An abrasive free slurry has been formulated using ionic and non-ionic surfactants with KMnO₄ as an oxidiser. Subsequently, the effect of these surfactants on the material removal rate (MRR) and surface planarity of semi-polar (11–22) GaN surface have been studied using chemical mechanical planarization (CMP) process. The formulated polishing slurries were characterized for their rheological properties such as shear thickening, thinning and viscosity as a function of shear rate. It was found that the polishing rate and surface planarity depend on the type of surfactant and its concentration. The estimated MRR values of various surfactants are seen to decrease from anionic to cationic to non-ionic in the order SDS > CTAB > TX-100 and the maximum MRR has been found to be 2.58 ± 0.1 m/hr for 0.5 wt% SDS surfactant containing slurry, under optimized conditions of other CMP parameters. In comparison to the cationic (CTAB) and non-ionic surfactants (TX-100), anionic surfactant (SDS) offered relatively good surface planarity with a remarkable root-mean-square (rms) surface roughness of 2 Å over a scan area of 1 × 1 μm².

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Gallium nitride (GaN) with non-polar and semi-polar orientations are better alternatives than polar orientations for applications such as visible and ultra-violet light emitting diodes (LEDs), blue, green and violet laser diodes and UV photodetector device. For instance, unlike c-plane orientation, semi-polar and non-polar orientations have large reduction or absence of built-in electric field resulting from spontaneous and piezoelectric polarizations resulting in good recombination (electron-hole pairs) efficiency. Alongside, it is well known that a very smooth, atomically flat surface with rms roughness ≤ 0.5 nm with defect-free surface is a pre-requisite for growth of high quality epitaxial layer. If the surface is very rough, there is little contact and therefore, an insufficient density of bonds between the substrate and the epilayer, which prevents subsequent bonding between them. However, most non-polar and semi-polar epitaxial layers are grown heteroepitaxially on miscut sapphire substrates resulting in rough surface morphology with sub-surface defects owing to the anisotropic nature of the growth. Removal of the surface defects and improvement in surface roughness can be achieved by a process called chemical mechanical planarization (CMP). Conventional CMP slurries containing abrasive particles often creates polishing related surface or subsurface damages while removing material from the semiconductor surfaces. Such polishing related defects can be eliminated by abrasive free CMP which has many potential advantages in polishing various semiconductor surfaces for the opto- and micro-electronics devices. This is primarily due to its ability to create low surface and subsurface defect density with atomically flat surface topography, decreased dishing and erosion, simple post cleaning, economically feasible and prolongation of the polishing pad lifetime. Therefore, it is essential to formulate polishing slurry without abrasive and study its subsequent surface modification of III-V nitride semiconductors and characterize the surface for its topography after the CMP process with a reasonable polishing rate. The ionic environment of the polishing slurry gets significantly altered in presence of any surfactant and hence affects its flow behavior and in turn the polishing rate and surface finish. It has been reported that surfactant in the polishing slurry act as a lubricating agent that reduces the friction coefficient leading to improved polishing rate and surface quality simultaneously unlike those obtained from slurry without any surfactant. In this viewpoint, the role of surfactants on slurry stabilization and complex formation in presence and absence of abrasive particles and its subsequent effect on the polishing rate, selectivity and surface quality have been investigated rather often in Cu CMP. For instance, Hong et al. and Bernard et al. reported that electrostatic attraction promotes strong adsorption of surfactant molecules on Cu surface and subsequent formation of a compact protective layer. This layer established a balanced mechanical force and chemical dissolution regardless of the presence and the absence of abrasive particles. As a consequence, improved surface planarity with a reasonable material removal rate was obtained. Additionally, surfactant also may act as a lubricating agent and abrasive particles stabilizer. To the best of our knowledge, however, there have been very few reports describing the effect of the polishing slurry containing surfactant–abrasive–oxidant and surfactant–oxidant on the polishing rate and surface planarity of GaN by CMP. Recently, our group found that anionic surfactant suppresses chemical dissolution reactions and stabilizes charged micelle in the slurry containing abrasive nanoparticles, which improve the material removal and surface properties of c-plane (0001) GaN surface. In addition, it has been found that surfactant not only stabilized the abrasive particles but also involves in some complex formation and surface modification of GaN surface. An abrasive free polishing (or without the use of any externally added abrasive particles) has been demonstrated using various transition metal elements based oxidizer for polar nitride surfaces (Ga face of GaN and Al face of AlN).

