Heavily phosphorus-doped nano-crystalline diamond electrode for thermionic emission application

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Abstract

Thermionic energy conversion is one of the promising technologies for transforming thermal energy into electrical energy. A stable cathode electrode with high conductivity and low work function is required to realize this application. It is already well known that hydrogen-terminated diamond exhibits negative electron affinity, which is a great advantage of an electron emission electrode. In this study, we focus on phosphorus doping, which gives n-type donors with 0.57 eV in single crystal diamond to control the conductivity of diamond, in an attempt to develop a nano-crystalline diamond (NCD) electrode for thermionic emission by heavily phosphorus doping. Phosphorus concentration and structural characterization were performed by secondary ion mass spectroscopy and Raman spectroscopy, respectively. The thermionic emission properties were characterized in vacuum as a function of cathode temperature from 300 to 600 °C. The work function of heavily phosphorus-doped NCD electrode was estimated based on the Richardson-Dushman equation, and the effect of heavily phosphorus doping on thermionic emission was briefly discussed.

1. Introduction

Thermionic energy conversion, which can directly convert heat energy into electricity, is one of the most promising technologies for waste heat recovery applications [1-9]. It is expected reutilize unused thermal energy such as exhaust from industrial plants, automobiles, and renewable resources such as geothermal and hot spring resources. This energy conversion system consists of a hot cathode emitter and cooler anode collector separated by a vacuum gap. When the electrons in the cathode have sufficient thermal energy to overcome the material's work function, they can emit into a vacuum. This electron emission is the force driving this energy conversion, and provides electricity when the system is connected to a certain load. The current density of this thermionic emission is expressed by the Richardson-Dushman equation mainly using the material work function, temperature, Richardson constant, etc. In order to realize a thermionic energy converter, a lower work function cathode electrode with lower resistivity is required for efficient electron emissions [2,4].

The concept of thermionic energy conversion was proposed in the 1950s by both NASA and the Soviet space program. The experimental conversion efficiencies eventually reached around 10-15 % [1,2], when the emitter electrode was heated up to 1260°C with Cs⁺ ions vapor to lower the work function. The space charge cloud on the emitter electrode is one major obstacle preventing the next electron emission. The gate electric that applies a magnetic field along the electron trajectory suppresses this space charge cloud and can improve the conversion efficiency [4]. The photon excitation also assists the thermionic emission, enhancing the efficiency up to 40% according to a theoretical calculation [6,7]. The thermionic energy convertor, however, has not yet been commercialized because of this high temperature operation. An electrode with lower work function is required to overcome this high temperature issue,.

The negative electron affinity (NEA) of hydrogenated diamond surface is very promising for

electron emission applications [10-14]. Impurity doped nano-crystalline diamond (NCD) film is one of the candidates for this cathode. For example, nitrogen-doped NCD films have shown good thermionic emission properties of several mA/cm² at 500 °C with a work function of 1.4 eV, and demonstrated thermionic energy conversion at 500 °C [3,12]. Several groups have reported on phosphorus doping in NCD film. A phosphorus impurity can also be incorporated into the substitution site in NCD film, which was identified by phosphorus bound exciton emission of cathodoluminescence study [15]. A lower work function around 0.6 eV on phosphorus-doped diamond has been reported, while its thermionic emission property is far behind that of nitrogen-doped NCD film [13]. A possible reason for this could be an insufficient phosphorus doping level of around 10¹⁹ cm⁻³.

In this study, we focus on heavily phosphorus-doped NCD film, and investigate its potential as a thermionic emission electrode. The initial substrate seeding process and doping conditions were optimized for heavy doping with phosphorus concentration over 10²⁰ cm⁻³. The improved emission property, which is comparable to the reported nitrogen-doped NCD film, was obtained, and the effect of heavily phosphorus doping on thermionic electron emission was briefly discussed.

2. Experimental procedures

Phosphorus-doped NCD films were grown by plasma-enhanced chemical vapor deposition (CVD) using hydrogen, methane, and phosphine gas mixtures. The microwave power, stage temperature, pressure, CH₄/H₂ flow ratio, and PH₃/CH₄ flow ratio were 750 W, 900 °C, 25 Torr, 1 %, 100 %, respectively. Substrates used were n-type silicon, molybdenum, and SiO₂ insulating plats. In our CVD reactor, NCD films up to 2 inch size in diameter can be grown. Before CVD growth, each substrate was treated by nano-diamond colloidal solution with sonic wave, followed by rinse process with deionized water, and then installed in the CVD reactor. The average particle size of

nano-diamond colloid is around 3-6 nm and this solution has long term stability. This is a promising method of achieving high density nano-diamond seeding on the substrate.

