Highly conductive boron-doped nanocrystalline silicon-carbide film prepared by low-hydrogen-dilution photo-CVD method using ethylene as a carbon source

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Abstract

Boron-doped nanocrystalline silicon-carbide (p-nc-SiC:H) films with a low-concentration of hydrogen-dilution were grown by a mercury-sensitized photo-chemical vapor deposition method using silane (SiH_4), hydrogen (H_2), diborane (B_2H_6), and ethylene (C_2H_4) as a carbon source. From the Raman and FTIR spectrum measurements, the p-nc-SiC:H film is composed of nanosize crystal silicon embedded in a hydrogenated amorphous silicon-carbide matrix. A dark conductivity as high as 1.7×10^{-1} S/cm, with an optical bandgap at 2.0 eV, and a crystal volume fraction of 50%, were obtained. We tested these films as window material for amorphous silicon solar cells, obtaining an initial conversion efficiency of 10.4% without using any back reflectors. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Boron-doped hydrogenated microcrystalline silicon-carbide (p-μc-SiC:H) films have been used as a p-type material in hydrogenated amorphous silicon (a-Si:H) based solar cell because they have higher electrical conductivity, optical transmittivity, carrier mobility, and dopability than conventional p-type hydrogenated amorphous silicon-carbide (p-a-SiC:H) thin films. Electron cyclotron resonance chemical vapor deposition (ECR CVD) [1], glow discharge (GD) [2], and plasma enhanced chemical vapor deposition (PECVD) [3,4] techniques have been the typical growth methods of p-μc-SiC:H thin films. Hamakawa et al. have reported the highest conductivity (~10 S/cm) in p-μc-SiC:H films using the ECR CVD method with the extremely high hydrogen (H_2) dilution ratio of 74. However, the ECR CVD technique has the problems of non-uniform deposition over large area and requires very complicated equipment. On the other hand, a fairly high conductivity around 10^{-1} S/cm has been reported for the p-μc-SiC:H film by employing a considerably high power density (350 mW/cm^2) GD technique. A high conductivity of around 10^{-3} S/cm has been reported for the p-μc-SiC:H film using a high power

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density (150 mW/cm^2) PECVD method. However, these techniques have the problem of ion-damage on the growing film and interfaces because of the use of high power density. Besides, these results have been obtained with the significantly high H$_2$ dilution ratio of 50. However, hydrogen atoms are known to enhance the microcrystalline structure through high surface coverage and etching action, but these highly energetic particles involved in the high power processes degrade SnO$_2$ transparent conductive electrodes and interfaces. Another promising technique to fabricate μc-SiC:H thin film is photo-chemical vapor deposition (photo-CVD) method that is ion-damage free and simple.

Dasgupta et al. [5] have reported the fabrication of p-type μc-SiC:H having conductivity as high as 2.0×10^{-2} S/cm using acetylene (C$_2$H$_2$) as a carbon source by the photo-CVD technique with the H$_2$ dilution ratio of 30. Usually, methane (CH$_4$) is preferred carbon source owing to silane-like structure, but it is not suitable to the mercury-sensitized photo-CVD method due to the very low quenching cross-section of methane (0.06 Å^2). On the other hand, the quenching cross-section of C$_2$H$_4$ (25 Å^2) is larger than that of C$_2$H$_2$ (23 Å^2) [6]. Therefore, C$_2$H$_4$ is more suitable to this method. In this paper, we report for the first time the fabrication and properties of boron doped nanocrystalline silicon-carbide (p-nc-SiC:H) as a window material for a-Si:H solar cells using C$_2$H$_4$ as a carbon source by a photo-CVD technique with the low hydrogen dilution ratio of 20. Since crystalline grains of our samples are few nanometers in diameter, we use the terminology of nanocrystalline instead of microcrystalline.

2. Experimental

Films were grown in a mercury sensitized photo-CVD system described elsewhere [7] using the mixture of SiH$_4$, H$_2$, B$_2$H$_6$, and C$_2$H$_4$ reactant gases. A low-pressure mercury lamp with resonance lines of 184.9 and 253.7 nm was used as a UV light source to dissociate the mixture gases. In all depositions, the diborane doping ratio (B$_2$H$_6$/SiH$_4$), hydrogen dilution ratio (H$_2$/SiH$_4$), chamber pressure, mercury bath temperature and substrate

temperature were kept at 3000 ppm, 20, 0.46 torr, 20 and 250 °C, respectively. To investigate the effect of C$_2$H$_4$ addition on the film properties, we deposited films onto Corning 7059 glass substrates.