It is understood from the above critical literature survey that the ionic environment, viscosity and shear rates of the polishing slurry get significantly altered in presence of any surfactant and hence affects its flow behavior which in turn influence the polishing rate and surface finishing. However, there is still a dearth of systematic investigation on the role of ionic and non-ionic surfactants for GaN CMP using slurries free of abrasive particles. In the present work therefore, an effort has been made to elucidate the role of three different surfactants (anionic surfactant: sodium dodecyl sulfate (SDS), cationic surfactant: cetyl trimethylammonium bromide (CTAB), and non-ionic surfactant: Triton X-100 (TX-100) and its concentration in abrasive free slurries on the polishing rate and surface planarity of semi-polar (11–22) GaN surfaces. The polishing slurries were characterized for their rheological properties using rheometer. The surface topographical features have been studied using optical surface profiler and atomic force microscope. A remarkable local/global surface planarity has been obtained with rms surface roughness of 2 Å over a scan area of 1 × 1 μm² on abrasive free CMP processed semi-polar (11–22) GaN surface.
Experimental

Semi-polar (11–22) GaN (2-inch diameter and 2μm thick) epilayers grown on sapphire substrate by metal-organic hydride vapor phase epitaxy (MOVPE) was used to perform the experiment using a Buehler Ecomet 250 variable speed Grinder Polisher with Automet 250 power head. A Cabot D100 polishing pad was used for all the experiments. The wafer was bonded on a 2 inch stainless steel carrier using crystal bond 509 clear epoxy resin. All the CMP experiments were carried out at 90 rpm (platen velocity), 30 rpm (carrier velocity) and 38 kPa polishing pressure. The surfactant based CMP slurry is composed of oxidizer: 0.4 M potassium permanganate (KMnO₄), and three different surfactants, cationic surfactant: CTAB, anionic surfactant: SDS and non-ionic surfactant: TX-100. The slurry pH was maintained at 2 and delivered at a 10 ml/min flow rate between the wafer-pad interface using a peristaltic pump (Ravel, Model No. RH-P100VS-100). To confirm the reproducibility of the data, the experiment was repeated two times with typical polishing time for each experiment of 10 minutes. Conditioning of pad (down pressure applied by hand and at a platen rotational speed of 90 rpm for ten times) was performed after every 5 minutes of polishing using a diamond pad conditioner (Model no. S341038N-2A2 from M/s Abrasive Technology Asia Pacific Pvt. Ltd., Singapore). After every 10 minutes of polishing, the wafer was demounted from stainless steel carrier and washed repeatedly with deionized water, acetone and isopropyl alcohol in order to remove the thin Ga₂O₃ layer, surfactants and other possible residues with deionized water, acetone and isopropyl alcohol in order to remove the thin Ga₂O₃ layer, surfactants and other possible residues.

Results and Discussion

Rheological properties of slurries.—To understand the role of surfactant in the slurry formulation and its subsequent effect on material removal and surface planarity, rheological studies were conducted. Shear rate dependent viscosities of the slurries with three different surfactants and its concentration (0.5, 0.75 and 1 wt%) are plotted in Figs. 1a–1c. The slurry with 0.25 wt% surfactant does not show any differences in their rheological characteristics, compared to the surfactant free slurry (not shown here). From the curves, it is clear that surfactants can effectively regulate the rheological characteristics of the polishing slurry. It could most likely be associated with complex formation between oxidizer and surfactant, ionic strength and viscosity. The polishing slurry without surfactant shows shear thickening behavior throughout the entire shear rates, 20–100 (s⁻¹) with a sharp rise in viscosity at shear rate, 20 (s⁻¹). The rheological behavior of slurries containing anionic surfactant (SDS) with three different concentrations (0.5, 0.75 and 1 wt%) is completely different from the slurry without surfactant (Figs. 1a, 1c (inset)). No shear thickening behavior is observed (even at 1 wt% of SDS) throughout the entire shear rates, however a sharp rise in viscosity at lower shear rates for 0.75 and 1 wt% of surfactant is observed. Additionally, when shear rate reaches 35 (s⁻¹), the slurries of these two concentrations exhibited a significant shear thinning behavior and viscosity become almost stable up to the highest shear rate region (100 (s⁻¹)) studied. The viscosity is nearly stable throughout the entire shear rates (Newtonian fluid behavior) for 0.5 wt%, indicating excellent stability at all shear rates studied. No changes in viscosity as a function of shear rate indicates micelles at this concentration remain as small spherical ordered structures (SDS concentration at 1 wt% in this study is 0.0347 mol/dm³ which is well above its CMC in KMnO₄ solution- 80 × 10⁻⁴ mol/dm³). When increasing the concentration, these small micelles get to interact with each other leading to extended growth of micellar dimensions. The observed shear thinning behavior is possibly attributed to the arrangement of extended micelles into ordered structure with an increase in shear rate (as there is a repulsive force between SDS and MnO₄⁻).

