Photovoltaic characteristics of Pd doped amorphous carbon film/SiO$_2$/Si

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The Pd doped amorphous carbon (a-C:Pd) films were deposited on n-Si substrates with or without a native SiO$_2$ layer using magnetron sputtering. The photovoltaic characteristics of the a-C:Pd/SiO$_2$/Si and a-C:Pd/Si junctions were studied. It is found that under light illumination of 15 mW/cm$^2$ at room temperature, the a-C:Pd/SiO$_2$/Si solar cell fabricated at 350 °C has a high power conversion efficiency of 4.7%, which is much better than the a-C/Si junctions reported before. The enhanced conversion efficiency is ascribed to the Pd doping and the increase in sp$^3$-bonded carbon clusters in the carbon film caused by the high temperature deposition. © 2010 American Institute of Physics. [doi:10.1063/1.3478230]

The enormous potential of photovoltaic cells is widely acknowledged due to the shortage of fossil fuels and environmental issues.\(^1\) Until now, many materials have been reported for making solar cells but the cost of the current solar cells is extremely high to reach for daily life. Therefore, it is very important to find new kinds of clean and cheap photovoltaic materials. Recently, carbon materials have been investigated intensively as alternative photovoltaic materials because it is expected to have similar photovoltaic properties as Si and very cheap and stable.

Recently, carbon nanotube film/Si junction,\(^2\)–\(^4\) C$_{60}$ thin film/Si junction,\(^5\) amorphous carbon (a-C) film/Si junction\(^6\)–\(^11\) solar cells have been demonstrated. For example, the n-C/p-C/p-Si structure had a high power conversion efficiency ($\eta = 1.82\%$), which is much larger than that of the n-C/p-Si and p-C/n-Si heterojunctions.\(^7\) The photovoltaic characteristics of carbon films doped with the nonmetal elements have been reported.\(^5\)–\(^11\) However, there are few researches on photovoltaic characteristics of carbon films doped with metal elements. In this letter, we deposited Pd-doped a-C (a-C:Pd) films on n-Si substrates with or without a native SiO$_2$ layer and studied the photovoltaic characteristics of the a-C:Pd/Si and a-C:Pd/SiO$_2$/Si.

The a-C:Pd films were deposited on n-Si (100) substrates using direct current magnetron sputtering from Pd doped graphite target. The targets are cold-pressed composite disks, and the purities of the Pd and graphite are better than 99.9%. The silicon substrates are n-type materials with resistivity in the range of 2–5 $\Omega$ cm. Before deposition, the Si substrates were cleaned with following two methods: (1) The Si substrates were etched in hydrofluoric acid (HF) solution for 3 min and then ultrasonically cleaned in ethanol and acetone. (2) In order to reserve the native SiO$_2$ layer on the Si substrate and get the a-C:Pd/SiO$_2$/Si structure, the Si substrate was ultrasonically cleaned in ethanol and acetone without using HF solution. The deposition took place inside a chamber where the argon pressure was kept at 3 Pa and the Si substrates were kept at a given temperature.

A semitransparent copper surface electrode was deposited on top of the a-C:Pd films using magnetron sputtering. Such semitransparency ensures the absorption of the solar light by both the a-C:Pd film and the underlying Si substrate. The back electrodes contacted to the backside of Si substrates were made by indium solder. The experimental results show that the back electrodes have Ohmic contact to Si substrates. The current-voltage (I-V) characteristics of the photovoltaic cells were measured by using two-probe method with a Keithley 2400 source meter under illumination. The illumination was provided by a halogen tungsten lamp.

Figure 1 shows the schematic illustration of the a-C:Pd/SiO$_2$/Si photovoltaic cell. The scanning electron microscopy images (not shown in this letter) show that the thickness of the a-C:Pd films and the copper surface electrode are about 20 nm and 30 nm, respectively. The thin native SiO$_2$ layer on Si substrate is about 1.2 nm.\(^11\)

Raman spectra of the a-C film and a-C:Pd films are shown in Fig. 2. It is well known that the Raman spectrum of carbon materials can be fitted to the D band at 1350 cm$^{-1}$ and the G band at 1580 cm$^{-1}$. From these spectra, two main variations are observed as follows: (1) one obvious G peak around 1570 cm$^{-1}$ for the two films deposited at room temperature (RT) illustrates the diamondlike carbon characteris-

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tics of the two films and (2) the a-C:Pd film deposited at 350 °C has one obvious D peak, which suggest that the a-C:Pd film deposited at 350 °C contains much more sp²-bonded carbon clusters.

