Coaxial GaN/InGaN/GaN Nano-Heterostructures

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The optimization of the epitaxial quality and ordering of coaxial GaN/InGaN/GaN nano-heterostructures is the main focus of this study. Two approaches for the realization of upright ZnO nanipillars, used as templates for the epitaxially grown GaN layers, with their respective degrees of pattern arrangement are introduced. Consequently, the growth of coaxial GaN/InGaN/GaN quantum wells (for three different samples) along with the corresponding structural and optical properties is investigated. By comparing the optimized InGaN quantum well growth conditions in two different MOCVD reactors, we could reduce the FWHM of an intense room temperature photoluminescence peak of the InGaN quantum well at 3 eV from 300 meV to 190 meV. Cathodoluminescence mapping along the nanotubes revealed two main peaks that are emerging from the sides and top facets of the tubes backing an argument for different respective In incorporation.

1. Introduction

Gallium nitride nanotubes and nanorods have been receiving considerable attention as building blocks for nanophotonic technologies due to their unique high aspect ratios, promising the realization of photonic and biological nanodevices such as blue light emitting diodes (LEDs), short-wavelength ultraviolet nanolasers and nanofluidic biochemical sensors [1]. As a first step to realize the potential impact of these novel structures, the development of a process for fabricating dislocation free, position and diameter controlled nanostructures arrays is necessary. A variety of techniques have been utilized to synthesize GaN nanowires including laser ablation [2], metal-initiated Vapor-Liquid-Solid nanowire growth in metalorganic chemical vapor deposition (MOCVD) reactors [3] as well as hydride vapor phase epitaxy [4] . However, these approaches suffered from not having well ordered and upright pillars. On the other hand, there have been various methods to successfully grow high quality, upright and arranged ZnO nanorods [5]. Therefore, one approach for realizing GaN nano-structures in an upright and well ordered form is growing GaN epitaxially around ZnO nanorods as reported in our previous work [6].

ZnO decomposes by reacting with hydrogen or ammonia at elevated temperatures. Therefore, a multi-layer growth process (MGP) for the growth of GaN layers on ZnO templates by Metal Organic Vapor Phase Epitaxy (MOVPE) [7] has been developed. However, at the very last stage of growth at high temperatures , the ZnO may easily dissolve resulting in GaN nanotubes taking the original pattern of the ZnO pillars (Fig. 1). Furthermore, we have demonstrated the growth of a coaxial GaInN quantum well structure around the resulting GaN nanotubes [8]. In the present study, we investigated further the optimization of the afore-mentioned coaxial quantum well growth along with the corresponding

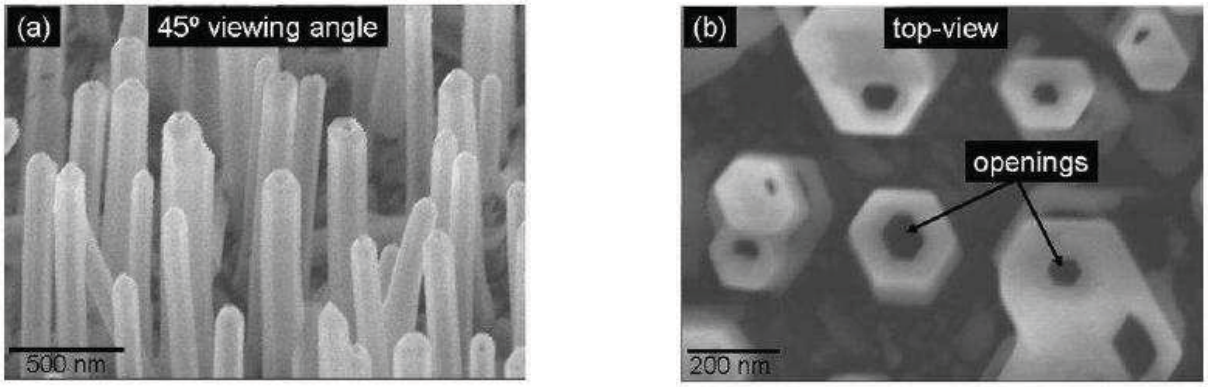

Fig. 1: GaN nanotubes grown around ZnO nanorods which dissolved during the MOVPE process [6].