![Figure 1. Shear rate dependent viscosities of the polishing slurries containing three different surfactants and its concentration, SDS (a), CTAB (b) and TX-100 (c), without surfactant (inset of c).](image-url)
Thus, the increase in viscosity during the shear rate reduction step is most likely a reversal of the shear thinning response. As the shear rate is reduced, entropic stresses become relatively more significant. As a result, the shear-induced ordered structure becomes random and highly disordered, leading to an overall resistance to flow. However, the dominance of the repulsive forces between the surfactant and the oxidant will break the agglomerates between them and thereby suppressing complex formation in the polishing slurry and hence no shear thickening is observed.

Figure 1b shows the change in rheological characteristics of CTAB containing slurry as a function of concentration. No notable shear thickening is observed throughout the entire shear rates for 0.5 and 0.75 wt% indicating the presence of only spherical micelles in the micellar system. However, the viscosity was gradually increased with decreasing shear rates. While the slurries containing 1 wt% showed a significant shear thickening behavior in intermediate shear rates (30–70 (s⁻¹)) with a sharp rise in viscosity at lower shear rate, 30(s⁻¹). In this case, the surfactant develops micelle as the studied concentration (0.0274mol/dm³ at 1 wt%) is well above its CMC (CMC of CTAB in KMnO₄ solution- 8.7 × 10⁻³mol/dm³). As CTAB concentration increases an abrupt change in the viscous nature and shear thickening is observed suggesting micelles are entangled with each other to form a network (transition from spherical to rod like shape). The shear-induced interlayer coagulation of micelles by strong hydrodynamic interaction is responsible for the shear thickening. Also, the complex formation between the micelle structure with a positively charged head group (N⁺(CH₃)₃) of CTAB and negatively charged oxidant species (such as MnO₄⁻) through electrostatic interaction contributes to the shear-induced agglomeration.

In contrast, the slurries containing non-ionic surfactant (TX-100) showed shear thickening behavior throughout the entire shear rates, 20–100 (s⁻¹) for 0.75 and 1 wt% with a sharp rise in viscosity at lower shear rates for 1 wt% (Fig. 1c). Whereas, the slurry containing 0.5 wt% has nearly stable viscosity without any notable shear thickening behavior throughout the entire shear rates. A gradual increase in viscosity has been observed upon increasing shear rate. The oxidation of polyoxyethylene chain in TX-100 by MnO₄⁻ produces complex species with highly agglomerated structures which, in turn, offers shear thickening behavior. This is expected to be much lesser for slurry with 0.5 wt% surfactant and therefore, no shear thickening is observed and more with increasing the surfactant concentration. Mixing of TX-100 and MnO₄⁻ under acidic medium produces a complex series of reactions leading to the degradation of polyoxyethylene chain of TX-100 by MnO₄⁻ which, in turn, changes the nature of the micelles. Under this circumstance, the Van der Waals attractive forces between oxidant species and the surfactant is expected to dominate and make the slurries unstable.

