Polarization Doped Nanowire Devices as an Alternative to Impurity Doping

By Santino Carnevale
Department of Materials Science and Engineering
The Ohio State University

In the past several decades, semiconductor materials have been used in a wide range of electronic devices. These devices include transistors, light emitting diodes, lasers, photodetectors, solar cells, and many more. Given such an impressive range of applications, one might wonder what makes semiconductors so different from other materials? At the heart of it, semiconductors are different from other materials because it is possible to control the electrical conductivity in semiconductors. Without this essential trait, none of the devices previously mentioned would be possible. And as semiconductor technologies have progressed, the line between semiconductors and insulators (materials that are generally not electrically conductive) has changed. That is, over time, researchers in search of new materials to meet the need of emerging applications find ways to control the conductivity in materials that were previously not conducting, thus changing an insulator to a semiconductor. However, this ability to modulate electrical conductivity using traditional methods can only go so far, and because of this limitation, new methods of controlling conductivity are desired. To explain this in greater detail, we'll first look at the method traditionally used to control conductivity, called impurity doping.

Impurity doping has been the key to controlling conductivity in semiconductors for decades. This method works by adding small concentrations of foreign atoms (i.e. impurities) to an otherwise nearly perfect semiconductor crystal. The electrical conductivity of the material is modulated by changing the concentration of the atoms added. Also, the type of atoms makes a difference as well, with different atoms resulting in one of two types of conductivity, n-type or p-

type. To illustrate this, let's look at how impurity doping works in Silicon (Si). Figure 1 includes a number of diagrams meant to illustrate how this process works. First, a section of the periodic table of elements is shown (Fig. 1A) to demonstrate atoms that can be used as impurity dopants in Si: Boron (B) and Phosphorus (P). Each Si atom has 4 electrons in its outermost electron shell. In a crystal of Si, each atom covalently bonds with four other Si atoms. This leads to a configuration like the one shown in Figure 1B, where each atom has a filled outer most electron orbital of 8 electrons, 4 from the atom itself, and one each from its neighbors.

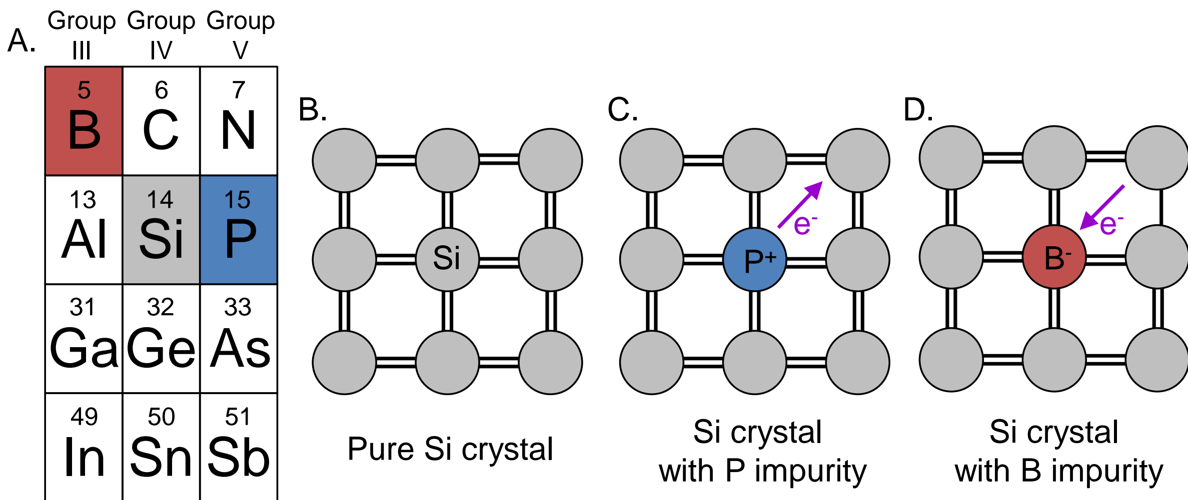

Figure 1 – A.) A small section of the periodic table of elements showing Si and commonly used dopants. B.) Schematic of a pure Si crystal with no dopants. C.) Schematic showing how P atoms add electrons to Si. D.) Schematic showing how B atoms add holes to Si.