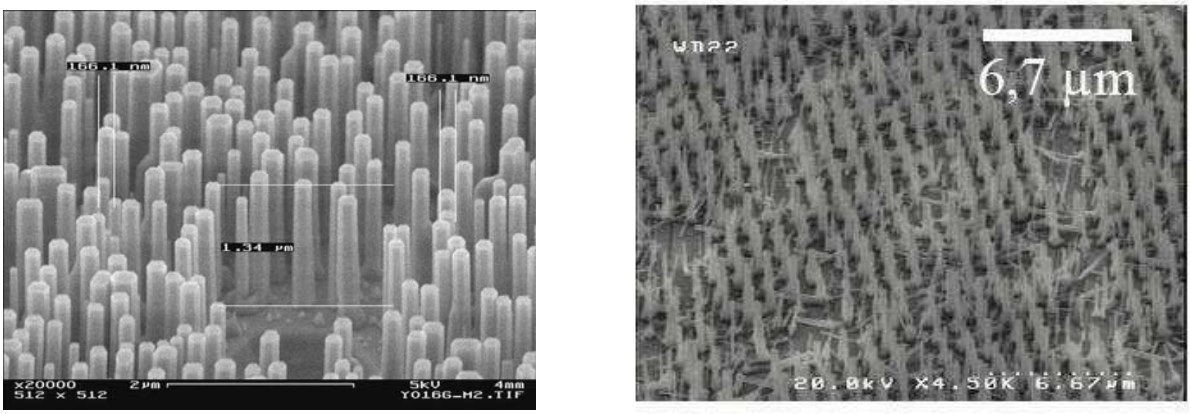

Fig. 2: ZnO nanorods grown on a-plane sapphire using a ZnO seed layer (left) [9] and using a gold catalyst (right) [10].

optical and structural characterizations using photoluminescence, transmission electron microscopy, scanning electron microscopy and cathodoluminescence. In addition, a new approach for the control of the arrangement and diameter of the ZnO pillar templates is described accompanied by the corresponding optical characterization of the overgrown coaxial GaN/InGaN/GaN heterostructures.

2. Experimental

The ZnO nanopillars used as templates in these studies have been grown using two different approaches. The first is a catalyst-free vapor-solid process on a-plane sapphire wafers which started with a ZnO nanocrystal nucleation seed layer using zinc acetate as precursor [9]. In a subsequent step, the nanorods were deposited at 845 °C with Ar as carrier gas where a ZnO/carbon powder was used as a precursor. Vertically aligned ZnO nanorods (Fig. 2 left) with typical diameters and heights of 100–300 nm and 1–2 µm were achieved, respectively.

However, this is a random process where the precise control of the position or ordering

of the rods is not controllable and the degree of reproducibility of such process is not quite high. Therefore, a second approach utilizing the structured patterning of a thin metal catalyst layer on the a-plane sapphire substrate before the ZnO pillar growth was attempted [10]. Around 2 nm of Au were deposited on the a-plane sapphire followed by the deposition of a monolayer of polystyrene spheres with a diameter of 1.4 µm. Then the sample is treated on a hot plate and in an oxygen plasma for fixing the spheres on the gold film and reducing their size, respectively. Finally, the gold film in the open windows between the spheres is wet etched and the spheres are removed in an ultrasonic bath. The final pattern of the gold catalyst takes the form of the Polystyrene sphere monolayer, where the periodic distance is dictated by the diameter of the spheres, the time in oxygen plasma and the wet etching time of the gold film. The ZnO pillar growth is thus enhanced mainly at the sites where the gold catalyst is positioned. A SEM picture of the subsequently grown ZnO pillars in an ordered form on the patterned gold catalyst is shown in Fig. 2 (right) with diameters of 100–300 nm and lengths of 1–1.5 µm, respectively. The ZnO templates are then transferred to our AIXTRON AIX 200 RF low pressure (LP) MOVPE system. Here, the precursors were trimethylgallium (TMGa) and NH_3. In the following, we compare three different samples. For sample A, the ZnO pillars were grown using the catalyst-free nucleaction seed layer. The subsequent GaN nanotube growth and the the In containing layers including the adjacent GaN barrier layer took place in two different MOVPE systems, respectively, in order to take advantage of the well established InGaN growth environment in the second system. A single coaxial quantum well was epitaxially grown. We have already reported about the characterization results for this sample in [8]. It is retrieved here for comparison.

For sample B, the sequence was exactly the same except for the facts that three coaxial quantum wells were grown and there was no growth interruption. InGaN growth took place in the same MOVPE system after the InGaN growth conditions have been optimized. Finally, sample C was a gold patterned ZnO template with the same GaN and InGaN growth conditions as sample B.

Photoluminescence carried out at room and low temperature was applied to investigate the band gaps of the grown multi-layer nano-structures. The shape of the grown nanopillars was mainly investigated by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) measurements revealing the dimensions of single rods and the heterostructure details for sample A are retrieved [8]. Low temperature cathodoluminescence was utilized to map the distribution of quantum wells for sample B.

3. Coaxial GaInN Quantum Wells

As mentioned above for sample A, the deposition of one InGaN quantum well took place in a second MOVPE system. Here, the growth was re-established by growing a thin GaN layer (about 7 nm) at 885 °C with triethylgallium (TEGa) as Ga precursor and N_2 as carrier gas. Then, the trimethylindium (TMIn) flow was switched to the reactor to grow a GaInN quantum well with nominally about 10 % In at a temperature of 830 °C. Finally, the temperature was set back to 885 °C for the growth of the outer GaN barrier layer, first grown with N_2 as carrier gas, then switching to H_2 for the last few nanometers. SEM

inspection showed that the diameters of the nanotubes have significantly increased and the tube openings were closed (Fig. 3 left).

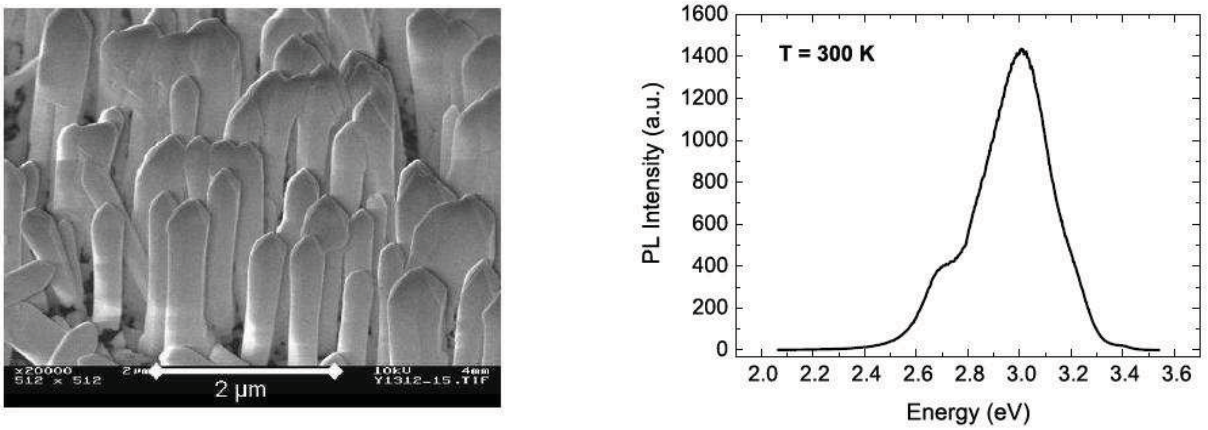

Fig. 3: Sample A: GaInN/GaN coaxial nanotube structures (left) and the corresponding room temperature photoluminescence spectrum (right) [8].

It seems that most material was deposited at the top of the tubes, indicating a less pronounced precursor diffusion down to the template surface. This may be a consequence of the fairly densely packed nanotubes and of the lower diffusivity of TMIn and TEGa as compared to TMGa, being even further pronounced by the lower growth temperature. In room temperature photoluminescence, a fairly intense peak at around 3 eV, the position expected for the GaInN quantum well, was observed (Fig. 3 right) with a full width at half maximum of 300 meV. TEM analysis (not shown here) showed a quantum well thickness of 4 nm, a covering spacer of 20 nm and a distance of 40 nm from the inner tube wall to the quantum well layer [8].

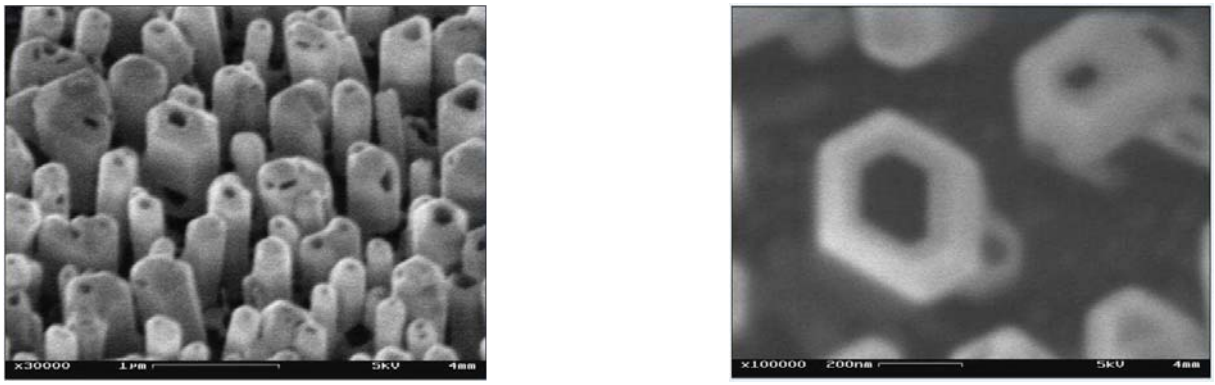

Fig. 4: Sample B: three GaN/GaInN/GaN coaxial nanotube heterostructures grown without growth interruption.

For sample B, three quantum wells were deposited directly after the epitaxial growth of the GaN tube in the same machine. Here, the InGaN quantum wells growth conditions were optimized for a barrier and quantum well thicknesses of 7 nm and 3 nm on c-plane sapphire, respectively, with an emission wavelength of 417 nm. Within that context, the barrier and

quantum well growth temperatures were 880 °C and 860 °C, respectively, using the same precursors and carrier gas as for sample A. As opposed to sample A, the tube openings were apparently observed (Fig. 4). This could indicate the process sensitivity with respect to the diffusivity of TMIn and TEGa to the temperature variations between the two machines. In room temperature photoluminescence, an intense peak with a narrower spectral width of 190 meV was observed at 3.086 eV indicating again the existence of a quantum well structure (Fig. 5 (left)). Note that the light-colored lines are just software created Gaussian fits for calculation purposes.

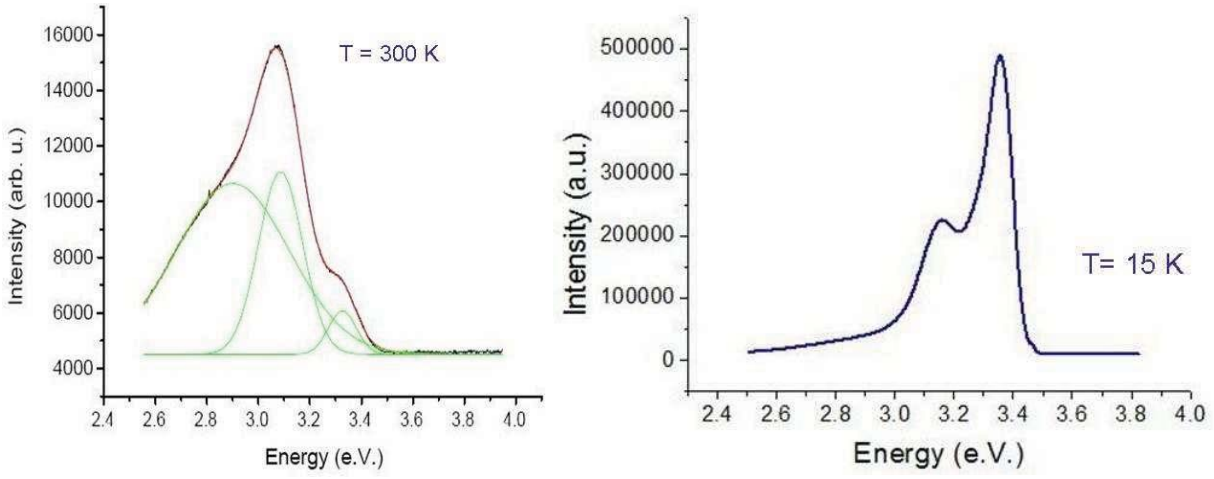

Fig. 5: Sample B: Room temperature and low temperature photoluminescence spectrum for three GaN/GaInN/GaN coaxial nanotube heterostructures.