**Effect of surfactants on material removal rate.—** Figure 2a–2c shows the effect of three surfactants (SDS, CTAB, and TX-100) and its concentration (0, 0.5, 0.75 and 1 wt%) on MRR of semi-polar (11–22) GaN surface under the present CMP processing condition. The estimated MRR values of various surfactants are seen to decrease from anionic to cationic to non-ionic in the order SDS > CTAB > TX-100. A maximum MRR has been obtained for SDS containing slurry, compared to those obtained from either surfactant free or CTAB/TX-100 containing slurries. During the CMP process the oxidizer present in the slurry (KMnO₄) undergoes catalytic conversion with some possible intermediate species of Mn (VI, V, IV and III) ions depending on the pH of the slurry. The most possible forms of Mn formed in the present study (pH-2) could be Mn (III) (reaction intermediates), and Mn (II) (reaction product) which act as an auto-catalyst in the oxidation process. Presence of surfactant in the slurry solution leads to the formation of the complex between the oxidizer and surfactant (as discussed in Rheological properties of slurries section). Further, dual-phase CMP polishing, oxidation reaction between MnO₄⁻ and GaN surface forms a soft layer of Ga₂O₃ under the suitable slurry chemistry and dissolves in the solution and removed subsequently by mechanical pressure. A maximum MRR 2.58 μm/hr has been achieved for the slurry containing 0.5 wt% SDS which is ~15% increase, compared to slurry without surfactant (2.24μm/hr). With further increase in concentration MRR decreases and the values are estimated to be 2.16μm/hr (~3% decrease) for 0.75 wt% and 1.87μm/hr (~16.5% decrease) for 1 wt% SDS. Second maximum MRR of 2.32μm/hr has been obtained when 0.5 wt% CTAB is used which is found to be a marginal increase of 0.08 μm/hr (~3.5% increase) compared to the surface polished without surfactant. Further increase in concentration led to decrease in MRR and was estimated to be 1.93 μm/hr (~13% decrease) for 0.75 wt% and 1.62μm/hr (~27.6% decrease) for 1 wt% CTAB. A minimum MRR has been obtained for TX-100 containing slurry compared to those obtained from either surfactant free or CTAB/TX-100 containing slurries. A significant reduction in MRR has been observed upon increasing the surfactant concentration, 1.27μm/hr (~43% decrease), 1.03μm/hr (~54% decrease) and 0.97μm/hr (~57% decrease) for 0.5, 0.75 and 1 wt% of TX-100 respectively.

The observed MRR trend as a function of surfactants is described with the anticipated mechanism in Figs. 3a, 3b. The polishing slurry without surfactant produces a direct interaction between the oxidant and the surface. Therefore, the slurry maintains the system entirely in edge/boundary lubrication (as shown in Fig. 3b) while all other slurries containing surfactant exhibit different degrees of lubrication behavior. Under this condition, reasonable material removal has been obtained but not the surface uniformity. In the case of anionic surfactant (SDS), there will be a repulsive force between the negatively charged head group of SDS – MnO₄⁻ species. Therefore, unlike other two surfactants, SDS will not affect the oxidation efficiency of MnO₄⁻. Moreover, the SDS micelles will be formed in the polishing slurry as there is no complex formation and the studied SDS concentrations are well above its critical micelle concentration in KMnO₄. Under this chemical environment, oxidation of Ga surface by MnO₄⁻ species will occur in presence of the SDS micelles. The dodecyl sulfate anion (DS⁻) present in the SDS micelle structures tends to adsorb directly on Ga-polar (+) surface of GaN through the electrostatic interaction. Also, it is likely that the Ga atoms on the m-plane have positively charged dangling bonds which can attract SDS micelles via negatively charged heads of DS⁻ through the electrostatic interaction. The adsorbed micelles form ordered structure and form a thin substantially permeable
liquid layer at lower surfactant concentration (0.5 wt%) \(^{33,36-38}\). This layer will assist to circulate the slurry equally throughout the wafer surfaces and hence the improved MRR and surface planarity are simultaneously observed through the appropriate lubrication effect and surface passivation. As the micelles structure gets elongated surface absorption will increase with increasing SDS concentration, the liquid layer thickness also increases, leading to high lubrication effect, which protects the surface from oxidization and hence decreased removal rate (see Fig. 3b).\(^{33}\) This layer is expected to be reasonably thin even upto 0.75 wt% as there is marginal (\(\sim 3\%\)) decrease in MRR. It is also evident from the rheological characteristics, the viscosity of the slurries increases with increasing surfactant concentration. Also, it has been reported that simply addition of surfactant in the polishing slurry improves the lubrication between the pad-wafer interfaces which decrease the friction coefficient regardless of the surfactant types.\(^{35}\)

