Fabrication of C-rich a-SiC Semiconductor Nanoparticles Having Variable Optical Gaps and Particle Sizes Using High-density Plasma in Localized Area

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ABSTRACT

Novel method of fabricating nitrogen-doped carbon-rich amorphous silicon-carbon alloy nanoparticles was successfully established using radio-frequency (r. f.) plasma-enhanced vapor deposition (CVD) system with a porous aluminum plate set between a cathode and an anode. Nanoparticles (Nps) were fabricated in high-density plasma regions generated in pores of the porous aluminum plate. Sizes of Nps were dependent on the transit time required for nuclei to pass through high density plasma regions during CVD synthesis. The average diameter of nitrogen-doped (N-doped) carbon-rich amorphous silicon-carbon alloys (C-rich a-SiC) Nps was successfully controlled within the range from 271.2 to 14.8 nm by changing the conditions of CVD synthesis: transit time, r. f. power, chamber pressure, and plate thickness. The optical gaps of C-rich a-SiC Nps were satisfactorily controlled by changing Si/C ratio at amorphous Si-C network in C-rich a-SiC (changing Si/C ratio of the source material used in CVD synthesis). The optical gaps of C-rich a-SiC Nps were controllable from 2.04 to 1.19 eV. The Nps showed photon-to-current conversion functionality in the photoelectrochemical measurement under 360 nm irradiation. In other words, C-rich a-SiC Nps are applicable to devices using photon-to-electron conversion in nano-meter size.

Keywords : C-rich a-SiC Nanoparticles, Variable Optical Gaps and Particle Sizes, High-density Plasma in Localized Area, Photon-to-current Conversion Functionality

1. Introduction

In recent years, semiconductor nanoparticles (Nps) and quantum-dots based on CdS, CdSe, Si, GaAs, InGaAs, TiO, ZnO, and SnO, have received much attention because they have been expected to have a wide range of application, such as optoelectronics (photovoltaic cell) and LED, catalysts (photocatalysts), and medical application (bio-medical imaging). Among various semiconductor materials, semiconductor Nps of CdS, PbS, and GaAs have been widely studied. However, these materials have high toxicity and cannot be used for the biomedical application. There are two challenges to overcome for wide-ranging practical applications (such as photocatalysts and bio-imaging) of semiconductor Nps. Firstly, the toxicity of semiconductor materials should be low. Secondly, diameters of the semiconductor particles should be controlled up to ca. 10 nm and semiconductor properties (e.g. band gaps) should be controlled in a wide range.

N-doped C-rich a-SiC that our research group has recently developed using plasma CVD synthesis is a promising candidate for such semiconductor materials because it has no-toxicity and optical gaps of C-rich a-SiC can be controlled from 1.25 to 2.76 eV by changing Si/C ratio at amorphous Si-C network in C-rich a-SiC. The objective of this study is to establish the CVD synthesis method of C-rich a-SiC Nps since their fabrication method has not been reported.

There are many reports relating vacuum and solution-processing methods that can fabricate Nps. Typical-vacuum-based fabrication techniques use the radio-frequency (r. f.) plasma reactor or laser ablation. Solution-processing method includes synthesis routes based on the reaction of silicon compounds such as SiCl or NaSi with selected salts or reducing agent. However, with these methods, diameters of Nps are variable only in a narrow range. These methods, therefore, cannot be applied for the fabrication of C-rich a-SiC Nps.

Our research group tried to establish the CVD synthesis method of fabricating Nps, which enables to control Nps diameters in a wide range (from sub-micrometer to a few nm), and focused on clusters generated in the plasma synthesis process. The diameters of the clusters were several nm and probably controllable by output power of r. f. power source.

The clusters of which sizes were below a few nanometers were formed in silane r. f. discharges and introduced in semiconductor (a-Si:H) thin films when the films were synthesized by the CVD method with high r. f. power (at the condition of high rate deposition). The C-rich a-SiC Nps of which optical gaps are variable will be achieved if the method that enables to extract the clusters (Nps) from the plasma is established.

It has been reported that nuclei of Nps formed through polymerization of radicals generated in plasma and Nps grew while depositing radicals on the surfaces of nuclei and Nps clumping. The formation rate of nuclei and the growth rate of Nps were accelerated in plasma with higher energy density (i.e. higher r. f. power) by higher densities of electrons and radicals. In this study, our research group devised a method for creating high energy density plasma regions in plasma of CVD synthesis system. When a conductive (aluminum) porous plate that is insulated from the cathode and the anode is set in plasma (Fig. 1(A)), electrons in plasma are trapped by the conductive porous plate. The plate is highly-negatively charged and high-
density plasma regions are generated in pores of the plate (Fig. 1(B)). Radio-frequency power is applied so that the lower electrode can function as a ground and the upper electrode as a highly negatively charged ($V_{DC} = ca. -500 V$) power electrode. Plasma is formed between the upper electrode and the conductive plate (Fig. 1(B)). Source materials are supplied and flowed down from the top of the plate. Nuclei are formed in plasma over the plate, passed through high-density plasma regions (inside pores of the plate), and swept downstream by the evacuation of the pump placed under the lower electrode. NPs grow while they pass through high energy density regions and can individually accumulate on the substrate above the lower electrode without depositing a film. The reason why a film is not deposited on the substrate is that plasma is not formed between the conductive porous plate and the lower electrode (ground).

The objective of this study is to develop a novel fabrication method of semiconductor NPs of which sizes and optical gaps are separately controllable. C-rich a-SiC semiconductor NPs are fabricated using plasma-enhanced CVD synthesis with the aluminum porous plate. The controllable ranges of sizes and optical gaps of the particles are checked. In addition, we try to elucidate the mechanism of C-rich a-SiC NPs formed by our unique plasma technique and establish the method.

