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Photovoltaic and spectral photoresponse characteristics of *n*-C/*p*-C solar cell on a *p*-silicon substrate

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Recent studies have shown the application of amorphous carbon as a semiconductor in C/Si heterojunction photovoltaic solar cells. In this letter, we report the rectifying current–voltage characteristics of the phosphorus-doped carbon/undoped-carbon (*n*-C/*p*-C) junction. The *p*- and *n*-carbon films were deposited by pyrolysis and ion-beam sputtering, respectively, on a *p*-Si substrate, using camphor as a natural carbon precursor. The preliminary photovoltaic characteristics of the cell reveals a short-circuit current density of 17.1 mA/cm^2, open-circuit voltage of 0.339 V, and photoelectrical conversion efficiency of 1.82%, a reproducible result, under air mass zero and 1 sun illumination conditions. The spectral photoresponse characteristics of the cell of the above configuration was explained in terms of transmission/absorption characteristics of the two individual carbon layers. [S0003-6951(00)00736-1]

The application of carbon, in the form of amorphous carbon (*a*-C or *a*-C:H) or diamond-like carbon (DLC) or C_{60}, as a semiconductor in optoelectronic devices such as photovoltaic solar cells has been attempted, although rather limited to date.[1–11] Most of the structures are *a*-C or DLC-based heterojunctions (with Si, GaAs, InP, etc.), including the patent held by Siemens AG, Germany.[1–5,8–11] Successful doping of *a*-C or *a*-C:H is a requirement for practical and more advanced solar cell structures. Doping of carbon with *n*- and *p*-type dopants such as phosphorus, nitrogen, and boron has been attempted by several researchers,[9–12] however, the prospect of doping this material (in particular, *p*-type doping, although undoped carbon exhibits *p* type) remains unclear.

Veerasamy *et al.* have reported a significant amount of work on tetrahedral amorphous carbon obtained by a filtered cathodic vacuum arc method. They have made an *n*-C/*p*-Si heterojunction diode[2] through successful *n*-type doping of *a*-C using phosphorus and nitrogen.[12] Also, Yu *et al.* have made a photovoltaic solar cell of configuration, carbonaceous film/*n*-Si, where the carbon film was obtained by pyrolyzing the 2,5-dimethyl-*p*-benzoquinone.[4] Furthermore, Krishna *et al.* have made a heterojunction solar cell of configuration *n*-C/*p*-Si where the *n*-C was obtained by ion-beam sputtering of phosphorus-doped camphoric carbon soot which in turn was obtained from a natural source, camphor.[11]

In this letter, we present our recent results on the rectifying behavior of an *n*-C/*p*-C junction made on a *p*-Si substrate and demonstrate the spectrophotovoltaic characteristics through transmission/absorption characteristics of the two individual carbon layers, *n*-C and *p*-C.

Camphor has been used as a source of carbonaceous thin film for ion-beam sputtering and pyrolysis. The details of the chemical structure of the camphor molecule and its structural advantages,[13] the experimental setup for the generation of carbon soot (used as a target for sputtering[11] of *n*-C), the target preparation, and the method of doping have been discussed elsewhere.[13,14] Phosphorus was used as an *n*-type dopant in the ion-beam sputtered films.

Quartz and crystalline silicon substrates were used for the deposition of carbon thin films. The substrates were cleaned, prior to the deposition, using a process that has been reported earlier.[11,14] The experimental details of sputtering can be found elsewhere.[11] Pyrolysis was carried out using a double furnace setup, one for heating the source material (camphor) and the other for controlling the deposition temperature, using Ar as a carrier gas. Camphor was placed in a quartz boat and heated between 110 and 140 °C by keeping it in furnace I. Different flow rates and deposition temperatures were exercised to obtain suitable optoelectrical properties. In this work, the vapor of camphor was carried, by Ar gas with a flow rate of 0.6 l/min, into furnace II where the substrates were kept at 650 °C for deposition of the carbon (*p*-C) films.

