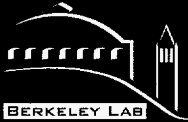
LBNL-39218
UC-404

CONF-960781--8



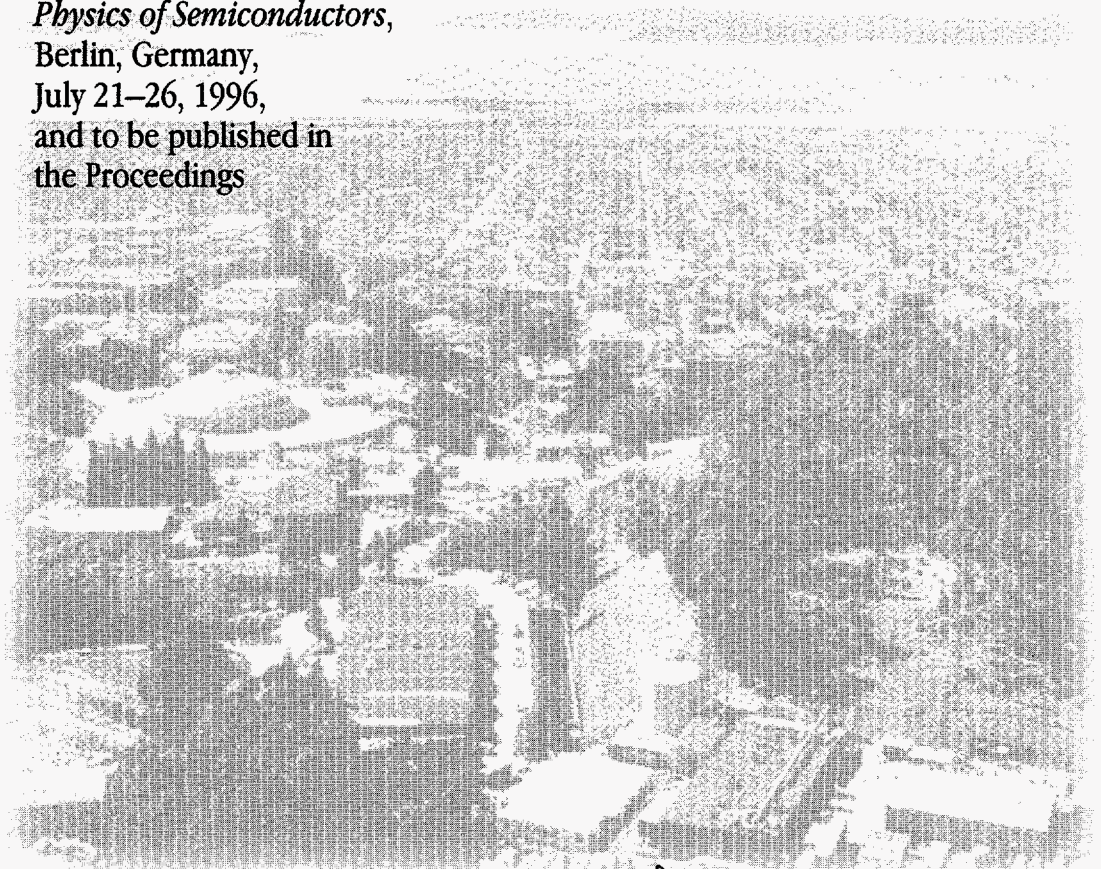
ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Strongly Localized Donor Level in Oxygen Doped Gallium Nitride

C. Wetzel, T. Suski, J.W. Ager III, W. Walukiewicz, S. Fischer, B.K. Meyer, I. Grzegory, and S. Porowski
Materials Sciences Division
Center for Advanced Materials

RECEIVED
DEC 10 1996
OSTI

August 1996
Presented at the
23rd International Conference on the Physics of Semiconductors,
Berlin, Germany,
July 21–26, 1996,
and to be published in
the Proceedings



DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory
is an equal opportunity employer.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LBNL-39218
UC-404

