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Fabrication and Properties of *a*-C:H/Boron-Doped Diamond Structure

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The fundamental regions of photovoltaic conversion from each band gap are considered ultraviolet light on diamond and visible light on amorphous carbon. This difference suggests that the cell that forms electric junctions using both materials shows photovoltaic efficiency under ultraviolet light and visible light. A photovoltaic cell with a hydrogenated amorphous carbon (*a*-C:H) film deposited on a boron-doped diamond layer was fabricated to confirm this suggestion. The *a*-C:H film was deposited by radio-frequency plasma-enhanced chemical vapor deposition (RF-CVD) on heavily boron-doped diamond, which was homoepitaxially grown by microwave plasma CVD on single-crystal diamond. The photovoltaic characteristics of the cell were obtained using xenon lamp irradiation and a UV filter. The open-circuit voltage and short-circuit current of the cell without the UV filter were –62 mV and 17.7 nA, respectively. The open-circuit voltage and short-circuit current decreased with insertion of the UV filter between the cell and the lamp. These results indicate that the photovoltaic effect of an *a*-C:H/boron-doped diamond cell can produce not only visible light but also UV light.

1. Introduction

Diamond as a wide-band-gap material is important for the development of ultraviolet (UV) detector devices. Polyakov *et al*. reported the photovoltaic characteristics of a UV detector formed by two opposing saw-patterned nickel electrodes on diamond.(1,2) The sensitivity of this diamond UV detector under UV light irradiation is 10^4 times higher than that under visible light irradiation. Koide *et al.* reported a Schottky photodiode formed using boron-doped diamond and tungsten carbide electrodes.(3) The device shows high sensitivity under deep-UV light irradiation. These reports on diamond

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photodetectors focused on wavelengths shorter than that of UV, because the band gap of diamond is 5.5 eV. In visible light irradiation, the photoelectromotive force of a cell made of only diamond is difficult to observe.

A few reports of photoelectric conversion in visible light have shown the photovoltaic capability of a *p*-*n* junction device whose narrow-band-gap material was deposited on diamond. Huth *et al*. used a cadmium telluride layer (band gap = 1.44 eV) to control conversion characteristics.(4) In their report, the *p*-*n* heterojunction consisted of diamond as a *p*-type layer and cadmium telluride as an *n*-type layer. The open-circuit voltage and short-circuit current under visible light irradiation were 0.23 V and 1.54 mA/cm^2, respectively. In these previous reports, it has been suggested that a device formed by a narrow-band-gap material and diamond can generate photoelectromotive force under visible light.

The band gap of amorphous carbon (*a*-C) films is determined by the sp^2 bonded carbon concentration from 0.8 eV of visible light to 3.0 eV of the near-UV region.(5) *a*-C films are highly chemically inert and nontoxic compared with cadmium telluride. Hence, devices that use *a*-C films deposited on diamond have potential for the development of photovoltaic cells for wide-range photovoltaic conversion. In this study, a hydrogenated amorphous carbon (*a*-C:H) film/boron-doped diamond multilayer cell was fabricated, and its photovoltaic characteristics were investigated.

2. Experimental Methods

The substrate used was single-crystal diamond (1.5 mm×2.0 mm×0.3 mm) synthesized by a high-pressure high-temperature method. The boron-doped diamond film used as the first layer was homoepitaxially grown by microwave-plasma-assisted chemical vapor deposition (MW-CVD) with methane (CH_4), hydrogen (H_2), and diborane (B_2H_6) on the diamond substrate.(6,7) Details of the MW-CVD system have been described elsewhere.(7–10) The *a*-C:H film used as the second layer was deposited on the boron-doped diamond layer and *p*-Si by radio-frequency plasma-enhanced CVD (RF-CVD). Pressure was controlled at 10 Pa, and RF power was kept at 80 W. The plasma gas and carbon source used were argon (Ar) and pure methane, respectively. Gas flow rate was maintained at 50 cm^3/min during the deposition. The distance from the substrate to the anode was kept at approximately 10 cm. The thickness of the *a*-C:H film was maintained at 200 nm to prevent direct electric contact between the boron-doped diamond and the electrode on the *a*-C:H film, because the surface roughness of boron-doped diamond was $R_a = 70$ nm.

The structures of the boron-doped diamond and *a*-C:H film were investigated. The structure of the *a*-C:H film was examined using a Fourier-transform infrared (FT-IR) spectrometer and a Raman scattering spectrometer. Raman spectra were obtained in the backscattering mode using an SHG-YVO_4 laser operating at a 532 nm wavelength. The optical band gap of the *a*-C:H film was estimated by ultraviolet-visible (UV/VIS) spectroscopy. The optical band gap E_{04} was considered to be the photon energy corresponding to an absorption coefficient of 10^4 cm^{-1} from UV/VIS spectra. The current-voltage (I-V) characteristics of the *a*-C:H film/ boron-doped diamond cell were investigated using a high-resistance meter and a digital direct-current power source.