Now suppose that one Si atom is removed from the crystal and replaced with a P atom. The P atom has 5 electrons in its outermost shell. Four of these electrons form bonds with the 4 nearest neighbor Si atoms, leaving the fifth electron only weakly bonded to the P atom. If the P atom absorbs a small amount of energy then the P atom is ionized and the weakly bonded electron leaves the atom and it is free to move about the material. This extra electron adds to the electrical conductivity of the material. So, if one wants to make highly conductive Si, they need

only add a large number of P atoms. Similarly, a B atom can be added to the Si. In this case, the B atom only has 3 outermost electrons, and will therefore take in an electron, leaving behind a missing electron, or hole. The presence of holes in a material also lead to increase electrical conduction, though with oppositely charged carriers compared to material that contains excess electrons. Semiconductors with each these two different kinds of charge carriers are called "n-type" (electrons carry charge) and "p-type" (holes carry charge). Many, but not all, of these devices utilize both n-type and p-type material, so it is necessary to be able to achieve both types of conductivity in any given semiconductor.

An important point should be stressed here. Impurity doping only works if the impurity atoms are ionized by absorbing a small amount of energy. The amount of energy needed to ionize a dopant is referred to as the ionization energy or the dopant's activation energy. This energy is usually supplied by thermal energy available at room temperature. Therefore, if a semiconductor is cooled to cryogenic temperatures, the impurities will no longer be ionized, the number of charge carriers decrease and so does the material's electrical conductivity. This reduction in conductivity with reduced temperature is referred to as freeze-out. Of course, most devices are not designed to operate at cryogenic temperatures, so impurity doping works fine in the vast majority of situations.

But as was previously mentioned, there is a problem with impurity doping that has become more apparent as researchers have pushed the boundaries of what is considered a semiconductor, and it involves the material parameter known as "band gap energy". The band gap energy of a semiconductor determines many of its most important characteristics. It determines the wavelength of energy a semiconductor emits when used in a device like a light emitting diode. It determines the range of wavelengths that a semiconductor will absorb, for

example if used in a solar cell. And it determines the maximum voltage that can be applied to a material before it fails, known as the breakdown voltage. Recently, semiconductors with a large band gap energy (called "wide band gap") have been sought after for a range of applications that current semiconductors cannot be used in, specifically optoelectronic devices (LEDs and lasers) that emit light in the ultraviolet part of the electromagnetic spectrum and high power transistors. Some common examples of wide band gap semiconductors are Gallium-nitride (GaN), Aluminum-nitride (AlN), Zinc-oxide (ZnO), and Silicon-carbide (SiC).

The difficulty with using wide band gap materials lies in the amount of energy needed to ionize dopants in these materials. At low band gaps, ionization energy is close to the level of thermal energy at room temperature. As band gap increases, ionization energy also tends to increase. For wide band gap materials, ionization energy is many times larger than thermal energy. Thus, these impurities will essentially be frozen-out at room temperature. This room temperature freeze-out makes it difficult to form highly conductive wide band gap semiconductors. Additionally, it is sometimes the case that only one type of conducting material (e.g. n-type or p-type) is possible to form in a given semiconductor. For example, it is currently not possible to form highly conductive p-type AlN or ZnO material.

Fortunately, there is a way to control the conductivity of wide band gap semiconductors without the need for impurity doping, and is called polarization-induced doping. Several wide band gap semiconductors have a non-centrosymmetric crystal structure known as wurtzite. This specific structure exhibits strong polarization phenomena. Polarization in a semiconductor is essentially a small separation in the positive and negative charge, called a dipole, within the crystal structure of the material. This separation can results in a number of ways, such as strain-induced (piezoelectric) or temperature-induced (pyrolectric) polarization, but what separates

semiconductors with the wurtzite structure from other semiconductors is the existence of spontaneous polarization. Like its name implies, spontaneous polarization exists in a wurtzite structure without the need of any specific external conditions. Spontaneous polarization exists in wurtzite structures because of a small separation in positions between anion and cation atoms in the structure and the strongly ionic character of the bond between these atoms.

