells, nuclear reactor and in industrial applications. Performance of any sensor is based on few important parameters, such as measuring range, sensitivity, selectivity, and response time. Apart from this, sensor operation at room temperature is of considerable interest in many areas of sensor technology. Comparative H₂ sensing performance of widely used materials with GaN NTs functionalized with Pt nanocluster is enlisted in table 5.1.

5.6.1 Materials and Methodology:

Mats of Pt functionalized GaN NTs were used for H₂ sensor. Prior to sensor application, the Pt coated samples were heated at 300 °C for 30 minutes to remove any unwanted lysine, used as a linker molecule between GaN NT and Pt nanocluster. H₂ sensor contact probes were made by sputtering a 5 nm Cr followed by 80 nm Au films on interdigitated electrodes with 1 mm spacing.

5.6.2 Pt Catalysed Hydrogen Sensing Properties of GaN Nanotube:

The H₂ oxidation on the Pt-decorated GaN NTs is investigated as a function of time over a wide range of H₂ concentration (25 - 200 ppm) in N₂ background, and temperature (RT to 473 K) as shown in figures 5.17(a,b). The material shows good sensitivity to H₂ with
Table 2: Comparative $H_2$ sensing properties of selected promising nano materials to that of

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Values reported in this work.
response time of 120 sec and recovery time of about 5 min at RT. At RT, Pt-decorated GaN NTs show relative sensitivities of 0.4 at 25 ppm, and 0.95 at 100 ppm level for H$_2$, which are factors of 10 as compared to that shown by control NTs. However, the relative sensitivities of H$_2$ increased to 3.8 at 25 ppm and 10.8 at 100 ppm at 373 K [Fig. 5.17(c)]. The reported value of 25 ppm of H$_2$ at RT using the NTs, in the present study, is the lowest ever reported in the GaN system. Wright et al.\textsuperscript{14} reported the previous lowest value with a relative response of 1.7 at 200 ppm of H$_2$ for 7 nm Pt sputter-coated GaN NWs with longer exposure time ~10 min at RT and 0.1 V bias condition. By comparison, Pt functionalized GaN NTs are found to be more sensitive than Pt sputter-coated on GaN NWs. Thus the uniform distribution of Pt

![Fig. 5.17 Time dependent changes in resistance of Pt decorated GaN NTs at (a) RT and (b) 373 K with different H$_2$ concentration; (c) relative sensitivity to H$_2$ at different temperatures for Pt coated and control NTs; (d) Arrhenius plot of the rate of change in resistances for the highest change in resistance (10-30 sec) with temperature.](image)
nanoclusters over NTs, using green chemistry methodology in the present study, is advantageous over sputter-coated film, and found to be more effective in catalytic dissociation of molecular $\text{H}_2$ at RT. An Arrhenius plot of the rate of change of resistance in Pt-decorated NTs with temperature is used to calculate the adsorption activation energy of 0.35 meV [Fig. 5.17(d)]. The value obtained here is found to be the lowest ever reported, as compared to other GaN systems. The calculated activation energy is well below the reported value of ~ 300 meV for Pt and Pd sputtered GaN NWs,\textsuperscript{14,15} which confirms the superiority in sensitivity and responsivity of our GaN NT based H$_2$ sensor.

5.6.3 Mechanism of Hydrogen Sensing in GaN Nanotube:

There is growing evidence which indicates that Schottky barrier formed between the metal and semiconductor surface gets altered as a result of a chemical reaction at the interface.\textsuperscript{45} Upon interaction with $\text{H}_2$ the excess electrons, generated as a result of catalytic oxidation of $\text{H}_2$ on Pt active sites, can easily exceed the Schottky barrier, and travel ballistically through the metal conduction band. These electrons possibly reach at the semiconductor surface where it would contribute to the conduction process resulting in the decrease of resistance at Pt-decorated GaN NTs interface. The low activation energy of Pt-decorated GaN NTs interface and small Pt nanocluster size distribution enhance the catalytic dissociation of $\text{H}_2$ through a non-adiabatic energy transfer route leading to a high value of sensitivity. Such $\text{H}_2$ sensor has also an important advantage over others in terms of the fact that the sensing elements can be effectively integrated with GaN based electronics leading to further miniaturization.

5.7 Summary:

Single crystalline GaN NTs with regular square facets are synthesized using the CVD technique. The NTs nucleate via a quasi VS process followed by self-agglomeration induced
facet formation limited by the differential growth rate along crystallographic faces. Green way of functionalizing NTs with well dispersed Pt nanoclusters exhibit noble catalytic properties. Catastrophic sensitization of Pt nanoclusters in GaN NTs matrix, leading to the rapid oxidation and photo-fragmentation process, can be controlled by modulating the gas phase kinetics as well as tuning the laser power irradiation. It is, thus, apparent that the sensitization of Pt nanoclusters is enhanced due to auto-amplified electronic cascades inside the nanoclusters, which reinforces the energy deposition in the close vicinity of the metal and semiconductor interface during gas phase kinetics as well as on high power laser irradiation. The process can be termed as laser-assisted catalysis.

H₂ induced decrease in resistance has been measured to the lowest value of 25 ppm level at RT with activation energy of 0.35 meV for Pt-decorated GaN NT surfaces, as compared to other GaN systems. These ideal surfaces can be used for multiple applications in realizing high throughput optoelectronic devices and sensors. The integration of nanoelectronic components with inbuilt sensing potential in a single microchip can go hand in hand.

5.8 References:


