



Nanoindentation Induced Elastic-plastic Deformation of GaN Nanomembrane on a Sapphire Substrate

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To cite this article:

Maha Khayyat, Eric Bourhis, Rami Elafandy, Tienkhee Ng, Boon Ooi. Nanoindentation Induced Elastic-plastic Deformation of GaN Nanomembrane on a Sapphire Substrate. *American Journal of Nanosciences*. Vol. 7, No. 1, 2021, pp. 15-22. doi: 10.11648/j.ajn.20210701.13

Received: January 4, 2021; **Accepted:** January 19, 2021; **Published:** January 28, 2021

Abstract: One of the main challenges of the production of a blue laser is the preparation of defect-free GaN layers. It is of high technological interest to characterize GaN nanomembrane mechanically for further advanced applications. The current study addresses the impact of applied stresses on GaN nanomembranes, which are placed on sapphire the substrates, using nanoindentation as a nondestructive test. The mechanical response of the 20, and 100 nm thin GaN nanomembrane were studied at different normal applied loads ranging from 1 mN down to 0.1 mN using the Berkovich nanoindentation technique. There were plastic deformation regions at the nanoindented GaN nanomembranes monitored by the load-displacement (*p-h*) curves. The depth of the deformed regions increased with increasing the applied loads on the diamond indenter. Beside the *in-situ* depth estimation of the residual nanoindentation using the instrumented nanoindentation machine, Atomic Force Microscopy (AFM) has been deployed as an *ex-situ* measurements of indentations depth. Scanning Electron Microscopy (SEM) provided us with surface images of the indented membranes. Indentation of the 100 nm thick GaN nanomembrane, where the effect of the substrate is reduced, showed discontinuity in the *p-h* curves. These discontinuity or pop-in events were attributed to a possible sudden initiation and propagation of threading dislocations in the GaN nanomembrane which was free of threading dislocation upon fabrication. It was suggested to employ μ -Raman spectroscopy methods to investigate the possible structural phase transformation of thicker GaN nanomembranes and to measure the compressive or tensile stresses within the center of the indented zones. Where the observed sudden load-displacements discontinuity or depth excursions during indentation of GaN nanomembranes can be attributed.

Keywords: Nanoindentation, GaN, Nanomembrane, Sapphire, AFM

1. Introduction

GaN is one of the most important optoelectronic semiconductors for its applications as white light source, blue diode leading to UV lithography.³ High dislocation density and related issues in GaN are one among few of the major hindrances for the application as blue laser.⁴ Thus, removal of stress is one of the prime objectives for opto-electronic device applications in GaN [1-3]. GaN is a wide band-gap III-V compound semiconductor. It usually has a wurtzitic structure

(α -GaN) with a direct band gap 3.4 eV at room temperature, which offers the potential for fabricating a variety of near ultraviolet (UV) optoelectronic devices, such as blue light emitting diodes [2, 3]. The successful fabrication of devices based on epitaxial GaN thin films requires better understanding of their mechanical characteristics, since the contact loading during processing or packaging can significantly degrade the performance of these devices [4]. Moreover, such devices will experience large thermal strains in addition to the growth strains leading to cracking thus posing problems for the development of GaN based devices. Therefore, there is a growing demand of

investigating the mechanical characteristics of materials, in particular in the nanoscale regime, for device applications [5,6]. More particularly, however, contact loading is a type of mechanical impact that semiconductor materials often inevitably experience during processing. This kind of loading may cause structural phase transformations and consequently change the band gap of the material [4]. Hence, the study of mechanical behaviour of GaN nanomembranes is the key research topic for their successful device application.

The indentation test represents a simple and quite unique approach for studying of metastable high-pressure phases of semiconductors, in addition to the mechanical properties of solid materials [4]. A combination of biaxial and hydrostatic stresses, as in the case of indentation, originating from dislocation related extended defects and point defects, respectively, are reported generally in epi-GaN [5]. Where Diamond Anvil Cells (DAC), shown only the effect of hydrostatic pressures. However, hydrostatic stress alone is estimated inside the indented region of epi-GaN without implication of any structural changes.

Lim *et. al* [7] explained indentation-induced plastic deformation under a pointed indenter for an isotropic solid. A theoretical study was carried out by another research group at University of Cambridge, Needs *et al*, 2003 on high pressures phases of group-IV, III-V and II-VI compounds, including GaN [8]. The plastic deformation of the III-V semiconductors under concentrated load was reviewed by Le Bourhis and Patriarche [9]. Indentation experiments involves pressing a geometrically well-defined piece of a very hard material, such as diamond, into another solid under a known load, creating very high stresses, both hydrostatic and shear, in the material indented [4]. For the purpose of studying the mechanical properties of materials and other related properties of thin

films nanoindentation technique should be employed. Instrumental nanoindentation allows monitoring the penetration of a diamond tip as a function of the applied load. Moreover, it offers us a method to monitor the threshold of plastic deformation by applying ultra-low loads, so we can avoid fracture as explained by Le Bourhis and Patriarche [10]. Using the instrumented nanoindenter one can deduce information about the elastic-plastic response of the thin film as well as their adhesion to the substrate [9, 10]. If a material underneath the indenter transforms into a new phase when certain stress conditions are met, changes in the slope of the loading/unloading curve or discontinuities in the loading/unloading curves are expected [11]. Previous work of mechanical properties of GaN thin films were carried out on relatively thick films, Jian [12] nanoindented 2 μm thick films grown on sapphire by MOCVD method, using TEM and CL techniques. Also, Lin *et al* [13] examined a 2 μm thick GaN thin film using nanoindentation and AFM techniques. Navamathavan *et. al* [14] carried out nanoindentation on 1-4 μm thick GaN thin films on sapphire. Geetha *et al* [15] carried nanoindentation experiments on 2 μm films of GaN and examined the residual microindentation using AFM. Bradby *et al* [16] studied the mechanical deformation of wurtzite GaN epilayers grown on sapphire substrates using spherical nanoindentation and cathodoluminescence (CL). In 2007 Khayyat *et. al* [17] studied the effect of temperature on structural phase transformation of Si, and recently in 2020 detailed simulation [18] and experimental [19] studies were carried out on the impact of temperature and growth parameters on GaN crystals during indentation which showed that strain increased with increasing temperature and growth conditions of the crystalline GaN films.

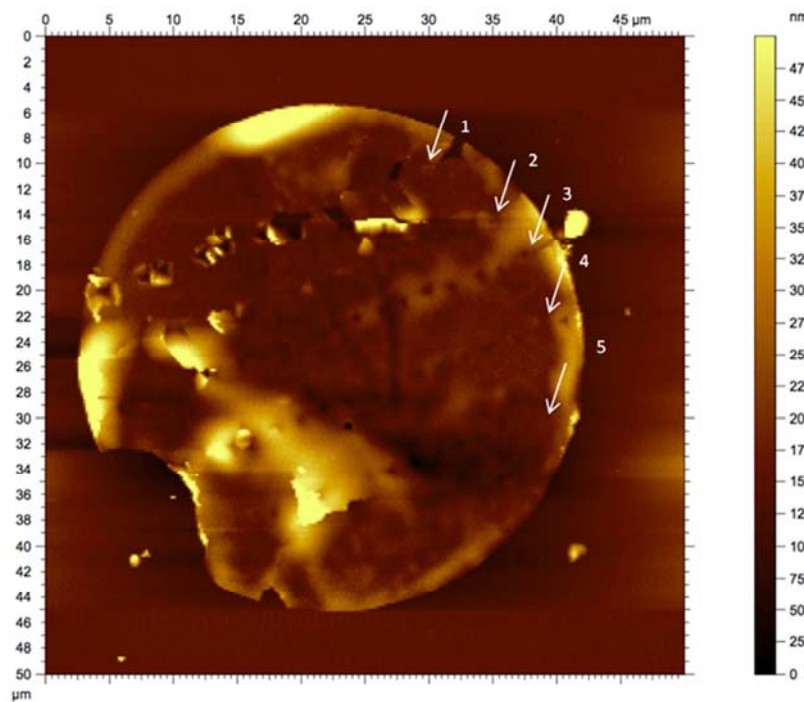


Figure 1. AFM image shows the 20 nm thick GaN nanomembrane on a sapphire substrate at various Berkovich indenter loads: first row marked with the arrow 1 shows indentation at 20 mN, arrow 2 at 1 mN, arrow 3 at 0.5 mN, arrow 4 at 0.2 mN, arrow 5 at 0.1 mN.

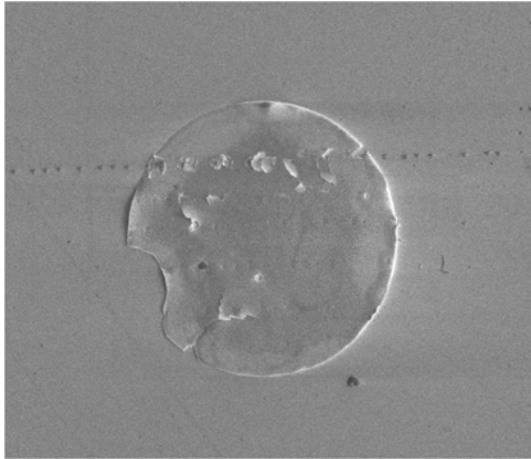


Figure 2. SEM micrograph of 20 nm thick GaN nanomembrane after undertaken nanoindentation, as shown in Figure 1 using AFM.

2. Experimental

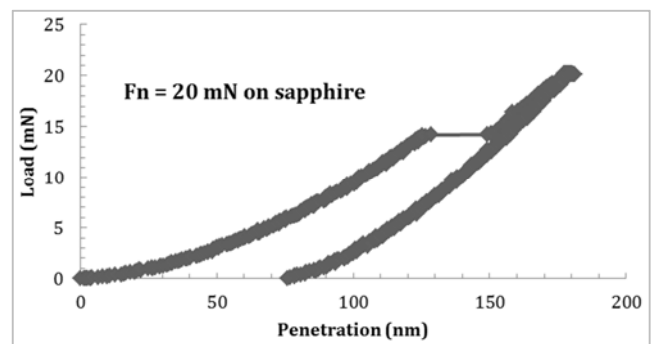
The process of fabrication the GaN nanomembranes was explained by Rami Elafandy *et. al* [20]. GaN nanomembranes of 20 nm and 100 nm thick and 50 μm diameter were prepared by chemical exfoliation of completely threading dislocation free single crystalline GaN nanomembranes, using UV-assisted electroless chemical etching. The GaN wafers were grown using hydride vapor phase epitaxy (HVPE) technique. The details of growth procedures in preparing these GaN can be found elsewhere [20-22]. Then exfoliated GaN nanomembranes were transferred mechanically by lifting them with a 40 nm thick tungsten probe then place them on a sapphire substrate [20].

Nanoindentations were carried out using the Nano-Hardness Tester CSEM Instrument, fitted with Berkovich diamond indenter (serial number; BC-33-SCB2) [24]. The 20 nm thick GaN nanomembrane was indented with a Berkovich indenter with peak loads of 20, 1, 0.5, 0.2, 0.1 mN (see Figures 1 & 2) at room temperature with a dwell time of 30 s, similarly the pausing and unloading time, where the rate varies according to the maximum normal applied loads. Instrumented nanoindentation allows for monitoring the penetration of a tip into a specimen as a function of load. The Young's modulus and hardness of these samples were determined from the load-depth curves using the method of Oliver and Pharr [25]. Similarly, The 100 nm thick GaN nanomembrane was indented at 0.5 mN and 0.2 mN. The samples to be examined were mounted on a glass cylinder. The mounted sample was placed on a flat base of the x-y-z translation stage of the machine to undertake nanoindentation at various normal indenter loads.

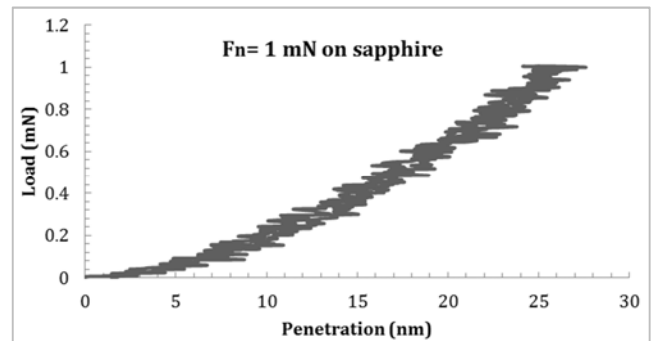
3. Results and Discussion

First, nanoindentation experiments were carried out on sapphire substrate to examine the elastic zone so we can examine the elastic-plastic response of GaN NM without an interference of the substrate. A representative loading-unloading curve of sapphire is shown in Figure 3 (a), where

the maximum normal applied load was 20 mN, applied at the 20 nm thick GaN nanomembrane. The average load is 13 ± 1.16 mN where pop-in occurs. The average hardness is 42.10 GPa, the hardness values have been measured using the projected contact areas obtained from Oliver & Pharr method [25]. This value of hardness is in general agreement with the previous reported measurements, Mao *et al.* [26] showed that the hardness of C plane of sapphire is 46.7 ± 15 GPa. On the other hand, there is a discrepancy in the published value of sapphire hardness, as Lim *et al.* [7] reported the value of the sapphire hardness to be 26 GPa. A curve obtained from indenting the surface of the sapphire substrate with 20 mN normal load. It shows an elastic loading up to 13 ± 1.16 mN where a discontinuity or a pop-in is observed on loading, and the unloading remains elastic.



