

Fabrication of silicon and carbon based wide-gap semiconductor thin films for high conversion efficiency

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Abstract. Nitrogen doped amorphous silicon carbide (N-doped a-SiC) thin films were fabricated by radio frequency plasma enhanced chemical vapor deposition (RF-PeCVD) method using mixed solution of tetramethylsilane (TES) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as a liquid source. Chemical composition of N-doped a-SiC thin film was Si:C = 1:4 and sp^2 -bonded carbon ratio was 0.75. N-doped DLC were multi-phase structure including a-SiC phase, sp^2 clusters and a-Si clusters. Optical gap and resistivity of the film were 1.68 eV and $4.32 \times 10^4 \Omega \text{ cm}$, respectively. From photocurrent measurement under UV exposure, it was clarified that the film functioned as n-type semiconductor materials with 4.87 % of quantum yield, which was on the same level as that obtained at anatase-type titanium oxide prepared by sol-gel method. To apply these films to solar cells, further improvements of optical gap and conductivity are necessary.

1. Introduction

The widespread use of a low-cost (7 yen/kWh) and high efficiency (40%) solar cell can contribute to reduce CO₂ emission from thermal power station and the amount of man-made carbon dioxide. Tandem-type solar cell composed of stacked layers of silicon and carbon-based semiconductors can achieve high efficiency solar cell at lower cost. To realize the solar cell, it is necessary to develop p- and n-type silicon and carbon-based semiconductors with band gap larger than 2.5 eV and high semiconducting properties applicable to electronic devices.

In the process of device fabrication, semiconductor layers should be synthesized on a conducting glass at a temperature below the melting point of the substrate. In this study, plasma-enhanced chemical vapor deposition (PeCVD) method was employed because amorphous thin film could be fabricated at low temperature. It has been reported that n-type semiconductor could be synthesized by incorporating phosphorous atoms in amorphous silicon carbide (a-SiC)[1]. This film, however, exhibited quite higher resistivity more than $10^4 \Omega \text{ cm}$ because the concentration of P atoms in a-SiC was not so high. The resistivity of a-SiC should be reduced less than $10^1 \Omega \text{ cm}$ to utilize the film for electronic devices.

To realize n-type semiconductive a-SiC film, nitrogen atoms were tried to be incorporated in a-SiC (N-doped a-SiC). Impurity level of N atoms in 4H-SiC has been reported to be 0.0653 eV under the conduction band of 4H-SiC. By incorporating N atoms, electrons in N impurity level can be easily activated and can function as carriers of n-type conduction at room temperature, which results in lower resistivity. In addition, a liquid source composed of hydrocarbons including impurity



(nitrogen) atoms and Si was used as source material of PeCVD. The atomic ratios of Si and C atoms in a-SiC can be easily controlled by changing the composition (Si:C) of the liquid source. By increasing Si/C ratio in a-SiC films, the ratio of sp^3/sp^2 hybrids can be easily enhanced. It results in widening the optical gap of a-SiC films. Moreover, impurity (nitrogen) atoms remained single bound to silicon atoms and were introduced in a-SiC film since source material was not completely decomposed in partially-ionized plasma. Therefore, higher carrier density and lower resistivity compared to those of a-SiC synthesized with N_2 , PH_3 and SiH_4 gases can be achieved, for nitrogen atoms generated from N_2 gas in plasma tend to be preferentially formed quite stable multiple bonding such as $=C=N-$ and $-C\equiv N$, which does not contribute to conductivities.

The purpose of this study is to realize n-type a-SiC semiconductor with optical gap of 2.5 eV and volume resistivity of $10^1 \Omega \text{ cm}$.

