AIP | Journal of Applied Physics

Stabilization of amorphous GaN by oxygen

F. Budde, B. J. Ruck, A. Koo, S. Granville, H. J. Trodahl et al.

Citation: J. Appl. Phys. **98**, 063514 (2005); doi: 10.1063/1.2014937
View online: http://dx.doi.org/10.1063/1.2014937
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v98/i6
Published by the AIP Publishing LLC.

JOURNAL OF APPLIED PHYSICS **98**, 063514 (2005)

Stabilization of amorphous GaN by oxygen

F. Budde, B. J. Ruck,[a] A. Koo, S. Granville, and H. J. Trodahl
MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand 6001

A. Bittar and G. V. M. Williams
Measurement Standards Laboratory, Industrial Research Ltd., P. O. Box 31310, Wellington, New Zealand 6315

M. J. Ariza
Grupo de Física de Fluidos Complejos, Departmento de Física Aplicada, Universidad de Almería, E-04120 Almería, Spain

B. Bonnet and D. J. Jones
Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques Unitè Mixte de Recherche (UMR) Centre National de la Recherche Scientifique (CNRS) 5072, Université Montpellier II, Place Eugène Bataillon, F-34095 Montpellier Cédex 5, France

J. B. Metson
Department of Chemistry, Auckland University, Private Bag 92019, Auckland, New Zealand 1020

S. Rubanov and P. Munroe
Electron Microscope Unit, University of New South Wales, Sydney, New South Wales 2052, Australia

(Received 8 June 2005; accepted 13 July 2005; published online 22 September 2005)

We have investigated experimentally the structure of disordered GaN films. The results suggest that it is not possible to stabilize an amorphous network in stoichiometric films, and the GaN instead consists of random-stacked nanocrystals of some 3-nm diameter. However, incorporation of 15% or more oxygen stabilizes an amorphous phase, which we attribute to the presence of nontetrahedral bonds centered on oxygen. The ionic favorability of heteropolar bonds and its strikingly simple constraint to even-membered rings are the likely causes of the instability of stoichiometric *a*-GaN. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2014937]

I. INTRODUCTION

The existence and stability of glasses and amorphous solids is poorly understood in detail,[1,2] despite extensive technological applications. The problem is exacerbated by their metastability; they can be formed only in nonequilibrium processes and their bonding configuration depends on the details of that process. At the most stable extreme there are covalently bonded materials which form continuous random networks in a simple quench from a melt, of which the twofold-bonded chalcogenide atoms are often a constituent. Tetrahedrally bonded materials require more rapid quenching, so that amorphous Si (*a*-Si) and Ge are formed by deposition from the vapor onto an ambient-temperature substrate, or by ion implantation or bombardment.[3] In the case of the III-V compounds, including GaN,[4–11] claims have been made for amorphous-material preparation by the same techniques as are used for Si, though these materials have been studied less than *a*-Si. We will argue below that in the case of GaN, the truly amorphous form is unstable in stoichiometric material.

There is ambiguity in characterizing a material as amorphous, for the difference between nanocrystalline and amorphous materials is one of the range over which atomic order persists. It is convenient to consider Si as a model for tetrahedrally bonded amorphous materials. In its amorphous form it consists of nearly ideally tetrahedrally bonded Si atoms with almost completely random dihedral angles.[3,12] That structure leads to first and second nearest-neighbor shells with the same coordination and at very similar distances as are found in crystalline Si, but there remains almost no clear order at larger distances. The amorphous form of a covalently bonded material is then characterized by a rapid loss of configurational order at distances beyond that at which the covalent bonding firmly constrains the configuration.

a-Si solar cell and thin-film transistor technologies have now led to a substantial industry, but that success has not been matched in the amorphous group III-V compounds. However, it has been suggested that the amorphous form of GaN (*a*-GaN) might be particularly interesting in this regard, because the relatively strong ionicity of the Ga–N bond would be expected to limit homopolar bonds that might otherwise introduce states in the gap separating the valence and conduction bands.[13] Attempts to form *a*-GaN have had mixed results as regards both its preparation and electronic and optoelectronic properties.[4–11] Many of the attempts have generated either a nanocrystalline or nonstoichiometric material, and it is unclear from a study of the literature that genuinely stoichiometric *a*-GaN can be formed.