In case of cationic surfactant (CTAB), there will be a reaction between the positively charged head group of CTAB and negatively charged MnO\(_4^-\) species leading to complex formation in the form of micelle through the electrostatic interaction (as discussed in Rheological properties of slurries section). This interaction forms a stern layered micelle structure in which counter ions (MnO\(_4^-\)) are strongly attracted by the surfactant head group (\(N^+ (\text{CH}_3)_3\)) and are located in their immediate vicinity (see Fig. 3a).\(^{29,30,39}\) The local concentration of the counter ion will be high at lower surfactant concentration which, in turn, increases the reaction rate.\(^{30,39}\) With the increasing CTAB concentration, number of micelles increases thus the accumulation of counter ions around each micelle decreases.\(^{30}\) As a result, insufficient oxidant species participate in Ga surface oxidation leading to a decrease in removal rate. Therefore, a marginal increase in removal (\(\sim 3.5\%\)) is observed at 0.5 wt% of CTAB, compared to surfactant free counterpart. Besides, it is also likely that the micelles composed of CTAB- MnO\(_4^-\) at this concentration are discrete in small-spherical dimension as evident in shear thickening throughout the entire shear rate in the shear rate dependent viscosity result.\(^{22}\) Therefore, uniform circulation of the slurry leading to increase in MRR is observed. However, with increasing concentration of the surfactant micelles get aggregated and influence the MRR adversely, which has exactly been observed for increasing CTAB concentration to 0.75 and 1 wt%.\(^{22,26}\) This has also been evident from the shear-induced agglomeration and abrupt increase in viscosity in the shear dependent viscosity measurement, leading to an overall stronger resistance to slurry flow. In addition, lubrication between wafer–pad interfaces increases upon increasing concentration of the surfactant, thus reducing shear forces and hence the removal rates.

In contrast to ionic surfactants, a significant reduction in MRR has been observed upon increasing the surfactant concentration in case of non-ionic surfactant (TX-100). This could be attributed to the following reasons. It has been reported that polyoxyethylene chains of TX-100 are oxidized by MnO\(_4^-\) under acidic medium.\(^{31}\) Likewise, under the present slurry environment, (slurry with pH-2) some of the MnO\(_4^-\) oxidation.
The rms surface roughness values (scan area $0.70 \times 0.96 \text{ mm}^2$) of semi-polar (11–22) GaN surfaces as a function of three different surfactants and its concentration.

| Surfactant con. | rms roughness ($R_q$) (nm) | Diff. in local/ global rms roughness (nm) | Total roughness ($R_t$) (nm) |
|-----------------|----------------------------|----------------------------------------|-----------------------------|
| Without surfactant | 4.6                        | 4.7                                    | ~62                         |
| SDS 0.5 wt %     | 1.8                        | 0.56                                   | ~14                         |
| 0.75 wt %       | 1.6                        | 1.0                                    | ~22                         |
| 1 wt %          | 1.4                        | 1.4                                    | ~25                         |
| CTAB 0.5 wt %   | 3.8                        | 2.7                                    | ~31                         |
| 0.75 wt %       | 2.8                        | 3.1                                    | ~38                         |
| 1 wt %          | 2.4                        | 3.7                                    | ~43                         |
| TX-100 0.5 wt % | 1.5                        | 1.4                                    | ~24                         |
| 0.75 wt %       | 1.1                        | 2.5                                    | ~33                         |
| 1 wt %          | 0.97                       | 2.8                                    | ~35                         |