2. Experimental

Nitrogen-doped amorphous silicon carbide films (N-doped a-SiC) were fabricated by radio frequency plasma enhanced chemical vapor deposition system (RF-PeCVD) (13.56 MHz, SAMCO Co., Ltd. Model BPD-1). N-doped a-SiC films were deposited on highly Sb-doped silicon (111) substrate ($0.02 \Omega \text{ cm}$ of resistivity) and insulating glass plate. Before the deposition, substrate on PeCVD equipment was heated to 100°C using 200 W of Ar plasma (50 sccm of Ar flow). As a liquid source, mixed solution of tetramethylsilane (TES) (Si and C sources) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (Si, C and N sources) at a ratio of $[HMDS]/[HMDS]+[TES] = 0.01$ was used. After the substrate was heated, vaporized liquid source was introduced into a reaction chamber by heating at 80°C . The source gas at a flow rate of 1 sccm and H_2 gas at a rate of 150 sccm were introduced simultaneously. N-doped a-SiC thin films were deposited using plasma at various RF powers (75, 100 and 150W) to make clear the correlation between the structure and properties of semiconductor. Deposition time was 40 minutes. During depositions, total pressure in the chamber was kept at 110 Pa. Typical film thickness of the deposited thin films was $2.70 \mu\text{m}$ that was observed by SEM measurement.

Chemical composition of N-doped a-SiC was examined by XPS measurement. Transmission spectra of N-doped a-SiC deposited on glass substrate were examined by UV-Vis spectrophotometer (JASCO Co., Ltd. V-670). Absorption coefficient α was calculated using equation (1).

$$\alpha = -\ln\{(T/100)/d \times 10^8\} \quad (1)$$

T is transmittance (%) and d is film thickness (\AA) of the sample film. Optical gap (E_{og}) was estimated from Tauc's plot using Tauc equation (2), which is the result of the conversion.

$$(\alpha h\nu)^{1/2} = B(E_{og} - h\nu) \quad (2)$$

$h\nu$ is energy of incident light, B is constant, and E_{og} is optical gap of the sample film. Properties of semiconductor (carrier density, carrier mobility, resistivity and conductive type) were determined by Hall measurement with van der Pauw method (Ecopia Co., Ltd. HMS-3000). Ohmic contacts were formed by 1 mm^2 nickel vapor deposited with resistance heating deposition system on the four corners of N-doped a-SiC thin film at 1 cm interval. These four electrodes were used for Hall measurement. Hall measurement was performed at room temperature. Potentiostat/galvanostat (Hokuto Denko Co., Ltd. HZ-3000 system) was used for photo-electrochemical measurement. Photocurrent measurement was performed with linear sweep voltammetry (LSV) using three electrode electrochemical cells. $0.2 \text{ M NaH}_2\text{PO}_4$ was used as electrolyte solution. The geometric area of working electrodes was 0.1 cm^2 . Sweeping rate was 5 mV sec^{-1} . Hg-Xe lamp (USHIO Co., Ltd. SP9-250DV) was used as UV sources.

3. Results and Discussion

3.1. Chemical composition

N-doped a-SiC thin film deposited on glass substrate at 100 W of RF power was highly transparent. The surface of N-doped a-SiC thin film was flat, smooth, and yellow in colour. Chemical composition of this N-doped a-SiC film was estimated by XPS measurement. The measurement within the range

of 0 eV to 1100 eV at scan rate of 10 eV min⁻¹ was performed. Peaks of Si 2p, C 1s, N 1s and O 1s were confirmed at 99 eV, 285 eV, 398 eV and 531 eV, respectively (Figure 1). From this result, it was clarified that the resulting film was consisted mainly of Si and C at a ratio of Si:C =1:4. It suggests that the deposited film contained relatively higher concentration of C atoms (Table 1). Nitrogen atoms that act as donor were confirmed to be 1.1 atom%.