2. Experimental Methods

2.1 Fabrication of C-rich a-SiC semiconductor NPs

N-doped C-rich a-SiC NPs were prepared by setting an aluminum porous plate between cathode and anode electrodes in r. f. plasma-enhanced chemical vapor deposition (r.f.-PeCVD) system (13.56 MHz, SAMCO Inc., BPD-1) (Fig. 1(A)). N-doped C-rich a-SiC NPs were generated and accumulated on highly Sb-doped silicon (111) substrates (resistivity of 0.02 $\Omega$ cm) and insulating glass plates. The substrates and plates were rinsed thoroughly by ultra-sonic cleaning in isopropanol for 15 minutes before being placed in a reaction chamber of CVD system and cleaned by sputtering with Ar plasma (200 W for 15 minutes). The interval between the anode and the cathode were set at 4 cm. Before the Nps fabrication, the substrates were heated up to 135 °C by Ar plasma exposure (200 W, 15 Pa). A mixed solution of tetramethylsilane (TMS) (Si and C sources) and 1,1,3,3-tetramethyldisilathane (TMDS) (C and N sources) at a ratio of TMDS/(TMDS + TMS) = 0.02 was used as a source material. The vaporized liquid source heated to 80 °C was introduced into the reaction chamber. The source gas at a flow rate of 1.0 sccm and H$_2$ gas at a rate of 50 or 163.5 sccm were introduced simultaneously. N-doped C-rich a-SiC NPs were fabricated under the condition that r. f. power was in the range from 100 to 50 W and chamber pressure was varied from 200 to 60 Pa. The fabrication time was 10 minutes. The fabrication conditions of N-doped C-rich a-SiC NPs having different average diameters were shown in Table 1.

2.2 Geometric structure of metal porous plate

The material of the porous plate was aluminum. The pore diameter was 5.0 mm and the pore interval was 5.0 mm. The plates of different thicknesses from 3.0 to 0.7 mm were prepared. A plate was set on four insulating quartz cylinders of which diameters were 1 cm and heights were 1.5 cm on the anode of CVD system. (Fig. 1(A))

2.3 Sintering process of N-doped C-rich a-SiC Nps on silicon substrates and glass plates

The resulting N-doped C-rich a-SiC NPs on silicon substrates and glass plates were rinsed thoroughly by ultra-sonic cleaning in isopropanol for 15 minutes before being placed in a reaction chamber of CVD system and cleaned by sputtering with Ar plasma (200 W for 15 minutes). The interval between the anode and the cathode were set at 4 cm. Before the Nps fabrication, the substrates were heated up to 135 °C by Ar plasma exposure (200 W, 15 Pa). A mixed solution of tetramethylsilane (TMS) (Si and C sources) and 1,1,3,3-tetramethyldisilathane (TMDS) (C and N sources) at a ratio of TMDS/(TMDS + TMS) = 0.02 was used as a source material. The vaporized liquid source heated to 80 °C was introduced into the reaction chamber. The source gas at a flow rate of 1.0 sccm and H$_2$ gas at a rate of 50 or 163.5 sccm were introduced simultaneously. N-doped C-rich a-SiC NPs were fabricated under the condition that r. f. power was in the range from 100 to 50 W and chamber pressure was varied from 200 to 60 Pa. The fabrication time was 10 minutes. The fabrication conditions of N-doped C-rich a-SiC NPs having different average diameters were shown in Table 1.

Table 1. Fabrication conditions of N-doped C-rich a-SiC NPs.

| Condition | r. f. power (W) | Pressure (Pa) | Hydrogen (sccm) | Plate thickness (mm) | Average particle diameter (nm) |
|-----------|----------------|--------------|-----------------|---------------------|-----------------------------|
| A         | 100            | 200          | 50              | 3.0                 | 271.2                       |
| B         | 80             | 200          | 50              | 3.0                 | 187.3                       |
| C         | 50             | 200          | 50              | 3.0                 | 120.2                       |
| D         | 50             | 100          | 50              | 3.0                 | 68.9                        |
| E         | 50             | 60           | 50              | 3.0                 | 37.1                        |
| F         | 50             | 60           | 50              | 1.5                 | 23.8                        |
| G         | 50             | 60           | 50              | 0.7                 | 14.8                        |
| H         | 50             | 60           | 163.5           | 0.7                 | 14.8                        |
| I         | 50             | 100          | 163.5           | 0.7                 | 52.1                        |
| J         | 50             | 100          | 163.5           | 1.4                 | 102.5                       |
| K         | 50             | 200          | 163.5           | 1.4                 | 212.3                       |
| L         | 100            | 200          | 163.5           | 3.0                 | 242.2                       |
glass plates were sintered (550 °C for 3 h under Ar atmosphere) to be adhered on the substrates because the adhesion between particles and substrates or plates was weak for performing photoelectrochemical measurements. Sintering process conditions were determined so as to change the surface morphology of N-doped C-rich a-SiC NPs in microscope measurement and the chemical composition of N-doped C-rich a-SiC Nps in XPS measurement before and after the sintering.

2.4 Structural evaluation for N-doped C-rich a-SiC Nps

2.4.1 Direct force microscope (DFM) measurement

The geometry of the Nps on glass plates without sintering was evaluated using the scanning atomic force microscope (Seiko Instruments Inc., SPA-400-DVM). DFM cantilever with a sharp tip of 0.2 mm attached at its end (Seiko Instruments Inc., SIDF-40) was used. The surface morphology of N-doped C-rich a-SiC Nps deposited on Si substrates was identical to that of the Nps fabricated on glass plates under the same deposition conditions. No significant difference was seen in the surface morphology before and after the sintering process.

2.4.2 XPS measurement of N-doped C-rich a-SiC Nps

The chemical composition of N-doped C-rich a-SiC Nps deposited on glass plates without the sintering process was examined by XPS measurement (Thermo Scientific, Model. KAlpha + X-ray Photoelectron Spectrometer System). X-Ray source was monochromated, micro-focused Al Kα (1.486.6 eV). Take-off angle was 90°. The experimental binding energy resolution was 0.5 eV. The energy levels were based on the gold 4f7/2 XPS line at 83.9 eV. The XPS measurements were carried out after two seconds surface sputtering by Ar+ ion (3,000 eV) in order to eliminate a surface oxidized layer. Spectra were deconvoluted with the software attached to the instrument. The chemical composition of N-doped C-rich a-SiC Nps deposited on Si substrates was identical to that of the Nps fabricated on glass plates under the same deposition conditions. No significant difference was seen in the chemical composition of N-doped C-rich a-SiC Nps before and after the sintering process.

