Photovoltaic characteristics of postdeposition iodine-doped amorphous carbon films by microwave surface wave plasma chemical vapor deposition

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The amorphous carbon thin films have been deposited on silicon and quartz substrates by microwave surface wave plasma chemical vapor deposition at low temperature (<100°C) in Ar/CH₄ phase gas. Doping of iodine has been done in the postdeposited films by exposing them in iodine vapor. The photovoltaic measurements of the films were carried out before and after iodine doping. The results show dramatic decrease of optical gap from 3.4 to 0.9 eV corresponding to nondoping to iodine doping conditions, respectively. The preliminary photovoltaic characteristics of the film deposited on *n*-type silicon substrate under light illumination (AM1.5, 100 mW/cm²) reveal a short-circuit current density of 1.15 μ A/cm², open-circuit voltage of 177 mV and fill factor of 21.7%. © 2005 American Institute of Physics. [DOI: 10.1063/1.2089168]

Carbon (C) is an attractive material for low cost and reasonably high efficiency solar cells. This remarkable element exists in different forms ranging from insulator diamond to metallic graphite to conducting/semiconducting nanotubes.¹ In recent research,^{1–7} amorphous carbon (*a*-C) has been shown to behave as a semiconducting material, which is able to accept dopants, shows photoconductivity and is suitable for optoelectronic devices.² However, there are some problems such as low conversion efficiency due to the sp^2/sp^3 bonding structure and the difficulties in controlling the conduction type, carrier concentration and optical band gap.³ When we attempt to utilize a-C as an alternative material in photovoltaic applications, control of the conduction type of a-C film is indispensable.⁴ Effective doping can modify optical and electronic properties, in particular optical band gap and photoconductivity, in semiconductor materials.⁵ Doping of *a*-C with *n*- and *p*-type dopants such as P, N and B has been attempted by several researchers.^{3–7} However, the doping prospect of a-C remains unclear. A new method of doping by iodine (I) called oxidation has been introduced by Shirakawa⁸ *et al.* for hydrocarbon polyacetylene (CH) $^{9-11}$ polyacetylene (CH)_r.

In this letter, we report the effects of postdeposition solid phase I doping on the photovoltaic properties of *a*-C thin films deposited on *n*-type silicon (*n*-Si) and quartz substrates by microwave (MW) surface wave plasma (SWP) chemical vapor deposition (CVD) at low temperature (<100 °C). The films were deposited on quartz and *n*-Si substrates by MW SWP CVD, a newly developed deposition method.^{12,13} Figure 1 shows the schematic drawing of the CVD system. The stage diameter of MW SWP CVD is about 20 cm, so that it allows deposition of relatively large area thin films, which is generally required for a high power electromagnetic wave source about 2.45 GHz microwave having up to 6 kW. Also, this method is useful to avoid plasma induced damages of the substrate surface. The CVD chamber was evacuated to a base pressure at approximately 3.5×10^{-4} Pa using a turbomolecular pump. For film deposition, we used Ar as carrier gas and CH₄ as source gas, and the gas flow rates were maintained as 280 and 10 sccm, respectively. The microwave power and gas composition pressure in the CVD chamber were maintained at 500 W and 60 Pa, respectively. The duration of film deposition for this experiment was 60 min. The substrates were cleaned beforehand by acetone and methanol in ultrasonic bath and then rinsed by ultrapure water. The Si substrates were etched with diluted hydrofluoric acid (10%) in order to remove the resistive native oxide layer over the surface. For I doping, we employed the pyrolysis of the MW SWP CVD deposited a-C films to I vapor for about 10 min-



FIG. 1. Schematic diagram of MW SWP CVD system.

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FIG. 2. Schematic diagram of cross-sectional view of the postdeposition I-doped *a*-C based device.

utes. Pyrolysis was carried out using a double furnace setup, one for heating the source material (I) placed in a quartz boat and the other for controlling the sample temperature, using Ar as a carrier gas.^{14,15}

A JASCO V-570 ultraviolet visible near-infrared (UV/ VIS/NIR) spectrophotometer is used to investigate the optical properties of the film. While Nanopics 2100/NPX200 is used to measure the film thickness. A current-voltage (I-V) characteristic of a-C/n-Si structure was measured by a JASCO SS-200W solar simulator.

The films deposited in this experiment are diamond-like a-C, which promises as a good quality semiconducting thin film for optoelectronic devices. Figure 2 shows the schematic diagram of cross-sectional view of the postdeposition I-doped a-C (a-C:I) based photovoltaic device.