Species participate in oxidative degradation of polyoxyethylene chain of the TX-100 micelles (shown in Fig. 3a). This has also been evident during the slurry reaction in which the permanganate color disappeared partially and become rather turbid (not observed in the other two surfactants) indicating instability of polyoxyethylene chain of TX-100. Consequently, inadequate MnO4$^-$ species participate in the oxidation of Ga surface leading to the least material removal. The complex oxidative degradation process of TX-100 involves breaking down of the primary hydroxyl group of TX-100 by MnO4$^-$ and thereby produces aldehyde (-CHO) group. Further, the oxidation of –CHO group would continue to produce the carboxylic acid and cleavage of the C–O bond of polyoxyethylene chain of the nonionic surfactant. In addition, it is expected that the formation of soluble MnO2–TX-100 complex in the reaction mixture through hydrophobic interaction rapidly depletes the auto-catalyst (Mn (II and III)) concentration affecting the MnO4$^-$ oxidation potential toward GaN. This has been further evidenced by a significant fluctuation in the viscosity and shear thickening at various shear rates in the rheological study of 0.75 and 1 wt% of TX-100. This is attributed to the shear-induced agglomerates of oxidized species and micelles, leading to an overall stronger resistance to slurry flow and therefore, largely reducing MRR for 0.75 and 1 wt% TX-100. This shear thickening behavior is dominant throughout the entire shear rates for TX-100 containing slurry, compared to the slurries containing other two surfactants and hence a significant drop in the material removal rate is observed.

**Effect of surfactants on surface planarity.**—To investigate the effect of the three different surfactants and its concentration on surface planarity of semi-polar (11–22) GaN surfaces, optical surface profiler images were collected over varying scan area sizes ($0.45 \times 0.35$, $0.60 \times 0.48$, $0.96 \times 0.70$ and $1.2 \times 0.96 \text{ mm}^2$), representative of the local/global surface planarity. Fig. 4a depicts the 3D optical surface profiler image of as-grown surface which revealed a highly coarse and irregular surface topography with rms surface roughness of 136.6 nm over a scan area of $0.96 \times 0.7 \text{ mm}^2$. The surface topography was further enlarged with the smallest scan area size ($0.45 \times 0.35 \text{ mm}^2$), which allows a direct visualization of 3D topography and revealed highly coarse surface with rms roughness of 85.3 nm (Fig. 4b). Surface polished without surfactant is fairly flat and defect free with rms surface roughness of 4.6 nm over a scan area of $0.96 \times 0.7 \text{ mm}^2$ (Fig. 4c).

Figs. 5a, 5b and 5c depicts the 3D optical surface profiler images of polished surfaces with three different slurries containing surfactants, 0.5 wt% of SDS (Fig. 5a), CTAB (Fig. 5b) and TX-100 (Fig. 5c). The rms surface roughness values (scan area $0.70 \times 0.96 \text{ mm}^2$) were found to be 1.5, 1.1 and 0.97 nm for 0.5, 0.75 and 1 wt% of TX-100 respectively, 1.8, 1.6 and 1.4 nm for 0.5, 0.75 and 1 wt% of SDS respectively and 3.8, 2.8 and 2.4 nm for 0.5, 0.75 and 1 wt% of CTAB respectively (Fig. 6a) (values are provided in Table I). The rms surface roughness values decreased from non-ionic to anionic to cationic in the order TX-100<SDS<CTAB and the best rms surface roughness has been achieved from the surface polished with TX-100 surfactant. This is most likely attributed to the mild material removal and absence of electrostatic complex formation between the surfactant and wafer surface. It has been observed that rms surface roughness improved for the surfaces polished with slurries containing all three surfactants compared to surfactant free slurry. This is due to the fact that, an...
addition of surfactant act as lubrication between the wafer-pad interfaces which reduces the friction coefficient.