2.4.3 Hall effect measurement of N-doped C-rich a-SiC Nps

Properties of the semiconductor were determined by Hall measurement with van der Pauw method (Ecopia Co., Ltd. HMS-3000). Ohmic contacts were formed by 1 mm² Au vapor deposited with a resistance heating deposition system on the four corners of the porous plate. Hence, we examined the correlation between particle sizes and these three synthesis conditions as below.

2.4.4 Optical gap measurement of N-doped C-rich a-SiC Nps

The optical gap (Eog) was estimated from Tauc's plot using Tauc's equation (Eq. (2)), which is the result of the conversion.

\[ \alpha = \ln\left(\frac{I_0}{100}\right) \times 10^8 \]  

(1)

\[ T = \text{transmittance (\%) and } d \text{ is film thickness (Å) of the sample film.} \]

\[ \text{The optical gap (Eog) was estimated from Tauc's plot using Tauc Eq. (2), which is the result of the conversion.} \]

\[ (a d h v)^{1/2} = B (E_{og} - h v) \]  

(2)

\[ hv \text{ is the energy of incident light, } B \text{ is constant, and } E_{og} \text{ is the optical gap of the sample film.} \]

2.4.5 Photoelectrochemical measurement of N-doped C-rich a-SiC Nps

A sign (n or p) of the semiconductor having lower mobility such as amorphous semiconductor cannot be judged accurately by Hall measurement only in many cases. In this study, it was determined by photoelectrochemical measurement with Potentio/galvanostat (Hokuto Denko Corporation HZ-3000 system). The measurement was performed with linear sweep voltammetry (LSV) using three electrode electrochemical cells. As an electrolyte solution, 0.2 M NaH2PO4 was used. A working electrode was the sintered N-doped C-rich a-SiC Nps on Si substrates. The geometric area of the working electrode was 0.1 cm². Platinum wire served as a counter electrode. A commercial Ag/AgCl (3 M KCl) electrode was used as the reference electrode. Before the measurement, the solution was bubbled for 15 minutes to remove dissolved O2 thoroughly. All the measurements were performed at room temperature (25 °C). Sweeping rate was 5 mV/sec⁻¹. Hg-Xe lamp (USHIO Co., Ltd. SP-9-250DV) was used as UV sources. The UV source was set at a distance of 9 cm from N-doped C-rich a-SiC Nps surface and UV lamp irradiated perpendicular to the surface of Nps. The quantum efficiency (QE) was calculated using the following Eq. (3).

\[ QE = \frac{N_e}{N_p} \]  

(3)

\[ N_e \text{ is the number of incident photons. } N_e \text{ is the number of electrons.} \]

\[ N_p \text{ and } N_e \text{ were calculated using the following Eqs. (4) and (5).} \]

\[ N_e = \frac{I_p}{e} \]  

(4)

\[ N_p = \frac{W}{E} \]  

(5)

\[ I_p \text{ is photo response current observed at } 3.0 \text{ V vs. Ag/AgCl, } e \text{ is elementary charge, } W \text{ is the photo intensity, and } E \text{ is photon energy of the light with wavelength of 360 nm.} \]

3. Results and Discussion

3.1 Mechanism of Nps formation in high-density plasma region and control method of Nps sizes

N-doped C-rich a-SiC Nps having the average diameter of 271.2 nm were fabricated by plasma CVD with the aluminum porous plate under the condition A indicated in Table 1. DFM image of the resulting N-doped C-rich a-SiC Nps was shown in Fig. 2(B).

Nps could not be obtained when CVD synthesis was performed without the aluminum porous plate (Fig. 2(A)). N-doped C-rich a-SiC Nps were fabricated only when high density plasma region was generated in pores of the plate as shown in Fig. 1(B). In the case that plasma was generated between the anode and the cathode (no porous plate) and high density plasma regions were not generated, thin films were deposited on the substrate surface without Nps formation. Thus, high density plasma regions in the pores seem to make a substantial contribution to fabricate Nps. If Nps were formed in plasma regions, particle sizes could be controlled by plasma conditions such as r. f. power or pressure of the reaction chamber. We tried to clarify the mechanism of Nps formation by verifying the relation between Nps sizes and the conditions of CVD synthesis.

The mechanism of cluster formation during the synthesis of semiconductor thin films using plasma CVD with higher r. f. power has been reported as follows. Nano-sized clusters were formed in two steps: The first step is the formation of nuclei by polymerization of dissociated reactive species (radicals) in plasma. The second is the growth of Nps by depositing radicals on the surface of nuclei.

Considering from the mechanism, the following three synthesis conditions of plasma CVD seem to affect particle sizes: The first condition is r. f. output power that is related to the rate of formation and the density of radical species in plasma. The second and third are the conditions related to the time of particle growth in plasma such as total pressure of the reaction chamber and the thickness of the porous plate. Hence, we examined the correlation between particle sizes and these three synthesis conditions as below.
3.1.1 Dependence of particle sizes on r. f. power

DFM images of Nps fabricated using the aluminum porous plate set in CVD with r. f. power of 100, 80, and 50 W are shown in Figs. 2(B)–2(D). The detailed conditions of Nps fabrication are shown in Table 1 (condition A, B, and C). From Fig. 2, average particle diameters of N-doped C-rich a-SiC Nps with 100, 80, and 50 W were estimated to be 271.2, 187.3, and 120.2 nm, respectively (Table 1). The values were decreased with decreasing r. f. power from 100 to 50 W. The higher the applied r. f. output power is, the higher the density of the radical species in plasma become. The higher density of the radical species induces the higher rate of particle growth (higher deposition rate at the nucleus surface). This results in the larger size of Nps.

3.1.2 Dependence of particle sizes on pressure in the reaction chamber

Figures 3(A)–3(C) show DFM images of Nps fabricated with different total pressure; (A) total pressure = 200 Pa, (B) 100 Pa, and (C)–(E) 60 Pa and different aluminum plate thicknesses; (A)–(C) thickness = 3.0 mm, (D) 1.5 mm, and (E) 0.7 mm (condition C to G).