The case of tetrahedrally bonded III-V compounds is also of special fundamental interest, for these materials add one further constraint to those in Si, namely, the need to

---

[a] Electronic mail: ben.ruck@vuw.ac.nz

accommodate predominantly heteropolar bonds. It is important in this regard that the most successful structural models for *a*-Si contain odd-membered rings of atoms,[14] and those would require at least one homopolar bond and are thus formed only at a substantial energy cost in the III-V's. Thus extensive extended x-ray-absorption fine structure (EXAFS) studies of amorphous III-As and -P films formed by ion bombardment have concluded that these necessarily contain homopolar bonds.[15] The nitrides are especially interesting, for they are the most ionic of the III-V compounds and will be the least tolerant of homopolar bonds. Molecular-dynamics studies suggest that these materials might still form an amorphous structure, but that they contain four- as well as six-membered rings, a wide range (85°–130°) of Ga–N–Ga and N–Ga–N bond angles, and a large fraction of triply coordinated ions with sp^2 bonds.[16] Such a structure is expected to display specific signatures, most clearly as regards the presence of sp^2-bonded ions. Thus, in addition to their potential optoelectronic use, these materials offer the possibility of determining the effects of an extra constraint on the stability of the amorphous phase.

II. SAMPLE FABRICATION

We have developed an ion-assisted deposition technique for the preparation of GaN.[11,17,18] The materials are grown in a vacuum system with a base pressure of 5×10^{-9} mbar using a Ga evaporation source and a Kaufmann-type ion source. The substrate temperature is held below 20 °C throughout the growth, and the resulting films are typically 150 nm thick. Rutherford backscattering spectroscopy (RBS) establishes that they are Ga rich for low ion energy, rising to stoichiometric GaN when the ion energy is above 300 eV.[18] At these energies the N_2^+ penetration depth is about 0.5 nm, which disturbs the top two atomic layers and encourages a reconstruction of the bonds; the preparation thus involves a deposit of energy intermediate between that of evaporated vapor deposition and ion bombardment. The oxygen concentration in the films is less than 1 at. %, but can be increased to over 20% by adding a water vapor partial pressure of 4×10^{-6} mbar. The oxygen appears to substitute for nitrogen, and excess N is trapped within the network as molecules.[19–21] We now report x-ray diffraction (XRD), Ga-edge EXAFS, and transmission electron microscopy (TEM), all of which yield information about the atomic configurational order.

III. RESULTS AND ANALYSIS

In earlier publications we reported that the procedure leads to amorphous GaN containing 10%–20% O in films prepared in a base pressure of 5×10^{-6} mbar (mainly water vapor).[11] In contrast, our near-stoichiometric films are nanocrystalline, as demonstrated by the XRD data in Fig. 1. These data were obtained using Co K-edge x rays, incident at grazing angle to avoid contamination of the spectra by substrate peaks. The trace labeled nc-GaN, taken on a film with little oxygen, shows a clear diffraction pattern, with a broadening corresponding to configurational order extending to only about 3 nm. Crystalline materials, with similar dimensions are also seen to fill high-resolution TEM images of these films. Interestingly, the XRD features do not agree with either the wurtzite nor the zinc-blende phases of GaN, but they show substantial agreement with the synthetic pattern labeled R.S. in the figure, a simulation for 3-nm diameter random-stacked nanocrystals. The Ga–Ga separation for the simulation was 0.324 nm, about 2% larger than the separations in either wurtzite or zinc-blende GaN. Scattering from N atoms and both dynamic and static short-range positional disorder (the Debye-Waller factor) are ignored in the simulation, which cannot then be expected to reproduce the magnitudes of the diffraction peaks faithfully, but with one exception the peak positions fit very well. That feature, at 36° in the pattern, may indicate that some of the nanocrystals have the zinc-blende structure.[22] It is significant in this context that oriented films with densities of stacking faults approaching the random-stacked density have been formed under a variety of deposition conditions.[23–25] The upper spectrum in Fig. 1 shows the XRD pattern for a film containing 23% oxygen, and the difference from nanocrystallinity is striking. All evidence of crystalline order is missing in the material with oxygen concentration above about 15%, at which every Ga atom might have one O in its first shell. Again in these films the TEM images are in agreement with an amorphous structure. The middle pattern in Fig. 1, for a film with an intermediate oxygen concentration, is a clear mixture of amorphous and nanocrystalline structures.