Strongly Localized Donor Level in Oxygen Doped Gallium Nitride

C. Wetzel, T. Suski, J.W. Ager III, and W. Walukiewicz

Materials Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, California 94720

S. Fischer and B.K. Meyer

1. Physikalisches Institut
Justus-Liebig-Universität Giessen
35392 Giessen, Germany

I. Grzegory and S. Porowski

Unipress
Polish Academy of Sciences
01-142 Warszawa, Poland

August 1996

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

STRONGLY LOCALIZED DONOR LEVEL IN OXYGEN DOPED GALLIUM NITRIDE

C. Wetzel, T. Suski, J.W. Ager III, and W. Walukiewicz
Lawrence Berkeley National Laboratory, Berkeley CA 94720, USA

S. Fischer and B.K. Meyer
1. Physikalisches Institut, Justus-Liebig-Universität Giessen, 35392 Giessen, Germany

I. Grzegory and S. Porowski
Unipress, Polish Academy of Sciences, 01-142 Warszawa, Poland

A classification in terms of the localization of donor defects in GaN is performed by Raman spectroscopy under large hydrostatic pressure. We observe a significant decrease of the free carrier concentration in highly O doped GaN epitaxial films at a hydrostatic pressure of 22 GPa. This indicates the presence of a strongly localized donor defect at large pressure. Monitoring the phonon plasmon coupled mode we find similarities with results on highly n-type bulk crystals. We refine the model of localized defects in GaN and transfer it to the AlGaN system.

1 Introduction

The problem of p and n-type doping in the alloys of AlGaN and InGaN are closely related to an identification of the origin of high background n-type conductivity in GaN as observed by many different growth processes. Both, native defects and unintentional incorporation of donor species [1] are typically considered. Namely the N vacancy and the Ga interstitial should act as strongly localized donor defects [3]. Oxygen on the other hand is known to be a highly efficient donor in GaN [1] and its proximity to N suggests it to be an effective mass type defect. Here we present a study of the nature of the dominant donors in highly O doped epitaxial films and small GaN bulk single crystals.

2 Experimental

Epitaxial GaN films at a thickness of 5 μm were grown on (0001) sapphire by hydride vapor phase epitaxy. Through small amounts of water vapor a doping with O was achieved. Free electron densities in the low 10^{19} cm^{-3} were found. Incorporation of O at this concentration was confirmed by Secondary Ion Mass Spectroscopy. Bulk GaN crystals were grown by high pressure synthesis. Small pieces of 200 μm in diameter have been selected for this study. The crystals are typically characterized by a free electron concentration in the mid 10^{19} cm^{-3}

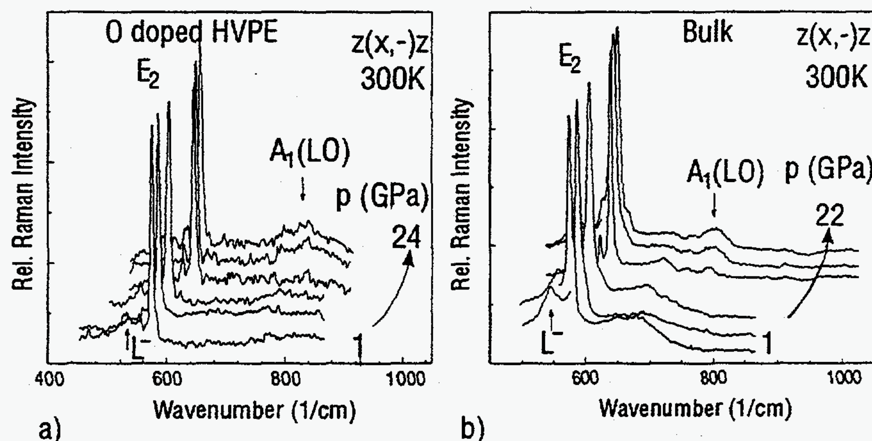


Figure 1: Raman spectra at various hydrostatic pressures for. a) O doped HVPE GaN film: The A_1(LO) mode appears at 22 GPa for the first time. b) The same mode appears first at 19 GPa and its intensity increases at 20 and 22 GPa. Spectra are normalized to the height of E_2 and offset for clarity.

and mobilities of 400 cm^2/Vs. Hydrostatic pressure was applied by means of a Mao-Bell-type diamond anvil cell using a methanol-ethanol mixture as a pressure medium. The pressure was determined by ruby fluorescence and the pressure dependence of the GaN E_2 phonon mode. Nonresonant Raman spectroscopy in z(x,-)z forward scattering geometry was performed using 100 mW of the 476.5 nm line of an Ar ion laser. All data were taken at room temperature.

2.1 Oxygen doped samples

Raman spectra of the highly O doped films as a function of hydrostatic pressure is presented in Fig. 1 a). At all pressure values the spectra are dominated by the E_2(high) mode (567 cm^{-1} at ambient pressure). This mode does not couple to the free electrons and is used as an internal intensity reference for the spectra. With increasing pressure this mode shifts towards higher energy at a rate of 3.75 cm^{-1}/GPa up to 24 GPa. For the lowest pressure of 1.4 GPa no contribution in the expected range of the A_1(LO) mode is observed. Due to the high carrier concentration and the limited mobility of the electrons this mode is overdamped and vanishes in the background signal. This can be

seen from a simulation of the lineshape in an oscillator model for the dielectric function. On the low energy side the phonon plasmon coupled mode L^- is observed close to the value expected for the $A_1(TO)$ [2]. There is no change on the high energy $A_1(LO)$ side until a pressure of 22 GPa. At this pressure, however, a strong contribution occurs centered at 835 cm^{-1}. There is very little further change at the highest measured pressure of 24 GPa.