Si 2p peak was measured at scan rate of 1 eV min⁻¹ within the range of 96 eV to 108 eV. The peak attributable to Si bonded Carbon (Si-C) and Si bonded to Si (Si-Si) were observed at 100.65 and 99.709 eV by waveform separation of the measured Si 2p peak in Figure 2. This result indicated that the resulting films include a-SiC phase and amorphous silicon (a-Si) clusters. Atom % of Si atoms in N-doped a-SiC was decreased from 18.1 to 13.3 atom% and C atoms was increased from 65.2 to 68.8 atom % with increasing in RF power during CVD synthesis (75 to 150 W), as shown in Table 1. Elevating plasma power might induce decomposition of source materials and increase of the rate of methyl cation formation, which resulted that large amounts of C atoms were introduced in a-SiC films.

C 1s peak for N-doped a-SiC film at 100 W was measured at scan rate of 1 eV min⁻¹ within the range of 283.8 eV to 284.6 eV. The peaks attributable to C-C (*sp*³) and C=C (*sp*²) were observed at 283.8 eV and 284.6 eV by altering waveform separation. The ratios of *sp*² and *sp*³ bonded carbon were calculated to be 0.75 and 0.25 from the ratio of peak areas of these carbons. This result indicates that N-doped a-SiC contains *sp*²-bonded carbon clusters.

The existence of *sp*² clusters in N-doped a-SiC fabricated at 75, 100, and 150W was examined by Raman spectroscopy. Broad peaks around 1500 cm⁻¹ were observed in all Raman spectra and the peaks were composed by G and D peak that typically observed at a-C films (Figure 4). It indicated that *sp*²-bonded carbons in a-SiC films form clusters. Size of cluster that can be estimated from the ratio of peak intensity of D and G peak (*I*_D/*I*_G) was gradually decreased with plasma power (8.47 μm at 75W, 6.13 μm at 150 W). Since C/Si ratio was increased with RF power in XPS spectra, the number of *sp*² cluster should be increased. The peaks attributable to a-Si (ca. 480 cm⁻¹) and a-SiC (ca. 750 cm⁻¹) could not be obtained in Raman spectra. It indicated that the proportion of a-Si clusters and a-SiC phase was relatively lower than *sp*² cluster. The position of G peak was sifted to lower wave number side with increasing Si atom % (lower RF power). This sift was caused by formation of Si-C bonding at *sp*² clusters (C=C-Si). Therefore, a-SiC phase and *sp*² clusters were connected and clear boundary between them might not be formed.

Figure 5 shows FTIR spectra for a-SiC with different RF power. In all spectra, peaks at ca. 2100, 1100 and 800 cm⁻¹ were observed. The peak at 2100 cm⁻¹ was attributable to Si-Hn stretching mode and the peak at 1100 cm⁻¹ was C-Hn wagging mode. The peak at ca 800 cm⁻¹ was Si-CH₃ stretching/wagging mode and the intensity of this peak was increased with increasing Si content (lowering of RF power). This observation supports that N-doped a-SiC includes a-SiC phase. The peak intensity (0.0335) at 2100 cm⁻¹ of N-doped a-SiC fabricated at 150 W was quite lower than those of N-doped a-SiC at 75 and 100W (0.0742 and 0.0702, respectively). It indicates that N-doped a-SiC at 150 W include small amount of a-Si cluster than that at 75 and 100 W because of lower Si atom%.

Figure 6 shows XRD spectra of a-SiC film. Broad peak centred at 43 degree, which was attributable to *sp*² cluster, was observed. It indicates that there is no long range ordering in a-SiC film.

Therefore, these spectroscopic data suggests that resulting a-SiC films were multi-phase structure including a-SiC phase, *sp*² clusters and a-Si clusters. C/Si ratios and the number of *sp*² clusters in N-doped a-SiC films were increased with RF power of CV synthesis.

