



# Supermagnetron plasma CVD of highly effective a-CN<sub>x</sub>:H electron-transport and hole-blocking films suited to Au/a-CN<sub>x</sub>:H/p-Si photovoltaic cells

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## ABSTRACT

Hydrogenated carbon nitride (a-CN<sub>x</sub>:H) films (0–500 nm) were deposited on p-Si wafers to make Au/a-CN<sub>x</sub>:H/p-Si photovoltaic cells using i-C<sub>4</sub>H<sub>10</sub>/N<sub>2</sub> supermagnetron plasma chemical vapor deposition. At a lower electrode RF power (LORF) of 50 W and an upper electrode RF power (UPRF) of 50–800 W, hard a-CN<sub>x</sub>:H films with optical band gaps of 0.7–1.0 eV were formed. At a film thickness of 25 nm (UPRF of 500 W), the open circuit voltage and short circuit current density were 247 mV and 2.62 mA/cm<sup>2</sup>, respectively. The highest energy conversion efficiency was 0.29%. The appearance of the photovoltaic phenomenon was found to be due to the electron-transport and hole-blocking effect of thin a-CN<sub>x</sub>:H film.

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## 1. Introduction

As state-of-the-art Si-based photovoltaic cells are still quite expensive, a new type of solar cell material based on various novel materials has recently become of interest to photovoltaic researchers. Hydrogenated amorphous carbon nitride (a-CN<sub>x</sub>:H) films with various CC bonding and disorder structures have been expected to become very important materials for photovoltaic cells because of their semiconducting properties. It has been shown that the structural, electrical, optical, and mechanical properties of amorphous carbon films can be greatly modified by the incorporation of hydrogen and nitrogen depending on the bonding configuration structure [1,2]. It is found, for example, that incorporated nitrogen increases the electrical conductivity, and that this effect is accompanied by a decrease in the associated activation energy as well as in the band gap energy ( $\pi$  and  $\pi^*$  states of sp<sup>2</sup> sites) [3,4].

Despite the availability of various reports related to the properties of a-CN<sub>x</sub> and a-CN<sub>x</sub>:H films, there have been few studies investigating the appropriate materials for various applications, such as diodes and photovoltaic cells [5–7]. The a-CN<sub>x</sub> and a-CN<sub>x</sub>:H films are formed by various deposition techniques, and their physical properties are dependent on the deposition conditions. Radio frequency plasma chemical vapor deposition (CVD) is a useful technique for the deposition of a-CN<sub>x</sub> and a-CN<sub>x</sub>:H films [1–4]. Among the RF plasmas, supermagnetron plasma is a high-density plasma and is suited to the high-rate deposition of films by a sputter-assisted plasma CVD [8]. By use of this supermagnetron plasma, hard a-CN<sub>x</sub>:H films with low

resistivity that show excellent field emission characteristics have been deposited [2]. A hard a-CN<sub>x</sub>:H film called nitrogen-doped diamond-like carbon (DLC:N) includes many sp<sup>3</sup> and sp<sup>2</sup> CC bonds and few CH bonds, and shows a low resistivity of 0.03 Ωcm [9]. The electrical conductivity of our a-CN<sub>x</sub>:H films was of n-type [10].

In this study, we deposited a-CN<sub>x</sub>:H films on p-Si substrates and measured the diode *I*–*V* characteristics. We report herein the optical properties of a-CN<sub>x</sub>:H films and the photovoltaic cell properties, including the short circuit current density (*I*<sub>SC</sub>), open circuit voltage (*V*<sub>OC</sub>), and energy conversion efficiency, for fabricated Au/a-CN<sub>x</sub>:H/p-Si heterojunction photovoltaic cells.

## 2. Experimental

a-CN<sub>x</sub>:H films were formed using a supermagnetron plasma CVD set up with two parallel magnetron electrodes [9]. Two RF power sources at the same RF frequency (13.56 MHz) were supplied to two electrodes through matching networks. A magnetic field of approximately 80 G was applied between two electrodes located 40 mm apart. The phase difference between the two RF voltages was fixed at 180°. Two kinds of Si and glass (SiO<sub>2</sub>) substrates were located on the lower electrode. Si wafers were used for measurement of the deposition rate, and glass substrates were used for measurements using the ultraviolet (UV) spectrometer. During film deposition, the lower electrode was heated to 100 °C using a heated oil circulator. Both substrates were apt to be easily heated to more than 100 °C by exposure to plasma. Using the intermittent plasma CVD technique with a 16.7% duty cycle at 6-min periods, we tried to suppress the overheating of the substrate.