The structural, optical, and electrical properties of the ion-beam sputtered carbon films have been discussed elsewhere.[11,14,15] In brief, both the pyrolysed and sputtered carbon films are found to be amorphous by x-ray diffraction and Raman scattering. The temperature dependence of the electrical conductivity measurements indicate the semiconducting nature of the deposited carbonaceous thin films. Furthermore, the x-ray photoelectron spectroscopy[11] and Fourier transform infrared measurements indicate the presence of sp^3-bonded carbons, up to a concentration as high as 30%, responsible for the optical gap and the semiconducting nature of these carbon thin films. The optoelectrical properties of *n*-C and *p*-C are summarized in Table I.

A schematic view of the *n*-C/*p*-C photovoltaic solar cell on the *p*-Si substrate, including the individual layer thick-

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TABLE I. Optoelectrical properties of pyrolysed (p-C) and ion-beam sputtered (n-C) carbon layers.

Property	Pyrolysis	Ion-beam sputtering
Absorption coeff. (α, cm^{-1})	10^5–10^6	10^4–10^5
Optical gap (E_{opt}, eV)	0.7	1.05
Conductivity (σ_{RT}, S cm^{-1})	10–10^2	10^{-1}–10
Conduction type	p-type	n-type
Carrier conc. (N, cm^{-3})	10^{20}	10^{18}

ness, is shown in Fig. 1. The front and back contacts of this cell were made with a gold (Au) electrode, using an electron-beam evaporation system. The surface area of the Au electrode was about 0.25 cm^2 and served as an active area for the cell. The contacts, Au to p-Si and to n-C, both showed Ohmic characteristic. Furthermore, the p-C to p-Si is Ohmic.

The current–voltage ($I-V$) characteristics of the n-C/p-C solar cell on the p-Si substrate, under dark, displayed a rectifying behavior. Having confirmed the other contacts (Fig. 1) as Ohmic, we attribute this rectifying behavior to the interface of the *pn* junction between the semiconducting n-C and p-C layers. When illuminated, at air mass zero (AM0) and 1 sun conditions, the cell exhibits a large photoresponse (Fig. 2). The photovoltaic parameters, such as the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and conversion efficiency (η), derived from the illuminated $I-V$ curve (Fig. 2), are summarized in Table II, and discussed in subsequent paragraphs.

It should be noted here that the substrate used in our solar cell structure is p-Si. Also, since the thickness of our carbon films is relatively thin, some amount of light may still reach the p-Si surface. Hence, despite the contact between p-C and p-Si being Ohmic, some contribution from the p-Si substrate to the photovoltaic properties of the n-C/p-C junction cannot be ruled out. Therefore, we have studied the transmission/absorption characteristics of the individual carbon layers and also made the heterojunctions, n-C/p-Si and p-C/n-Si, by depositing the respective films separately on p-Si and n-Si substrates, in order to understand the major role and contribution of the carbon films. The photovoltaic parameters of the two heterojunctions are collected in Table II for comparison. The enhanced photoresponse characteristics of the n-C/p-C junction over the heterojunctions studied by us and others are due to various reasons. A direct evidence for such an enhancement is also shown through the spectral response characteristics (Fig. 3) of this cell compared with the heterojunctions, n-C/p-Si and p-C/n-Si, discussed in subsequent paragraphs.

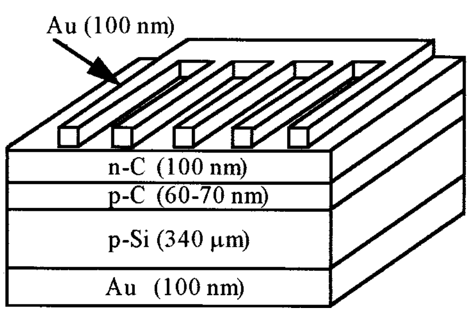

FIG. 1. Schematic view of the n-C/p-C photovoltaic solar cell on the p-Si substrate.