Spontaneous polarization allows for the formation of conducting semiconductors without the need for impurity doping. Figure 2 displays some simple ways in which conductivity can be modulated with spontaneous polarization. First, it should be noted that the amount of spontaneous polarization changes from material to material. In the case of the III-nitrides, AlN has a larger spontaneous polarization than GaN (Fig. 2A). In a homogenous slab of material, the dipoles that exist within the wurtzite structure do not lead to any net charge since the charge between adjacent dipoles cancel one another out. However, if two different materials are stacked one on top of the other (Fig. 2B and 2C), then adjacent charges will have different magnitudes. This means that there will be some net charge at the interface between the two dissimilar materials. Figure 2B and 2C shows the cases for AlN on GaN and $Al_{0.5}Ga_{0.5}N$ on GaN. In both cases, the change in spontaneous polarization across the interface leads to some amount of uncompensated charge. Since AlN has a larger spontaneous polarization than AlGaN, there will be more uncompensated charge at the AlN/GaN interface than the $Al_{0.5}Ga_{0.5}N$ /GaN interface.

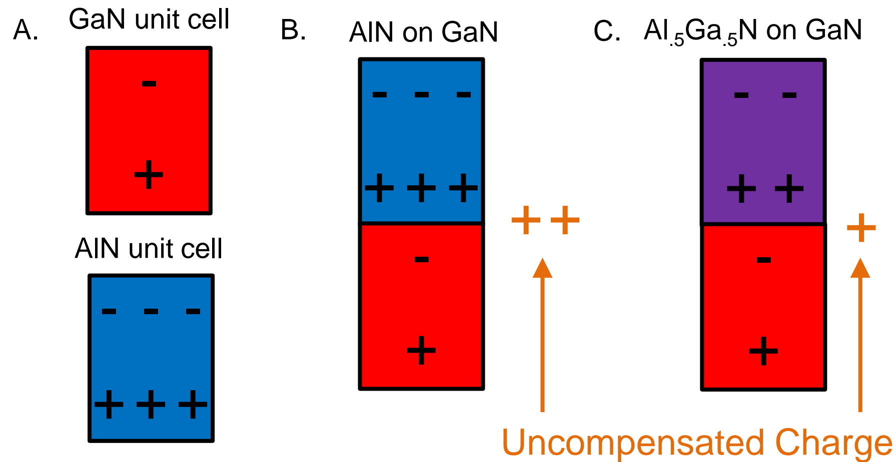

Figure 2 – A.) The unit cells of GaN and AlN, with dipoles denoted by + and – signs, and stronger dipoles denoted by more of + and – signs. B.) A stack of AlN on GaN, and the uncompensated bound charge at the interface. C.) AlGaN on GaN, and the uncompensated bound charge at the interface.

Some key points should be noted here. First, the orientation of the dipoles in the material is determined by the material's polarity. In the case provided, the charges are ordered positive to negative from bottom to top. Thus, there is a net positive charge at the interface. However, if the orientation of the crystal were inverted, the charge orientation would also invert, leaving a net negative charge at the interface.

Second, the net uncompensated charge at the interface is bound to material's crystal structure and is not in the form of charge carriers free to move about the material. That being said, the net charge at the interface will become compensate with free carriers with the opposite sign. This can happen in two ways. First, impurities can be included in the top layer to provide the necessary charge to compensate the net charge at the interface. In the examples shown (Fig. 3B) Si atoms can be added to the AlN to provide electrons that will move to the interface and neutralize the bound positive charge there. These Si impurities are not ionized by thermal energy, but rather by the presence of the polarization charge. Alternatively, it has been found that surface states of the material can act as the source of electrons at the interface[1], meaning

no impurities at all are needed in the material to provide electrons. Regardless of the source of the electrons, because of the bound polarization charge at the interface, a sheet of free electrons will form at the interface, called a two-dimensional electron gas (2DEGs). AlGaN/GaN heterostructures like this are commonly used in a common device called a high-electron mobility transistor (HEMT)[2].