To study the optical characteristics of *a*-C films, we carried out the reflectance and transmittance measurements by UV/VIS/NIR spectroscopy in the range of 200–2000 nm. The absorption coefficient (α) was calculated by the spectral reflectance and transmittance, and the film thickness data. The optical band gaps were obtained by Tauc plot.^{16,17} The Tauc optical band gap (E_g) was obtained from the extrapolation of the linear part of the curve at α =0 by using the Tauc equation

$$(\alpha h\nu)^{1/2} = B(E_{\varrho} - h\nu), \tag{1}$$

where *B* is the density of the localized state constant.⁴ Figure 3 shows a comparison of the dependence of α on spectral wavelength for the *a*-C film (thickness: 205 nm) before and after I doping. The α of the doped film in the visible wavelength region was found to be approximately 10^5 cm⁻¹. Figure 4 shows that the optical gap dropped from 3.4 to 0.9 eV corresponding to nondoping to I-doping conditions respectively. Our results of optical gap suggest that the I doping in



FIG. 3. Absorption coefficients of the *a*-C film vs spectral wavelength before and after I doping.



FIG. 4. Plots of $(\alpha h \nu)^{1/2}$ vs photon energy for the determination of the *a*-C film's optical gap.

a-C films results in more conductivity because the I content in the films induced graphitization by decreasing the optical gap.

Figure 5 shows the *I-V* characteristics of the *a*-C:I based device. It shows a rectifying curve in the dark,^{6,14} indicating the formation of a heterojunction between the *a*-C:I film and *n*-Si. When illuminated by the simulated solar light (AM1.5, 100 mW/cm²), this structure shows the photovoltaic behavior with a maximum open-circuit voltage (V_{oc}) of 177 mV and short-circuit current density (J_{sc}) of 1.15 μ A/cm². According to calculation, the fill factor was found to be 21.7%.

Although undoped *a*-C is reported theoretically to have weakly *p*-type conductivity in nature, the high density of intrinsic defects restricts its ability to dope efficiently, which is the main barrier for its electronic devices application when we attempt to utilize *a*-C as alternative material in optoelectronic devices. Hence, control of the conduction type of *a*-C film is indispensable. Unlike Si the microstructure of C is more complicated due to the presence of both σ and π states while Si and other group IV elements have only σ states. Since π states are more weakly bonded, they lie closer to the Fermi level (E_F) than the σ states. Therefore, filled π states



FIG. 5. The current-voltage (*I-V*) characteristics of a-C/n-Si structure under dark and light illumination (AM1.5, 100 mW/cm²). Illuminated area is about 0.5 cm².

from valence bands and empty π states from conduction bands determine the characteristics of gap states.^{4,5} The bonds σ and π are fixed and immobile. They form the covalent bonds between C atoms. The electrons in a conjugated double bond system are also relatively localized, though not as strongly bound as the electrons. Before a current can flow along the molecule, one or more electrons have to be removed or inserted. If an electrical field is then applied, the electrons constituting the bonds can move rapidly along the molecule chain. As mentioned before, the doping by I is called oxidation, which was introduced for $(CH)_x$, and it is shown in the following formula:

$$(CH)_{x} + (3n/2)I_{2} \rightarrow [(CH)_{x}]^{+n} + nI_{3}^{-},$$
 (2)

where *n* is the number of molecules. In this doping, the iodine molecule (I₂) attracts an electron from the $(CH)_x$ chain and becomes I₃. The $(CH)_x$ molecule is now positively charged. The lonely electron of the double bond, from which an electron was removed, can move easily. Consequently, the double bond successively moves along the molecule. The positive charge, on the other hand, is fixed by electrostatic attraction to the iodide ion, which does not move so readily. Since we need to increase the conductivity of *a*-C we applied this new doping method that was successful in conducting polymer.

In conclusion, we investigated the photovoltaic characteristics of the postdeposition solid-phase I-doped *a*-C films deposited by MW SWP CVD. To achieve our target to develop a carbon-based device for photovoltaic applications, we need to improve the optoelectronic properties of the films, such as absorption and photoconductivity. We succeeded to narrow the band gap of the films to 0.9 eV by I doping. Further research is in progress to optimize the dopants and to improve quality of the films by reducing the bonding defects. This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) under the Ministry of Economy, Trade and Industry (METI), Government of Japan. One of the authors, A.M.M.O., is grateful to ASJA International for its financial support.

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