The surface morphology was observed by differential microscopy with a Nomarski prism and atomic force microscope (AFM) using contact mode with SiN cantilever. The incorporation of impurity atoms was evaluated using secondary ion mass spectroscopy (SIMS). Cs⁺ accelerated at 14.5 keV was used as the primary ions, and the impurity concentration of phosphorus and hydrogen atoms was quantified using implanted standard samples with the accuracy around 40 %. The structural characterization was performed by Raman spectroscopy with a green laser of 532 nm at room temperature. Electrical properties of grown phosphorus-doped diamond films were measured by four probe methods as a function of temperature from room temperature to 600 °C. Ti (50 nm) / Pt (50 nm) / Au (150 nm) contacts were deposited on the diamond by electron-beam evaporation followed by thermal annealing in Ar atmosphere at 420 °C for 30 min.

Thermionic electron emission measurements were conducted in a UHV system with a base pressure $< 2 \times 10^{-8}$ Torr. Before the emission measurements, the samples were again exposed to hydrogen plasma to obtain their NEA property on a doped diamond surface. The diamond emitters were mounted on a sample stage with a radiation heater. The emitter and molybdenum collector were separated by an Al₂O₃ spacer with 300 μm gap in a vacuum. The emission current was measured by a Keithley 4200-SCS source-measurement unit.

3. Results and discussion

Figure 1 shows surface images of phosphorus-doped NCD films grown on a silicon wafer with a diameter of 1 inch (a), molybdenum substrate with a size of 14 mm square (b), and SiO₂ insulating substrate with a size of 10 mm square (c). The films are homogeneous, smooth, and transparent. As shown in Fig. 2, typical surface roughness of phosphorus-doped NCD films grown on the silicon

wafer was RMS of 9 nm with thickness around 250 nm. The grain size is 20-80 nm, while the preferential facet structure cannot clearly be obtained.

Figure 3 shows the typical SIMS profile of grown phosphorus-doped NCD film. The solid curve clearly indicates that the phosphorus atoms are incorporated into the film with uniform depth distribution. The maximum concentration successfully reached around $5 \times 10^{20} \text{ cm}^{-3}$. The broken curve indicates the data for silicon atoms, and its intensity goes down to the background level in the film region, indicating that the film is dense enough without any pin holes. Boron atoms were also the back ground level of the SIMS measurements, while large amounts of hydrogen over 10^{21} cm^{-3} were detected in the film. This could be due to the effect of heavy doping as well as grain boundaries in a typical NCD film [16]. Details are still under investigation.

The film structure was characterized by Raman spectroscopy using a 532 nm green laser. The laser spot diameter was 1 μm . As shown in Fig. 4, the peaks consist mainly of three components, which are typically observed in impurity doped NCD films. The first one is a sharp sp^3 peak around 1332 cm^{-1} related to diamond structure, the second is a small shoulder around 1350 cm^{-1} related to D-band due to a disordered graphite component, and the third is broad peak around 1650 cm^{-1} related to G-band due to a graphite component. No big difference can be obtained between the center and edge parts of the sample, indicating that structure components are almost homogeneous in structure.

Figure 5 shows the change of resistivity measured by the four probe method as a function of temperature from room temperature to 600 °C. The resistivity decreases down to be 0.5 Ωcm with an increase in the measurement temperature. The activation energy estimated from the slop of this Arrhenius plot is around 50 meV. Non-metallic property can be obtained even in such heavily phosphorus concentration of $5 \times 10^{20} \text{ cm}^{-3}$.

Figure 6 shows the thermionic emission properties of typical heavily phosphorus-doped NCD film

as a function of hot cathode temperature from 300 to 600 °C. The cathode of phosphorus-doped NCD film and anode Mo electrode were separated by a vacuum gap with insulating Al_2O_3 spacer of 300 μm . These spacers don't touch the surface of phosphorus-doped NCD emitter as shown in insert schematic of Fig.6. The thermionic electron emission starts around 2 V, and saturates around 6 V in every temperature condition. The saturation current density increases with an increase in the cathode temperature. The maximum current density of 8 mA/cm^2 is obtained at 600 °C, which is comparable to that of the reported nitrogen-doped NCD film. The thermionic emission current was only observed from hydrogen-terminated surface. The reproducibility of these emissions has been confirmed in the present temperature range, indicating that the hydrogen termination on phosphorous-doped NCD can survive at around 600 °C.