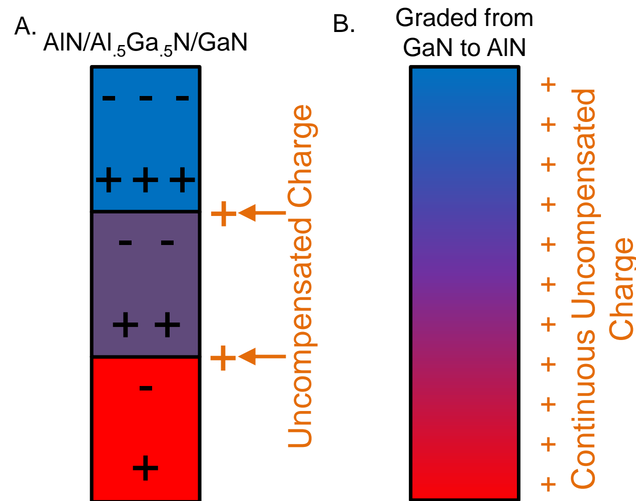

Figure 3 – A.) Schematic showing a stack of material with abrupt increases in % Al in the material. B.) Material continuously graded from GaN to AlN, and the resulting continuous polarization-induced charge.

The preceding example of an abrupt interface displayed the basic principles of polarization-induced doping. This idea can be extended to a series of abrupt interfaces where each layer has a progressively composition. A potential structure like this is shown in Figure 3A. Here, the change in spontaneous polarization from GaN to AlN is shared between two interfaces, leading to two sheets of charges. This same idea can be applied to a linearly graded heterostructure (Fig. 3B). Again focusing on the III-nitrides, if a layer of material is graded from GaN to AlN, the size of the dipole in the material will get progressively larger. This means that instead of a sheet of charge at only one or two interfaces, the same amount of charge is smeared throughout the entire graded structure. This has been shown previously in graded AlGaN

layers[3-5]. As previously mentioned, the polarization-induced charge depends on the polarity of the material. This means that by linearly grading from GaN to AlxGa1-xN along the wurtize [0001] direction (called Ga-face material) will result in a slab of free electrons in the graded section(i.e. n-type material), while the same material graded along the [000-1] direction (called N-face) will result in a slab of free holes (i.e. p-type material). N-type material shown in this way was first shown in the early 2000's [3]. P-type materials were achieved using polarization-induced doping in 2010 [4], and has been repeated experimentally [5, 6]. One small difference between the n-type and p-type graded structures is the presence of impurities. It has been found that adding impurities is not necessary to form polarization-induced n-type AlGaN layers, while there are varying reports on whether it is necessary in p-type layers, with some groups saying it is necessary[4] and some groups saying it is not[6].

In all of these reports, layers are graded at most over a 30% change in composition (that is, either GaN to $Al_{.3}Ga_{.7}N$ or AlN to $Al_{.7}Ga_{.3}N$). This is because AlN and GaN have a different spacing between atoms (lattice parameter) and grading between the two materials leads to strain in the material. When enough strain builds up, the material relaxes either through the formation of extended defects. This relaxation is terrible for a device because it greatly reduces material quality. So by grading over only a narrow range of compositions, researchers have been able to prevent relaxation. This is a problem because in order to maximize the amount of polarization-induce charge in the material it is necessary to grade over the largest possible range of compositions (i.e. GaN to AlN). Therefore, the strain induced in a graded layer prevents researchers from taking full advantage of polarization-induced doping.

Luckily, there is a way to form graded AlGaN material without incorporating strain-related defects. The key to this is using material formed in a nanowire geometry instead of a

planar geometry, which is more traditionally used in electronic devices. It is widely known that the geometry of a nanowire (specifically the large sidewall surface area) accommodates strain better than a planar structure[7]. This means that it is possible to form structures in a nanowire without the formation of dislocations that would never be possible to achieve in a planar geometry[8]. This should allow for AlGaN nanowires graded over the entire compositional range, thus taking full advantage of polarization-doping in the III-nitrides.

III-nitride nanowires have been formed using a number of techniques including chemical vapor deposition[9], metalorganic chemical vapor deposition[10, 11], and plasma-assisted molecular beam epitaxy (PAMBE)[12]. In this study, PAMBE is the preferred growth method. III-nitride nanowires grown by PAMBE have previously been shown to have exceptionally high material quality[12]. They also grow on Si(111) substrates, opening the possibility of integrating III-nitride devices with Si based technologies.