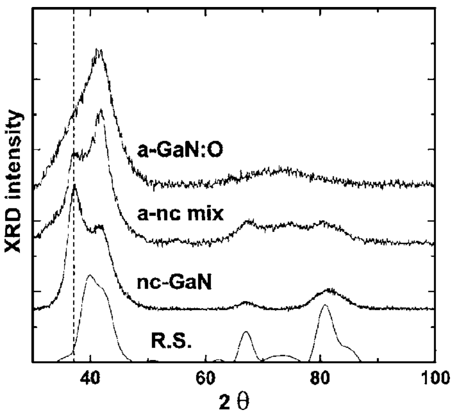

FIG. 1. XRD patterns from stoichiometric nanocrystalline (nc) GaN, an amorphous (*a*) film with 23% O and a mixed nc-*a* film. R.S. is a simulated pattern for random-stacked nanocrystals with an average diameter of 3-nm. The text discusses the 36° peak (vertical dashed line) for nc material which is not reproduced by the simulation.

These conclusions are corroborated by the Ga-edge EXAFS data in Fig. 2. These data, obtained in the electron yield mode at LURE synchrotron facility, are extracted from the measurements covering the k range from 3 to 12 Å^{-1}. The first neighbor peak is consistent with four nitrogen atoms at a similar distance to that in crystalline GaN.[17] It should be noted, however, that our EXAFS data, which are not phase corrected, cannot distinguish between backscattering from nitrogen or from oxygen atoms. The second nearest-neighbor peak shows marked differences between nanocrystalline and amorphous films. Those films prepared without oxygen are characterized by an intense second maximum corresponding to backscattering from 12 gallium at-

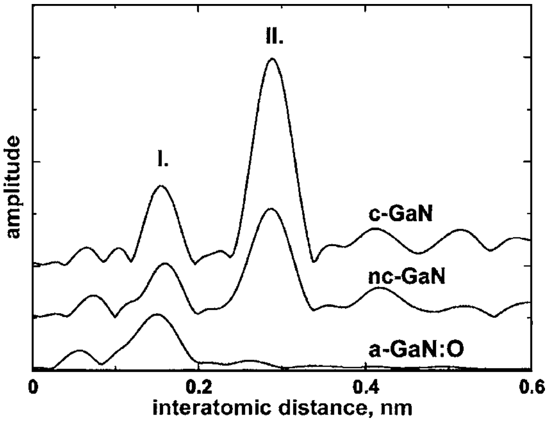

FIG. 2. 1st (I.) and 2nd (II.) neighbor peaks in the Fourier-transformed k^3-weighted EXAFS data for a nanocrystalline and an amorphous film, compared with a crystalline film.

oms. In contrast, films containing oxygen show almost no second neighbor peak, not unlike the EXAFS spectra of *a*-Si, *a*-Ge, and other amorphous III-V compounds.[15,26] The loss of intensity signals a high degree of static disorder. It is worth noting also that the first neighbor peak in the amorphous film's EXAFS shows no evidence of skewing towards longer bond lengths, as would be expected if homopolar Ga–Ga bonds were present.[15]

The amorphous versus nanocrystalline transition is manifest in a remarkably sudden function of the O concentration, as evidenced by the bright-field 200-keV TEM image and diffraction patterns shown in Fig. 3. The image is of a film prepared in a chamber in which a partial pressure of water vapor continually dropped, so that the oxygen concentration, determined by secondary-ion-mass spectroscopy (SIMS) [Fig. 3(a)], fell from about 25% at the substrate to a minimum of 7% before rising to 15% toward the surface in contact with air. Despite the gradual variation in O concentration through the film, the image shows a sharp separation where the structure changes from amorphous adjacent to the substrate to nanocrystalline nearer to the outer surface.

