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Photovoltaic Characteristics of Heterojunction Diode Comprising Boron-Doped Ultrananocrystalline Diamond/Hydrogenated Amorphous Carbon Composite Film and n-Type Silicon

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Abstract

Heterojunction diodes, which comprise boron-doped p-type ultrananocrystalline diamond/hydrogenated amorphous carbon composite (UNCD/a-C:H) films prepared by coaxial arc plasma deposition and n-type Si substrates, were electrically investigated to evaluate the photovoltaic characteristics. The diode showed a typical diode behavior. Photodetection for 254 nm monochromatic light, which is predominantly attributable to photocurrents generated in UNCD grains, was evidently confirmed in the heterojunctions. Since dangling bonds are detectable by electron spin resonance spectroscopy, their control might be a key for improving the rectifying action and photodetection performance.

1. Introduction

Ultrananocrystalline diamond/hydrogenated amorphous carbon composite (UNCD/a-C:H) films, wherein nanosized diamond grains are embedded in an a-C:H matrix, contain a very large number of grain boundaries (GBs) in the films, which is a distinctive structure specific to UNCD/a-C:H films. The electrical properties of UNCD/a-C:H films, mainly prepared by chemical vapor deposition (CVD), have received considerable attention [1].

We have reported that UNCD/a-C:H films prepared by pulsed laser deposition (PLD) and coaxial arc plasma deposition (CAPD) possess large optical absorption coefficients of more than 10^5 cm^{-1} in the photon energy range between 3 and 6 eV, which differs from those of UNCD/a-C:H films prepared by CVD. The both method, of which the depositions are physically carried out in a pulsed process, enable the growth at low substrate temperatures and require no pretreatment of substrates. As for the films prepared by PLD, it has been demonstrated that their p- and n-type conduction accompanied by enhanced electrical conductivity are possible by boron and nitrogen doping, respectively [2,3]. Their superior optical and electrical properties are advantageous for their application as photodiodes. Between PLD and CAPD, there is a distinctive difference: a hydrogen atmosphere during the deposition is not necessary for diamond crystallite formation by CAPD [4], although it is not necessary for that of PLD. The growth mechanism in CAPD should be distinct from not only that in CVD but also that in PLD.

Heterostructures comprising semiconducting carbon films and Si substrates have been studied for the purpose of applying them in optoelectric device such as UV detectors and solar cells [5,6]. Aside from their attractive applications, single-crystalline Si substrates, whose physical parameters are well known, are suitable for investigating the electrical properties of pair materials in heterojunctions.

In this study, boron doping for inducting p-type conduction was examined for UNCD/a-C:H films prepared by CAPD. The photovoltaic characteristics of boron-doped UNCD/a-C:H films were investigated through the electrical evaluation of heterojunctions comprising p-type UNCD/a-C:H films and n-type Si substrates.

2. Experimental procedure

Heterojunction diodes comprising boron-doped UNCD/a-C:H films and n-type Si substrates, wherein boron-doped UNCD/a-C:H films were deposited on Si substrates by CAPD with 5 at.% boron-blended graphite targets at a substrate temperature of 500 °C and a hydrogen pressure of 53 Pa, were prepared. The resistivity and thickness of the Si substrates were 1 Ω cm and 260 μm, respectively. For ohmic back-surface electrodes, Ti were deposited on Si substrates. For front ohmic contacts, Pd and Au were successively deposited on the films. After that, the UNCD/a-C:H film was etched with exposing to oxygen plasma to form cylindrical structures. The boron content of the films was estimated by X-ray photoemission spectroscopy using a MgKα line, and argon ion etching was employed to measure the boron content distribution in the depth direction. Current–voltage (I–V) was performed at room temperature in the dark and under illumination of 2 mW UV light with a monochromatic wave length of 254 nm. Capacitance–voltage (C–V) measurements were conducted to estimate the carrier density of the UNCD/a-C:H film. Electron spin resonance (ESR) spectra were observed in the X-band frequency range at room temperature.

3. Results and discussion

The boron content of the films deposited with 5 at.% boron-blended targets was estimated to be 4 at.% from the X-ray photoemission spectra. The electrical conductivity at room temperature was 6×10^{-2} Ω^{-1} cm^{-1}, whereas that of undoped films was difficult to measure owing to the films

being insulating. The p-type conduction of the boron-doped films was confirmed thermally.