i-C<sub>4</sub>H<sub>10</sub> (50 sccm) and N<sub>2</sub> (120 sccm) were introduced into the CVD chamber through each mass flow controller. In this way, a-CN<sub>x</sub>:H films were formed at a N<sub>2</sub> concentration of 70%. The gas pressure in the

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chamber was maintained at 4 Pa. The film thicknesses were measured by profilometry. The hardness of the films was determined by a dynamic ultra-micro-hardness tester (DUH-200; Shimadzu) by analyzing the displacement vs. the load curve. The optical band gap was estimated from the Tauc formula using optical absorption data specified by the UV/VIS/NIR spectrometer at normal incidence, which has been commonly used for amorphous materials. By plotting the  $(\alpha h\nu)^{1/2}$  versus the photon energy  $h\nu$ , the optical band gap was determined from the intercept of the linear portion of the plot on the energy axis [11].

The p-Si wafers (0.02  $\Omega\text{cm}$ ) used for the photovoltaic cells were cleaned in HF:H<sub>2</sub>O (1:20) solution to remove the native oxide layer on the surface before film deposition. a-CN<sub>x</sub>:H film was deposited on the cleaned p-Si substrate. Gold contacts with a thickness of 30 nm were deposited for the solar cell by a magnetron sputter deposition system on the a-CN<sub>x</sub>:H surfaces. The contact of the gold with the a-CN<sub>x</sub>:H film was found to be ohmic. The 30-nm-thick gold film was semitransparent in visible light. Back ohmic contacts between the p-Si and Al film-like wire were made using conductive silver pastes. The current–voltage (*I*–*V*) characteristics of the Au/a-CN<sub>x</sub>:H/p-Si photovoltaic cell were measured with a semiconductor parameter analyzer. The photovoltaic behavior of the fabricated heterojunctions was investigated under illumination by a Xenon arc lamp (L2274; Hamamatsu Photonics) equipped with a UV cut filter with a wavelength ranging from 380 to 2000 nm (close to AM 1.5).

### 3. Results and discussion

a-CN<sub>x</sub>:H films were deposited on Si and glass substrates at a lower electrode RF power (LORF) of 50 W as a function of the upper electrode RF power (UPRF). The deposition rate was estimated using a net time with plasma generation (during intermittent runs). The deposition rates of films increased with the UPRF (50–800 W) from 51 to 99 nm/min. The optical band gap of the a-CN<sub>x</sub>:H films vs. UPRF was measured, as shown in Fig. 1. The optical band gap decreased with an increase in the UPRF from 50 to 800 W. The maximum optical band gap was 1.0 eV, and the minimum was 0.7 eV. At 500/50 W, the DC self-bias voltage of the lower electrode was approximately –150 V. The hardness of the a-CN<sub>x</sub>:H films was measured at LORF of 50 W as a function of UPRF (50–800 W) and was found to be almost constant (about 30 GPa); the hardness was also sufficiently greater than that of our quartz glass wafer (about 22 GPa).

*I*–*V* characteristics of a Au/a-CN<sub>x</sub>:H/p-Si photovoltaic cells were measured in the dark, as shown in Fig. 2. They showed a rectifying curve in the dark, indicating the formation of a heterojunction

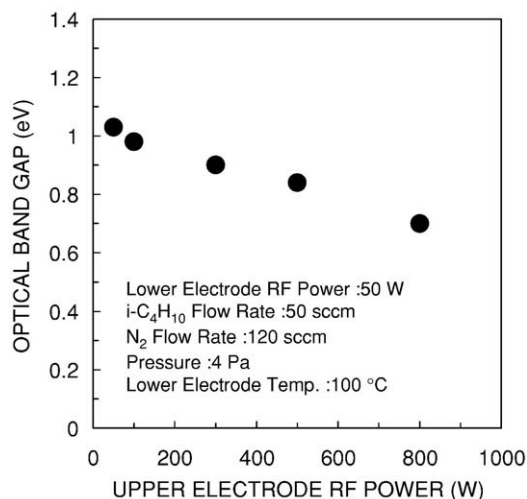


Fig. 1. UPRF dependences of the optical band gap in a-CN<sub>x</sub>:H films deposited at LORF of 50 W.

