Research Article

Journal of RAMAN SPECTROSCOPY

Received: 9 October 2008 Accepted: 28 March 2009 Published online in Wiley Interscience: 12 june 2009

(www.interscience.wiley.com) DOI 10.1002/jrs.2336

The mechanism of the recrystallization process in epitaxial GaN under dynamic stress field: atomistic origin of planar defect formation

C. R. Das,[a] S. Dhara,[a,b]* H. C. Hsu,[c] L. C. Chen,[c] Y. R. Jeng,[d] A. K. Bhaduri,[a] Baldev Raj,[a] K. H. Chen[c,e] and S. K. Albert[a]

The mechanism of the recrystallization in epitaxial (0001) GaN film, introduced by the indentation technique, is probed by lattice dynamic studies using Raman spectroscopy. The recrystallized region is identified by micro-Raman area mapping. 'Pop-in' bursts in loading lines indicate nucleation of dislocations and climb of dislocations. These processes set in plastic motion of lattice atoms under stress field at the center of indentation for the initiation of the recrystallization process. A planar defect migration mechanism is evolved. A pivotal role of vacancy migration is noted, for the first time, as the rate-limiting factor for the dislocation dynamics initiating the recrystallization process in GaN. **Copyright © 2009 John Wiley & Sons, Ltd.**

Supporting information may be found in the online version of this article.

Keywords: GaN; recrystallization; indentation; dislocation; Raman spectroscopy

Introduction

GaN is one of the most important optoelectronic semiconductors in its applications as a white light source and blue diode, leading to UV lithography. The blue diode laser has an enormous potential as the read and write head for high density digital versatile disk (DVD) memories and printing (typically calculated for 1200 dpi having ~17 μm spot size with 1 mm depth of field using 6 mm optics). Its most imminent application is in white-light-based (using diode-laser-based RGB) compact display devices. However, high dislocation density in GaN is one of the major hindrances in its application as blue laser. Several techniques have been adopted for the diminution of dislocation densities in GaN,[1] including our recent report on recrystallization under indentation.[2] A layer-by-layer defect formation in GaN is studied using structural studies,[3] without a detailed atomistic model of its origin and dynamics. It necessitates a detailed study of the lattice dynamics in the stress-free region, as well as in the strained volume for comparison. Investigation of phonon modes in Raman scattering process is well established, and is one of the potential methodologies to understand lattice dynamics at the atomic level.

We report here the mechanism of recrystallization in wurtzite (WZ) epi-GaN film under indentation. Lattice dynamical studies by probing phonon modes reveal the possible mechanism of defect migration, which actually influences the recrystallization process. Defect nucleation and its dynamics in GaN are also studied for an atomistic view of the process where the role of both point (vacancy) and extended (dislocation) defects is noted for the first time.

Experimental

An undoped epi-layer of 6 μm thickness (0001) GaN/Al_2O_3 grown by MOCVD with threading dislocation (TD) $<5 \times 10^8$ cm^{-2} (TDI, USA) along with an intrinsic carrier concentration of $\sim 3 \times 10^{17}$ cm^{-3} is used for the present study. The sample is indented using a microindenter with a Berkovich diamond tip. The data presented in this report exploits indentation conditions of load 100–400 mN; same loading–unloading rate of 1–50 mN s^{-1}, and holding time 5 s. Excitation wavelength of 632.8 nm of He–Ne laser is used for the micro-Raman spectroscopic studies (probed volume <1 μm^3) in the back-scattering geometry. A liquid-nitrogen-cooled CCD detector is used for recoding the scattering intensity.

