Fabrication of Diamond Ultraviolet Light Emitting Diodes

Janay Frazier
Optical Engineering, Norfolk State University

NNIN REU Site: Howard Nanoscale Science and Engineering Facility, Howard University, Washington, DC
NNIN REU Principal Investigator: Dr. Gary Harris, Howard Nanoscale Science and Engineering Facility, Howard University, Washington DC
NNIN REU Mentor: James Griffin, Howard Nanoscale Science and Engineering Facility, Howard University
Contact: j.a.frazier@spartans.nsu.edu, gharris1124@gmail.com, jagriffin@howard.edu

Abstract:

Ultraviolet light emitting diodes (UV LEDs) have been used in a variety of applications and as a result are becoming cheaper to fabricate. LED products have reached 12 watts at 914 amperes. Initial UV LEDs were fabricated with GaN films grown on sapphire substrates. The main disadvantage of this fabrication technology is the difficulty in growing high quality GaN films on sapphire because of the large lattice mismatch. Diamond has a wide energy band gap of 5.47 eV, which makes it attractive for opto-electrical applications. Its high thermal conductivity makes it an excellent material for UV LED fabrication. In this work, diamond UV LEDs were fabricated by growing high-quality diamond films on silicon and silicon carbide (SiC) substrates by hot filament chemical vapor deposition (HFCVD). Methane was used as the carbon source gas with solid source boron used as the p-type dopant and N used as the n-type dopant. Hall measurements confirmed a hole concentration of approximately 3 × 10^{19} cm^{-3}, a carrier mobility of 73 cm^2/V-sec, and a resistivity of 5 × 10^{-3} Ω-cm.

Introduction:

Light emitting diodes are semiconductor light sources that are fabricated from a p-n junction that emits light when activated. When a suitable voltage is applied to the contacts, free electrons recombine with holes within the device. Once recombination happens, photons are emitted as a function of the bandgap energy of the semiconductor material.

The objectives of this work were to grow high quality diamond films on silicon and silicon carbide substrates, dope the diamond films with boron (p-type) and nitrogen (n-type) dopants, and characterize the diamond epitaxial films by Raman spectroscopy, scanning electron microscopy, Hall effect measurements, and current-voltage (I-V) measurements. The final objective was to fabricate ultraviolet light emitting diodes by photolithography.

The semiconductor material used for the fabrication of the ultraviolet light emitting diodes was diamond. Diamond behaves as an insulating material as a result of its covalent carbon bonds but can be rendered electrically conductive by doping.

Methodology:

To grow diamond heteroepitaxially, wafers must be seeded with nanodiamond slurry or “Opalseed” mixture. This process was done by placing the wafers in a 1:1 ratio mixture of nanodiamond slurry and methanol, and sonicated for 10 minutes for nanodiamond adhesion. After rinsing with methanol, the wafers were blow-dried with nitrogen gas. The samples were then loaded into the HFCVD reactor for growth. Growth conditions were as follows: hydrogen and methane flow rates of 80 sccm and 1 sccm respectively, growth pressure of 20 torr and a substrate temperature of 750°C. These conditions yielded a growth rate of about 0.16 µm/hr. P-type doping of diamond was accomplished by placing a piece of 99.7% boron in the center of the substrate holder and very close to the hot filaments (1-2 mm) during growth. N-type doping was performed by introducing nitrogen-15 gas into the chamber during growth at an elevated substrate temperature (>>750°C).

Results:

Current-voltage measurements on unannealed titanium-gold contacts on diamond revealed ohmic behavior indicating degenerate boron doping, see Figure 1. Hall measurements on boron doped diamond yielded a mobility, resistivity and carrier concentration of 73 cm^2/V-s, 5 × 10^{-3} Ω-cm, and 3 × 10^{19} cm^{-3} respectively. Raman spectroscopy measurements of undoped diamond indicated a sharp intense peak at 1333 cm^{-1} while the boron doped diamond indicated a less intense 1333 cm^{-1} peak and a broad intense peak at 1219 cm^{-1}, shown in Figure 2, characteristic of heavy boron doping [1].
Nitrogen doping to produce n-type diamond was not successful. Previous work [2] had indicated that nitrogen doping in diamond produces defects that trap free carriers and produces insulating diamond. The incorporation of nitrogen-15 and growth at an elevated substrate temperature did not change the outcome. Therefore no p-n junction was created within the final device structure due to a lack of n-type carriers.

**Conclusions:**

High quality diamond films were grown by HFCVD and doped with boron. Hall effect measurements and Raman spectroscopy verified the presence of boron doping at very high concentrations (greater than $3 \times 10^{19}$ cm$^{-3}$). While nitrogen doping to produce n-type carriers in diamond proved unsuccessful, there are a number of elements in groups V and VI of the periodic table that may prove effective as an n-type dopant in HFCVD, with phosphorus as the leading candidate. Once the n-type doping problem is solved, fabrication of ultraviolet light emitting diodes should be straightforward. Growth of polycrystalline diamond on silicon and silicon carbide may prove detrimental to device performance. Therefore growth of diamond on diamond substrates is preferable, even with their small size and large cost.

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**References:**