Silver electrodes as extraction electrodes were deposited on the boron-doped diamond and *a*-C:H film surfaces by sputtering deposition, as shown in Fig. 1. A xenon (Xe) discharge lamp was used as a light source to illuminate the cell. Figure 2 shows the intensity of each wavelength of the Xe lamp. A polymer sheet as a UV filter was placed in front of the lamp during the I-V characteristic measurement under the condition without UV irradiation. The polymer sheet was removed during the irradiation with UV light and visible light. The cell holder was cooled by water flow to maintain temperature during the measurement.

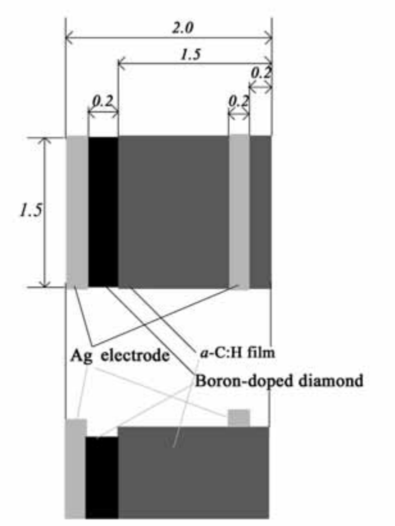

Fig. 1. Electrode pattern of *a*-C:H /boron-doped diamond photovoltaic cell.

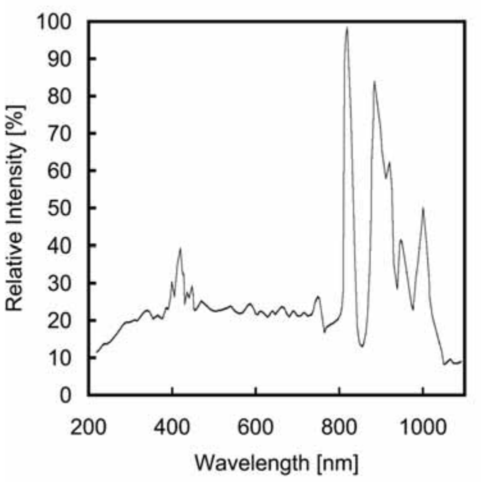

Fig. 2. Relative intensity of Xe lamp as a function of wavelength.

3. Results

Figure 3 shows the Raman spectra of the diamond substrate, boron-doped diamond and *a*-C:H film. The Raman spectrum of the diamond substrate shows a single sharp peak that can be assigned to the T_{2g} zone center phonon line from the diamond structure at 1332 cm^{-1}. The Raman spectrum of the epitaxial boron-doped diamond shows two broad peaks and one sharp peak. The positions of these three peaks were similar to those in previous reports on heavily doped diamond;(11–14) thus, these peaks could be assigned following the structures in those reports. The wide signal from 1070 to 1290 cm^{-1} represented a combined peak of signal optical phonons caused by boron atoms incorporated into the diamond structure. The other broad peak at 510 cm^{-1} was attributed to the B-B structure of the boron incorporated into diamond. The sharp signal at 1328 cm^{-1} that shifted from 1332 cm^{-1} as a result of the strain from the incorporated boron could be assigned to the T_{2g} phonon mode from the diamond structure. The Raman spectrum of the *a*-C:H film shows that the G (graphitic)-band at around 1530 cm^{-1} and the D (disorder)-band at around 1350 cm^{-1} indicate the presence of *a*-C films. The peak at 520 cm^{-1} was attributed to the Si substrate. The D-band and G-band were fitted assuming a Gaussian distribution, and the integrated ratio of these peaks, I_D/I_G, was calculated. I_D/I_G was 0.78, suggesting that the sp2-bonded cluster size in the a-C:H film is a few nanometers, because I_D/I_G indicates the cluster size of continuous sp^2 bonded carbon.15,16)

Figure 4 shows the FT-IR spectrum of the *a*-C:H film. The absorption bands at wave numbers in the range of 2800–3000 cm^{-1} can be assigned to the stretching vibrational modes of the CH, CH_2 and CH_3 structures. The absorption band at the wave number of approximately 1650 cm^{-1} is assigned to the stretching vibrational mode of the C=C bond.

