Diamond p-i-n-nanoC Diodes forElectron Emitters

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Abstract: *Electron emitters are widely deployed in traveling wavetubes (TWTs) for communications, radar applications, and scientific apparatus like free electron lasers. These instruments typically utilize cathodes that release an electron current through application of thermal energy or high electric fields. A novel electron emitter approach exploits the negative electron affinity surface of diamond in a modified semiconductor p-i-n diode. Under a forward bias electrons are injected into the conduction band of the diamond diode and a fraction are emitted into vacuum. Electron emission occurs at room temperature and low electric fields. We have prepared a modified diamond p-i-n diode that included a highly conducting nanostructured carbon (nanoC) contact layer utilizing plasma-enhanced chemical vapor deposition (PECVD) on a single crystal boron doped substrate. Emitter devices with various geometries were then fabricated using photo-lithography. After a hydrogen passivation step individual devices were characterized in vacuum. Under a forward bias the p-i-n-nanoC diodes displayed light emission indicative of bipolar transport. With a typical diode current of 0.1A an electron emission current approaching 0.4mA was measured from a single device sized 1.2mm x 0.2mm.*

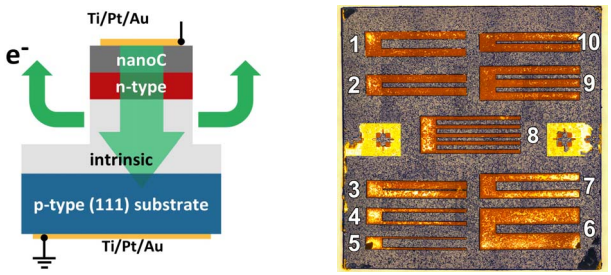
Keywords:diamond; plasma-enhanced chemical vapor deposition; electronic material; doping; electron emission

Introduction

Electron sources are a key component for a wide range of applications including telecommunications, radar and analysis instruments like x-rays and free electron lasers [1].The typical electron source for these devices presents a thermionic electron emitter. Its electron emission is governed by the law of Richardson-Dushman that describes the emission current as a function of emitter temperature and thermal emission barrier, i.e. work function. To establish a significant emission current requires an emitter with low work function and its operation at elevated temperatures. Diamond has long been investigated for electron emission applications as its surfaces can attain negative electron affinity (NEA) characteristics for which the vacuum level is shifted below the conduction band minimum (CBM), thus, eliminating a surface barrier for electron emission [2]. A diamond device configuration can be conceived in the form of a p-i-n diode that would allow injection of electrons into the conduction band (CBM) from where a fraction can be released through the NEA surface [3]. We present electron emission results from a modified diamond p-i-n diode that utilizes a nitrogen doped highly conducting nanostructured carbon (nanoC) contact layer.

Experimental

Plasma-enhanced CVD of diamond p-i-n-nanoC diodes: Diamond p-i-n-nanoC diodes were prepared on a (111) surface oriented single crystal, boron doped (p-type) substrate sized 3mm x 3mm x 0.25mm. Secondary ion mass spectroscopy (SIMS) of the substrate measured a boron concentration $>1x10^{20}cm^{-3}$. Prior to diamond deposition the substrate was cleaned by a wet-chemical process including a boil in $H_2SO_4/H_2O_2/H_2O$, 3:1:1, at 220°C for 15 min followed by an HF treatment for 5 min and a final boil in $NH_4OH/H_2O_2/H_2O$, 1:1:5, at 75°C for 15 min. After each step the substrate was rinsed with DI water. The sample was then loaded into a plasma-enhanced CVD system based on an ASTeX AX5250 reactor that is solely used for intrinsic diamond growth with a base pressure in the low 10^{-8}Torr range through oil-free pumping. Prior to diamond deposition the substrate was exposed to a pure hydrogen plasma at a hydrogen flow rate of 400sccm and substrate temperature of about 750°C. Intrinsic diamond growth commenced under the addition of methane (7sccm) and oxygen (0.75sccm) at a total gas flow rate of 400sccm. At a chamber pressure of 60Torr and a microwave power of 1050W, a substrate temperature of ~900°C was recorded by a dual-wavelength optical pyrometer. Its interference signal allowed in situ thickness monitoring during film growth with a final thickness of about 10μm. The n-type diamond layer was grown in a dedicated plasma-enhanced CVD reactor that utilized a 200ppm trimethylphosphine (TMP) in hydrogen gas mixture. A similar hydrogen plasma surface cleaning process initiated the n-layer growth that commenced by introduction of 60sccm TMP/H_2, 0.5sccm methane and hydrogen carrier gas establishing a total gas flow rate of 400sccm. With a microwave power of 2000W and a chamber pressure of 62Torr, a substrate temperature of ~850°C was measured. The thickness of the phosphorus doped diamond layer was about 300nm. SIMS of similar films communicated a phosphorus doping concentration of $\sim3x10^{19}cm^{-3}$. The final layer presented a nitrogen doped nanostructured carbon layer that was grown in a plasma-enhanced CVD system utilizing 100sccm of nitrogen, 20sccm of methane, 10sccm of argon and 5sccm of hydrogen. At a chamber pressure of 20Torr and microwave power of 900W, a temperature of ~900°C was recorded. The final thickness of this nanostructured carbon (nanoC) layer was about 200nm. The nitrogen incorporation of similar films was measured by SIMS to $\sim3x10^{21}cm^{-3}$. This layered structure, shown schematically in Figure 1, was then processed by photo-lithography to prepare various emitter geometries as displayed in Figure 1(b).