The full body of evidence then raises an interesting question: Why does GaN require impurities to form the amorphous phase, while the similarly bonded *a*-Si is formed so readily? The local bonding order is identical, so one must look for an explanation beyond that scale. The one strong symmetry lost in *a*- versus *c*-Si is the disordering of the dihedral angle, but the similar energies of wurtzite and zincblende GaN and the prevalent random stacking suggest that the dihedral angle is even more weakly constrained than in Si. Evidently the heteropolar bonding and its implied absence of odd-membered rings destabilize *a*-GaN and encourage the growth of nanocrystalline material. The conclusion agrees with the presence of homopolar bonds in *a*-III-V compounds involving less strongly ionic bonds,[15] and with the predominance of threefold bonds in molecular-dynamics simulations of *a*-GaN.[16] Furthermore, it has been reported that even heavily ion-damaged stoichiometric GaN retains crystalline short-range order,[27] and an amorphous phase forms only if a sufficient ion dose is applied to render the material Ga rich.[28]

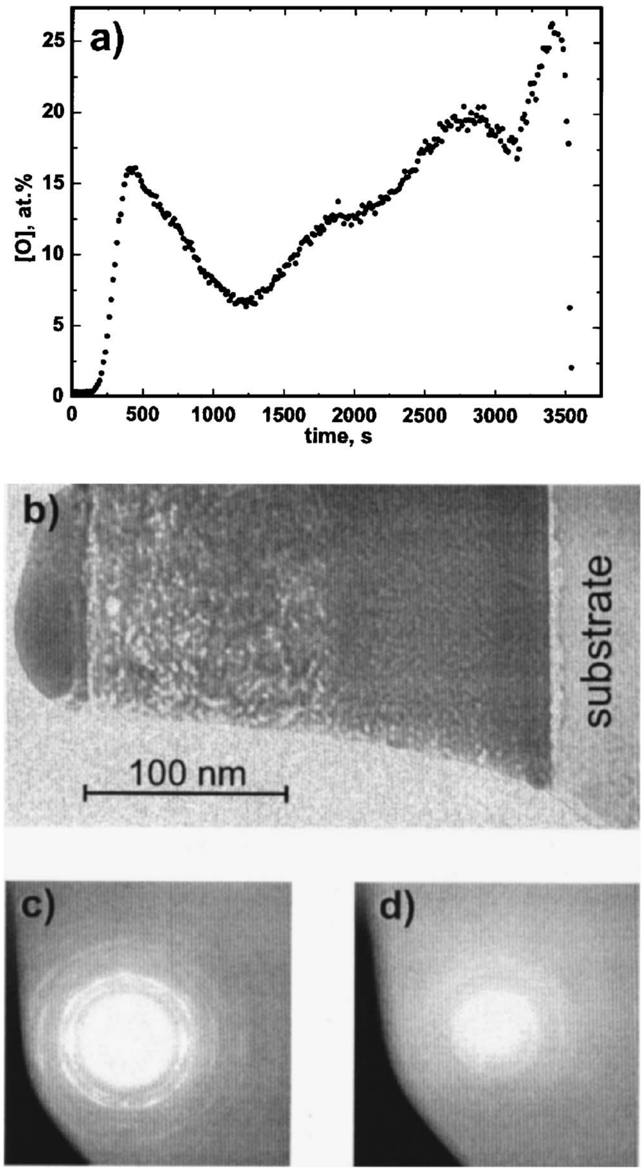

FIG. 3. (a) Oxygen concentration through a film determined by SIMS (calibrated by RBS). (b) Bright-field TEM image of a film with graded oxygen concentration. An interface running close to the center, separating an amorphous oxygen-rich layer from a nanocrystalline, is clearly visible. (c) and (d) Selected area electron-diffraction patterns from the two layers.