Moreover, a wide blue luminescence peak - also noticeable for sample A - centered around 2.8 eV is observed, which has been reported by Wang et al. to be attributed to carbon incorporation from the TMGa incomplete dissociation at low temperatures during the deposition of the first layers of GaN [11]. Another shoulder peak at 3.33 eV was observed that could be attributed to either band gap emission of some remaining ZnO or a possible stacking fault in GaN or even some InGaN layers with less In incorporation along different facets of the GaN nanotube (namely: the side walls or the top ring of the tube). In low temperature photoluminescence (Fig. 5 right), the intensity of the InGaN quantum well peak was shifted to 3.16 eV and was increased by a factor of 2.5 with the same spectral width of 190 meV. The peak at 3.33 eV was increased by a factor of 5 whereas the blue luminescence peak was suppressed. Furthermore, low temperature cathodoluminescence mapping along the rods has been undergone (Fig. 6 and Fig. 7). It was shown that the emission of the lower energy peak that is attributed to the InGaN quantum well mainly emerged from the top of the tubes (Fig. 6), whereas the higher energy peak emission emerged from sides and bottom of the tubes (Fig. 7). Five minutes hydrochloric acid (HCL) treatment was undergone to a twin sample to etch away any remaining ZnO, however the spectrum did not show a significant decrease of the peak at 3.33 eV, thus supporting more the assumption of a stacking fault or a an InGaN phase separation on the different facets of the tubes.

The ZnO pillars of sample C were less dense and more ordered than those of samples

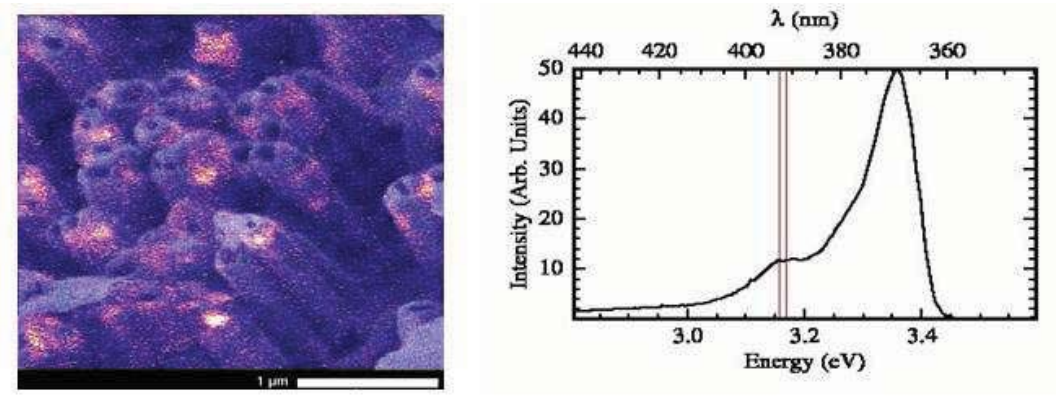

Fig. 6: Low temperature cathodoluminescence mapping along the nano-tubes for sample B under detector window centered at 393 nm.

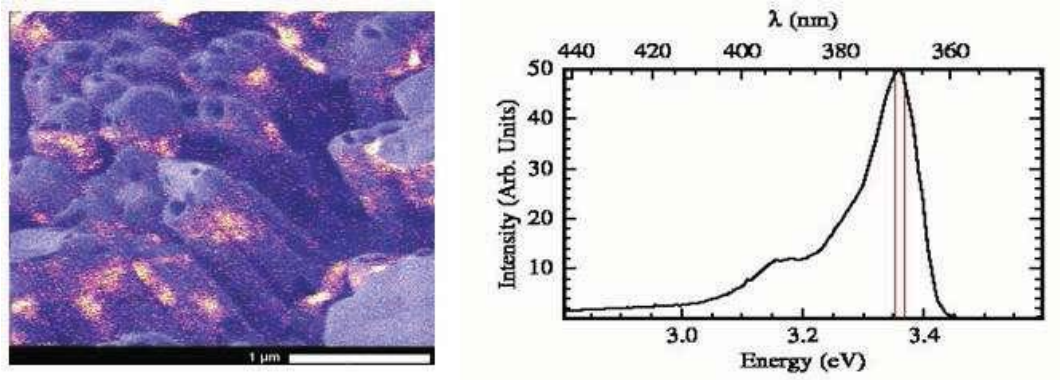

Fig. 7: Low temperature cathodoluminescence mapping along the nano-tubes for sample B under detector window centered at 370 nm.