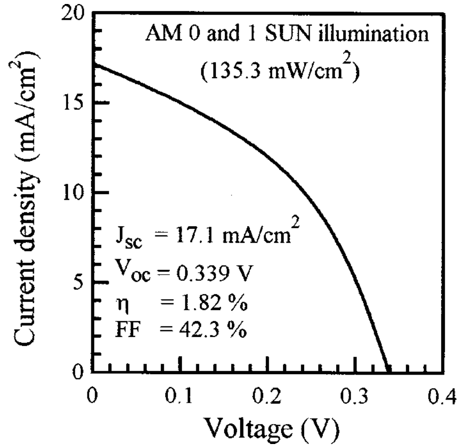

FIG. 2. Current density–voltage characteristics of the n-C/p-C solar cell on p-Si substrate.

It is clear from Fig. 2 and Table II that the n-C/p-C junction reveals relatively high V_{oc} over the two heterojunctions. Also, the p-C/n-Si heterojunction reveals V_{oc} better than 0.21 V, which is fairly large in comparison to that of the n-C/p-Si heterojunction (0.15 V), though the two cannot be compared as the type of Si used was different. However, by considering the role of carbon, we relate the enhanced V_{oc} (0.34 V) of the n-C/p-C junction on the p-Si substrate (Fig. 2) over the two heterojunctions (Table II), and in particular to p-C/n-Si, due to the junction between the n-C and p-C. The particular reference to p-C/n-Si is made since the two junctions (n-C/p-C and p-C/n-Si) can be compared by substituting n-C for n-Si (E_{opt},1.1 eV) as they possess a similar optical band gap although differ in their carrier concentration ($N_{n\text{-C}} > N_{n\text{-Si}}$, 10^{15}–10^{16} cm^{-3}, also see Table I). And, the higher $N_{n\text{-C}}$ is the cause for the enhanced V_{oc} in the n-C/p-C *pn* junction solar cell. Furthermore, when we look at the optical absorption characteristics of the n-C and p-C layers (Table I and Fig. 4), the p-C shows maximum absorption behavior compared to the n-C, particularly at longer wavelengths (>800 nm). Therefore, the p-C is expected to contribute to the large current and thereby the efficiency for the cell of configuration n-C/p-C on the p-Si substrate over the two heterojunctions, and in particular to n-C/p-Si (since the two can be compared by assuming a thin layer of p-C insertion between the n-C and p-Si and as to the similar environment of p-Si), which is what exactly is reflected in Fig. 2 and Table II. Furthermore, the dark (not shown) and illuminated (Fig. 2) $I-V$ characteristics reveal large leakage current and high series resistance responsible for the low V_{oc} and FF of the n-C/p-C solar cell.

Figure 3 shows the spectral response [quantum efficiency (QE)] of the n-C/p-C solar cell. For comparison, the QE characteristics of n-C/p-Si and p-C/n-Si heterojunctions are also shown in Fig. 3. It is clear from Fig. 3 that the

TABLE II. Photovoltaic parameters of the n-C/p-C solar cell on the p-Si substrate and the two heterojunctions, n-C/p-Si and p-C/n-Si.

Structure	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
n-C/p-C on p-Si	17.10	0.339	42.3	1.82
n-C/p-Si	8.77	0.147	45.6	0.44
p-C/n-Si	7.44	0.213	21.6	0.26

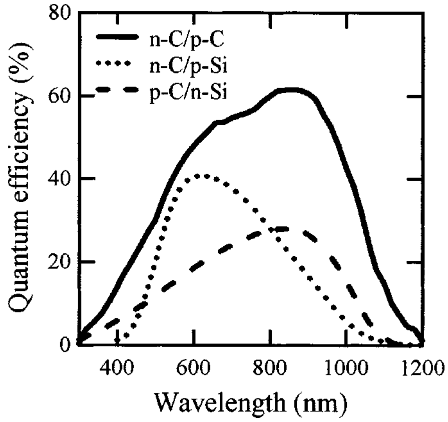

FIG. 3. Quantum efficiency of the *n*-C/*p*-C solar cell on the *p*-Si substrate. The contributions from *n*-C and *p*-C are explained through the QE plots of *n*-C/*p*-Si and *p*-C/*n*-Si heterojunctions.