2.2 Bulk crystals with unknown donor

Raman data for a series of pressure values for the bulk crystals are given in Fig. 1 b). The occurrence of the $A_1(LO)$ mode in this material has been reported before [4]. Here however, more details are obtained on the very onset at lower pressure. Both, E_2 and L^- behave similar to the ones in the oxygen doped material. The earliest observation of the A_1LO) mode is at 19 GPa. At 20 GPa the mode has increased in area by 3.5 and by another 1.4 at 22 GPa.

3 Discussion

The occurrence of the $A_1(LO)$ mode is interpreted as the result of a decreased concentration of the free carriers [5,4]. In bulk GaN crystals such an effect has been explained by a strongly localized donor defect emerging from the conduction band at large hydrostatic pressure. From Fig. 1 b) we find that there actually is a gradual onset of this mode with pressure which indicates a continuously increasing binding energy for larger pressure. A localization energy of 126 meV at 27 GPa was found [4]. This is consistent with the assumption of a strongly localized donor defect exhibiting a much smaller pressure coefficient than the bandgap. Such a level can be caused by several defects: a typically strongly localized native defect or an otherwise delocalized hydrogenic defect undergoing a pressure induced transformation into a localized one.

Large discrepancies in reported electron concentrations and detectable impurity concentrations support the first model. N vacancies or Ga interstitials should act as a donor and in a model for the pressure behavior of such as donor we find its resonant level ~ 400 meV above the conduction band minimum ($p \sim 0$). Carriers would autoionize from the defect to the edge of the conduction band. They would bind in the coulomb potential of the fixed positive charge they left behind and again form a hydrogenic defect. However, the center of this potential corresponds to the high lying resonant state and acts as a repulsive potential barrier. In the consequence we find a positive central cell correction to the binding energies of perfect effective mass type donors in a dilute system.

In the other model commonly assumed quasi hydrogenic donor impurities such as Si or O would induce a localized gap state under hydrostatic pressure. We recently showed that Si doped GaN films do not exhibit a carrier freeze out up to the largest applied pressure of 30 GPa[6].

Altogether we find that the dominant donor in O doped HVPE GaN films and small bulk GaN crystals from pressure synthesis show a similar pressure behavior inducing at localized gap state in the range of 17 - 22 GPa.

From the established similarities of application of hydrostatic pressure and the alloying with Al in the AlGaAs system a similar effect is expected for the nitrides. Assuming a linear dependence of the bandgap energy in $Al_xGa_{1-x}N$ with x and the theoretical pressure dependence of the bandgap,[7] a transition pressure of 19 GPa would correspond to $x = 0.2$. This indicates that this localized defect can be the reason for doping problems in $Al_xGa_{1-x}N$ for $x \geq 0.2$. Si on the other hand should be a good donor up to at least $x = 0.3$.

Acknowledgments

The authors wish to thank Professors E.E. Haller and P.Y. Yu for experimental support and helpful discussion. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. W. Seifert, R. Franzheld, E. Butter, H. Sobotta, and V. Riede, Cryst. Res. Technol. **18**, 383 (1983).
2. A. S. Barker Jr. and M. Ilegems, Phys. Rev. B **7**, 743 (1973).
3. P. Boguslawski, E.L. Briggs, and J. Bernholc, Phys. Rev. B, **51**, 1725 (1995).
4. C. Wetzel, W. Walukiewicz, E.E. Haller, J.W. Ager III, I. Grzegory, S. Porowski, and T. Suski, Phys. Rev. B, **53**, 1322 (1996).
5. P. Perlin, T. Suski, H. Teisseyre, M. Leszczynski, I. Grzegory, J. Jun, S. Porowski, P. Boguslawski, J. Bernholc, J.C. Chervin, A. Polian, and T.D. Moustakas, Phys. Rev. Lett., **75**, 296 (1995).
6. C. Wetzel, A.L. Chen, T. Suski, J.W. Ager III, and W. Walukiewicz, Seventh Inter. Conf. High Pressure Semiconductor Physics, Schwäbisch-Gmünd, Germany (1996) *unpublished*.
7. N. E. Christensen and I. Gorczyca, Phys. Rev. B **50**, 4397 (1994).