Average diameters of Nps estimated from Fig. 3 are 37.1, 23.8, and 14.8 nm. The thicknesses of aluminum plates are respectively 3.0, 1.5, and 0.7 mm (Table 1). The values of average diameters decreased from 37.1 to 14.8 nm with a decrease in plate thicknesses. The nuclei were found to grow in high density plasma region in pores of the porous plate because the particle diameter was reduced with a decrease in length of high density plasma regions at the constant r. f. power and the constant pressure.

3.1.3 Dependence of particle sizes on aluminum plate thicknesses

In order to identify whether the plasma regions affect particle growth, the length of high density plasma regions were varied by changing the aluminum plate thickness from 3.0 to 0.7 mm. Figures 3(C)–3(E) show DFM images of the particles fabricated with varying aluminum plate thicknesses from 3.0 to 0.7 mm. The detailed conditions of Nps fabrication are included in condition E, F, and G in Table 1. Average diameters of Nps estimated from Fig. 3 are 37.1, 23.8, and 14.8 nm. The thicknesses of aluminum plates are respectively 3.0, 1.5, and 0.7 mm (Table 1). The values of average diameters decreased from 37.1 to 14.8 nm with a decrease in plate thicknesses. The nuclei were found to grow in high density plasma region in pores of the porous plate because the particle diameter was reduced with a decrease in length of high density plasma regions at the constant r. f. power and the constant pressure.

The mechanism of Nps formation mentioned above was shown in Fig. 4. Vaporized source materials were introduced into the reaction chamber and decomposed to electron and cationic species in plasma. Cations were attracted to the cathode side and electrons were attracted to the anode side in plasma. Electrons were trapped by the aluminum porous plate, and then, the plate was negatively charged. Cationic species were enclosed in the pores by the attractive force from negatively charged porous plates. The concentration of radical species in pores became higher and high-density plasma regions were generated in the pores of the plate. Nuclei formed in plasma between the cathode and the aluminum plates passed through the pores and were grown in high density plasma regions. Nps accumulate on the substrate by down force from the evacuation of the pump. The C-rich a-SiC thin films were not formed on the substrate because plasma was generated between the cathode and the aluminum plate.
The sizes of Nps were successfully controlled by r.f. output power, pressure in the reaction chamber, and thickness of the porous aluminum plate in our system. The particle sizes were shrunk to the diameter of 14.8 nm by decreasing r.f. power and sizes of high density plasma (growth region).

3.2 Control of optical gaps of N-doped C-rich a-SiC Nps and its photoelectrochemical characterization

3.2.1 Optical gap control of Nps with a diameter of 15 nm by changing the composition of source materials used in CVD synthesis

The Nps sizes were successfully controlled in the range from 250 to 15 nm as shown in the previous section. In this section, we try to regulate the optical gaps of Nps. In our previous publication, the optical gaps of N-doped C-rich a-SiC semiconductor films can be controlled from 1.25 to 2.76 eV by changing Si/C ratio at amorphous Si-C network in multi-phase structure of the resulting C-rich a-SiC.

In this study, we tried to fabricate N-doped C-rich a-SiC Nps having different Si/C ratios by adding n-hexane to source materials used in CVD synthesis in order to control their optical gaps. Semiconductor properties were examined by Hall effect measurements and photoelectrochemical measurements.

N-doped C-rich a-SiC Nps with a diameter of 15 nm and various optical gaps were fabricated by changing volume ratios of source materials (TMS : TMDS : n-hexane; 50 : 1 : x (x = 0, 1, 9)) in the synthetic condition H in Table 1. Average diameters and results of Hall effect measurements of the resulting Nps were summarized in Table 2. Tauc’s plots obtained from transmittance and absorption spectra of N-doped C-rich a-SiC Nps are shown in Fig. 5(A).

Table 2. The results of Hall effect measurement, photoelectrochemical measurement, DFM measurement, and estimated band position of N-doped C-rich a-SiC Nps with a diameter of 15 nm.

| Volume of n-hexane | Optical gap E_{opt} (eV) | Carrier density (10^{11} cm^{-2}) | Carrier mobility (cm^2 V^{-1} s^{-1}) | Conduction type | Onset potential for H_2 evolution (V vs. Ag/AgCl) | Onset potential for photocurrent (V vs. Ag/AgCl) | Quantum efficiency (%) | Potential of valence band top (V vs. SHE) | Potential of conduction band edge (V vs. SHE) | Average particle diameter (nm) |
|-------------------|--------------------------|----------------------------------|----------------------------------|---------------|---------------------------------|---------------------------------|---------------------|--------------------------------|--------------------------------|---------------------|
| 0                 | 2.04                     | 4.43                             | 3.93                             | n             | −0.857                          | 1.214                          | 0.72                | 0.545                          | −1.795                          | 14.8 |
| 1                 | 1.86                     | 4.02                             | 4.24                             | n             | −0.961                          | 1.219                          | 0.45                | 0.455                          | −1.705                          | 16.2 |
| 9                 | 1.19                     | 2.10                             | 4.82                             | n             | −0.872                          | 1.354                          | 0.21                | 0.120                          | −1.370                          | 13.7 |

Optical gaps of N-doped C-rich a-SiC Nps were estimated from Tauc’s plots.

As shown in Table 2, optical gaps of N-doped C-rich a-SiC Nps with 15 nm was successfully controlled in the range from 2.04 to 1.19 eV by increasing the ratios of n-hexane in source materials used in CVD synthesis. The average diameters of Nps were in the same range (approximately 15 nm). The change of the optical gaps of Nps was not caused by changing diameters but Si/C ratio. Semiconductor properties of N-doped C-rich a-SiC Nps with 15 nm fabricated on glass plates (insulator) were examined by Hall measurement at room temperature. Carrier densities and carrier mobility were summarized in Table 2.

The signs of Hall coefficient of all N-doped C-rich a-SiC Nps with 15 nm were negative, which indicates n-type conduction. Carrier densities and carrier mobility were in the range of ca. 4 × 10^{11} cm^{-2} and 4 cm^2 V^{-1} s^{-1}, respectively. Carrier densities slightly decreased from 4.43 × 10^{11} cm^{-2} to 2.10 × 10^{11} cm^{-2} by adding n-hexane to source materials.