(a)



(b)

Figure 3. (a) a representative curve of indenter load (y) in mN vs. penetration depth (x) in nm of a Berkovich indenter into sapphire substrate showing the pop-in or excursion event for an indenter load of 13 ± 1.16 mN. (b) Loading and unloading curves of a Berkovich indenter in the sapphire at room temperature under 1 mN.

At this relatively high load of 20 mN, the GaN nanomembrane shattered into flakes upon nanoindentation, and the indenter tip penetrates to the substrate. Based on that, we excluded the measurements of 20 mN nanoindentation of the 20 nm thick GaN nanomembrane. Nanoindenting the 20 nm thick GaN nanomembrane at 1 mN shows that there is not any plastic deformation, as it confirmed by the loading-unloading curve (see Figure 3 (b)). The slope of the loading curve of sapphire, at $F_n=1$ mN, almost coincides with the slope of the unloading curve.

Figures 5 and 6 show AFM images and profiles of 1 mN and 0.1 mN nanoindentations of 20 nm thick GaN nanomembrane. The image of 1 mN nanoindentation shows perfect impressions without any trace of radial crack is observed, similarly, the 0.1 mN nanoindentation shows no cracks, as one would expect at this ultra-low indenter loads. The AFM profiles of 1 mN and 0.1 mN (see Figures 5&6) show material pile-up near the indented zones, revealing the elastic-plastic behaviour of the 20 nm thick GaN nanomembrane [15].

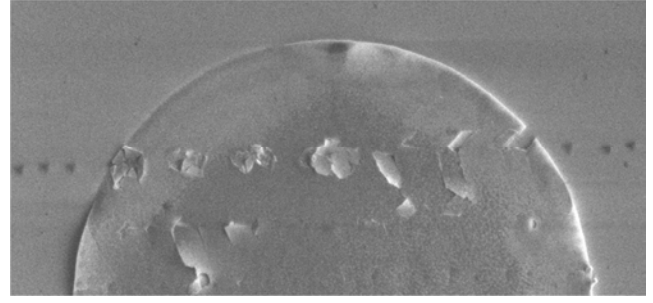
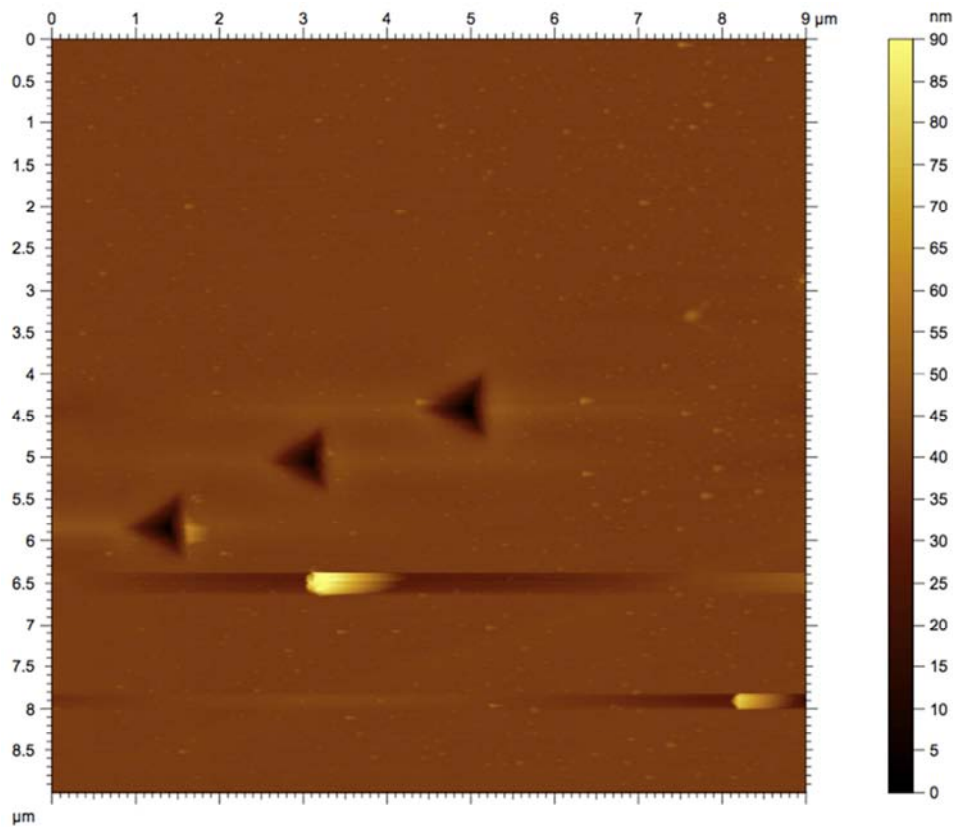
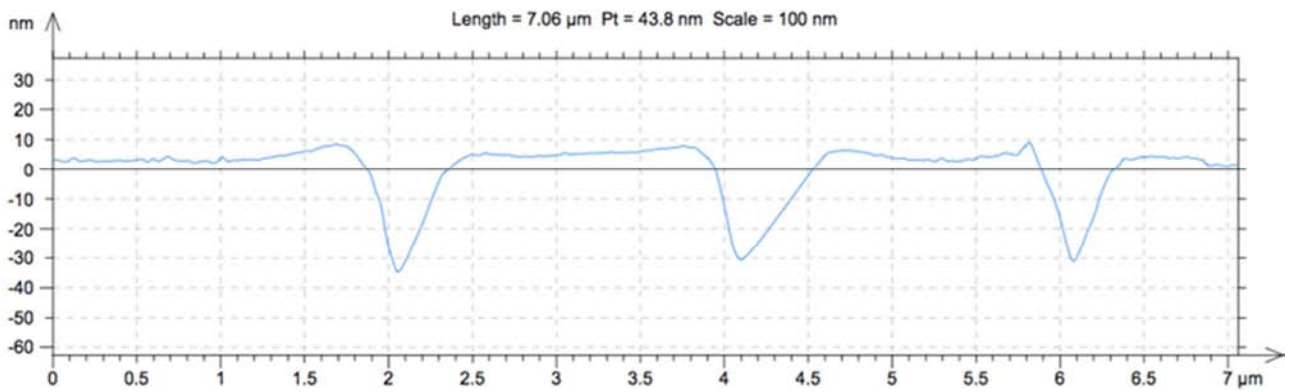