As a proof of concept, graded AlGaN nanowire structures will be used to form polarization-induced nanowire light emitting diodes (PINLEDs). These nanowires are designed to emit light in the ultraviolet portion of the electromagnetic spectrum. This specific emission is chosen because UV LEDs currently suffer from low efficiencies because it is difficult to form p-type AlGaN material[13], making this application a good match for using polarization-induced doping. Our efforts in forming PINLEDs have been previous published[14, 15]. The remainder of this text will summarize the key findings in these publications.

Nanowires grown by PAMBE form in a self-assembled process on Si(111) substrates. Growth occurs such that the wurtzite material's c-axis is perpendicular to the Si surface. A scanning electron image of the nanowires on the substrate is shown in Figure 4A. Each of the nanowires consists of two graded sections that sandwich the LED's active region (Fig. 4B). The

bottom graded section starts at GaN and ends with AlN. If one assumes that the nanowires have a Ga-face polarity, this bottom graded layer will be n-type. The next layer is a thin section of GaN. This thin layer forms a quantum well, which serves to trap electrons and holes in the center of the wire so that they can radiatively recombine with one another. Because the quantum well is made from GaN, the light emitted from these devices will have an energy close to 3.4 eV, which corresponds to emission at a wavelength of ~365 nm. After the GaN quantum well, the next layer is graded from AlN to GaN. Again, assuming Ga-face polarity, this top section will be p-type. To reinforce the charge present from the polarization, both the bottom and top layers are doped with appropriate impurities (Si in the base for n-type and Mg in the top for p-type). The grading sections aside, this n-p structure is a classic LED design. To make the as-grown nanowire ensemble into a device, a thin layer of metal is evaporated onto the nanowire tops using standard semiconductor processing techniques, and a second piece of metal is placed on the Si wafer. These two metal pieces act as electrodes to drive a current through the nanowires.

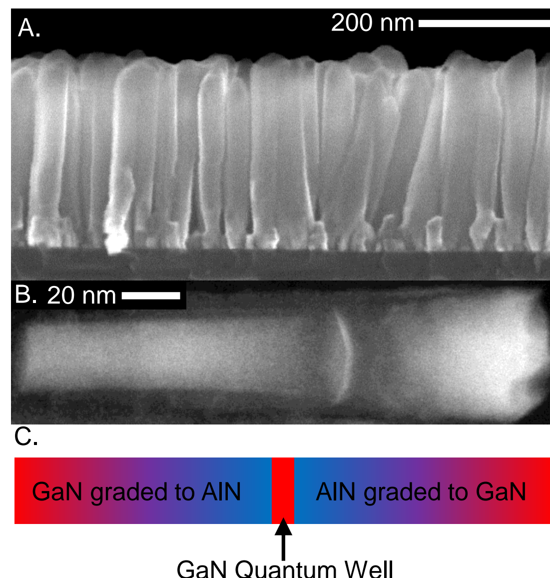

Figure 4 – A.) A scanning electron microscope image of graded AlGaN wires grown on Si(111) substrates. B.) A scanning transmission electron microscopy image of an individual nanowire heterostructure. C.) Schematic showing the nanowire design. Image in B taken by P. J. Phillips, previously published by author in Ref. 14.

The optical characteristics of this device are shown in Figure 5. When a current is driven through the device, light is emitted. This phenomenon is called electroluminescence. The electroluminescence spectra of the device taken at a range of currents shows that as current is increase, more light is emitted (Fig. 5A), which is exactly how an LED should operate. The emission of the nanowires is centered near 365 nm, which corresponds to the correct emission for a GaN quantum well. An example of a PINLED under operation is also provided (Fig. 5A, insert). The round, purple circle corresponds to the area of the nanowires covered with thin metal. Finally, the current density as a function of applied voltage shows normal LED characteristics. The devices are rectifying, meaning that current is only driven in the devices with the correct applied voltage, in this case a positive voltage applied to the nanowire tops. The device turns on at approximately +4 V, which is within the expected range for such devices.