The carrier densities of N-doped C-rich a-SiC thin films having optical gaps of 2.76, 1.78, and 1.25 eV (Si44-N-a-SiC, Si17-N-a-SiC, and Si18-N-a-SiC) were reported to be 1.78 × 10^{14}, 3.05 × 10^{13}, and 2.02 × 10^{14} cm^{-3}, respectively. The carrier mobility was respectively 3.16, 2.71, and 5.70 × 10^{-1} cm^2 V^{-1} s^{-1}. Although the carrier mobility of Nps was in the same range as that of thin films, the carrier densities of Nps were one order of magnitude lower than those of thin films. The chemical structure of N-doped C-rich a-SiC Nps probably reduce the activation of carriers.

3.2.2 Chemical compositions of Nps with a diameter of 15 nm

Chemical compositions of N-doped C-rich a-SiC Nps with 15 nm fabricated using a source material of TMS : TMDS : n-hexane = 50 : 1 : x (x = 0 and 9) were examined by XPS measurement performed within the range from 0 to 1,100 eV at a scan rate of 10 eV min^{-1} (0.1 eV step^{-1}). XPS spectra of N-doped C-rich a-SiC Nps fabricated with n-hexane = 0 is shown in Fig. 6. On the surfaces of both N-doped C-rich a-SiC Nps, peaks of Si2p, C1s, N1s, and O1s were confirmed at 99, 285, 398, and 531 eV, respectively. The atomic concentrations of N-doped C-rich a-SiC Nps were estimated from the peak area in XPS spectra and the sensitivity factors of the atomic assigned (Table 3). N-doped C-rich a-SiC Nps were found to be mainly composed of C, Si, and O atoms. N atom of approximately 2 atom% was introduced as n-type impurity.

The atomic ratios (C : Si : N) of N-doped C-rich a-SiC Nps with n-hexane = 0 and 9 were estimated to be 26 : 32 : 3 and 53 : 17 : 0.7, respectively. The atomic concentrations of Si44 and Si18-N-a-SiC thin films are also shown in Table 3. The optical gap of Si44-N-a-SiC thin film (2.76 eV) was close to that of Nps with n-hexane = 0 (2.04 eV). The optical gap of Si18-N-a-SiC thin film (1.25 eV) was close to that of Nps with n-hexane = 9 (1.19 eV). As shown in Table 3, Si/(C + Si) ratio of Nps with n-hexane = 0 (0.45) is close to that of Si44-N-a-SiC thin film (0.49), and Si/(C + Si) ratio with n-hexane = 9 (0.25) is close to that of Si18-N-a-SiC thin film.
SiC thin film (0.21). Therefore, it was summarized that optical gaps of N-doped C-rich a-SiC Nps changed when Si/C ratio were changed at amorphous Si-C network in multi-phase structure of the amorphous silicon-carbon alloys as in the case of C-rich a-SiC films that our research group previously reported. 

In Table 3, N atom% of N-doped C-rich a-SiC with 15 nm and n-hexane = 0 (2.98 atom%) was higher than that of N-doped C-rich a-SiC with 15 nm and n-hexane = 9 (0.69 atom%). This difference may cause the difference in carrier densities between N-doped C-rich a-SiC with 15 nm and n-hexane = 0 (4.43 × 10¹³ cm⁻³) and N-doped C-rich a-SiC with 15 nm and n-hexane = 9 (2.10 × 10¹³ cm⁻³) (Table 2).

3.2.3 Optical gap control of Nps having various diameters

N-doped C-rich a-SiC Nps with a diameter of 50 nm and various optical gaps were fabricated by changing the volume ratio of source materials (TMS : TMDS : n-hexane; 50 : 1 : x (x = 0, 1, 6)) under the fabrication condition I indicated in Table 1. N-doped C-rich a-SiC Nps with 100 nm and various optical gaps were fabricated with TMS : TMDS : n-hexane in the ratio of 50 : 1 : x (x = 0, 1, 3) (condition J). N-doped C-rich a-SiC Nps with 200 nm and various optical gaps were fabricated with TMS : TMDS : n-hexane in the ratio of 50 : 1 : x (x = 0, 1, 3) (condition K). N-doped C-rich a-SiC Nps with 250 nm and various optical gaps were fabricated with TMS : TMDS : n-hexane in the ratio of 50 : 1 : x (x = 0, 1) (condition L).

Figure 5. (A) Tauc’s plots for N-doped C-rich a-SiC Nps with a diameter of 15 nm and n-hexane (a) x = 0, (b) x = 1, and (c) x = 9. (B) Tauc’s plots for N-doped C-rich a-SiC with 100 nm and n-hexane (a) x = 0, (b) x = 1, and (c) x = 3. (C) Tauc’s plots for N-doped C-rich a-SiC with 250 nm and n-hexane (a) x = 0 and (b) x = 1.

Figure 6. XPS spectra of N-doped C-rich a-SiC Nps with a diameter of 14.8 nm and n-hexane = 0. Sweep rate = 10 eV min⁻¹.

Table 3. Chemical compositions of N-doped C-rich a-SiC Nps with diameters of 15 and 100 nm by XPS measurements.