The description above suggests an obvious explanation for the stabilization of the amorphous phase by O. The bonding configuration of such high concentrations of a chalcogenide in disordered GaN is unlikely to be exclusively tetrahedral, as evidenced by observations that in high concentrations oxygen impurities in *c*-GaN reside in dislocations and grain boundaries rather than as a simple nitrogen substituent.[29,30] We suggest that it forms either twofold or fourfold bonds, primarily with Ga ions, which reduces the density of exclusively tetrahedral bonds and permits a space-filling network even within the even-membered ring constraint. Alternatively there may be twofold or threefold O ions forming bridges between Ga and N ions, reducing the constraints both as regards odd-membered rings and nontetrahedral bonds.

These data raise the question as to which, if any, of these configurations are suitable for optoelectronic devices. The strong ionicity of the bonds in GaN that was at the core of the suggestion that *a*-GaN might be a useful optoelectronic material is itself the constraint that prevents the formation of *a*-GaN, at least by the ion-assisted deposition (IAD) techniques described in this paper. Optical-absorption data show quite clearly that the nanocrystalline films have an absorption edge very close to the 3.4 eV that is found in crystalline GaN, but there is a tail to lower energies indicating the existence of states in the gap.[17,21] The edge is still sharp, so that the 200-nm-thick films are transparent across the visible. Amorphous GaN:O films have a larger band gap, an edge which is as sharp as found in nanocrystalline films, and a photoconductivity which is larger by several orders of magnitude.[17,21]

IV. CONCLUSIONS

In summary we have identified IAD conditions leading to stoichiometric GaN, but those conditions lead only to a nanocrystalline structure, with nearly random-stacked nanocrystals of about 3-nm diameter. The picture that emerges suggests that amorphous GaN is not as stable as *a*-Si, despite the similarity of bonding in the two materials. It is likely that the heteropolar character of the bonds in GaN, which adds a further constraint preventing the formation of odd-membered rings, is responsible for the apparent instability of *a*-GaN. On the other hand, clearly amorphous films do form with the introduction of oxygen into the bonding network, which we associate with a relaxation of constraints on the bonding network by the presence of nontetrahedral bond configurations centered on oxygen.

ACKNOWLEDGMENTS

We acknowledge the New Zealand Foundation for Research, Science and Technology for financial assistance through its New Economy Research Fund, and through doctoral (AK) and postdoctoral (BJR) fellowships, and the Royal Society of New Zealand for support under the Centre of Research Excellence programme.