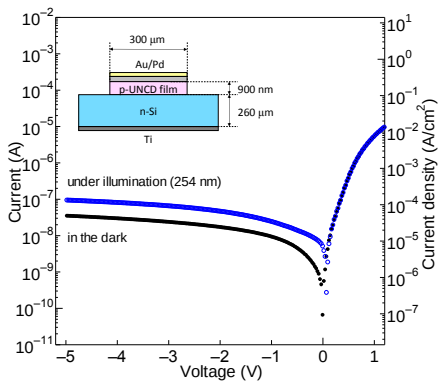

Fig. 1 I–V characteristics of heterojunction diode conmprising boron-doped UNCD/a-C:H films and n-type Si in dark and under illumination of 254 nm monochromatic light. The inset schematically illustrates the diode structure.

Figure 1 shows the I–V characteristic curve for the heterojunction diode comprising the p-type UNCD/a-C:H film and n-type Si substrate in the dark and under illumination of 254 nm monochromatic light. The inset illustrates the schematic of the diode. The I–V curve shows a typical rectification action of pn junction diodes in the dark and boron-doped UNCD/a-C:H films clearly act as a p-type semiconductor. Under illumination of UV light, an increase of current in applying reverse voltage were confirmed comparing that in the dark. Thus, photogenerated carriers are evidently observed although the effective irradiation area is limited to the side face of the cylindrical structure. The 254 nm light detection including the signal/noise ratio was clearly better than that of commercial GaN photodiodes. It is considered that photocarriers might generate at a large number of UNCD grains in the film and that they are transported through the a-C:H matrix. Since the photon energy of 254 nm light is too large for effective photocarrier generation in Si and a-C:H, the contribution of UNCD grains might be predominant.

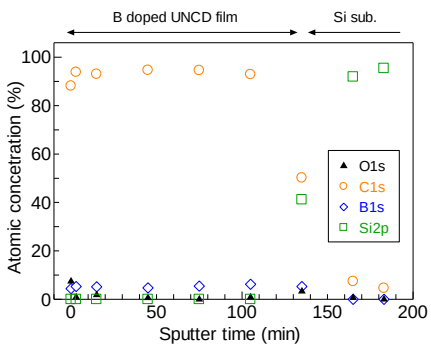

Fig. 2 Depth dependence of chemical composition of UNCD/a-C:H film, measured by X-ray photoemission spectroscopy combined with argon ion etching.

In order to investigate the depth dependence of the boron content, X-ray photoemission spectroscopic measurement combined with argon ion etching was employed for a 50-nm film prepared under the same conditions as the heterojunction film. The depth dependence of the chemical composition is shown in Fig. 2. The decrease in the carbon content simultaneous with an increase in the silicon content indicates that the etching penetrates the film. The boron content does not significantly change in the depth diction.

From the C–V measurement of heterojunction diodes it was confirmed that a depletion region clearly expands into the UNCD/a-C:H film. The built-in potential was estimated to be approximately 0.6 eV. The active carrier concentration of the UNCD/a-C:H film were calculated to be 0.9-1.5×10^{16} cm^{-3} with that (5×10^{15} cm^{-3}) of Si substrate.

The presence of dangling bonds, which is considered as recombination centers, in the films was investigated by ESR. The ESR spectrum exhibits a clear signal associated with carbon dangling bonds. It implies that a detectable number of dangling bonds exist in the film. Possible origins of the signal might are dangling bonds at GBs, defects in UNCD grains, and defects in an a-C:H matrix. The appropriate termination of dangling bonds should be a key factor for enhancing the photovoltaic performance.

4. Conclusions

Photovoltaic characteristics of boron-doped UNCD/a-C:H films prepared by CAPD were investigated. The heterojunction diode evidently detects 254 nm monochromatic light, and photocarriers generated in UNCD grains are expected to be transported through the a-C:H matrix. Since the UNCD/a-C:H films contain dangling bonds detectable by ESR, the appropriate termination of dangling bonds should be key for the application of boron-doped UNCD/a-C:H films in optoelectronic devices.

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