We investigated the results of Raman spectroscopy measurements and the deposition ratio of p-nc-SiC:H films to elucidate the effects of C$_2$H$_4$ addition and hydrogen dilution on the formation of the silicon-carbide film. Dark conductivity (σ_d) was measured using Al coplanar electrode configuration. The activation energy (E_a) for the electrical σ_d was extracted from the Arrhenius plot. The optical absorption coefficient and film thickness were measured by a spectroscopic ellipsometer.

3. Results

Fig. 1 presents the effect of variation of the C$_2$H$_4$ gas flow ratio (C$_2$H$_4$/SiH$_4$) against the σ_d, its activation energy (E_a), and deposition rate (R_d) of 120–140 nm thick p-nc-SiC:H films. The σ_d of the films decreases nearly exponentially as the C$_2$H$_4$/
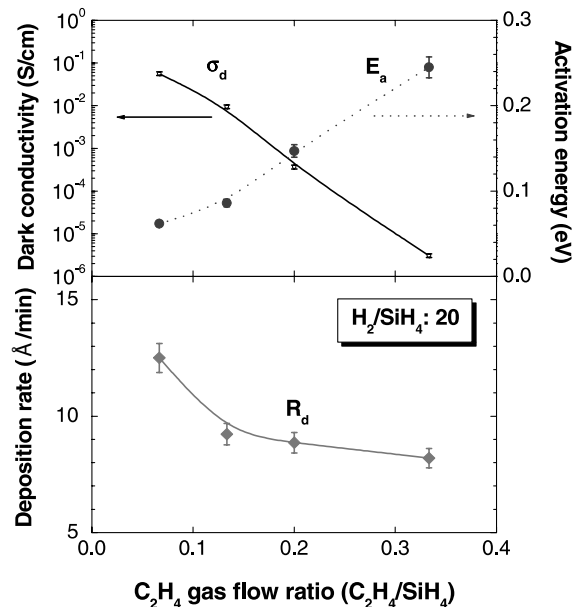

Fig. 1. Effect of variation of the C$_2$H$_4$/SiH$_4$ on the dark conductivity, activation energy, and deposition rate of films.

SiH_4 increases. In contrast, the E_a value increases with increasing the C_2H_4/SiH_4. In case of R_d value, it reduces as the C_2H_4/SiH_4 increases, but the extent of decrease is small when the C_2H_4/SiH_4 is more than 0.13.

Fig. 2 shows the absorption spectra of the p-nc-SiC:H films fitted by the effective medium approximation method [8]. However, some estimation errors caused by their rough surfaces and size effect could not be excluded perfectly. From this figure, it is found that the optical bandgap of E_{04} (the value of the photon energy for which the optical coefficient is 10^4 cm^{-1}) improves very slightly as the C_2H_4/SiH_4 increases due to the decrease in the optical absorption in the visible region. However, the extent of the E_{04} improvement with the C_2H_4/SiH_4 increases for the higher hydrogen diluted films [9].