Table 1 Chemical composition of N-doped a-SiC by XPS measurement

Plasma power(W)	Si[atom%]	C[atom%]	N[atom%]	O[atom%]	C <i>sp</i> ²
75	18.1	65.2	1.1	16.8	0.840
100	17.6	68.5	1.1	13.9	0.750
150	13.3	68.8	1.1	17.8	0.786

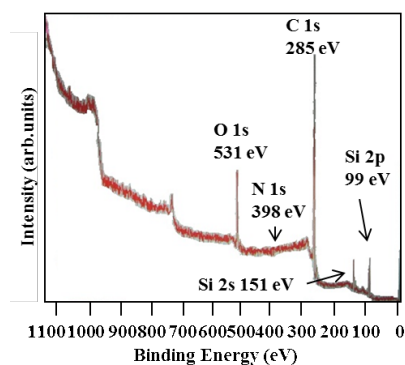


Figure 1 XPS spectrum of N-doped a-SiC

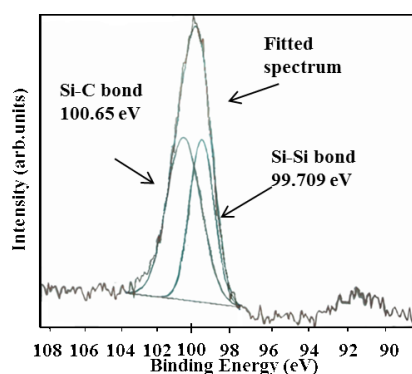


Figure 2 XPS Si 2p spectrum for N-doped a-SiC, scan rate, 1 eV min^{-1}

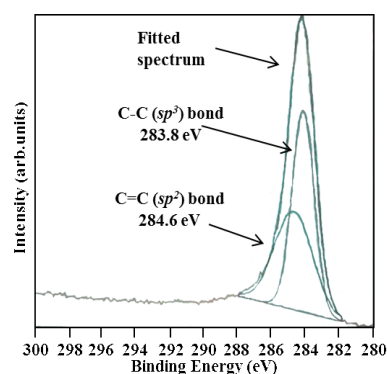


Figure 3 XPS C 1s spectrum for N-doped a-SiC, scan rate, 1 eV min^{-1}

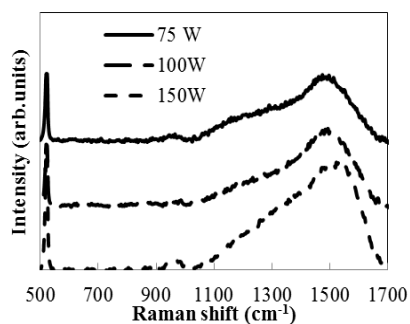


Figure 4 Raman spectra of N-doped a-SiC

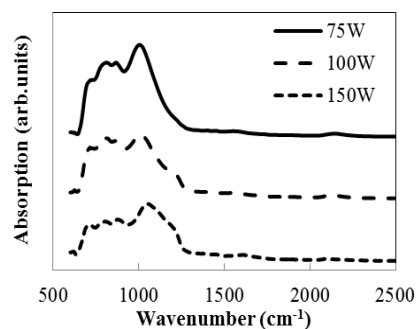


Figure 5 FTIR spectra of N-doped a-SiC

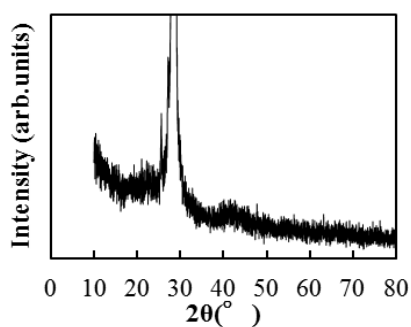


Figure 6 XRD spectrum of N-doped a-SiC

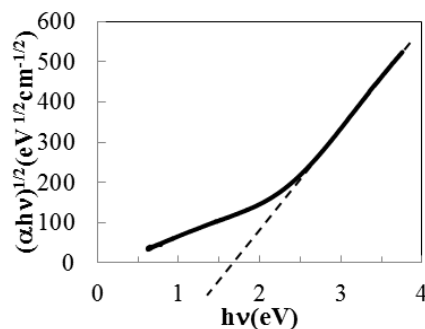


Figure 7 Tauc plot of N-doped a-SiC

3.2. Semiconductor properties

Semiconductor properties were examined using N-doped a-SiC deposited on glass substrate (insulator) by Hall measurement. Carrier density, carrier mobility, and resistivity of N-doped a-SiC synthesized with various RF power were shown in Table 2. The resistivity of N-doped a-SiC at 100W was relatively low and on the same level as the reported value of P-doped a-SiC fabricated using PeCVD, $10^4 \Omega \text{ cm}$ [1].