Results and Discussion

Lattice dynamics of GaN under indentation

The structural transformation is studied close to the indented region using micro-Raman spectroscopy (Fig. 1(a)). The E_2 (high) mode at 570 cm^{-1}, measured outside the indented region,

* Correspondence to: S. Dhara, Metallurgy and Materials Group, Indira Gandhi Center for Atomic Research, Kalpakkam-603102, India; Department of Electrical Engineering, Institute for Innovations and Advanced Studies, National Chen Kung University, Tainan-701, Taiwan. E-mail: s_dhara2001@yahoo.com

a Metallurgy and Materials Group, Indira Gandhi Center for Atomic Research, Kalpakkam-603102, India

b Department of Electrical Engineering, Institute for Innovations and Advanced Studies, National Chen Kung University, Tainan-701, Taiwan

c Center for Condensed Matter Sciences, National Taiwan University, Taipei-106, Taiwan

d Department of Mechanical Engineering, National Chung Cheng University, Chia-Yi 621, Taiwan

e Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei-106, Taiwan

 Copyright © 2009 John Wiley & Sons, Ltd.

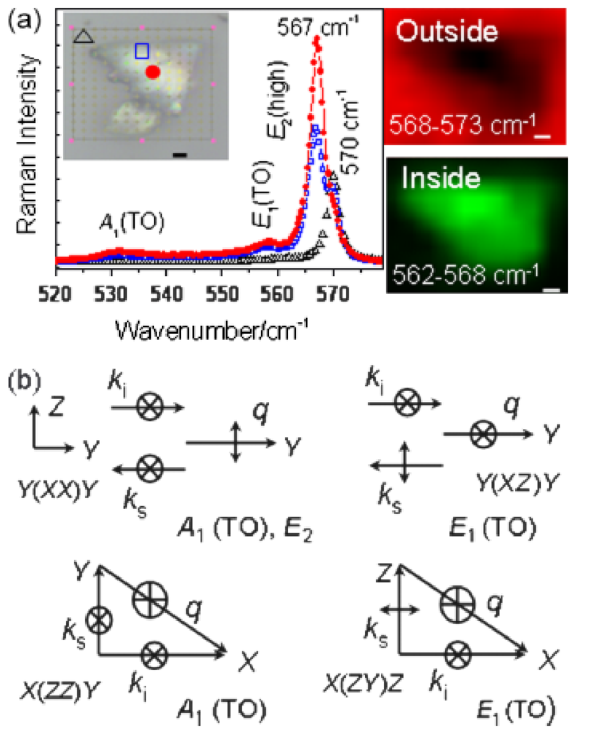

Figure 1. (a) Micro-Raman spectra for epi-GaN outside and different regions inside the indentation spot. Inset shows corresponding optical image of the indentation spot. Area mappings of the outside and inside of the indentation spot, using different spectral regions indicated in the picture, are shown at the outset. Scale bar is 1 µm. (b) Different Raman scattering configuration for WZ crystal in the backward (top) and right-angled (botttom) direction corresponding to E_2, and TO modes of E_1 and A_1 symmetries for usual incident and scattering notations. [Drawn after Fig. 6 of Ref. [6]. Reprinted with permission from C. A. Arguello, D. L. Rousseau, S. P. S. Porto, *Phys. Rev*. **1969**, *181*, 1351. Copyright 1969 by the American Physical Society (http://prola.aps.org/abstract/PR/v181/i3/p1351_1)]. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

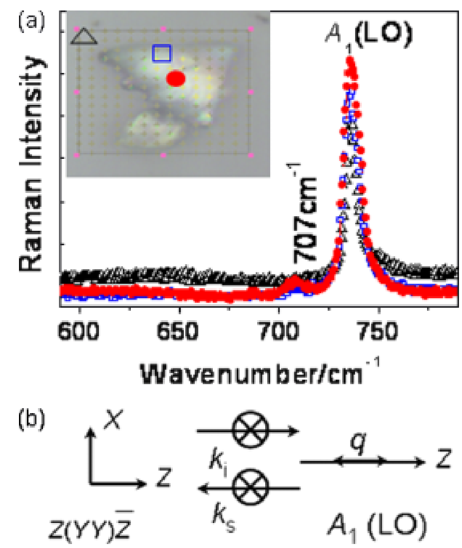

Figure 2. (a) Micro-Raman spectra for epi-GaN outside and different regions inside the indentation spot. Inset shows corresponding optical image of the indentation spot. Scale bar is 1 µm. (b) Raman scattering configuration for WZ crystal in the backward-scattering direction corresponding to LO mode of A_1 symmetry for usual incident and scattering notations. [Drawn after Fig. 6 of Ref. [6]. Reprinted with permission from C. A. Arguello, D. L. Rousseau, S. P. S. Porto, *Phys. Rev*. **1969**, *181*, 1351. Copyright 1969 by the American Physical Society (http://prola.aps.org/abstract/PR/v181/i3/p1351_1)]. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