(a) (b)

Fig. 1. (a) Schematic of the diamond p-i-n-nanoC diode and (b) top view of the diamond device die (3mm x 3mm) with various emitter geometries where the Ti/Pt/Au contact to the nanoC layer is visible.

*Device processing:*Various device geometries (see Figure 1(b)) were etched utilizing an aluminum hard mask and O_2/SF_6 plasma with a final mesa depth of 7µm. Electrical contacts to the nanoC layer and the backside of the boron doped substrate were deposited by e-beam evaporation using Ti/Pt/Au metallurgy with thicknesses of 50nm/50nm/300nm, respectively. The final stage in device processing presented exposure of the patterned diamond die to a hydrogen plasma for 5min at a temperature of 850°C. The hydrogen passivated die was then loaded into the characterization chamber with a base pressure of ~$5x10^{-9}$Torr. Adsorbates were desorbed in an annealing step at about 600°C for 15min and after cool-down to room temperature electrical characterization commenced.

Results and Discussion

Electrical contact to individual devices was established through a gold plated tungsten probe and each device was characterized in an I/V sweep with results shown in Figure 2.

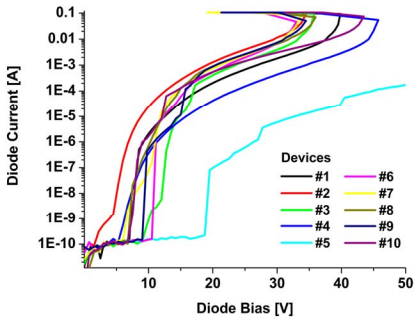
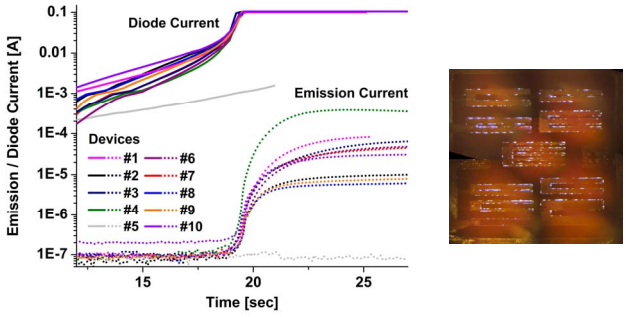


Fig. 2. I/V characteristics of all p-i-n-nanoC diodes from the device die shown in Figure 1(b).

The devices exhibited a turn on ranging from 5-10V and the maximum diode current of 0.1A was limited by the source-measure unit. In a next step an electron collector was positioned about 500µm above each device center and biased at 500V. Individual diodes were successively biased in forward direction ranging from 0-50V and the time dependent emission current for each device recorded as shown in Figure 3(a). Upon diode operation light emission was observed from each device (see Figure 3(b)) which was attributed to exciton generation. Recombination of excitons with transverse-optical (TO) phonons results in deep UV emission around 240nm and broader emission around 350nm and 500nm due to defects and nitrogen impurities [4]. The non-uniform emission was attributed to the reduced thickness of the nanoC layer (200nm) and the phosphorus-doped diamond layer (300nm).



(a) (b)

Fig. 3. Electron emissioncharacterization of devices shown in Figure 1. (a) The solid lines present the diode forward current and the emission current is shown by the dotted lines. (b) Individual diodes under forward bias display light emission.

A closer investigation of the emission characteristics indicated the presence of a diode current threshold of about 0.05A after which the emission current sharply increased. For diode #4 with a finger width of 50µm, the emission current approached 0.4mA at a current density of 71A/cm^2. The reduced emission current from other diode structures was attributed in part to the increased finger width of 100µm and the reduced current density ranging from 1.8-43A/cm^2. This suggests an optimization prospect through emitter geometry including intrinsic layer thickness and mesa depth. Optimization of the n-layer and nanoC layer thicknesses and their doping concentrations should further provide an increased diode and emission current.

Acknowledgements

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