A and B since the approach of the structured patterning of the gold film mentioned in the experimental section has been utilized. The InGaN quantum well growth conditions were exactly the same as those for sample B. As shown in Fig. 8 (left), the GaN tubes with their coaxial quantum wells took the same arrangement as the original ZnO pillars. However, the diameters of tube openings were considerably reduced (Fig. 8 (right)). In low temperature photoluminescence (Fig. 9), a sharp peak showing the donor bound exciton emission of GaN at 3.46 eV with spectral width of 14 meV was observed. This is in addition to a newly observed peak at 3.41 eV that is assumed to be stacking fault of GaN, blue luminescence and the afore-mentioned unclarified peak around 3.33 eV.

Surprisingly, the InGaN quantum well peak at 3.16 eV, previously discussed for sample B, did not show any sign in the spectrum. Probably, the TMIn and TEGa diffusion on a lower density of pillars is more homogeneously distributed along the rods leading to lower In incorporation on the top ring facets of the tubes, thus reducing the emission of the afore-mentioned InGaN peak. However, still CL and TEM of that sample are needed for confirmation of the afore-mentioned argument. Notably, the wide blue luminescence at low temperature for sample C is considerably high compared to sample B that could indicate a possible manifestation of gradient of In incorporation.

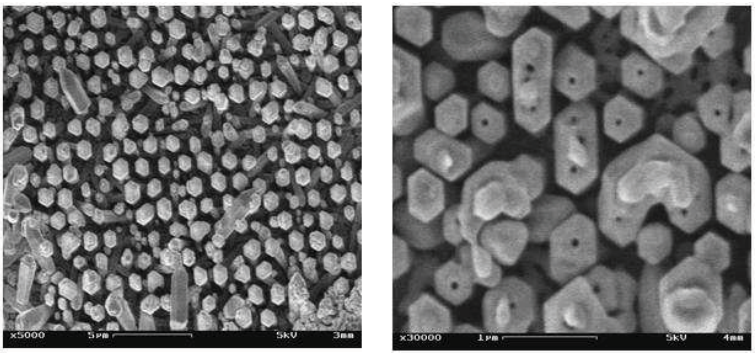

Fig. 8: Sample C: SEM pictures of the coaxial GaN/InGaN/GaN nano-heterostructures showing a relatively ordered pattern (left) and a smaller tube opening diameter compared to sample B (right).

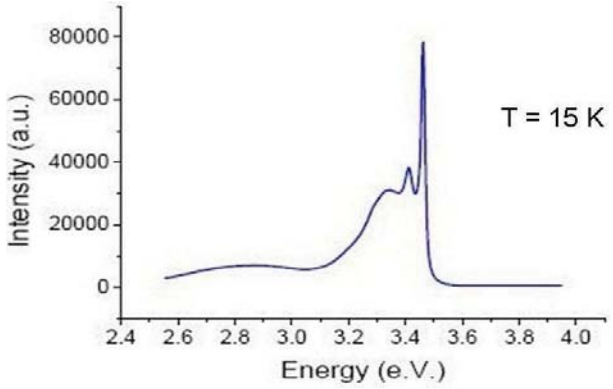

Fig. 9: Low temperature photoluminescence for sample C: coaxial GaN/InGaN/GaN quantum wells overgrown around a less dense and more ordered ZnO pillar template.

4. Conclusion

Based on cathodoluminescence mapping along the coaxial GaN /InGaN/GaN nanoheterostructures, we assume that the In incorporation along the nanotubes is different along the sides and the top ring facets, respectively. Moreover, low temperature photoluminescence for the more ordered and less dense structures revealed the disappearance of an InGaN peak at 3.16 eV and the appearance of a more intense and wide blue luminescence peak. This could indicate that for the more ordered structures, a gradient of In incorporation along different facets exists which would be attributed to higher diffusivity of TMIn and TEGa.

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