To estimate the local/global surface planarity, rms surface roughness collected from the smallest (0.45 × 0.35 mm²) and largest (1.2 × 0.96 mm²) scan areas were used. The difference in rms roughness of the as-grown surface was found to be 51 nm. This difference decreased to 4.7 nm for the surface polished without surfactant, 0.56, 1.0, 1.4 nm for 0.5, 0.75 and 1 wt% of SDS respectively, 2.7, 3.1 and 3.7 nm for 0.5, 0.75 and 1 wt% of CTAB respectively and 0.5, 0.75 and 1 wt% of TX-100 respectively (values are provided in Table I). The local/global surface roughness differences as a function of various surfactants are seen to be decreased from anionic to non-ionic to cationic in the order SDS < TX-100 < CTAB. The least surface roughness differences was found be to 0.56 nm for 0.5 wt% SDS concentration which is ∼99% improved surface planarity, compared to as-grown surface and ∼88%, compared to the surface polished without surfactant. As shown in Figure 3b, when a small amount of SDS (0.5 wt%) is present in the polishing slurry, the surfactant molecules in the form of micelles cannot cover the surface densely, the micelle forms a porous cluster and solution pass through the liquid cavities. The SDS micelles absorb to the Ga-polar surface through DS⁻ with the nonpolar tails extending into the solution (this is absent in the other two surfactants as there is no electrostatic interactions and only physically absorbed surfactant molecules are anticipated). Under this condition, the slurry is uniformly spread throughout the wafer surfaces and the applied pressure distribution is also uniform, therefore, improved surface planarity can be achieved after a balance between the chemical and mechanical effects is established. However, when the concentration of SDS increased further in the slurry, the GaN surface would have covered densely with ordered arrangement of DS⁻ which could have separated the slurry from the surface leading to rather unbalanced chemical and mechanical effects. This is consistent with the discussions made earlier about the material removal of SDS containing slurries in Effect of surfactants on material removal rate section. Also, when the surface polishing is performed at less lubricating condition (without surfactant), within wafer-non-uniformity will not generally be achieved due to the presence of the edge zones (solid-solid-interaction) between the pad-wafer interfaces resulting in non-uniform surface roughness.  

A significant difference in total roughness (Rₜ – peak (Rₚ)-to-valley (Rᵥ)) has been observed for various surfactants, the lowest global rms surface roughness and Rₜ values are plotted in Figure 6b. The measured Rₜ roughness values are affected by the variations in topography caused by irregular surface morphology and sharp hillocks. These hillocks associated with mixed dislocations were produced during the growth of GaN epilayers. Rₜ values (scan area 0.70 × 0.96 mm²)
The observed overall trend in $R_t$ upon increasing surfactant concentration is most likely associated with the following reason. The layer at low surfactant concentration resulting in efficient suppression of peak-to-valley height difference. If the layer formed on the surface is too thick upon increasing concentration, total surface planarity will generally not be achieved. This is because both the high (peak) and low (valley) topographies present on the wafer surface will receive nearly the same polishing rate.\textsuperscript{36}

The surface topographical features at the atomic scale were also analyzed using AFM measurement. Figure 7a represents the 2D AFM image of the as-grown semi-polar (11–22) GaN surface, which revealed highly rough and non-uniform topography with 139 nm rms surface roughness over a scan area of $1 \times 1 \mu m^2$. Whereas, 2D AFM image of the polished surface using 0.5 wt% SDS containing slurry revealed good surface planarity with atomic terrace and a moderately defect-free surface with 0.2 nm rms surface roughness over a scan area of $1 \times 1 \mu m^2$ (Fig. 7b).

Conclusions

This investigation indicates that understanding the effect of ionic and non-ionic surfactants in the slurry solution is critical for slurry formulation and improved CMP performance. Efficient abrasive free CMP slurry consisting of environmental friendly anionic surfactant SDS has been identified as the best slurry to improve the polishing rate and surface planarity of semi-polar (11–22) GaN surface simultaneously. A $\sim 15\%$ increase in MRR of 2.58$\mu$m/hr has been achieved using the slurry containing 0.5 wt% of SDS compared to that for the slurry without surfactant (2.24$\mu$m/hr) under similar experimental conditions. Concurrently, the total surface roughness ($R_t$) was found to be 14 nm, which was $\sim 77\%$ improved surface planarity compared to the surface polished by slurry without surfactant (62 nm). The anticipated mechanism has been proposed for the observed trends in material removal and surface planarity as a function of three different surfactants.

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Figure 7. 2D AFM images of representative rough as-grown (11–22) GaN surface over a scan areas of $10 \times 10 \mu m^2$ (a) and polished surface using slurry containing 0.5 wt% SDS over a scan area of $1 \times 1 \mu m^2$ (b).

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