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## Hydrogenation effects on minority carrier lifetime in ultrananocrystalline diamond/amorphous carbon films prepared by coaxial arc plasma deposition

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**Abstract:** Ultrananocrystalline diamond (UNCD)/hydrogenated amorphous carbon (a-C:H) composite (UNCD/a-C:H) films, which comprise a large number of diamond grains whose diameters are less than 10 nm embedded in an amorphous carbon matrix, possess large optical absorption coefficients and the conduction type can be controlled by nitrogen and boron doping, accompanied by enhanced carrier densities. Therefore, UNCD/a-C:H is a new candidate semiconductor applicable to photovoltaics. In this work, the minority carrier lifetime ( $\tau$ ), which is an important factor in the photovoltaic action, was experimentally measured by a microwave reflected photoconductivity decay method, and effects of hydrogenation of films on  $\tau$  was investigated.  $\tau$  of UNCD/a-C:H films and UNCD/nonhydrogenated amorphous carbon (a-C) composite (UNCD/a-C) films were estimated to be 0.43 and 0.21  $\mu$ s, which evidently indicates that the hydrogenation enlarge  $\tau$ . This might be because dangling bonds that act as trap centers for minority carriers are terminated by hydrogen atoms.

**Keywords:** ultrananocrystalline diamond; minority carrier lifetime; hydrogenation;  $\mu$ -PCD

### 1. INTRODUCTION

Ultrananocrystalline diamond (UNCD)/hydrogenated amorphous carbon (a-C:H) composite (UNCD/a-C:H) films are composed of a large number of diamond grains whose diameters are less than 10 nm and an a-C:H matrix. UNCD/a-C:H films possess the following specific characteristics: (i) the appearance of additional energy levels in the bandgap of diamond [1] is theoretically predicted; (ii) large optical absorption coefficients ranging from visible to ultraviolet region [2,3], which might be due to (i); (iii) n and p-type conduction can be produced by nitrogen and boron doping, which is completely different from that for singlecrystalline diamond [4,5]. These specific properties might be due to the existence of large number of grain boundaries [6]. Owing to the above-mentioned properties, UNCD/a-C:H films are new candidates for photovoltaic materials.

In our previous research, we have experimentally demonstrated that the production of n and p-type conduction accompanied by enhanced electrical conductivities is possible by doping nitrogen and boron respectively, for UNCD/a-C:H films prepared by pulsed laser deposition and coaxial arc plasma deposition (CAPD) [7,8,9]. In addition, on the basis of the doping results, we have fabricated heterojunctions comprising boron-doped UNCD/a-C:H films and n-type Si and comprising nitrogen-doped UNCD/a-C:H films and p-type Si substrates, and experimentally demonstrated their photodetection [10,11,12]. On the other hand, it has been unknown that key factors that predominantly affect the photovoltaic properties of UNCD/a-C:H. There have been no researches on the lifetime of minority carriers ( $\tau$ ) in UNCD/a-C:H, which should be an important factor in photovoltaic action, thus far, to our knowledge.

We have ever reported that the hydrogenation of UNCD/a-C:H films strongly affect the electrical properties of the films [13]. Similarly, to hydrogenated

amorphous Si films, it is expected that hydrogenation has an important role in the termination of dangling bonds in UNCD/a-C:H films also.

In this work,  $\tau$  of undoped UNCD/a-C:H and UNCD/nonhydrogenated amorphous carbon (a-C) composite (UNCD/a-C) films were experimentally measured to study the hydrogenation effects on  $\tau$ . In addition, the potential of UNCD/a-C:H films as photovoltaic materials is discussed from the viewpoint of  $\tau$ .