Figure 4. The 20 nm thick GaN nanomembrane after indenting at 10 mN indenter load, see the flakes of the GaN nanomembrane at the nanoindented zones.



(a)



(b)

Figure 5. (a) 1 mN nanoindentations on 20 nm thick GaN nanomembrane. It shows perfect impressions without any traces of radial cracks are observed. (b) nanoindentations profile.

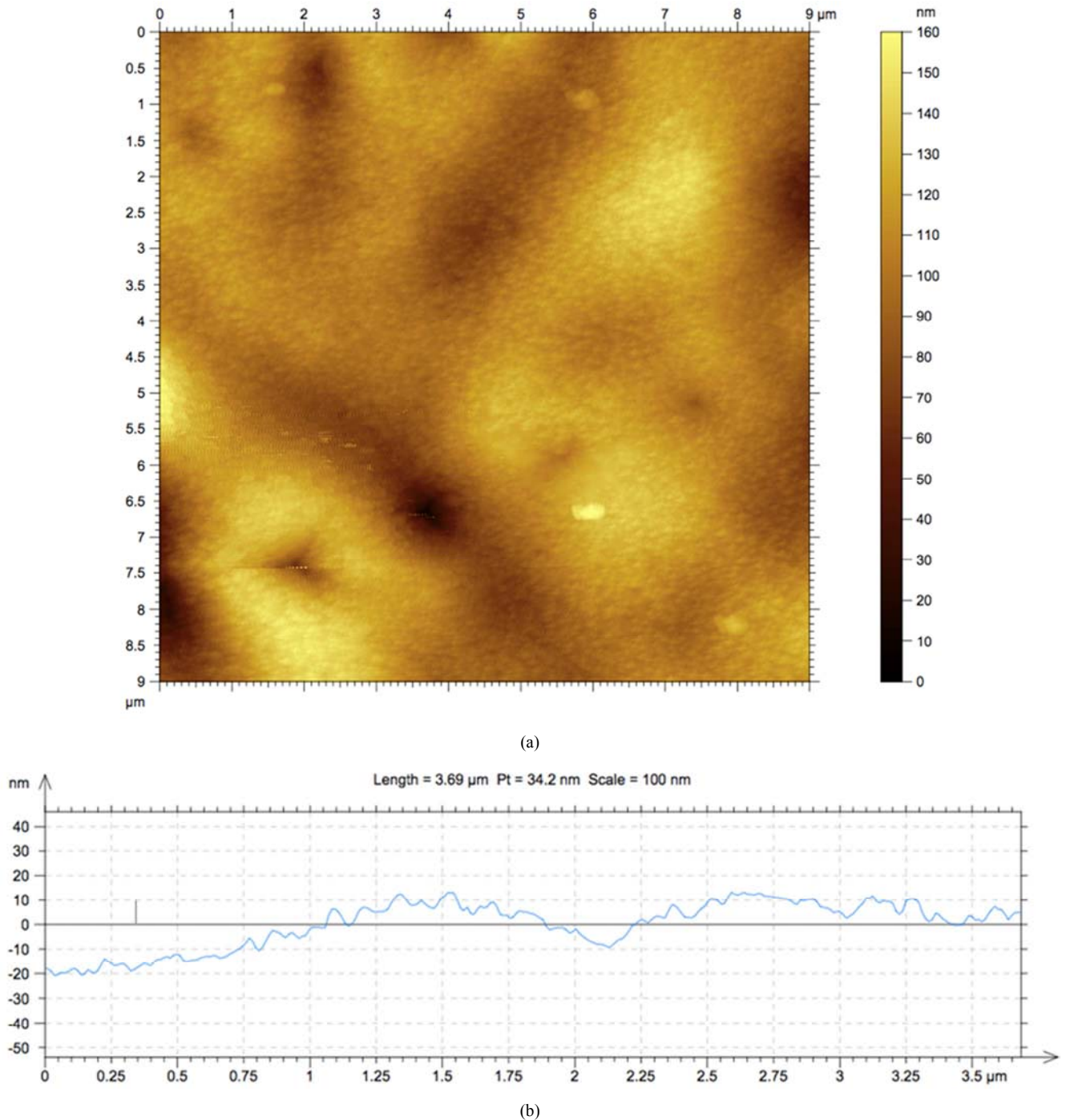


Figure 6. (a) AFM image of 0.1 mN indenter load nanoindentation of 100 nm thick GaN nanomembrane. (b) nanoindentation profile.

Figure 7 (a:c) shows the load-penetration curves of nanoindentation on 20 nm thick GaN nanomembrane at ultra- low loads. As it is shown in the load-penetration curves, as the indenter load increases, 0.1 mN, 0.2, mN, 0.5 mN, 0.1 mN, the penetration depth increases. It is important to note that all these values remain below the membrane thickness indicating that the interface between the membrane and the substrate is not reached by the indenter tip extremity.

Nanoindenting the 100 nm thick GaN nanomembrane show elastic-plastic deformation as shown in Figure 8.

Typical nanoindentation p-h curves of GaN nanomembrane subjected to the maximum indentation loads of 0.5 mN and 0.2 mN. The curves exhibit irregularities during loading characterized by pop-in. The frequency of such events was estimated to be about 60%. Such discontinuities correspond to a sudden deformation of the sample and generally attributed to the onset of plasticity.

The curves (Figure 8 a & b) exhibit a single discontinuity at an indentation depth of 27 nm corresponding to the applied load of 0.5 mN, and 30 nm at 0.2 mN. No other pop-in event was observed when indentation load was further increased.

Lin *et al.* [13] observed pop-in events took place at 16 nm at applied load 0.16 mN, and attributed the discontinuity or pop-in to dislocation associated phenomenon. Navamathavan [6] observed a single pop-in event at 0.4 mN indenter load, penetration depth 20 nm of GaN thin films (1-4 μm thick). They attributed the pop-in to the lattice mismatch of the GaN epitaxial film with respect to the substrate or/and sudden propagation of threading dislocation [4]. It was observed by Bradby [16] there are discontinuity observed during loading when the maximum load is above

the elastic-plastic threshold. This behavior was correlated by Bradby *et al.* with multiple slip bands revealed by XTEM [16]. The physical mechanism responsible for the 'pop-in' event may be due to the interaction behavior of the indenter tip with the pre-existing threading dislocation present in the films during mechanical deformation [27]. It was observed that the 'pop-in' depth is correlated with the lattice mismatch of the epitaxial thin film with the substrate, the higher the lattice mismatch the shallower the critical 'pop-in' depth [27, 28].