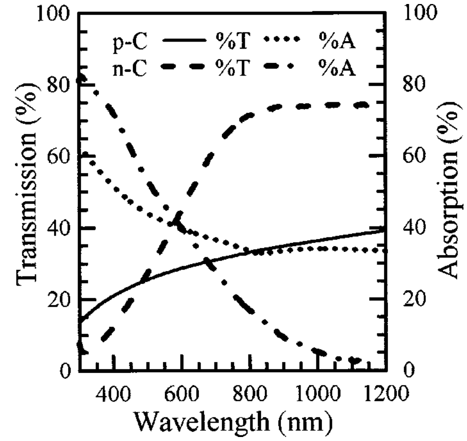

FIG. 4. Transmission (*T*) and absorption (*A*) characteristics of *n*-C and *p*-C thin films (on quartz). The large % of *T* of *n*-C, thereby the % of *A* of *p*-C in the wavelength range>800 nm, and a relatively large % of *A* of *n*-C in the wavelength range<800 nm indicate the active role of the two layers for the enhanced spectral response characteristics of the *n*-C/*p*-C junction on *p*-Si over the two heterojunctions shown in Fig. 3.

QE has improved significantly for the *n*-C/*p*-C junction over the two heterojunctions. A relatively sharp QE has been observed for the *n*-C/*p*-Si cell with a peak maximum more towards the lower wavelength (around 600 nm). On the other hand, a broad distribution over a wide range of wavelengths, from much less than 400 nm to almost up to 1200 nm, with enhanced QE (peaking at around 900 nm, similar in behavior to that of the *p*-C/*n*-Si solar cell) has been observed for the *n*-C/*p*-C solar cell. The enhanced QE of the *n*-C/*p*-C cell over the two heterojunctions is explained to some extent based on the fundamental absorption characteristics of the individual layers. The absorption and transmission spectra of the *n*-C and *p*-C layers are shown in Fig. 4. The *n*-C exhibits more than 75% of the light transmission (<10% of absorption), whereas the *p*-C exhibits more than 30% of the light absorption for the wavelength range >800 nm, thereby the function and the role of *p*-C for the enhancement of QE at wavelengths >800 nm in Fig. 3 is understood. On the other hand, at wavelengths <800 nm, the main contribution comes from *n*-C owing to its relatively large absorption characteristics (Fig. 4). However, once again, as mentioned before, some contribution from *p*-Si cannot be ruled out as our films are relatively thin and some percentage of light may still reach the *p*-Si surface.

Although the results presented here sufficiently encourage and prompt further study to understand the detailed mechanism involved in this structure, the cell suffers to some extent due to the involvement of *p*-Si. The existing problem can only be best solved by making a cell of configuration *n*-C/*p*-C on a nonsilicon substrate, preferably on a glass substrate, although it seems to be difficult at present due to buckling of carbon on glass substrates when we try for multiple layers or a large film thickness (>100 nm or so). Alternatively, the thickness of *p*-C should be sufficiently large such that light cannot reach the substrate. Efforts toward these directions to overcome the existing problems are in progress. These are our preliminary and recent finding. Moreover, the aim of this letter is to establish and show the formation of a junction between the two carbon layers, and hence, a more precise conclusion on the quantitative analyses will only be drawn at a later stage.

In summary, thin films of amorphous carbon deposited by ion-beam sputtering and pyrolysis methods, using camphor as a natural source, are used in the fabrication of a photovoltaic solar cell of configuration *n*-C/*p*-C on a *p*-Si substrate and we have studied the photoelectrical properties. We observe the rectifying nature of the *n*-C/*p*-C junction. The spectral response characteristics are explained through the combination of the individual heterojunctions, *n*-C/*p*-Si and *p*-C/*n*-Si, and have proved the nature of *n*-C/*p*-C, to eliminate any ambiguity due to the *p*-Si substrate. Furthermore, the contributions of *p*-C and *n*-C, and thus the *n*-C/*p*-C junction to the photovoltaic parameters and quantum efficiency, are demonstrated in terms of the transmission/absorption characteristics of the individual carbon layers.

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