Invited Paper

Fundamental differences between traditional III-V compounds and Nitride Semiconductors

Theodore D. Moustakas

Department of Electrical and Computer Engineering, Materials Science and Engineering Division, Photonics Center, Boston University, USA, moustakas@bu.edu.

Nitride semiconductors, grown heteroepitaxially on a number of substrates such as sapphire and SiC, have been found to have a high concentration of extended defects [1]. Such include, for example, threading dislocations, stacking faults and compositional inhomogeneities due to phase separation and partial alloy ordering. Paradoxically the performance of optoelectronic devices, such as LEDs and lasers, based on Nitride semiconductors is insensitive to this high concentration of defects, while the performance of similar devices based on traditional III-V compounds requires orders of magnitude smaller concentration of defects [2, 3]. In this paper I am arguing that these observations are related to differences in the chemical bonding and the crystal structure of these two families of semiconductors.

A. The influence of the Chemical Bonding: The traditional III-V compounds are mostly covalent materials. Thus, the intrinsic surface states due to dangling bonds occur in a narrow half-filled band near the center of the energy gap. Due to their position in the energy gap these states are potent non-radiative recombination centers and thus are enhancing the recombination rate at the surface region. Furthermore, dangling bonds in edge dislocations contribute also states close to the middle of the gap, and this accounts for the poor performance of minority type devices such as LEDs and lasers at high concentration of edge dislocations. Also, these surface states pin the Fermi level close to the middle of the gap and thus, the barrier height of metallic contacts is independent of the workfunction of the metal.

On the contrary the chemical bonding in Nitride semiconductors is mostly ionic [4, 5]. As discussed by Shockley, the ionicity of the chemical bond between their atoms results in the bunching of the surface states near the band edges [6]. A direct observation of intrinsic surface states in GaN was reported by Dhesi and co-workers using angle resolved photoemission studies [7]. These authors reported the existence of states near the valence band maximum and identified them as surface states, since they have sp_z character and are destroyed upon hydrogenation. On the other hand Kocan et al. [8] reported by in-situ XPS during growth that the position of surface Fermi level depends sensitively on the Ga/N ratio during growth. The surface Fermi level was found to vary from $E_F - E_v = 2.89$ eV under nearly stoichiometric growth conditions to $E_F - E_v = 1.65$ eV under Ga-rich conditions where metallic Ga forms on the surface. Theoretically the surface electronic structure of GaN and InN was investigated by Van de Walle and Segev [9] under group-III rich conditions of growth. Under these conditions the surface is covered by a laterally contracted double layer of Ga, which affects the surface reconstruction and thus, the surface electronic structure. It is obvious from these experimental and theoretical studies that the surface states introduced by a reconstruction associated with the excess Ga on the surface of the GaN are not the same as the intrinsic surface states that can be revealed by cleaving the semiconductor in vacuum or by thorough cleaning the semiconductor surface through chemical etching.

In this paper I am discussing the role of the intrinsic surface states, which are revealed by cleaving in vacuum or etching the semiconductor. Such intrinsic surface states are also likely to be present in GaN films grown under nitrogen-rich conditions of growth, which is the case during growth by MOCVD or MBE using ammonia or high power nitrogen plasma. These intrinsic surface states are not recombination centers but traps and are not likely to pin the Fermi level.

The position of the intrinsic surface states affect the performance of minority carrier devices based on Nitride semiconductors. Specifically, surface recombination and surface depletions are absent in such devices, while they are prominent in devices based on traditional III-V compounds. Also, dangling bonds

in edge dislocations, which are the majority of threading dislocations in these materials [1], are not expected to be non-radiative recombination centers but traps like dangling bonds in free surfaces. This then can account for the insensitivity of the performance of GaN based LEDs to high concentration of threading dislocations. Furthermore, if the surface is unpinned one expects that the design of metal contacts to both electronic and optoelectronic devices to depend on the work function of the metal. This is indeed the case since contacts to the n-GaN is done with metals whose work function is equal or smaller than the electron affinity of GaN, and contacts to p-GaN is done by using high workfunction metals [4].