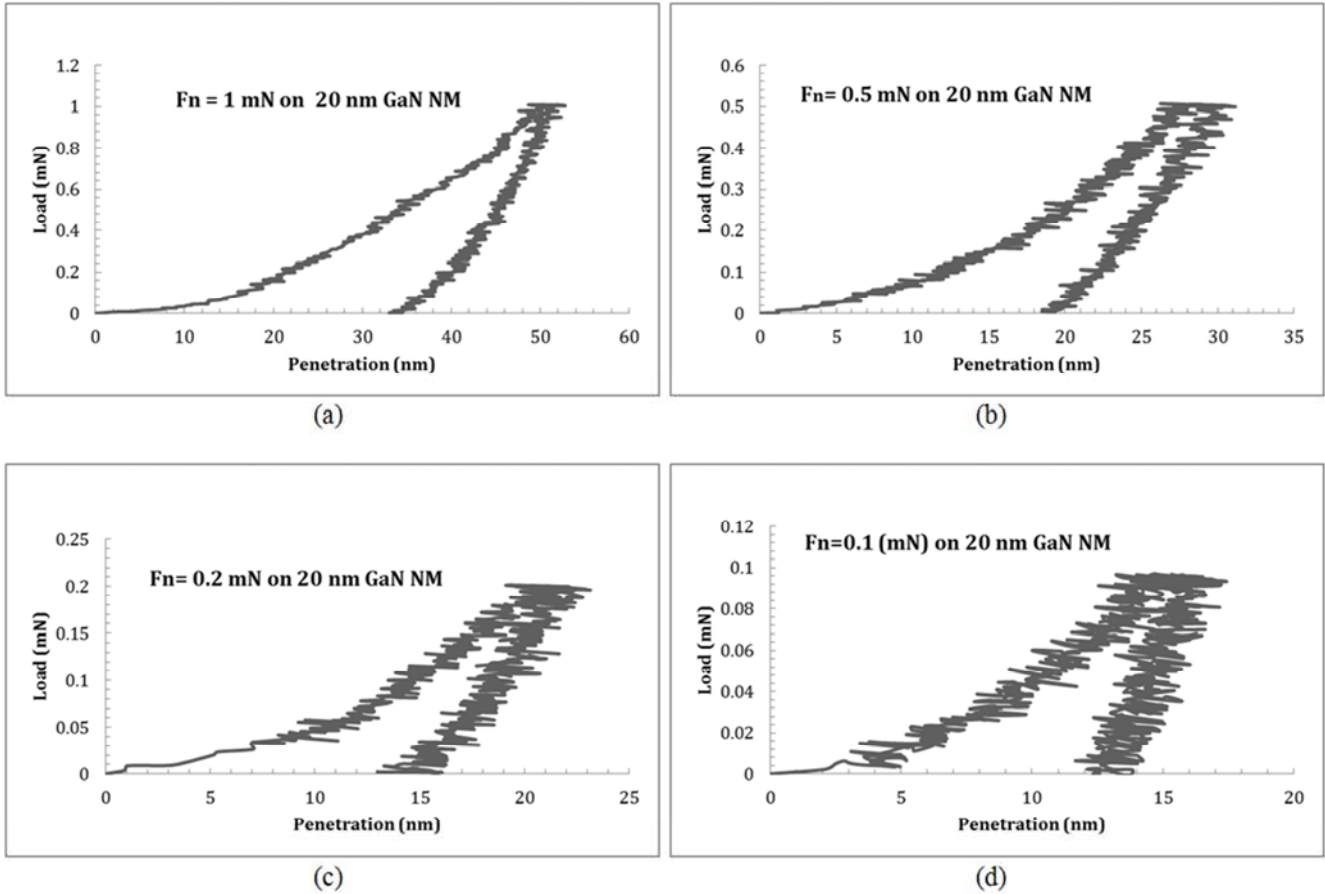


Figure 7. (a) Loading and unloading curves of a Berkovich indenter on 20 nm thick GaN nanomembrane at 1 mN. (b) at 0.5 mN normal indenter load. (c) at 0.2 mN. (d) at 0.1 mN.