resembles the reported value of epi-GaN on sapphire substrate. The inset shows the spots measured out along with the insides of the indentation mark recorded in the optical microscope attached to the spectrometer. However, micro-Raman measurements inside the indented region show a redshift of the phonon mode to 567 cm^{-1} gradually from the interface region (edge of the spot) to the center of indented spot. This value is close to the calculated and measured value for the E_2 (high) phonon of bulk GaN and GaN nanostructure under stress-free conditions.[4,5] Double peaks are observed for the interface region close to the edge of the indentation (Fig. 1(a)), showing contributions from both the stressed region outside and the stress-free region inside the indented region. Raman area mapping (outset of Fig. 1(a)) using the spectral part of 568–573 cm^{-1} shows the red (bright in the grayscale) region lying outside the indented region and 562–568 cm^{-1} shows the green (bright in the grayscale) region lying inside the indented region. It clearly shows that the 567 cm^{-1} signal originates from the stress-free region inside the indented mark and the 570 cm^{-1} peak originates from the stressed region of the sample.

Two additional peaks at 531 and 559 cm^{-1} (Fig. 1(a)), corresponding to the A_1(TO) and E_1(TO) modes respectively, are also observed in the indented region. According to the selection rule in the WZ crystal of GaN, the TO phonon modes are forbidden in the backscattering geometry for the (0001) oriented planes.[5] However, small disorientations of the crystallites in the indented region allow the phonon modes corresponding to other crystalline orientations, as shown in the schematics (Fig. 1(b)) for the WZ crystal.[6,7] It can be also mentioned that the phonons (Fig. 1(b)) corresponding to the E_2 (high), and TO modes belonging to A_1 and E_1 symmetries are along the X and/or the Y direction (confined mostly to the XY plane). Therefore, the lattice modes in the XY plane are vibrant. After indentation, the surface of the epi-GaN is no longer flat, and, in the 'V'-grooved geometry, a right-angled scattering is not obscured. Therefore, we have considered both the backward and right-angled scattering processes. From the evolution of the E_2 (high) and TO phonon modes, collected in the backscattering geometry, it seems that stress is released in the planar direction so that the Raman modes along X or Y or both gets modified. Interestingly, the peak position ~736 cm^{-1} corresponding to the A_1(LO) mode, in the different regions close to the indentation spot (Fig. 2(a)), shows no shift in the position. The Raman scattering configuration in the WZ crystal (Fig. 2(b)),[6,7] for a phonon corresponding to the LO mode of A_1 symmetry is always (leaving quasi-LO modes in the right-angled scattering process) along the Z direction (normal to the XY plane). Thus, with no change in the peak position of the A_1 (LO) mode, it is obvious that the lattice modes normal to the XY plane remain unaltered. It is also well known that defects in GaN propagate in the planar direction. A layer-by-layer model of defect accumulation in epi-GaN is envisaged from Rutherford backscattering (RBS)-based channeling experiments supported by cross-sectional transmission electron microscopic imaging.[3] Thus, the overall evolution of the phonon modes may be due to nucleation of dislocation and release of its stress field under indentation stress to set in planar motion at the center of the indentation region by dislocation climb. Dislocation climb in the material is reported under very high hydrostatic stress owing to indentation, even though test temperature is a relatively small fraction of the melting temperature of the material.[8]

Copyright © 2009 John Wiley & Sons, Ltd.