| Sample | Optical gap Eₒ (eV) | C (atom%) | Si (atom%) | N (atom%) | O (atom%) | Si/ (C + Si) | sp²/ (sp² + sp³) | Quantum efficiency (%) |
|--------|---------------------|-----------|------------|-----------|-----------|--------------|------------------|------------------------|
| N-doped C-rich a-SiC Nps with 15 nm and n-hexane x = 0 | 2.04 | 25.81 | 32.01 | 2.98 | 39.20 | 0.45 | 0.734 | 0.71 |
| N-doped C-rich a-SiC Nps with 15 nm and n-hexane x = 9 | 1.19 | 52.57 | 17.49 | 0.69 | 29.25 | 0.25 | 0.775 | 0.05 |
| N-doped C-rich a-SiC Nps with 100 nm and n-hexane x = 3 | 1.25 | 45.44 | 17.11 | 0.74 | 36.71 | 0.27 | 0.749 | 0.11 |
| Si44-N-a-SiC thin film | 2.76 | 45.9 | 44.1 | 2.30 | 7.70 | 0.49 | 0.578 | 1.22 |
| Si18-N-a-SiC thin film | 1.25 | 68.2 | 17.6 | 2.84 | 11.4 | 0.21 | 0.665 | 3.43 |
The average diameters of the resulting Nps were summarized in Table 4 and Tauc’s plots of C-rich a-SiC Nps are shown in Fig. 5(B) and (C). Optical gaps of N-doped C-rich a-SiC Nps having a diameter from 50 to 250 nm were gradually decreased with an increase in the volume ratio of n-hexane in source materials as in the case of N-doped C-rich a-SiC Nps with 15 nm. The lower limits of optical gaps of all N-doped C-rich a-SiC Nps were approximately 1.2 eV. The average diameters of Nps fabricated under the same condition were almost in the same range, even when volume ratio of n-hexane in source materials was changed. Therefore, the changes of the optical gaps of Nps having various diameters were caused by the change of Si/C ratio at amorphous Si-C network in C-rich a-SiC Nps.

The optical gaps of C-rich a-SiC Nps were successfully controlled by changing Si/C ratio of source materials used in CVD synthesis. The range of optical gap control at C-rich a-SiC semiconductor Nps with 15 nm was wide, from 2.04 to 1.19 eV, while that at Nps with 250 nm was relatively narrow, from 1.24 to 1.18 eV. Seemingly, the method to control the sizes and optical gaps of Nps separately by fabrication conditions and compositions of source materials has been reported for the first time. The particle sizes were controlled in the range from 250 to 15 nm and optical gaps were controlled from 2.0 to 1.2 eV.

As shown in Table 4, the signs of Hall coefficient of all N-doped C-rich a-SiC Nps having various diameters and optical gaps were negative, which indicates n-type conductivity. Carrier densities and carrier mobility of all N-doped C-rich a-SiC Nps having various diameters and optical gaps were in the range of ca. $4 \times 10^{13}$ cm$^{-3}$ and 4 cm$^2$V$^{-1}$s$^{-1}$, respectively. Although the carrier mobility of Nps was in the same range as that of N-doped C-rich a-SiC thin films (as in the case of N-doped C-rich a-SiC Nps with 15 nm), the carrier densities of Nps were one order of magnitude lower than those of N-doped C-rich a-SiC thin films. The method to enhance carrier densities of Nps should be developed to use Nps as semiconductor materials for electronic device.

### 3.2.4 Photoelectrochemical properties of C-rich a-SiC Nps having various diameters

In this study, photoelectrochemical measurement was employed to determine conduction types and to examine photon-to-current conversion functionality of N-doped C-rich a-SiC Nps for verifying whether Nps are applicable to photovoltaic system. The photoelectrochemical measurement does not require fabricating p-n junction and can be performed by only one (n- or p-) type semiconductor material. Photoelectrochemical studies are frequently carried out to obtain better understanding of the nature of semiconductor/solution interface. The measurement was performed using a standard photoelectrochemical set up. Current-voltage curves of N-doped C-rich a-SiC Nps fabricated under various conditions were measured in the dark and under irradiation with Hg-Xe light. The results are shown in Fig. 7. Under the dark condition, cathodic currents ($I_h$) evolution at approximately $-1.2$ V vs. Ag/AgCl were observed at all N-doped C-rich a-SiC Nps fabricated in this study. Significant anodic currents were not observed at a higher potential region over 0 V vs. Ag/AgCl. The results indicate that N-doped C-rich a-SiC Nps exhibited rectification behavior of the n-type semiconductor because N-doped C-rich a-SiC Nps has excess electrons. The positions of conduction band edges and valence band top were estimated from the valence band top of $-5.75$ eV at a-Si0.2C0.8 by UPS and the observed optical gaps. The values of all N-doped C-rich a-SiC Nps are summarized in Table 2 and 4. The positions of conduction band edges were ca. $-1.5$ V vs. SHE. In Fig. 7, the onset potentials for H$_2$ evolution (the potential when the cathodic current reaches $0.1 \mu$A cm$^{-2}$) were

| Sample | Volume of n-hexane (cm$^3$) | Optical gap (eV) | Carrier mobility (10$^3$ cm$^2$V$^{-1}$s$^{-1}$) | Carrier density (cm$^{-3}$) | Conduction type | Onset potential for photocurrent (V vs. Ag/AgCl) | (V vs. SHE) | Estimated band position of N-doped C-rich a-SiC Nps having various diameters. |
|--------|-----------------------------|------------------|-----------------------------------------------|----------------------------|----------------|-----------------------------------------------|------------|--------------------------------------------------------------------------------|
| N-doped C-rich a-SiC Nps with 50 nm | 0 | 1.79 | 4.77 | 4.21 | n | -1.037 | 0.487 | n | 0.81 | 0.820 | 0.576 | 1.522 | 0.76 | 0.520 | 0.81 | 0.487 | n | 0.81 | 0.820 | 0.576 | 1.522 | 0.76 | 0.520 | 0.81 |
| N-doped C-rich a-SiC Nps with 100 nm | 1 | 1.54 | 4.21 | 4.11 | n | -0.807 | 0.902 | n | 0.807 | 1.522 | 0.76 | 0.520 | 0.81 | 0.487 | n | 0.81 | 0.820 | 0.576 | 1.522 | 0.76 | 0.520 | 0.81 |
| N-doped C-rich a-SiC Nps with 200 nm | 2 | 1.24 | 3.65 | 4.11 | n | -0.613 | 1.547 | n | 0.81 | 0.820 | 0.576 | 1.522 | 0.76 | 0.520 | 0.81 | 0.820 | 0.576 | 1.522 | 0.76 | 0.520 | 0.81 |
| N-doped C-rich a-SiC Nps with 250 nm | 3 | 1.18 | 3.49 | 4.49 | n | -0.63 | 1.299 | n | 0.81 | 0.820 | 0.576 | 1.522 | 0.76 | 0.520 | 0.81 | 0.820 | 0.576 | 1.522 | 0.76 | 0.520 | 0.81 |
ca. –0.9 V vs. Ag/AgCl at all N-doped C-rich a-SiC Nps, and higher than that of the conduction band edges by ca. 0.6 V. Consequently, the estimated positions of valence and conduction states are slightly lower than the actual edge of conduction band and top of valence band. These results also indicate that the reactivity toward H2 evolution at all N-doped C-rich a-SiC Nps surfaces was quite high.