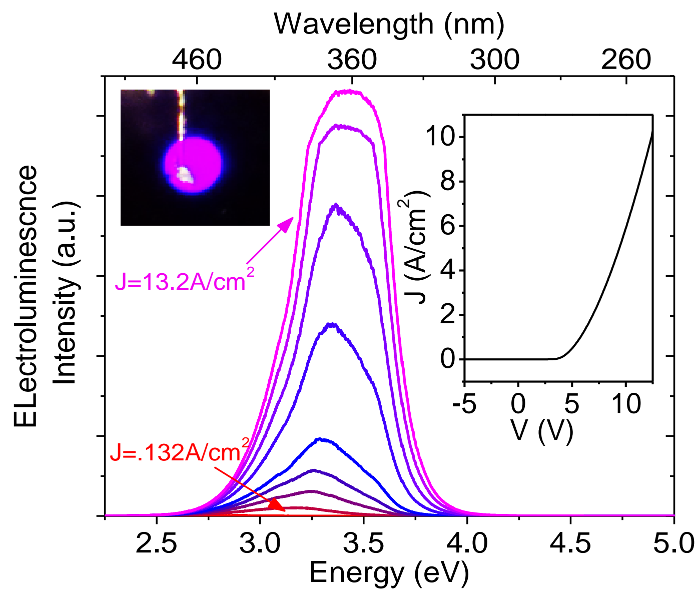

Figure 5 – Electroluminescence a polarization-induced nanowire light emitting diode (PINLEDs) operating under a range of currents. (Inset: Image of an illuminate PINLED). Data previously published by author in Ref. 14.

Based on the results shown in Figure 6, it should be clear that these nanowires operate properly as LEDs. But what evidence do we have that the device is using polarization-induced

doping? After all, as previously mentioned, these nanowires are compositionally graded as well as being impurity doped. To test if the dopants were ionized by thermal energy or by polarization charge, electrical measurements of the device were taken at a range of temperatures from room temperature down to 15K. If the impurities are thermally ionized then the device should show a large change in conductivity at cryogenic temperatures. However, if the dopants are ionized by polarization charge, then there should be a small change in device operation at low temperatures. The results are shown in Figure 6. The current density running through a PINLED device at a constant voltage is shown as a function of temperature. There is virtually no change in device operation even at temperatures as low as 15K. There is some initial drop in current, but this is only by a small amount, from roughly 6 A/cm^2 to 4 A/cm^2. As a comparison, the expected freeze-out for Si and Mg impurities in both GaN and AlN are provided (Fig. 6, dotted lines). The concentrations of electrons and holes due to thermally activated impurities should fall by more than 6 orders of magnitude at cryogenic temperatures. The fact that the current density barely changes in the device measured here is clear evidence that the impurities included in the structure are ionized by polarization charge and not thermal energy. Therefore, these devices do take advantage of polarization-induced doping.

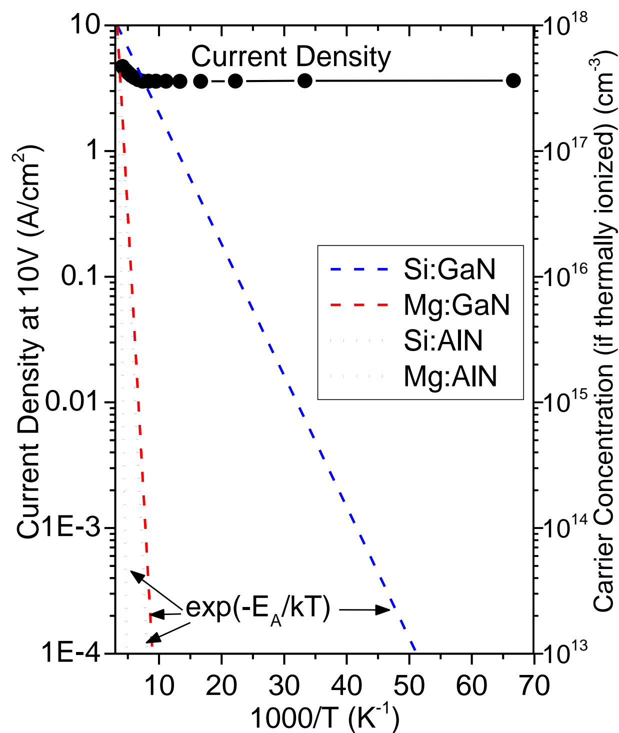

Figure 6 – Current density in a PINLED device as voltage is kept constant at 10V. The temperature dependence of carrier concentration is provided for context. Data previously published by author in Ref. 15.