Fig. 3 depicts a Raman spectrum of a 420 nm thick p-nc-SiC:H film prepared at $C_2H_4/SiH_4 = 0.07$, with a σ_d of 1.7×10^{-1} S/cm. As shown in this figure, it can be decomposed into two peaks; one stands for the crystalline Si (c-Si) with peak position at around 520 cm^{-1} and the other is the much broader amorphous Si peak around 480 cm^{-1}. There is no crystalline SiC (c-SiC) peak
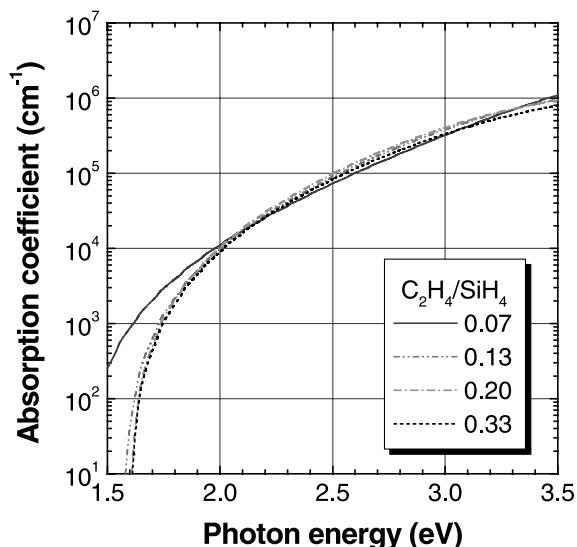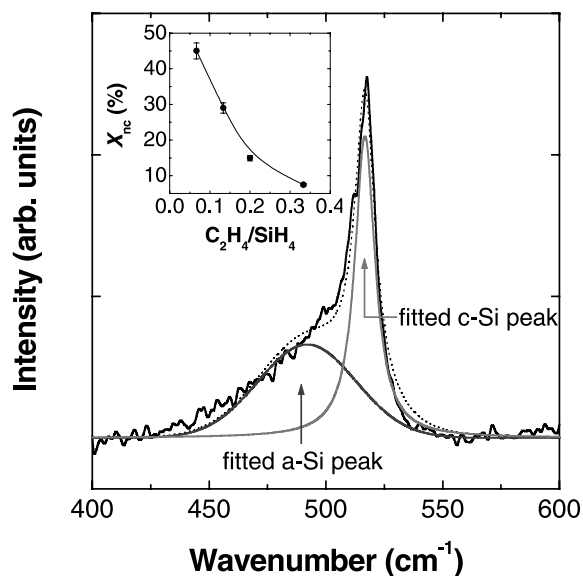

Fig. 3. Raman spectrum of a p-nc-SiC:H film prepared at $C_2H_4/SiH_4 = 0.07$. The inset represents the dependence of crystal volume fraction of p-SiC:H films on the C_2H_4/SiH_4.

observed in the range of 750–970 cm^{-1}, which confirms the absence of c-SiC grains. From these spectra, it is clear that these nanocrystalline films consist of c-Si grains embedded in hydrogenated amorphous silicon-carbide (a-SiC:H) matrix. The degree of crystallinity can be indicated by the crystal volume fraction. It is the ratio of the area under c-Si peak to the sum of that and the area under the a-SiC:H peak, corrected by the ratio of the Raman cross-section for c-Si to a-SiC:H [2]. In this paper, we used the non-corrected crystal volume fraction (X_{nc}). In other words, we assume the ratio of the Raman cross-section as 1 because crystalline grains are few nanometers in diameter, as estimated from Raman line shape [10,11]. Therefore, it is easy to calculate the X_{nc} from this Raman spectrum, which is found to be about 50%. We also estimated the respective X_{nc} of 120–140 nm thick films (see Fig. 1). These are represented in the inset graph of Fig. 3. The X_{nc} reduces severely with increasing the C_2H_4 addition.

Fig. 4 shows the result of X-ray diffraction on the 420 nm thick film. In this figure, dotted line represents a background signal caused by the contribution of the Corning 7059 glass substrate

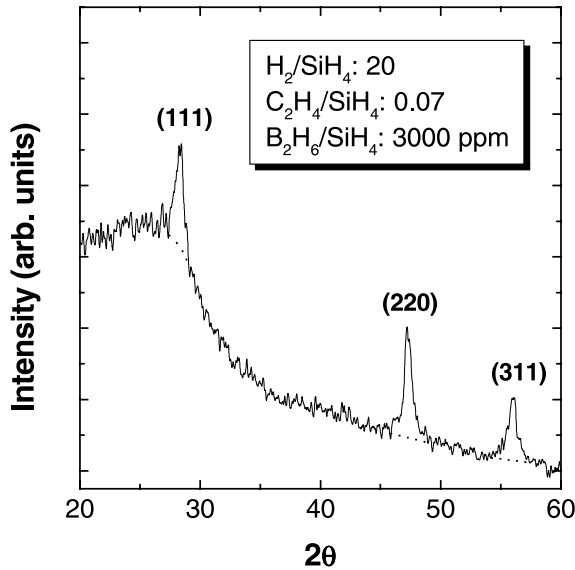Fig. 2. Absorption coefficient spectra with the variation of the C_2H_4/SiH_4.