Journal of RAMAN SPECTROSCOPY

A small peak at ∼707 cm^{-1} shows up in the spectra collected from the regions inside the indentation. Changes are observed in the lattice vibrations with the size of the crystal reducing to a few nanometers. It is prominent where the phonon is confined to the surface, giving rise to a wavenumber that falls between the TO and the LO modes.[9] The dielectric constant $\varepsilon(\omega)$ is negative in between the LO and the TO mode. This is the region where the surface optic (SO) phonon appears, and the electromagnetic field associated with the SO phonon is localized at the surface of the material. The surface phonon frequency and intensity mainly depend on the size and the shape of the nanostructured material. The expression for SO phonon in spherical clusters is given by the following:[9]

$$\omega^2{}_{\mathrm{SO}} = \omega^2{}_{\mathrm{TO}} \frac{\varepsilon_0 + 2\varepsilon_m}{\varepsilon_\infty + 2\varepsilon_m} \quad (1)$$

where ϖ_{TO} is the frequency of the TO phonon, ε_0 and ε_∞ are the static and high frequency dielectric constant of the material, and ε_m is the dielectric constant of the medium. Here, we use 10.4 and 5.8 for the values of ε_0 and ε_∞ respectively for GaN.[10] The dielectric constant of the medium (air) is taken as 1. Taking A_1(TO) at 561 cm^{-1} for GaN in Eqn (1), we get the SO phonon wavenumber at 707 cm^{-1}, which matches the observed peak (Fig. 2(a)). Thus, the origin of this new peak can be assigned to the SO mode of GaN.

Nucleation and dynamics of defects under indentation stress field

Further, we explore the role of nucleation as well as the motion of dislocation and rate-limiting factors in the recrystallization process. A detailed description of compliance curve along with 'pop-in' bursts in the loading line is reported in our earlier studies,[2] and also shown in Fig. S1 (Supporting Information) for high and low loads. Recent findings suggest that the origin of an initial 'pop-in' in crystals could be explained in terms of homogeneous[11–13] or heterogeneous[14] dislocation nucleation under the penetrating tip. High values of hydrostatic and shear stress are present within the plastic volume beneath the indentation, and the latter is responsible for the plasticity. After the indenter is pressed into the material, instant plasticity ('pop-in') occurs as soon as the shear stress crosses the theoretical stress (estimated in Appendix A of Supporting Information for the present study). The mechanism responsible for the 'pop-in' bursts appears to be associated with the nucleation and movement of dislocation sources.[14,15]

A hardness value of ∼10 GPa is achieved in our indentation study,[2] and the value is comparable to the bulk value of GaN.[16] It is also observed that the hardness of the GaN film is also sensitive to the loading rate (strain rate), as shown in Fig 3(a). At a lower strain rate, the hardness is found to be ∼10 GPa and increases with the strain rate. Increasing hardness with strain rate can be explained with the increase in the dislocation density owing to its multiplication[17] by the shear stress component following the strain gradient plasticity model.[18] The stress relaxation at the tip of the indentation can be understood from the strain rate exponent[19] $m = \partial \ln H / \partial \ln \dot{\varepsilon})$ and activation volume[13,18] $V_A = 3\sqrt{3} k_B T (\partial \ln \dot{\varepsilon} / \partial H)$ (Boltzmann constant, k_B, and absolute temperature, T) analysis. These two parameters are used to determine the possible deformation mechanism for a given material. It also provides quantitative measures of the sensitivity of hardness, H, to the strain rate, $\dot{\varepsilon}$, and insight into the deformation mechanisms. The values of m and V_A are calculated to be around 0.26 and $0.3b^3$ from the linear plots of ln H *versus* ln $\dot{\varepsilon}$ (Fig. 3(b)) and ln $\dot{\varepsilon}$ *versus* H (Fig. 3(c)) respectively, at the peak load of 100 mN. The