From the least square fittings to the data using Richardson-Dushman equation as shown in Fig.7, the work-function and Richardson constant of heavily phosphorus-doped NCD film are estimated to be 2.3 eV and around 15 $\text{A}/\text{cm}^2\text{K}^2$, respectively. This estimation is quite reasonable in the present setup, in which the anode electrode is Mo metal with work function of typically 4.3 eV. The flat band condition of this configuration is around 2 V. The thermionic emission should start at 2 V, which is in good agreement with the experimental result as shown in Fig.6.

Generally, the surface of phosphorus-doped diamond has a large number of surface states, which cause strong upward band bending at the diamond surface. This band bending prevents electron emission into the vacuum even in the case of NEA [17]. The trend is consistent with Ohmic contact issue in n-type diamond with large barrier height of 4.3eV. The phosphorus doping itself cannot modify surface states, but can reduce the space charge width of a band bending surface. This narrowing of space charge width leads electrons effectively to the top surface of phosphorus-doped diamond, and the thermionic emission property can be improved by heavy doping. In the present study, the simple hydrogenated diamond surface was used for characterizations, while further

enhancement would be expected by a modified surface with a strong NEA property such as Li-O, Mg, etc [18,19].

4. Summary

Heavily phosphorus-doped NCD diamond films were grown by plasma-enhanced chemical vapor deposition for thermionic emission cathode. The phosphorus atoms of $5 \times 10^{20} \text{ cm}^{-3}$ were successfully incorporated into films when the gas flow ratio of phosphine and methane was 1. It was confirmed that the grown phosphorus-doped diamond films have a typical NCD structure with a combination of sp^3 diamond grains and sp^2 graphitic grain boundaries. Thermionic emission properties were measured in a vacuum as a function of temperature from 300 to 600 °C. The maximum current density was recorded as 8 mA/cm² at 600 °C, which is a value comparable to that of the reported nitrogen-doped NCD film. From the least-squares fitting to the data using Richardson-Dushman equation, the work function and Richardson constant of heavily phosphorus-doped diamond are estimated to be 2.3eV and 15 A/cm²/K², respectively. The results clearly indicate that the heavily phosphorus-doped NCD film is also a strong candidate for thermionic emission applications.

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Figure captions

Figures 1 Photographs obtained for heavily phosphorus-doped nano-crystalline diamond film grown on three types of substrate. (a) silicon substrate with a diameter of 1 inch, (b) molybdenum substrate with a size of 14 mm square, (c) SiO₂ insulating substrate with a size of 10 mm square.

Figure 2 AFM image obtained for heavily phosphorus-doped nano-crystalline diamond film grown on Si substrate. The image was observed using contact mode with SiN cantilever. The scan area is 5 × 5 μm.

Figure 3 Impurity depth profile of heavily phosphorus doped nano-crystalline diamond film grown on Si substrate. Solid and broken curves indicate the data for phosphorus and silicon, respectively. The phosphorus concentration was quantified using implanted standard sample.

Figure 4 Raman spectra obtained for heavily phosphorus-doped nano-crystalline diamond film grown on Si substrate. (a) center, (b) edge. Excitation wavelength is 532 nm.

Figure 5 Change of resistivity measured by the four probe method as a function of temperature from room temperature to 600 °C.

Figure 6 Thermionic electron emission properties as a function of operation temperature from 300 to 600 °C obtained for heavily phosphorus-doped nano-crystalline diamond film grown on Mo substrate. The insert figure indicates the schematic description of measurement setup for thermionic emission current.

Figure 7 Arrhenius plot of thermionic emission property obtained for heavily phosphorus-doped nano-crystalline diamond film grown on Mo substrate. From least-squares fitting to the data using Richardson-Dushman equation, the work function and Richardson-Dushman constant are estimated to be 2.3 eV and $15 \text{ A/cm}^2/\text{K}^2$, respectively.

Figures 1 (Diamond and Related Materials, Hiromitsu Kato)

Figure 2 (Diamond and Related Materials, Hiromitsu Kato)

Figure 3 (Diamond and Related Materials, Hiromitsu Kato)

Figure 4 (Diamond and Related Materials, Hiromitsu Kato)

Figure 5 (Diamond and Related Materials, Hiromitsu Kato)

Figure 6 (Diamond and Related Materials, Hiromitsu Kato)

Figure 7 (Diamond and Related Materials, Hiromitsu Kato)