Fig. 4. X-ray diffraction pattern of a 420 nm thick p-nc-SiC:H film deposited onto Corning 7059 glass.

and full line depicts a superposition of signals caused by the p-nc-SiC:H layer and the substrate. Three peaks corresponding to (1 1 1), (2 2 0), and (3 1 1) directions of c-Si are observed. A simple calculation using the FWHM of (2 2 0) peak and Scherrer's formula leads to an average grain size of 11 nm. This large value is attributed to the ion-damage free processing by the photo-CVD.

We performed the FTIR analysis of a 420 nm thick film deposited onto a bare Si wafer in order to obtain the evidence of SiC:H formation. Among the samples under consideration, this sample was prepared under the lowest C_2H_4/SiH_4, 0.07. We present the FTIR transmission spectrum of this film in Fig. 5. The shoulders at around 657 and 789 cm^{-1} confirm the formation of SiC:H [5,12,13]. This film possess about 1–2 at.% C, which roughly determined from the Auger results [9].

To confirm the possibility for applying these p-nc-SiC:H films as window material, we have fabricated nc-SiC:H/a-Si:H heterojunction solar cells which have the simple structure of Glass/SnO_2/p-a-SiC:H(7.8 nm)/p-nc-SiC:H(12 nm)/i-a-Si:H (600 nm)/n-μc-Si:H(40 nm)/Al. The typical photo current–voltage (J–V) characteristic of solar cell is shown in Fig. 6. To prevent open-circuit voltage
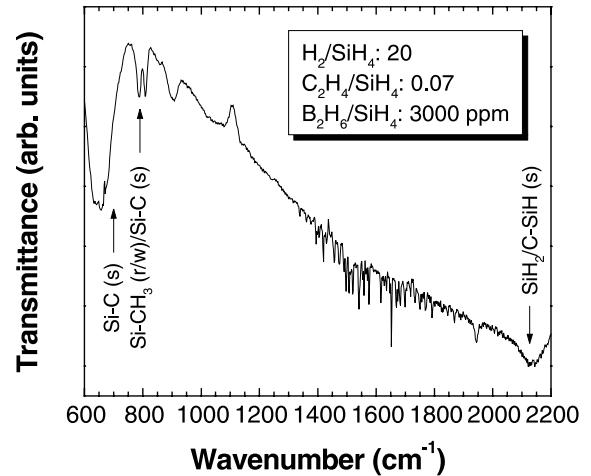

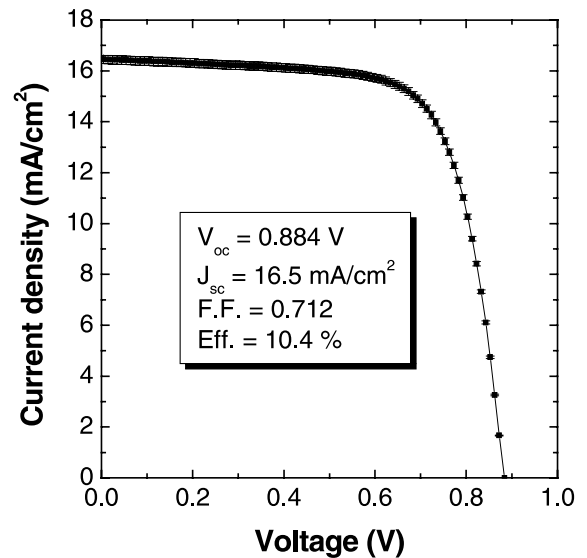Fig. 5. FTIR transmission spectrum of a 420 nm thick p-nc-SiC:H film.

Fig. 6. J–V characteristic of a glass/SnO_2/p-a-SiC:H/p-nc-SiC:H/i-a-Si:H/n-μc-Si:H/Al solar cell (AM 1.5, 100 mW/cm^2). The cell area is 0.09 cm^2.