### 2. EXPERIMENTAL

UNCD/a-C:H films with thickness of approximately 200 nm were prepared on insulating singlecrystalline Si substrates with electrical resistivities of more than 10 k $\Omega$ -cm at a substrate temperature of 550  $^{\circ}$ C and under a hydrogen pressure of 53 Pa by CAPD (Ulvac ARL-300) with a graphite target, similarly to our previous studies [14,15,]. UNCD/a-C films were deposited under a base pressure of less than 10<sup>-4</sup> Pa. A coaxial arc plasma gun

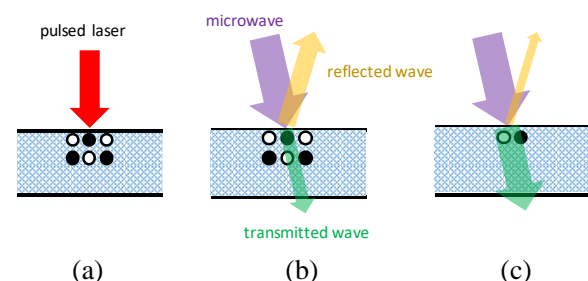


Fig. 1. Schematic diagram of  $\mu$ -PCD measurement principle. (a) generation of excess carriers by pulsed laser irradiation, (b) strong reflection of microwave in case of a large number of excess carriers, and (c) weak microwave reflection in case of a small number of excess carriers.

with a capacity of 720  $\mu\text{F}$  was operated at a voltage of 100 V. The repetition rate of pulsed arc discharges was 5 Hz, and the distance between the substrate and the target was 15 mm. Both undoped films exhibit weak p-type conduction.

$\tau$  in the films was investigated from the excess-carrier ( $\Delta n$ ) recombination kinetics analyzed by microwave reflected photoconductivity decay ( $\mu$ -PCD) [16,17,18]. The  $\mu$ -PCD decay curves were measured by a semiconductor wafer lifetime measuring system (KOBELCO, LTA-1512EP). Excess carriers were generated by a 5 ns laser pulse with a wavelength of 349 nm, as shown in Fig. 1(a), and photoconductivity decay was measured from the reflectivity of microwaves with a frequency of 26 GHz. The reflection of microwave is proportional to the number of excess carriers, as shown in Fig. 1(b) and 1(c). High-sensitivity measurements were realized by the differential detection of the reflected microwave intensity between the areas with and without laser irradiation.

### 3. RESULTS and DISCUSSION

Photoconductivity decay curves can be divided into three modes on the basis of the decay rate: Auger recombination and Shockley–Read–Hall (SRH) recombination without and with the carrier-trapping effect [16,17]. The decay curve was fitted well using the following equation:

$$I = I_1 \exp\left(-\frac{t}{\tau_{\text{Auger}}}\right) + I_2 \exp\left(-\frac{t}{\tau_{\text{SRH}}}\right) + I_3 \exp\left(-\frac{t}{\tau_{\text{SRH-trapping}}}\right) \quad (1)$$

Here,  $I_1$ ,  $I_2$ , and  $I_3$  are the coefficients, and  $\tau_{\text{Auger}}$ ,  $\tau_{\text{SRH}}$ , and  $\tau_{\text{SRH-trapping}}$  are the time constants for the three decay modes, respectively. The initial rapid decay is attributed to the Auger recombination process. Since the optical absorption coefficients of UNCD/a-C:H and UNCD/a-C films are extremely large, all the incoming photons are expected to be absorbed within the films.  $\Delta n$  is much larger than the majority-carrier concentration at equilibrium. Therefore, the fast decay mode arising from the multicarrier recombination might be inevitable [19]. The second component decay is caused by the SRH recombination mechanism without the carrier-trapping effect.  $\tau_{\text{SRH}}$  predominantly determines the minority-carrier lifetime [20]. Therefore, in this work, we regard  $\tau_{\text{SRH}}$  as  $\tau$ . The slow decay is attributed to SRH recombination with the carrier trapping effect.