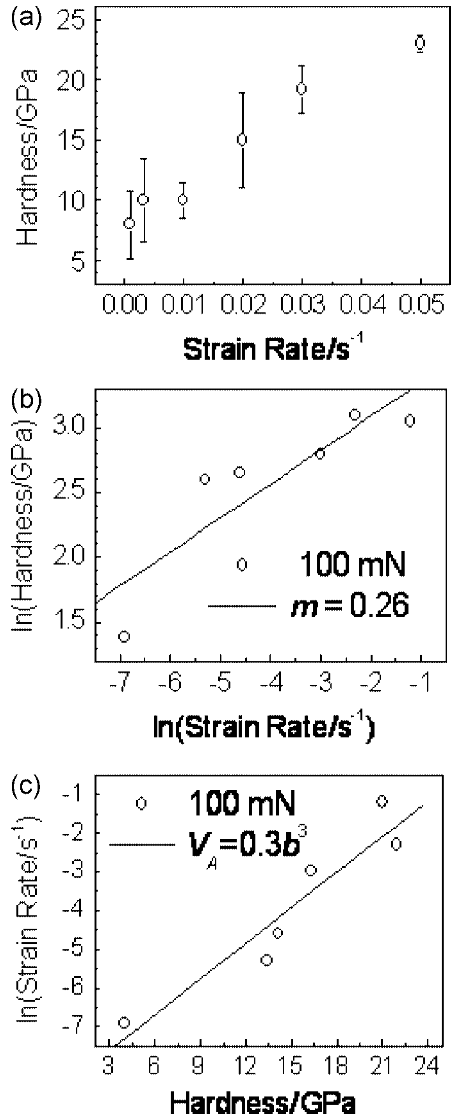

Figure 3. (a) Variation of hardness with indentation strain rate. (b) Typical log–log plot of hardness *versus* strain rate and (c) log (indentation strain rate) *versus* hardness plot for the peak load of 100 mN.

value of V_A is comparable to the average vacancy volume (∼$0.7b^3$) in GaN, considering both Ga and N vacancies are present.[20] It can be mentioned that, with an increase in the peak load of 200 mN, the value of m decreases to 0.06 (Fig. S2(a), Supporting Information) and V_A increases to $1.6b^3$ (Fig. S2(b), Supporting Information). It is generally accepted that a high m is indicative of a smaller V_A.[21] Thus, the magnitude of V_A extracted from our experiment is reflective of the atomic-scale event; therefore, one can assume that the point defect (vacancies)–related process is the rate limiter for the plastic deformation process.

Atomistic simulation studies on perfect single crystals have shown that dislocation nucleate either homogeneously[11–13] or heterogeneously[14] beneath the indenter in the material. $V_A \sim 0.5b^3$ is reported for homogeneous dislocation nucleation in single crystal Pt.[22] Though self-diffusion is slow at ambient temperature, authors argue that a rise in temperature for the material beneath the indenter is due to an adiabatic process,[23] and the high pressure gradient can cause the high diffusivity of vacancy to the high-pressure region to release the compressive stress from

Copyright © 2009 John Wiley & Sons, Ltd.

the material. In a separate study, the same idea is also proposed by Schuh *et al*.[14] The vacancy concentration (considering intrinsic carrier primarily contributed from vacancy-like defects in GaN) can be estimated to be $\sim 10^{17}$ cm^{-3}. The lower activation volume and the high vacancy concentration, from the preexisting defects, such as vacancies, suggest a heterogeneous dislocation nucleation model. The formation of a homogeneous dislocation loop may not be possible because of the large requirement of activation energy in this process.[14,22] A stress-induced crystallization has been also reported in Ge at a temperature as low as 400 K.[24] Observation of in-plane phonon dynamics and low activation volume for vacancy migration suggests that climb of dislocation by vacancy is the rate-limiting factor for stabilizing the recrystallization process.

Conclusion

Here, we address an important issue of the recrystallization process in GaN under indentation stress. Heterogeneous nucleation of dislocation, originated by shear stress within the plastic zone, is evidenced in the indentation process. The release of stress takes place by climb of dislocation due to high hydrostatic stress present in the plastic volume. Vacancy migration is found to equilibrate the recrystallization process by limiting the dislocation motion. The mechanism of the crystallization process is clearly evaluated with lattice dynamics studies. The present study implies important clues for reducing residual stress in a GaN epi-film, and the findings will have broad technological repercussions.

Acknowledgements

One of the authors (CRD) would like to thank C. Phaniraj of IGCAR, India, for his valuable discussion.

Supporting information

Supporting information may be found in the online version of this article.