(V_{oc}) lowering due to the deterioration of SnO_2 under hydrogen circumstances, we inserted a 7.8 nm thick p-a-SiC:H film between the SnO_2 film and the p-nc-SiC:H film prepared by a direct photo-CVD method. This cell area is 0.09 cm^2. Its typical performances are V_{oc} = 0.884 V, short-cir-

cuit current $(J_{sc}) = 16.5$ mA/cm^2, fill factor = 0.712, and efficiency = 10.4% (AM 1.5, 100 mW/cm^2).

4. Discussion

From these results, we can find the role of the H$_2$ dilution and C$_2$H$_4$ addition on the growth mechanism of the p-nc-SiC:H films prepared by the photo-CVD. H$_2$ dilution of SiH$_4$ causes hydrogen coverage on the growing surface of film. Such coverage by atomic hydrogen enhances the surface diffusion coefficient of the precursors decomposed by the UV light, and thereby the precursors adsorbed at the growing surface are able to find energetically suitable sites [14,15]. This results in the nucleation of crystallites by decreasing the structural disorder and retarding the deposition rate. In addition, hydrogen atoms are thought to be responsible for nanocrystallization by breaking weak Si–Si bonds. This structural improvement gives rise to the significant enhancement in the σ_d and the slight increase in the optical bandgap.

On the other hand, it is well-known feature that high carbon contents hinder the nanocrystallization of SiC:H films. It can be considered that the decrease in the R_d with the increase in the C$_2$H$_4$/SiH$_4$ is caused by the selective surface-etching behavior of mercury-sensitized H$_2$ radicals [14–16]. As the C$_2$H$_4$/SiH$_4$ increases, photodissociated hydrocarbon species increase near the growing surface and thus the adsorbed hydrocarbon species also increase. Since these adsorbed hydrocarbon precursors can be more easily etched than adsorbed silane precursors, the R_d of SiC film decreases. However, these phenomena are limited at the higher C$_2$H$_4$/SiH$_4$. From the Figs. 1 and 2, it is found that the carbon content (C_c) in film enhances with increasing the C$_2$H$_4$/SiH$_4$. Since the σ_d of carbon (C) is lower than that of silicon (Si), the σ_d decreases considerably with the increase in the C_c. However, the optical bandgap of E_{04} improves very slightly as the C$_2$H$_4$/SiH$_4$ increases. It can be attributed that the lower optical absorption in visible range due to the incorporation of C is compensated by the degradation of crystallinity under the considerably low (20) H$_2$/SiH$_4$ condition.

The high J_{sc} of solar cell achieved without any back reflector can be ascribed to a good ion-damage-free interface between p-nc-SiC:H and i-a-Si:H layers formed by the photo-CVD method. It also ascertains a considerable potential of this p-a-SiC:H/p-nc-SiC:H double p-layer for a-Si:H-based solar cells. We are trying to improve the conversion efficiency by optimizing the p-nc-SiC:H layer.

5. Conclusions

In summary, highly conductive p-nc-SiC:H films were successfully prepared by the photo-CVD using SiH$_4$, H$_2$, B$_2$H$_6$, and C$_2$H$_4$ gas as a carbon source. A σ_d as high as 1.7×10^{-1} S/cm, together with a crystal volume fraction of 50%, was obtained under the condition of C$_2$H$_4$/SiH$_4$ = 0.07. Considering the low H$_2$ dilution ratio of 20, this high conductivity shows the possibility of producing very high quality p-nc-SiC:H thin films with higher hydrogen dilution. We investigated the effects of C$_2$H$_4$ addition on the formation of nc-SiC:H films by inspecting the electrical, optical, and structural properties. By virtue of these efforts, we found that the carbon atoms introduced to the growing surface play an important role on the film properties. From the reduced σ_d and crystal volume fraction, it is clear that high C_c suppresses the nucleation of nanocrystallites. Based on these results, we employed for the first time these p-nc-SiC:H thin films, prepared by the mercury-sensitized photo-CVD technique using C$_2$H$_4$ source, as window material of a-Si:H-based solar cells. We obtained 10.4% efficiency for the solar cell using a p-a-SiC:H/p-nc-SiC:H double p-layer. We will be able to further improve the film quality and solar cell performance by optimizing the deposition conditions and the cell structure.

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