In Fig. 7, the photo-induced anodic currents (photocurrents) were observed at all N-doped C-rich a-SiC Nps surfaces. The surface morphology of N-doped C-rich a-SiC Nps observed with DFM was not changed before and after I–V measurement under UV exposure. It indicates that the origin of the current flow is not dissolution reaction of N-doped C-rich a-SiC but oxygen evolution and/or surface oxidation. The observed photocurrents indicate that N-doped a-SiC Nps show the photon-to-electron conversion functionality and have a potential ability to be applied to electronic devices such as photovoltaic cells.

Current-voltage curves of N-doped a-SiC Nps with 15 nm and n-hexane = 0 were measured in the dark and under irradiation with Hg-Xe light through the optical filter U-360 (bandpass filter of 360 nm; 3.4 eV) and G-533 (bandpass filter of 533 nm; 2.3 eV) (not shown). The photocurrents were observed under irradiation with Hg-Xe light through U-360, but not observed through G-533. In Fig. 8(A), the n-type semiconductor. The flat band potentials of N-doped a-SiC Nps with 15 nm and n-hexane = 0 did not function under irradiation with light under G-533, the anodic current under irradiation with Hg-Xe light was attributable to the photo-induced anodic currents (not the anodic current accelerated by heat of UV light).

The onset potentials of the photocurrent (the potential when the cathodic current reaches 0.1 µA cm⁻²) observed at all N-doped C-rich a-SiC Nps in Fig. 7 are summarized in Table 2 and 4. The onset potentials (from 0.447 to 1.700 V vs. Ag/AgCl) are relatively higher than the estimated values of valence band top (from 0.115 to 0.545 V vs. SHE). If the top of valence band is higher than 1.23 V vs. NHE (the standard potential toward oxygen evolution), the onset potential of photocurrent should be close to the flat band potential of the n-type semiconductor. Flat band potentials of N-doped C-rich a-SiC Nps are seemingly close to the edge of conduction band. The valence band top of N-doped C-rich a-SiC Nps was, however, lower than 1.23 V vs. NHE. Because fermi levels should be set at the potentials close to 1.23 V vs. NHE to occur oxygen evolution at the N-doped C-rich a-SiC Nps surface, the onset potentials of oxygen evolution were observed in higher potential regions.

The quantum efficiencies of N-doped C-rich a-SiC Nps fabricated under various conditions were estimated from the photocurrent at 3.0 V vs. Ag/AgCl using the wavelength of 365 nm and the intensity of Hg-Xe lamp of 2.5 mW cm⁻² (photons were completely absorbed in the film), and summarized in Table 2 and 4.

Figure 8(A) shows the relation of the quantum efficiencies with Nps sizes and optical gaps obtained at N-doped C-rich a-SiC Nps in this study. Nps sizes and optical gaps seem to have an effect on quantum efficiencies and two trends are seen; One of them is that the quantum efficiencies were decreased with a decrease in optical gaps of Nps having same diameters. The other is that the quantum efficiencies of Nps having larger diameters were higher than those of Nps having small diameters when the optical gaps of Nps were same.

As shown in Table 2 and 4, the potentials of valence band top of N-doped C-rich a-SiC Nps having lower optical gaps (N-doped C-rich a-SiC Nps with 15 nm and n-hexane = 9, with 50 nm and n-hexane = 6, with 100 nm and n-hexane = 3, with 200 nm and n-hexane = 2, and with 250 nm and n-hexane = 1) were ca. 0.1 V vs. SHE and significantly lower than 1.23 V vs. NHE (the standard potential toward oxygen evolution). This lower potential of valence band top may contribute to lower quantum efficiencies.

Figure 8(B) shows the relation between quantum efficiencies and carrier densities obtained at all N-doped C-rich a-SiC Nps. The quantum efficiencies linearly increased with an increase in carrier densities. The carrier densities of N-doped a-SiC Nps having lower optical gaps fabricated by adding n-hexane to source materials (e.g. N-doped a-SiC Nps with 15 nm and n-hexane = 9; 2.10 x 10¹³ cm⁻³) were approximately half of those of N-doped a-SiC Nps without n-hexane (e.g. N-doped a-SiC Nps with 15 nm and n-hexane = 0; 4.43 x 10¹³ cm⁻³). The decrease of carrier densities by adding n-hexane are also considered as one of the contributing factors lowering quantum efficiencies of N-doped a-SiC Nps having lower optical gaps.
Carried densities considerably affected the results that, in case of Nps having same optical gaps, the quantum efficiencies of Nps having larger diameters were higher than those of Nps having smaller diameters. The degradation of carried densities was caused by adding n-hexane. The amount of n-hexane used in fabrication of Nps having larger diameters (e.g. N-doped a-SiC Nps with 250 nm and n-hexane = 0; E_{og} = 1.24 eV) was lower than that of Nps having smaller diameters (e.g. N-doped a-SiC Nps with 15 nm and n-hexane = 9; E_{og} = 1.19 eV). It results in higher quantum efficiencies of Nps having larger diameters. The study about the mechanism of degradation in carried densities by n-hexane is in progress.

The quantum efficiencies of all N-doped C-rich a-SiC Nps were one order of magnitude lower than those of N-doped C-rich a-SiC thin films even when optical gaps of Nps and films were same, as shown in Table 2, 3, and 4. The difference of quantum efficiencies may be caused by several factors. For one thing, the thickness of the layer that N-doped a-SiC Nps accumulated on Si substrates is lower than that of Si44-N-a-SiC thin film: N-doped a-SiC Nps with 15 nm and n-hexane x = 0 was ca. 50 nm and Si44-N-a-SiC thin film was ca. 100 nm (not shown). Since UV light absorption of Nps is considered to be low, quantum efficiencies of Nps are low. For another, carried densities of N-doped a-SiC Nps are one order of magnitude lower than that of Si44-N-a-SiC thin film, previously mentioned. The lower carried densities of Nps may induce lower quantum efficiencies.