Figure 3 shows the current density-voltage (J-V) characteristics of the a-C:Pd/SiO₂/Si photovoltaic cell fabricated at 350 °C under dark and white light illumination of 15 mW/cm² at RT. It can be seen that the device has a good rectifying behavior without light illumination. Under the illumination of 15 mW/cm², this structure shows photovoltaic behavior with an open-circuit voltage (V_OC) of 0.33 V and a short-circuit current density (J_SC) of 3.5 mA/cm². Under the same light condition, the power conversion efficiency (η) and fill factor of this structure are found to be 4.7% and 0.61, respectively, which are much better than those of the a-C/Si junctions reported before.6–11

In our study, we also prepared a-C/Si, a-C:Pd/Si, and Fe(Ni)-doped a-C/Si junctions. It is found that the a-C/Si and Fe(Ni)-doped a-C/Si junctions prepared at RT behave no obvious photovoltaic characteristics under illumination. In contrast, the a-C:Pd/Si junction prepared at RT exhibits an eminent photovoltaic characteristics with a V_OC of 0.079 V and a η of 0.002% under the illumination of 15 mW/cm². Therefore, the Pd doping can greatly improve the photovoltaic characteristics of the a-C/Si junction, which may be ascribed to that the Pd doping can help to produce much more carriers under illumination. Furthermore, the a-C:Pd/Si fabricated at 350 °C exhibits a higher V_OC of 0.18 V and a higher η of 0.91%, and the a-C:Pd/SiO₂/Si solar cell shows the highest V_OC (0.33 V) and J_SC (3.5 mA/cm²) and η (4.7%), due to the native SiO₂ layer.

Usually, the enhanced η is mainly attributed to the V_OC and the series resistance (R_S) of the device. The effect of the R_S on η can be understood from the equivalent circuit of a solar cell shown in Fig. 4(a). Under illumination, by ignoring the shunt resistance (R_SH), the short-circuit current can be expressed by formula (1) (Ref. 3)

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J_{SC} = J_L - J_D = J_L - J_S \left[ \exp \left( \frac{qJ_{SC}R_S}{mkT} \right) - 1 \right],
\]

where J_L, J_D, and J_S are the photocurrent density, the forward biased current density, and the reverse saturation current density of the solar cell, respectively. The q, m, k, and T are the absolute temperature, respectively. For a given forward bias V, the resistance of the diode is much smaller than R_S under dark [Fig. 4(a)]. By neglecting the R_SH, the forward bias V mainly drops on R_S under dark. Therefore, by the dark I-V curve [Fig. 4(b)], it can be found that the R_S of the a-C:Pd/Si prepared at RT is much bigger than that of the a-C:Pd/Si prepared at 350 °C. Figure 4(b) shows that the dark I-V curves of the a-C:Pd/SiO₂/Si and a-C:Pd/Si prepared at 350 °C are basically coincident. Thus, the two solar cells can be considered to have equivalent R_S. According to the formula (1), J_SC is largely enhanced when R_S decreases significantly. The remarkably decreasing R_S of the device is attributed to the increase in sp²-bonded carbon clusters in the a-C:Pd film caused by the high temperature deposition (Fig. 2).

Figure 5 shows the energy-band diagram of the a-C:Pd/SiO₂/Si solar cell fabricated at 350 °C, where E_F and E_V are the Fermi level and energy gap, respectively. E_C and E_V are the conductance-band energy and valence-band energy, respectively. According to the Raman spectrum of the a-C:Pd film deposited at 350 °C, we can get the positions
of D and G peaks and the ratio of their intensities, which demonstrate that the a-C:Pd film deposited at 350 °C is a graphitelike a-C film with a relatively small energy gap (E_g < 1 eV).\textsuperscript{13–15} Under illumination, the small E_g caused by the high temperature deposition makes electron transition easier, which can help the a-C:Pd film to generate much more carriers. The Hall effect measurement shows that the a-C:Pd film deposited at 350 °C is a quasi-intrinsic semiconductor with a very small Hall coefficient (~0). The E_g of the Si substrate is about 1.1 eV.

As discussed above, the Pd doping and high temperature deposition can help the a-C:Pd film to produce much more carriers under illumination, which increases the conversion efficiency. Besides, the large V_{OC} of the solar cell can further enhance the conversion efficiency. Under illumination, the electrons and holes generated in the a-C:Pd film and the Si substrate are collected by virtue of the built-in electric field at the junction, where holes and electrons are directed to the a-C:Pd film and the n-Si substrate, respectively. Thus, the formation of the charge accumulation layer on both sides can reduce the built-in electric field barrier, and the reduced barrier is equal to the V_{OC}. Thereby, the V_{OC} depends on the barrier height of the junction.\textsuperscript{16} The increase in sp\textsuperscript{2}-bonded carbon clusters in the a-C:Pd film deposited at higher temperature can lead to a higher barrier height for a-C:Pd/Si. And, the SiO\textsubscript{2} layer in the a-C:Pd/SiO\textsubscript{2}/Si can further increase the barrier height.\textsuperscript{17} Thus, the high barrier height generates the high V_{OC} under illumination, which can increase the power conversion efficiency. Therefore, the a-C:Pd/SiO\textsubscript{2}/Si solar cell exhibits the remarkably enhanced power conversion efficiency, with the high V_{OC} and J_{SC}.

In summary, the a-C:Pd/SiO\textsubscript{2}/Si and a-C:Pd/Si junctions have eminent photovoltaic characteristics. Under light illumination of 15 mW/cm\textsuperscript{2}, the a-C:Pd/SiO\textsubscript{2}/Si solar cell fabricated at 350 °C has a high power conversion efficiency of 4.7%, which is ascribed to the Pd doping and the increase in sp\textsuperscript{2}-bonded carbon clusters in the carbon film. This study shows that the a-C:Pd/SiO\textsubscript{2}/Si structure has great potential in photovoltaic solar cells for its high power conversion efficiency, low cost, and it is highly chemical and environmentally stable.

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\textsuperscript{1}J. Potocnik, \textit{Science} \textbf{315}, 810 (2007).