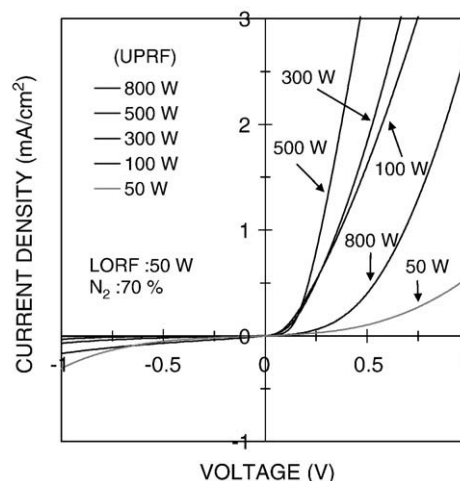


Fig. 2. *I*–*V* characteristics of the Au/a-CN<sub>x</sub>:H/p-Si photovoltaic cells measured under darkness. a-CN<sub>x</sub>:H films were deposited at 50–800/50 W.

between the a-CN<sub>x</sub>:H film and the p-Si substrate. a-CN<sub>x</sub>:H films with a thickness of 25 nm and a 70% N<sub>2</sub> concentration were deposited at a LORF of 50 W and UPRF of 50–800 W. At a forward current density of 1 mA/cm<sup>2</sup>, the forward voltage (*V*<sub>F</sub>) of the 500/50 W solar cell reached a minimum (0.28 V). With a decrease of UPRF from 500 to 50 W or an increase of UPRF from 500 to 800 W, the values of *V*<sub>F</sub> (forward current density of 1 mA/cm<sup>2</sup>) were increased. The increase of *V*<sub>F</sub> with the decrease in UPRF from 500 to 50 W is ascribed to an increase in resistivity, which usually varies proportionally to the optical band gap [9]. The cause of the increase of *V*<sub>F</sub> with an increase of UPRF from 500 to 800 W is believed to be degradation of the a-CN<sub>x</sub>:H/p-Si interface. The rationale is as follows. In response to the increase of UPRF from 500 to 800 W, the plasma potential was increased and higher energy positive ions were irradiated on a p-Si substrate. As a result, higher energy ions were implanted in the p-Si surface and degraded the a-CN<sub>x</sub>:H/p-Si interface.

The open circuit voltage (*V*<sub>OC</sub>) and short circuit current density (*I*<sub>SC</sub>) of the photovoltaic cells were measured under illumination by a Xenon lamp (close to AM 1.5), as shown in Fig. 3. With increases of UPRF from 50 to 500 W, *V*<sub>OC</sub> and *I*<sub>SC</sub> increased. However, with a further increase of UPRF from 500 to 800 W, *V*<sub>OC</sub> and *I*<sub>SC</sub> decreased. With the change of UPRF, the variation ratio of *V*<sub>OC</sub> was relatively small

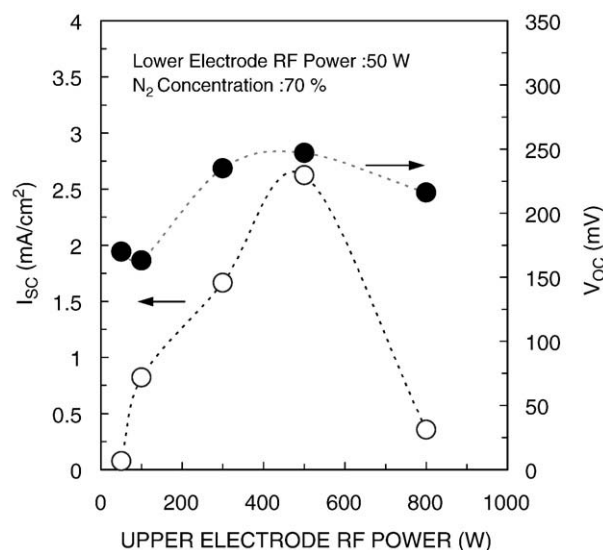


Fig. 3. *V*<sub>OC</sub> and *I*<sub>SC</sub> of the photovoltaic cells measured under the illumination of a Xenon lamp. a-CN<sub>x</sub>:H films were deposited at 50–800/50 W.

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