There are two possibilities to explain the causes of low resistivity; (1) Increase of carrier density (decrease of resistivity) by introducing N atom as a donor, (2) Enhancement of carrier mobility by forming (carbon) nanocrystal in the film. Carrier density and resistivity of non-doped a-SiC were $3.49 \times 10^{14} \text{ cm}^{-3}$ and $5.17 \times 10^4 \Omega \text{ cm}$, respectively. By incorporating N atoms in a-SiC, carrier density was increased by 100-fold ($4.79 \times 10^{14} \text{ cm}^{-3}$) and resistivity was decreased to $4.32 \times 10^4 \Omega \text{ cm}$. It was, therefore, clarified that N atom might act as n-type donor (cause 1). Carrier mobility of N-doped a-SiC was within the range of $10^{-1} \Omega \text{ cm}$ that was fairly lower than that of bulk SiC. In Raman spectra, peaks attributable to sp^2 clusters were observed. Hence, π -electron on sp^2 -bonded carbon might be related closely to the conductivity of N-doped a-SiC (sp^2 clusters contribute to shorten the length of hopping conduction) (cause 2). This assumption was supported by the fact that the lowering of the resistivity at a-SiC fabricated at 150 W of RF power (higher C contents) in Table2.

Table 2 Optical gap, carrier density, carrier mobility, resistivity and conduction typefor N-doped a-SiC

Plasma Power (W)	Optical gap (eV)	Carrier density (cm^{-3})	Carrier mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Resistivity ($\Omega \text{ cm}$)	Conduction type
75 (N-doped)	1.69	3.05×10^{13}	2.71×10^0	7.57×10^4	n
100 (Undoped)	1.68	3.49×10^{12}	1.11×10^1	5.17×10^4	n
100 (N-doped)	1.68	4.79×10^{14}	2.98×10^{-1}	4.32×10^4	n
150 (N-doped)	0.585	6.75×10^{14}	7.85×10^{-1}	1.18×10^4	n

3.3. Optical properties

Optical gap of N-doped a-SiC at 100 W of RF power was estimated to be 1.68 eV in Figure 7. This value was 0.67 times lower than the target value, 2.5 eV and 0.52 times lower than 3.26 eV of crystalline 4H-SiC band gap [2]. Optical gap of N-doped a-SiC was related closely to sp^2 clusters in N-doped a-SiC, which were conformed in Raman spectra.

The colour of N-doped a-SiC changed from yellow to dark brown by increasing RF power from 100 W to 150 W employed in PeCVD synthesis. C/Si ratios were increased with RF power, as mentioned above. Optical gap was monotonically decreased from 1.68 eV to 0.59 eV with RF power (C/Si ratio). It has been reported that optical gap of amorphous carbon was inversely proportional to the average number of six-membered ring that was included in sp^2 clusters. a-C including sp^2 clusters with 10 rings exhibited 1.68 eV of optical gap and a-C that has sp^2 clusters with 120 rings was 0.59 eV. The number and average size (number of rings) of sp^2 cluster might affect strongly the value of optical gap. Similar tendency was confirmed in literature relating a-SiC prepared using PeCVD method [3].