References

[1] (a) J. Gierak, E. Bourhis, R. Jede, L. Bruchhaus, B. Beaumont, P. Gibart, *Microelectron. Eng.* **2004**, *73–74*, 610; (b) Y. Chen, R. Schneider, S. Y. Wang, R. S. Kern, C. H. Chen, C. P. Kuo, *Appl. Phys. Lett.* **1999**, *75*, 2062.
[2] S. Dhara, C. R. Das, H. C. Hsu, B. Raj, A. K. Bhaduri, L. Chen, C. K. H. Chen, S. K. Albert, A. Ray, *Appl. Phys. Lett.* **2008**, *92*, 143114.
[3] (a) S. O. Kucheyev, J. S. Williams, S. J. Pearton, *Mater. Sci. Eng. R-Rep.* **2001**, *33*, 51; (b) V. Narayanant, K. Lorenz, W. Kima, S. Mahajan, *Philos. Mag. A* **2002**, *82*, 885.
[4] V. Y. Davydov, Y. E. Kitaev, I. N. Goncharuk, A. N. Smirnov, J. Graul, O. Semchinova, D. Uffmann, M. B. Smirnov, A. P. Mirgorodsky, R. A. Evarestov, *Phys. Rev. B.* **1998**, *58*, 12899.
[5] T. Azuhata, T. Sota, K. Suzuki, S. Nakamura, *J. Phys.:Condens. Matter.* **1995**, *7*, L129.
[6] C. A. Arguello, D. L. Rousseau, S. P. S. Porto, *Phys. Rev.* **1969**, *181*, 1351.
[7] H. Harima, *J. Phys.: Condens. Matter.* **2002**, *14*, R967.
[8] O. Sahin, O. Uzun, U. Kolemen, N. Ucar, *Physica B.* **2007**, *399*, 87.
[9] R. Ruppin, R. Englman, *Rep. Prog. Phys.* **1970**, *33*, 149.
[10.] O. Madelung, *Semiconductors: Data Handbook* (3rd edn), Springer: Berlin, **2004**, Section 2.9.
[11] J. Li, K. J. Van Vliet, T. Zhu, S. Yip, S. Suresh, *Nature (London).* **2002**, *418*, 307.
[12] I. Szlufarska, A. Nakano, P. Vashista, *Science.* **2005**, *309*, 911.
[13] A. Guldstone, K. J. Van Vliet, S. Suresh, *Nature (London).* **2001**, *411*, 656.
[14] (a) C. A. Schuh, J. K. Mason, A. C. Lund, *Nat. Mater.* **2005**, *4*, 617; (b) J. K. Mason, A. C. Lund, C. A. Schuh, *Phys. Rev. B.* **2006**, *73*, 054102.
[15] C. L. Kelchner, S. J. Plimpton, J. C. Hamilton, *Phys. Rev. B.* **1999**, *58*, 11085.
[16] M. D. Drory, J. W. Ager III, T. Suski, I. Grzegory, S. Porowski, *Appl. Phys. Lett.* **1996**, *69*, 4044.
[17] H. Siethoff, *Mater. Sci. Eng., A.* **2004**, *386*, 68.
[18] W. D. Nix, H. Gao, *J. Mech. Phys. Solid.* **1998**, *46*, 411.
[19] A. A. Elmustafa, D. S. Stone *J. Mech. Phys. Solids* **2003**, *51*, 357.
[20] C. D. Gu, J. S. Lian, Q. Jiang, W. T. Zheng, *J. Phys. D: Appl. Phys.* **2007**, *40*, 744.
[21] J. Neugebauer, C. G. Van de Walle, *Phys. Rev. B.* **1999**, *50*, 8067.
[22] M. A. Tschopp, M. D. McDowell, *J. Mech. Phys. Solids* **2008**, *56*, 1806.
[23] C. H. Tsai, S. R. Jian, J. Y. Juang, *Appl. Surf. Sci.* **2008**, *254*, 1997.
[24] D. Shahrjerdi, B. Hekmatsoar, L. Rezaee, S. S. Mohajerzadeh, *Thin Solid Films.* **2003**, *427*, 330.

Copyright © 2009 John Wiley & Sons, Ltd.