Figures 2(a) and 2(b) show photocurrent decay curves of UNCD/a-C:H and UNCD/a-C films. Both films exhibit fast decay components due to the Auger recombination process corresponding to the first term in the equation (1). And slow decay components due to the SRH recombination mechanism with the carrier-trapping effect corresponding to the third term in the equation (1) also are apparently observed. After the estimation of these fast and slow decay components by partial fitting, decay components due to the SRH recombination mechanism without the carrier-trapping effect corresponding to the second term in the equation (1) were derived by reproducing the experimental decay curves totally.  $\tau_{\text{SRH}}$  of the UNCD/a-C:H and UNCD/a-C films were estimated to be 0.43 and 0.21  $\mu\text{s}$ , respectively.

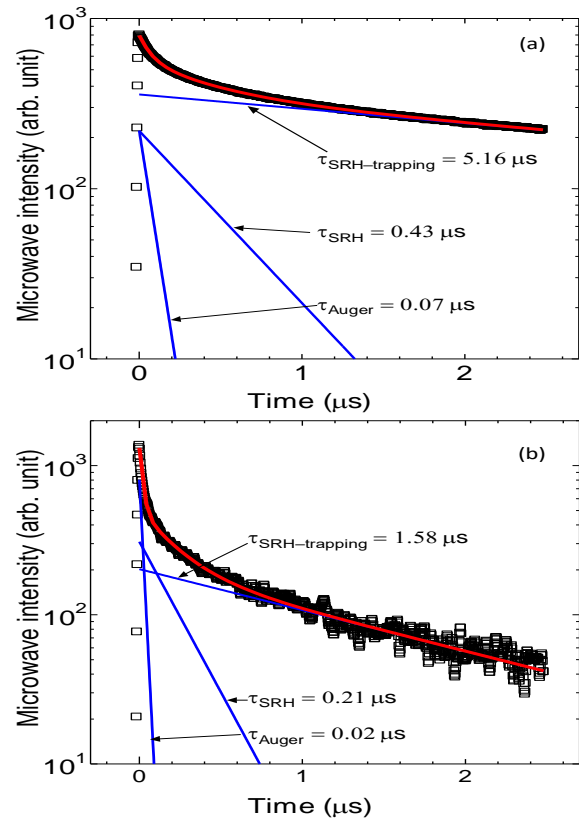


Fig. 2. Photoconductivity decay curves of (a) UNCD/a-C:H and (b) UNCD/a-C films. Red lines are reproduced curves based on equation (1) and blue lines are component decay curves of the reproduced curves.

The microwave intensity decay of the UNCD/a-C film is totally fast as compared to that of the UNCD/a-C:H film, which evidently indicates that the recombination of excess carriers actively occurs in the UNCD/a-C film. In our previous studies, on the basis of several spectroscopic measurements results, we have reported that a large number of dangling bonds at grain boundaries (GBs) between UNCD grains and those between UNCD grains and an a-C:H matrix are preferentially terminated by hydrogen atoms [21,22]. Dangling bonds are naturally expected to act as recombination centers. Thus, the enlarged  $\tau$  by hydrogenation might be because dangling bonds that act as trap centers for excess carriers are terminated by hydrogen atoms.

### 4. CONCLUSIONS

In this work,  $\tau$  in the UNCD/a-C:H and UNCD/a-C were experimentally investigated by  $\mu$ -PCD, and the values were 0.43 and 0.21  $\mu\text{s}$ , respectively. To apply the UNCD/a-C:H films to photovoltaics, double or triples values are required from the viewpoints of the optical absorption coefficients of UNCD/a-C:H. It was found that hydrogenation is effective for enlarging  $\tau$ , which might be because dangling bonds that act as trap centers for excess carriers are terminated by hydrogen atoms. We have never optimize the hydrogenation of UNCD/a-C:H films thus far from the viewpoints of enhancing  $\tau$ . In addition, we have no ideas concerning key factors in the chemical bonding structure of UNCD/a-C:H that predominantly affect  $\tau$ . In order to enhance  $\tau$ , further studies on the hydrogenation and chemical bonding structures are required.

## 5. ACKNOWLEDGEMENT

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