3.4. Photo-electrochemical properties

The performance of photo-electron conversion at N-doped a-SiC was examined by photo-electrochemical method (Figure 8) to check applicability for photo voltaic system. The value of the current with exposure to Hg-Xe lamp (photocurrent) at N-doped a-SiC (the ratio of sp^2 carbon = 75 atom%) fabricated at 100 W of RF power was achieved to be $153 \mu\text{A cm}^{-2}$ (Figure 8). This value was on the same level as that obtained at anatase-type titanium dioxide thin films prepared by sol-gel method. Quantum yield of the thin film was calculated using the value of photocurrent. The quantum yield of photo-excited electron at N-doped a-SiC was calculated to be 4.87 % using 365 nm of

wavelength and 11.8 W cm^{-2} of intensity of Hg-Xe lamp (photons were completely absorbed in the film). This value was lower than half of the values reported in [4] and [5] (15 % at anatase-type titanium dioxide prepared by sol-gel method [4] and 10 % at a-SiC by PeCVD [5]). It is necessary to enhance quantum yield of N-doped a-SiC.

The a-SiC film reported in literature has shown higher resistivity ($\sim 10^4 \Omega \text{ cm}$). In this study, relatively lower resistivity of N-doped a-SiC was obtained by controlling the amount of sp^2 carbon content (higher C/Si ratio > 1.0), resulting in the higher photocurrents at N-doped a-SiC film. Both currents with and without exposure to Hg-Xe lamp were monotonically increased with increasing RF power ($=sp^2$ carbon content) from 75 W to 150 W, as shown in Figure 9. The increase of both currents might be caused by lowering of resistivity of a-SiC films with increase in sp^2 content. These results support that the increasing in sp^2 content (the lowering resistivity) plays important role for higher photo-electron conversion efficiency. However, by increasing RF power up to 200 W, photocurrent values were monotonically decreased. This is because excess sp^2 carbons in N-doped a-SiC worked as recombination center of photo excited carries. Therefore, the amount of sp^2 content in N-doped a-SiC film should be moderately controlled.

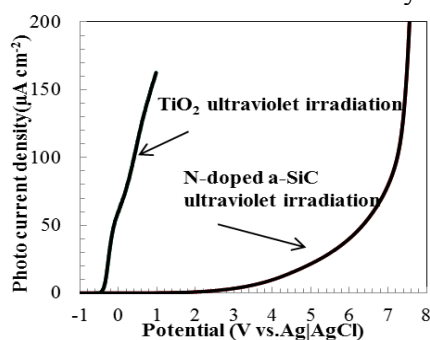


Figure 8 Current-voltage curves with exposure to Hg-Xe lamp of N-doped a-SiC

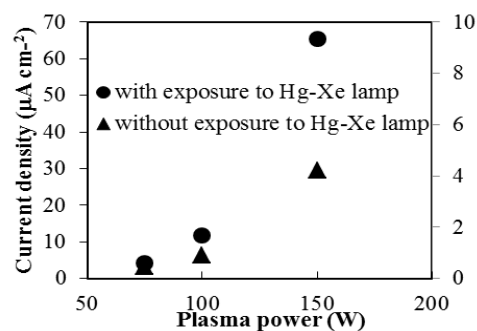


Figure 9 Current-voltage curves with, without exposure to Hg-Xe lamp of N-doped a-SiC

4. Conclusion

n-type a-SiC film with high performance, which can be utilized to electronic device, could be fabricated by optimizing the size and number of sp^2 clusters that was included in multi-phase structure of the film. The resulting N-doped a-SiC with 10 six-membered rings in sp^2 clusters shows 1.68 eV of optical gap and $153 \mu\text{A cm}^{-2}$ of photo-current. Quantum yield was on the same level as that obtained at anatase-type titanium oxide prepared by sol-gel method. It is, however, necessary to increase optical gap and conductivity in order to make the utilization possible. The size enlargement of sp^2 cluster brings higher conductivity but induces a lower optical gap. It suggests that another approach should be employed to develop N-doped a-SiC semiconductor with specific performance. Improvement of optical gap will be attempted by incorporating many Si atoms to increase a-SiC phase in N-doped a-SiC films. Moreover higher conductivity will be attempted by incorporating other impurity atoms like S that do not form insulating components such as SiN.

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