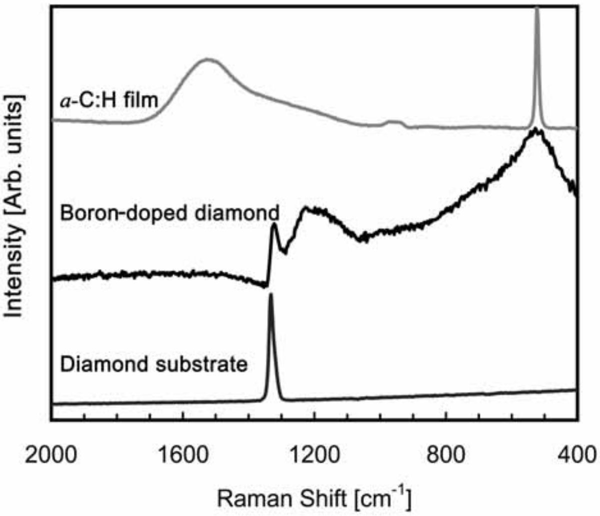

Fig. 3. Raman spectra of diamond substrate, boron-doped diamond and *a*-C:H film.

Furthermore, the absorption bands at wave numbers of approximately 1350–1500 cm^{-1} are assigned to the bending vibrational mode of CH_2 and CH_3 bonds. The IR spectrum suggests that there is a large amount of hydrogen in the *a*-C:H film.

Figure 5 shows the absorption coefficient spectrum and Tauc plot of *a*-C:H film obtained by the UV/VIS measurement. The Tauc plot of the *a*-C:H film did not exhibit

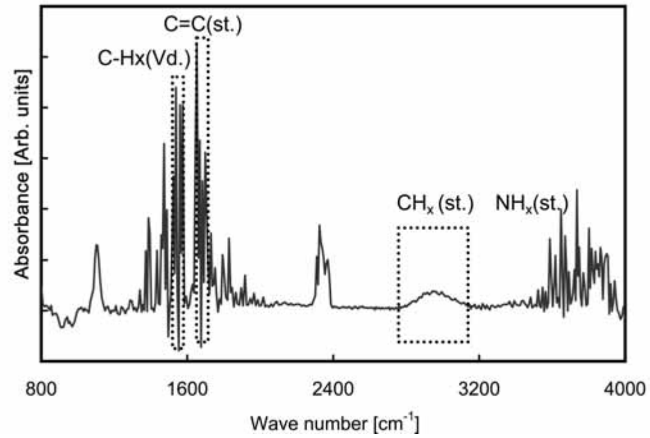

Fig. 4. IR spectrum of *a*-C:H film deposited on Si substrate.

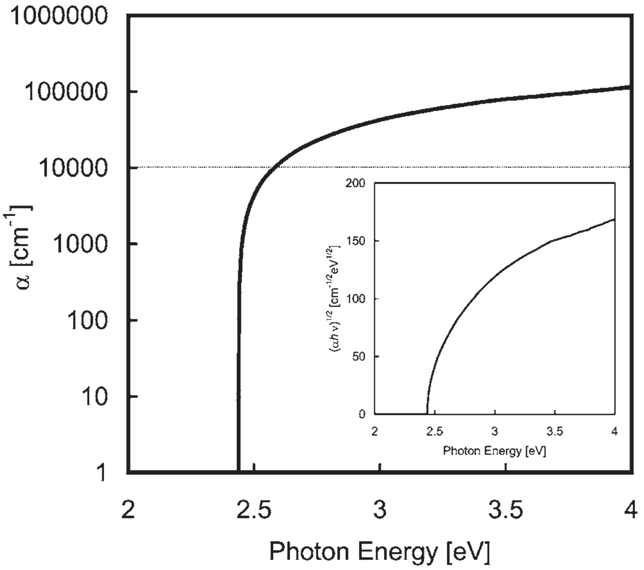

Fig. 5. Absorption coefficient spectrum and Tauc plot of *a*-C:H film.

a linear region. Hence, the band gap of E_{04} was used for band gap estimation. The band gap of E_{04} was calculated to be 2.6 eV for the *a*-C:H film. The photon energy at 2.6 eV is 430 nm in wavelength. This range looks blue in the visible-light region. The band gap indicates that the *a*-C:H film has the same effect as the CdTe layer reported by Huth *et al.*(4) in photovoltaic devices.

The hole mobility and hole concentration are important factors to understand the electronic structure of the cell *a*-C:H film/boron-doped diamond cell. Iihara *et al.* reported that the hole mobility and hole concentration of boron-doped diamond with a resistivity of 23 Ω • cm are 3.3 $cm^2V^{-1}S^{-1}$ and 10^{15} cm^{-3}, respectively.(17) In this study, the hole mobility and hole concentration of boron-doped diamond were thought to have similar values because the resistivity of our boron-doped diamond was 150 Ω • cm. However, the hole mobility and hole concentration of the *a*-C:H film are not presented, because the resistivity of the film was too high for the hole measurement. Estimation of these values is an issue that must be addressed in the future to understand the electronic structure of the *a*-C:H film/boron-doped diamond cell.