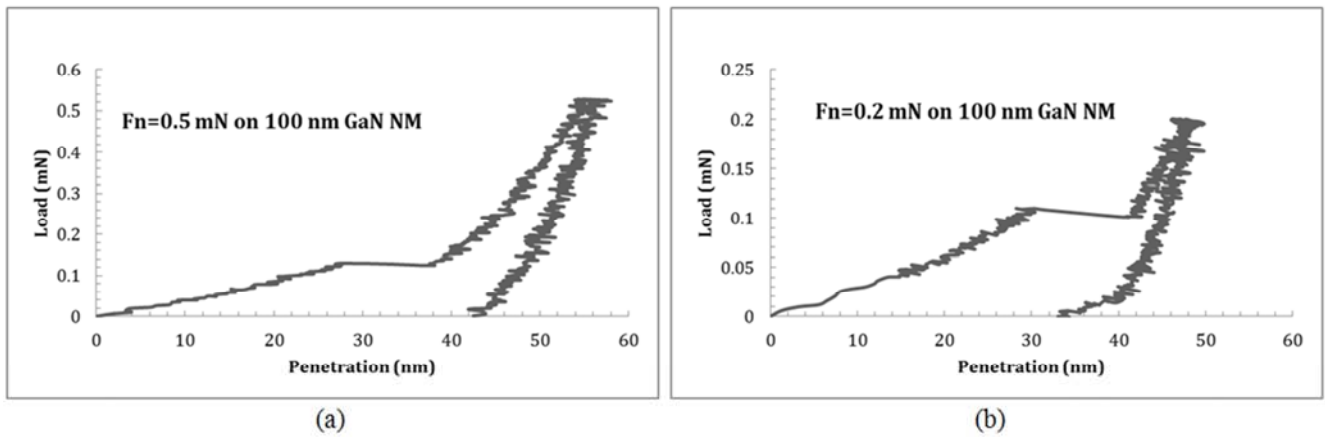


Figure 8. (a) load vs. penetration curve of a Berkovich indenter into 100 nm GaN nanomembrane for a load of 0.5 mN. (b) at 0.2 mN.

Table 1. Shows the Vickers hardness value of the 20 nm and 100 nm thick GaN nanomembrane at various applied loads. The fluctuations in the value of the hardness of GaN crystals can be explained by the growth conditions induce a change in the nitrogen vacancy concentration and consequently the hardness value [18, 28].

Indenter load (mN)	Hv (GPa) 20 nm thick GaN NM.	Hv (GPa) 100 nm thick Ga NM.
1	5.46	N/A
0.5	8.87	5.07
0.2	6.12	2.54
0.1	3.98	N/A

* not available

The pop-in event was attributed to the lattice mismatch of the epitaxial films with respect to the substrate [23, 27]. Other possible mechanism that would explain the observed behaviour is the formation and propagation of dislocations in GaN thin films [28]. GaN grown on sapphire substrates suffer from high density of threading dislocation [29, 30]. However, the GaN nanomembranes examined in the current study are threading dislocation (TD) free as it confirmed by TEM measurements [20]. Based on that, the pop-in events cannot be attributed to the extension of the TD pre-existed in the film. It might be a sign of an initiation of TD within the nanomembranes. On the other hand, this observation of the discontinuity event was observed in Si, and it has been linked to phase transformations [11]. However, to investigate the possible structural phase transition within the center of the indented zones, one should undertake a relatively high load at thicker membranes to apply the laser beam of a controlled diameter and measure the Raman scattering spectra [31].

Nanoindentation was employed to study the mechanical properties of thin films [32], such as the GaN nanomembranes under consideration.

4. Conclusion

The elastic-plastic behaviour of materials associated with various microstructures, micro/nano-mechanic techniques such as nanoindentation have been well established and widely used. Based on this, the mechanical deformation behaviour of GaN nanomembranes placed on sapphire substrate was studied using nanoindentation. At high loads there are cracking and fragmentation was observed at GaN nanomembranes. Nanoindentations at ultra-low loads, ranging from 1 mN to 0.1 mN show perfect impressions without any traces of radial cracks. Load-displacement curves of both the 20 nm and 100 nm thick GaN nanomembranes show elastic-plastic deformation as it was exhibited by the change of the slope of the loading-unloading curves. Moreover, the 100 nm thick GaN nanomembrane show a single pop-in event at the loading curve on 0.5 and 0.2 mN applied loads. The excursion or the pop-in was attributed to the possible initiation of threading dislocation (TD) in the nanomembrane which was TD free upon fabrication. The Vickers hardness value of the 20 nm thick GaN nanomembrane is higher than that of the 100 nm thick nanomembrane. Clearly, the 20 nm thick GaN hardness measurements was affected by the hard substrate. To investigate the possible phase transition in the GaN nanomembrane, nanoindentation should be undertaken

at slightly thicker membrane to be monitored by the micro Raman spectroscopy.

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