[1] C. A. Angell, Science **267**, 1924 (1995); A. P. Sokolov, *ibid.* **273**, 1675 (1996).
[2] J. Gump, I. Finkler, H. Xia, R. Soorykumar, W. J. Bresses, and P. Boolchand, Phys. Rev. Lett. **92**, 245501 (2004); Q. Yan, T. S. Jain, and J. J. de Pablo, *ibid.* **92**, 235701 (2004); J. A. Floro, P. G. Kotula, S. C. Seel, and D. J. Srolovitz, *ibid.* **91**, 096101 (2003); Z. H. Stachurski, *ibid.* **90**, 155502 (2003); M. Celino and C. Massobrio, *ibid.* **90**, 125502 (2003).
[3] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979).
[4] T. Hariu, T. Usuba, H. Adachi, and Y. Shibata, Appl. Phys. Lett. **32**, 253 (1978).
[5] M. Kuball, H. Mokhtari, D. Cherns, J. Lu, and D. I. Westwood, Jpn. J. Appl. Phys., Part 1 **39**, 4753 (2000).
[6] Z. Hassan, K. Ibrahim, M. E. Kordesch, W. Halverson, and P. C. Colter, Int. J. Mod. Phys. B **16**, 1086 (2002).
[7] H. Chen, K. Chen, D. A. Drabold, and M. E. Kordesch, Appl. Phys. Lett. **77**, 1117 (2000).
[8] Y. Kang and D. C. Ingram, J. Appl. Phys. **93**, 3954 (2003).
[9] S. Nonamura, S. Kobayashi, T. Gotoh, S. Hirata, T. Ohmori, T. Itoh, S. Nitta, and K. Morigaki, J. Non-Cryst. Solids **198–200**, 174 (1996).
[10] T. Miyazaki, T. Fujimaki, S. Adachi, and K. Ohtsuka, J. Appl. Phys. **89**, 8316 (2001).
[11] A. Bittar, H. J. Trodahl, N. T. Kemp, and A. Markwitz, Appl. Phys. Lett. **78**, 619 (2001); A. Koo, U. D. Lanke, B. J. Ruck, S. Brown, R. Reeves, I. Liem, A. Bittar, and H. J. Trodahl, Mater. Res. Soc. Symp. Proc. **693**, I10.10.1 (2002).
[12] R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).
[13] P. Stumm and D. A. Drabold, Phys. Rev. Lett. **79**, 677 (1997).
[14] D. E. Polk, J. Non-Cryst. Solids **5**, 365 (1971).
[15] C. J. Glover, M. C. Ridgway, K. M. Yu, G. J. Foran, T. W. Lee, Y. Moon, and E. Yoon, Appl. Phys. Lett. **74**, 1713 (1999); M. C. Ridgway, G. de M. Azevedo, C. J. Glover, K. M. Yu, and G. J. Foran, Nucl. Instrum. Methods Phys. Res. B **199**, 235 (2003).
[16] K. Chen and D. A. Drabold, J. Appl. Phys. **91**, 9743 (2003).
[17] A. Koo *et al.*, *Proceedings of the 26th International Conference on the Physics of Semiconductors* (IOP, Edinburgh, Scotland, 2002).
[18] U. D. Lanke *et al.*, Mater. Res. Soc. Symp. Proc. **693**, 16.10.1 (2002).
[19] J. B. Metson, H. J. Trodahl, B. J. Ruck, U. D. Lanke, and A. Bittar, Surf. Interface Anal. **35**, 719 (2003).
[20] B. J. Ruck *et al.*, Phys. Rev. B **70**, 235202 (2004).
[21] B. J. Ruck *et al.*, J. Appl. Phys. **96**, 3571 (2004).
[22] J. H. Kim and P. H. Holloway, Appl. Phys. Lett. **84**, 711 (2004).
[23] H. Siegle, L. Eckey, A. Hoffmann, C. Thomsen, B. K. Meyer, D. Schikora, M. Hankeln, and K. Lischka, Solid State Commun. **96**, 943 (1995).
[24] B. Yang, A. Trampert, O. Brandt, B. Jenichen, and K. H. Ploog, J. Appl. Phys. **83**, 3800 (1998).
[25] A. Munkholm *et al.*, Appl. Phys. Lett. **72**, 2972 (1998).
[26] C. J. Glover, G. J. Foran, and M. C. Ridgway, Nucl. Instrum. Methods Phys. Res. B **199**, 195 (2003); M. C. Ridgway, C. J. Glover, K. M. Yu, G. J. Foran, C. J. Clerc, J. L. Hansen, and A. Nylandsted Larson, Phys. Rev. B **61**, 12586 (2000).
[27] S. O. Kucheyev, J. S. Williams, C. Jagadish, J. Zou, and G. Li, Phys. Rev. B **62**, 7510 (2000).
[28] S. O. Kucheyev, J. S. Williams, C. Jagadish, G. Li, and S. J. Pearton, Appl. Phys. Lett. **76**, 3899 (2000).
[29] K. S. A. Butcher, J. Appl. Phys. **92**, 3397 (2002).
[30] J. Elsner, R. Jones, M. I. Heggie, P. K. Sitch, M. Haugk, T. Frauenhein, S. Öberg, and P. R. Briddon, Phys. Rev. B **58**, 12571 (1998).