The degradation in quantum efficiencies seems to be caused by the structural difference of C-rich a-SiC between Nps and thin films. In the next section, the degradation cause is clarified using XPS measurement in terms of structure change by micro-participation of N-doped C-rich a-SiC.

Reproducibility was examined by multiple measurements of current-voltage curves of N-doped C-rich a-SiC Nps with 15 nm and n-hexane = 0 under irradiation with Hg-Xe light (not shown). The photocurrent at 3.0 V vs. Ag/AgCl after 10 measurements decreased to 68% of the initial value. It indicates that the surface of N-doped C-rich a-SiC Nps may be oxidized and its activity toward photo-induced oxygen evolution reaction was decreased.

3.2.5 Analysis of the structure of N-doped C-rich a-SiC Nps by XPS C 1s spectra

In Table 3, the quantum efficiency of N-doped C-rich a-SiC Nps with a diameter of 15 nm and an optical gap of 2.04 eV (0.71%) was compared with that of N-doped C-rich a-SiC thin film with the optical gap of 2.76 eV (Si44-N-a-SiC) (1.23%). The quantum efficiencies of Nps were quite lower than that of Si44-N-a-SiC, even though Si/(C + Si) ratios obtained from XPS measurements are on the same level. The difference in the quantum efficiencies may be caused by the difference in the N-doped C-rich a-SiC structure.

C-rich a-SiC has a multiphase structure in which amorphous Si-C network (Si : C = x : 1\(-x\)), carbon-like clusters (sp\(^2\)-hybridized carbon cluster), and silicon-like clusters (Si-cluster) coexist. We tried to clarify the structural evolution (to change the ratio of three phases) of N-doped C-rich a-SiC Nps with decreasing Si/C ratios by XPS measurements as below.

C1s peaks of N-doped C-rich a-SiC Nps with 15 nm deposited using source solutions of TMS : TMDS : n-hexane in the ratio of 50 : 1 : x (x = 0, 9) were measured by XPS at a scan rate of 1 eV min\(^{-1}\) (0.01 eV step\(^{-1}\)) within the range from 280.0 to 290.0 eV. C1s spectra of N-doped C-rich a-SiC Nps with 15 nm were shown in Figs. 9(A) and 9(B).

The peaks attributable to C-C (sp\(^3\)), C=C (sp\(^2\)), C-Si, C-O, and C-N were observed at 284.8, 283.3, 282.8, 285.8 and 286.3 eV by altering waveform separation, as shown in Figs. 9(A) and 9(B). The sp\(^2\) and sp\(^3\) bonded carbon (sp\(^2\)/sp\(^3\)) ratios were calculated from the ratios of peak areas of the carbons and summarized in Table 3. The value of sp\(^2\)/sp\(^3\) of N-doped C-rich a-SiC Nps with 15 nm and 2.04 eV (0.734) was quite higher (ca. 1.5 times) than that of Si44-N-a-SiC thin films (0.578). This difference may cause the lower quantum efficiency. The value of sp\(^2\)/sp\(^3\) including in N-doped C-rich a-SiC Nps with 15 nm was increased up to 0.775 by adding n-hexane to source materials used in CVD synthesis. The quantum efficiency of N-doped C-rich a-SiC Nps with 15 nm and 1.19 eV further decreased to 0.05%. This may be because excess sp\(^2\) carbons in N-doped C-rich a-SiC Nps work as the recombination center of photo excited carriers.

Figure 9(C) shows C1s peaks for N-doped C-rich a-SiC Nps with 100 nm and 1.25 eV. As shown in Table 3, the optical gap of N-doped C-rich a-SiC Nps with 100 nm and 1.25 eV was close to that of N-doped C-rich a-SiC Nps with 15 nm and 1.19 eV. The quantum efficiency of N-doped C-rich a-SiC Nps with 100 nm and 1.25 eV (0.11) was slightly higher than that of N-doped C-rich a-SiC Nps with 15 nm and 1.19 eV (0.05). The value of sp\(^2\)/sp\(^3\) including in N-doped C-rich a-SiC Nps with 100 nm and 1.25 eV (0.749) was lower than that in N-doped C-rich a-SiC Nps with 15 nm and 1.19 eV (0.775). These results suggest the hypothesis that the degradation of quantum efficiencies was caused by excess sp\(^2\) carbons.

The amount of sp\(^2\) content in N-doped C-rich a-SiC Nps and carrier densities of Nps should be controlled to have higher quantum efficiencies and be applied to the devices using photon-to-electron conversion functionality, such as photovoltaic cells and photocatalysts.

4. Conclusions

Novel method of fabricating N-doped C-rich a-SiC semiconductor Nps was developed. By using our unique plasma CVD...
Figure 9. XPS C1s spectra for N-doped C-rich a-SiC Nps with a diameter of 15 nm and n-hexane (A) x = 0 and (B) x = 9. (C) XPS C1s spectra for N-doped C-rich a-SiC Nps with a diameter of 100 nm fabricated with n-hexane x = 3. Sweep rate = 1 eV min⁻¹.

Unique technique developed in this study is very useful method for fabricating Nps of other materials such as a-Si, a-C, and Ge. Our method using plasma CVD can create Nps of other materials of any size within the range from 271.2 to 14.8 nm by changing the condition of CVD synthesis.

The challenge to overcome for applying N-doped C-rich a-SiC Nps practically is to improve carrier densities and photon-to-electron conversion efficiencies up to the levels of practically used semiconductor materials. The degradation of photon-to-electron conversion efficiency may be caused by the recombination between photo excited carriers and holes at sp² clusters included in N-doped C-rich a-SiC and the lower carrier density. The amount of sp² content in N-doped C-rich a-SiC Nps and carrier densities of Nps should be controlled to achieve higher quantum efficiencies for the optoelectronic applications.

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