Figure 6 shows the I-V characteristics of the *a*-C:H film/boron-doped diamond cell. The cell generated a photoelectromotive force under light irradiation. The open-circuit voltages under Xe lamp irradiation with and without the UV component were –62 mV and –30 mV, respectively. The voltage difference between the two conditions suggests that an *a*-C:H film/boron-doped diamond cell can generate a photoelectromotive force attributable to UV radiation. The short-circuit current under Xe lamp irradiation using the UV filter was 8.6 nA. The short-circuit current increased to 17.7 nA under Xe lamp irradiation without the filter. Hence, the efficiency of photovoltaic conversion in the *a*-C:

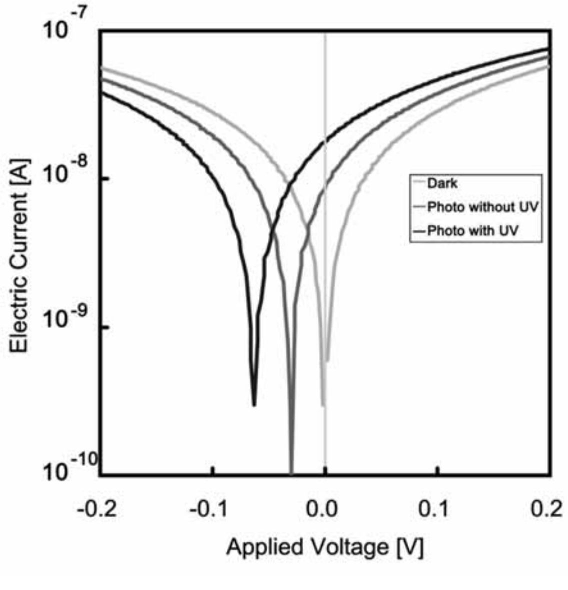

Fig. 6. I-V characteristics in the dark and under Xe lamp irradiation.

H film/boron-doped diamond cell was observed under not only visible light irradiation but also UV light irradiation. Assuming that the effective light-emission area of the cell for both UV and visible light was 0.02×0.15 mm^2, we derived the efficiency and fill factor of the cell to be approximately 1.4×10^{-4}% and 0.26, respectively.

To confirm that these photons were converted to electric power at the boundary of the *a*-C:H film and boron-doped diamond, the same electrodes as those of the *a*-C:H film/boron-doped diamond cell were placed on the boron-doped diamond, and the I-V characteristics of the device were obtained. Figure 7 shows the I-V characteristics of the Ag/boron-doped diamond/Ag structure under Xe lamp irradiation. The electronic structure of the junction between electrodes and the boron-doped diamond was an Ohmic junction because the I-V characteristics under dark condition indicated symmetry at V = 0. The characteristics of these three structures obtained under irradiation and in the dark were the same. Hence, the boundary of the boron-doped diamond and undoped diamond presented no photovoltaic efficiency. These results clarified that the junction between the *a*-C:H film and the boron-doped diamond layer in an *a*-C:H film/boron-doped diamond cell can generate a photovoltaic force.

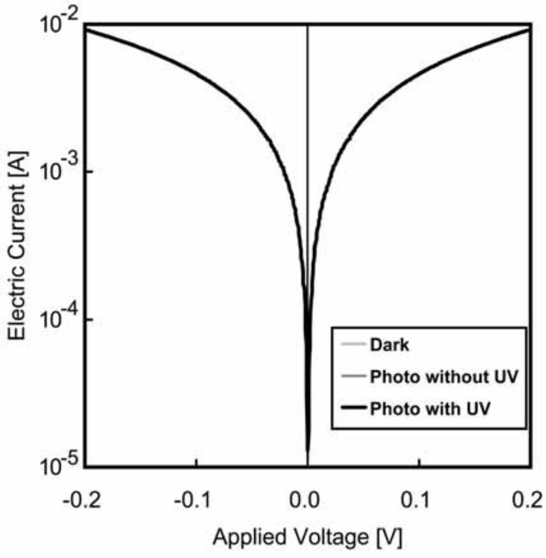

Fig. 7. I-V characteristics of Ag/boron-doped diamond/Ag structure in the dark and under Xe lamp irradiation.

4. Summary

A multilayer cell in which an *a*-C:H film was deposited on boron-doped diamond exhibited photovoltaic conversion from UV light and visible light. The open-circuit voltage and short-circuit current of the cell under Xe lamp irradiation without a UV filter were –62 mV and 17.7 nA, respectively. The photovoltaic characteristics of the cell showed differences between the cases with and without a UV filter under Xe lamp irradiation. The *a*-C:H film/boron-doped diamond cell can be used as a photovoltaic cell for UV light and visible light.

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