B. The influence of the crystal structure: The equilibrium crystal structure of Nitride semiconductors is the wurtzite; however, they can also exist in the metastable zincblende structure. The enthalpy of formation of these two allotropic forms differs only by a few meV. Since these materials are grown at temperatures higher than 1000 K the conversion between the two phases occurs easily by the formation of stacking faults along the closed packed (0001) and (111) planes. As a result basal plane stacking faults are abundant in all nitride semiconductors. Since a basal plane stacking fault can be viewed as a monolayer of a cubic domain embedded into a wurtzite matrix and since the cubic GaN has a smaller energy gap by 0.1 to 0.2 eV compared to wurtzite GaN [10], one expects that basal plane stacking faults introduce band structure potential fluctuations. Such potential fluctuations are beneficial for devices such as LEDs since they induce exciton localization and thus efficient radiative recombination [5, 11]. This is to be contrasted with the traditional III-V compounds whose equilibrium structure is cubic and a basal plane stacking fault is the equivalent of a monolayer of a wurtzite structure embedded into a cubic matrix. Since the wurtzite structure has a larger energy gap than its zincblende structure, the stacking faults in III-V compounds introduce band structure potential fluctuations which are not favoring exciton localization.

In conclusion arguments were presented that the intrinsic surface states of Nitride semiconductors should occur close to the band edges and thus they are traps rather than recombination centers. Similarly, dangling bonds in edge dislocations are also expected to be traps. Furthermore, we argued that the basal plane stacking faults, which are abundant in Nitride semiconductors, introduce band structure potential fluctuations which are beneficial for LEDs since they induce exciton localization.

[1] Zuzanna Liliental-Weber, in Semiconductors and Semimetals, Vol. **57**, Edited by J. I. Pankove and T. D. Moustakas (Academic Press, New York, 1998), Chapter 3.

[2] S. D. Lester, F. A. Ponce, M. G. Graford and D. A. Steigerwald, "High dislocation densities in high efficiency GaN-based light-emitting diodes", Appl. Phys. Lett. vol. 66**,** pp. 1249-1251, 1995

[3] F. A. Ponce and D. P. Bour, "Nitride-based semiconductors for blue and green light-emitting devices" Nature **386**, pp. 351-359, 1997

[4] J. S. Foresi and T. D. Moustakas, "Metal contacts to gallium nitride", Appl. Phys. Lett., vol. 62**,** pp**.** 2859-2861, 1993

[5] T. D. Moustakas, "The role of extended defects on the performance of optoelectronic devices in nitride semiconductors", Phys. Status Solidi A **210,** pp**.** 169-174, 2013

[6] W. Shockley, "On the surface states associated with a periodic potential", Phys. Rev. Vol. 56, pp. 317-323, 1939

[7] S. S. Dhesi, C. B. Stagarescu, K. Smith, D. Doppalapudi, R. Singh and T. D. Moustakas, "Surface and bulk electronic structure of thin-film wurtzite GaN" Phys. Review B, vol. 56, pp. 10271-10275, 1997

[8] M. Kočan, A. Rizzi, H. Lüth, S. Keller, and U. K. Mishra, "Surface potential at as-grown GaN (0001) MBE layers", Phys. Status Solidi B, vol. 234, pp. 773-777, 2002

[9] Chris G. Van de Walle and David Segev, "Microscopic origins of surface states on nitride surfaces", J. Appl. Phys., vol. 101, pp. 081704 -1-6, 2007

[10] T. Lei, T. D. Moustakas, R. J. Graham, Y. He and S. J. Berkowitz**,** "Epitaxial Growth and Characterization of Zinc-blende Gallium Nitride on (001) Silicon," J. Appl. Phys., vol. 71, pp. 4933-4943, 1992

[11] T. D. Moustakas, Influence of Extended Defects on Optoelectronic and Electronic Devices" Lester Eastman Conference on High Performance Devices 2012 (7-9 August 2012) IEEE Xplore Digital Library DOI 10.1109/lec.2012.6410991