Finally, a series of samples were grown with different doping schemes to see the effects of removing specific impurities from the device. Samples were grown with the following doping schemes: impurities in both the n- and p-type layers, impurities only in the p-type layer, and no impurities in either. The electroluminescence of these three devices is shown in Figure 7. All three devices provide comparable electroluminescence for low current densities (Fig 7A). At higher currents, the device with impurities in both the n- and p-layers is the brightest. This shows two things. First, it shows that by adding impurities the PINLEDs can become more reliable at higher currents, and therefore have a better chance of being used in commercially available devices. Second, it also shows that it is possible to create p-type material in graded AlGaN nanowires solely through polarization-induced doping. These results provide the first evidence that this is possible. It is also the first ever formation of an LED or p-n diode without the use of

impurity doping. Future work will focus on refining these devices to increase electroluminescence output and push the possibilities of polarization-induced doping further.

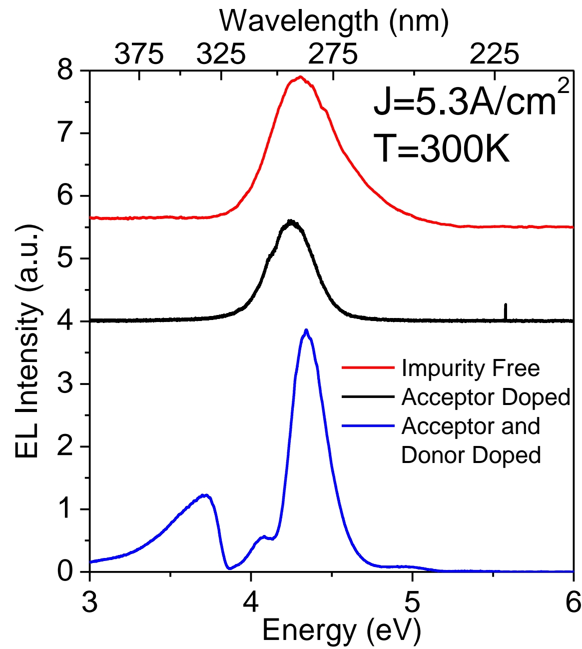

Figure 7 – Electroluminescence characteristics of three PINLED devices with doping in different sections of the nanowires. Data previously published by author in Ref. 14.

To sum, the traditional method for controlling semiconductor conductivity, impurity doping, has been successfully used for many decades. Unfortunately, there is some difficulty when using this technique to control conductivity in wide band gap materials. Polarization-induced doping provides an alternative method to controlling conductivity in many wide band gap materials. There are many benefits to using nanowires instead of planar material to form structures that utilize polarization-induced doping. As a proof of concept we have recently published results showing that is possible to use compositionally graded AlGaN nanowires to form polarization-induced LEDs. Electroluminescent and electrical measurements prove normal device operation, while variable temperature electrical measurements show that impurities in the devices are ionized by the presence of polarization-induced charge and not by thermal energy.

Finally, it is even possible to fabricate working LEDs from graded nanowires that do not include impurity dopants. Polarization-induced doping should open up many new possibilities for device designers, and could play a major role in the future of semiconductor-based devices.

References

[1] J. Ibbetson, P. Fini, K. Ness, S. DenBaars, J. Speck and U. Mishra, "Polarization effects, surface states, and the source of electrons in AlGaN/GaN heterostructure field effect transistors," *Appl. Phys. Lett.,* vol. 77, pp. 250-252, JUL 10, 2000.

[2] M. Khan, A. Bhattarai, J. Kuznia and D. Olson, "High-Electron-Mobility Transistor Based on a Gan-Alxga1-Xn Heterojunction," *Appl. Phys. Lett.,* vol. 63, pp. 1214-1215, Aug 30, 1993.

[3] D. Jena, S. Heikman, D. Green, D. Buttari, R. Coffie, H. Xing, S. Keller, S. DenBaars, J. S. Speck, U. K. Mishra and I. Smorchkova, "Realization of wide electron slabs by polarization bulk doping in graded III-V nitride semiconductor alloys," *Appl. Phys. Lett.,* vol. 81, pp. 4395-4397, DEC 2 2002, 2002.

[4] J. Simon, V. Protasenko, C. Lian, H. Xing and D. Jena, "Polarization-Induced Hole Doping in Wide-Band-Gap Uniaxial Semiconductor Heterostructures," *Science,* vol. 327, pp. 60-64, JAN 1, 2010.

[5] S. Li, T. Zhang, J. Wu, Y. Yang, Z. Wang, Z. Wu, Z. Chen and Y. Jiang, "Polarization induced hole doping in graded AlxGa1-xN (x=0.7 similar to 1) layer grown by molecular beam epitaxy," *Appl. Phys. Lett.,* vol. 102, pp. 062108, FEB 11, 2013.

[6] S. Li, M. Ware, J. Wu, P. Minor, Z. Wang, Z. Wu, Y. Jiang and G. J. Salamo, "Polarization induced pn-junction without dopant in graded AlGaN coherently strained on GaN," *Appl. Phys. Lett.,* vol. 101, pp. 122103, SEP 17, 2012.

[7] N. Thillosen, K. Sebald, H. Hardtdegen, R. Meijers, R. Calarco, S. Montanari, N. Kaluza, J. Gutowski and H. Luth, "The state of strain in single GaN nanocolumns as derived from micro-photoluminescence measurements," *Nano Letters,* vol. 6, pp. 704-708, APR, 2006.

[8] S. D. Carnevale, J. Yang, P. J. Phillips, M. J. Mills and R. C. Myers, "Three-Dimensional GaN/AIN Nanowire Heterostructures by Separating Nucleation and Growth Processes," *Nano Lett.,* vol. 11, pp. 866-871, FEB, 2011.

[9] H. J. Choi, J. C. Johnson, R. R. He, S. K. Lee, F. Kim, P. Pauzauskie, J. Goldberger, R. J. Saykally and P. D. Yang, "Self-organized GaN quantum wire UV lasers," *J Phys Chem B,* vol. 107, pp. 8721-8725, AUG 28, 2003.

[10] Y. J. Dong, B. Z. Tian, T. J. Kempa and C. M. Lieber, "Coaxial Group III-Nitride Nanowire Photovoltaics," *Nano Letters,* vol. 9, pp. 2183-2187, 2009.

[11] F. Qian, S. Gradecak, Y. Li, C. Wen and C. Lieber, "Core/multishell nanowire heterostructures as multicolor, high-efficiency light-emitting diodes," *Nano Lett.,* vol. 5, pp. 2287-2291, NOV, 2005.

[12] K. A. Bertness, N. A. Sanford and A. V. Davydov, "GaN Nanowires Grown by Molecular Beam Epitaxy," *IEEE J. Sel. Top. Quantum Electron.,* vol. 17, pp. 847-858, JUL-AUG, 2011.

[13] A. Khan, K. Balakrishnan and T. Katona, "Ultraviolet light-emitting diodes based on group three nitrides," *Nat. Photonics,* vol. 2, pp. 77-84, FEB, 2008.

[14] S. D. Carnevale, T. F. Kent, P. J. Phillips, M. J. Mills, S. Rajan and R. C. Myers, "Polarization-Induced pn Diodes in Wide-Band-Gap Nanowires with Ultraviolet Electroluminescence," *Nano Letters,* vol. 12, pp. 915-920, FEB 2012, 2012.

[15] S. D. Carnevale, T. F. Kent, P. J. Phillips, A. T. M. G. Sarwar, R. F. Klie, S. Rajan and R. C. Myers, "Graded nanowire ultraviolet LEDs by polarization engineering," *Proc. SPIE,* vol. 8467, pp. 84670L-1-84670L-11, October 11, 2012.