Amorphous silicon oxide and its application to metal/n-i-p/ ITO type a-Si solar cells[1]

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Abstract -- P-type and n-type amorphous silicon oxide (a-SiO) films with a microcrystalline Si phasewere deposited by plasma CVD using a gas mixture of SiH_4-CO_2-H_2-B2H_6 and SiH_4-CO_2-H_2-PH_6 respectively. These films had lower absorption coefficients than conventional a-SiO due to larger oxygen contents and microcrystalline phase, but their conductivities were still high since they contained some microcrystalline Si phase. Furthermore, it was found that it is easier to make microcrystalline a-SiO than a-SiC films at low substrate temperature. By applying these films to the p-layer of metal/nip/ITO type cells, higher performance was obtained, compared to the cells with conventional microcrystalline Si p-layer deposited at lower temperature and conventional a-SiO p-layer. From these results, we consider that these novel a-SiO films with microcrystalline Si phase are a promising material for the window layer of a-Si solar cells.

Keywords : solar cells, amorphous silicon oxide, microcrystalline phase

บทคัดย่อ -- ฟิล์มชนิดใหม่ที่มีส่วนผสมระหว่างอะมอร์ฟัสซิลิกอนออกไซด์และผลึกซิลิกอนขนาดเล็ก แบบพีและเอ็นสามารถสร้างด้วยวิธีพลาสม่า CVD จากก๊าซผสมของ SiH_4-CO_2-H_2-B2H_6 และ SiH_4-CO_2-H_2-PH_6 ได้ ฟิล์มชนิดนี้มีสัมประสิทธิ์ของการดูดกลืนแสงที่ต่ำกว่าฟิล์มชนิดอะมอร์ฟัสซิลิกอนออกไซด์แบบเดิม เนื่องจากมีส่วนผสมของออกซิเจนมากขึ้น และมีส่วนที่เป็นผลึกอยู่ด้วย แต่ยังคงมีคุณสมบัติที่นำไฟฟ้าได้ดีอีกด้วย เนื่องจากมีส่วนที่เป็นผลึกอยู่ เมื่อนำไปประยุกต์ใช้เป็นชั้นพี ของเซลล์แสงอาทิตย์แบบ Metal / nip / ITO พบว่า เซลล์แสงอาทิตย์ที่ได้มีประสิทธิภาพสูงขึ้น ทำให้สามารถสรุปได้ว่า ฟิล์มชนิดใหม่ที่ค้นพบนี้ เป็นฟิล์มที่เหมาะที่จะใช้ในชั้นรับแสงของเซลล์แสงอาทิตย์

คำสำคัญ : เซลล์แสงอาทิตย์, อะมอร์ฟัสซิลิกอนออกไซด์, ผลึกขนาดเล็ก

1. Introduction

Recently, we have demonstrated that hydrogenated amorphous silicon oxide(a-SiO:H) films deposited by plasma CVD using a gas mixture of SiH_4-CO_2-H_2 have a better film quality than conventional a-SiC films. Applying this a-SiO layer to the p-layer of glass/SnOJpin/metal, we have obtained 12.5% for 1 cm^2 area cell [1]. To achieve higher photovoltaic performance, we have concentrated on developing wider bandgap materials having the same electrical properties. Further more, we also considered a different device structure which is (inverted pin) type structure since I layer can be deposited at higher substrate temperature in this cell structure.

For wider bandgap materials, a-SiC with microcrystalline Si phase (,ac-SiC) has been developed by Y. Hattori et al. using ECR plasma CVD [2] and by K. Hanakiet al. [3] or S. Guha et al. using RF plasma CVD [4]. It was reported that higher performance were obtained with these p-type ,ac-SiC films [2,5]. However,

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up to date there are no reports on a-SiO with microcrystalline Si phase (,u c-SiO) and its application to the cell.

In this paper, we have studied for the first time p-type and n-type ,ac-SiO films deposited by RF plasma CVD using a gas mixture of SiH_4-CO_2-H_2-B_2H_6 and SiH_4-CO_2-H_2-PH_3 , respectively. Their film structure were evaluated and their optical and electrical properties were also measured and compared with those of conventional p(a-SiO) films. To compare the properties of these ,ac-SiO films, we have also tried to deposit p(yc-SiC) film from the gas mixture of SiH_4-C_2H_2-H_2-B_2H_6 under the same deposition condition. Furthermore, we will report the results of applying these p(,ac-SiO) films to the p-layer of metal/nip/ITO type cell.

2. Experimental

In this experiment, to deposit ,ac-SiO films, CO_2 was introduced to the gas mixture under normal deposition conditions for,uc-Si deposition. Table 1 shows the details of our typical deposition condition for ,ac-SiO films. Films having thicknesses of 200-300 nm were deposited on the Corning glass and c-Si substrate. The microcrystallization and the film structure were evaluated by X-ray diffraction, Raman, and FT-IR spectroscopy. The oxygen and carbon contents in the films were measured by ESCA while the hydrogen content was evaluated from FT-IR spectra. To evaluate their electrical and optical properties, dark conductivity and photoconductivity measured under AM 1.5, 100 mW/cm^2 , optical bandgap , and absorption coefficient were used.For cell fabrication, n-, i- and p-layers were deposited in different chambers in order to suppress the dopant contamination into the i-layer.

Table 1 Typical deposition condition used for the deposition of p(yc-SiO) and n(yc-SiO)

CO_2 /(SiH_4 + CO_2)	0-0.6
H_2 /SiH_4	160-320
B_2H_6(PH_3)/SiH_4	0.6-1.0%
Substrate temperature	100-250°C
Pressure	1.0 Torr
RF power density	50 mW/cm^2

3. Results and discussion

3.1. Film structure

3.1.1. Contents of silicon, oxygen, carbon and hydrogen

Table 2 shows the contents of silicon, oxygen, carbon, and hydrogen in p(,ac-SiO) films, compared with those in conventional p(a-SiO) films. As can be seen from this table, p (,ac-SiO) film has a higher oxygen content in the film than the a-SiO film which results to its higher bandgap. On the other hand, the carbon content in,uc-SiO films is also less than detection limit (0.5%). The hydrogen content in,ac-SiO films is about half of conventional p (a-SiO) film which is normally observed in ,uc-Si films.

3.1.2. Microcrystallinity

It is confirmed from the Raman spectra that there is a distinct narrow peak at around 520 cm-' corresponding to the TO phonon mode of crystalline Si in the above-mentioned p(yc-SiO) films, meaning that these films contain some microcrystal-line phase. However, the peak intensity becomes smaller with an increase of CO_2 gas ratio , showing that the microcrystal-lization becomes more difficult with more oxygen. It is found that besides a large mount of oxygen, this crystalline Si phase also makes the absorption of ,ac-SiO films lower.

Furthermore, we have evaluated the crystallite size and volume fraction of ,μc-si in p(,ac-SiO) films from the measured X-ray diffraction pattern. Their data are shown in Table 3. As expected, the crystallite size and volume fraction become smaller with an Increase of oxygen

Table 2 :ontents of silicon, oxygen, carbon and hydrogen in p(yc-SiO) films

Type	CO_2 /(CO_2 + SiH_4)	Si (%)	O (%)	C (%)	H atom /cm^3
p(a-SiO)	0.67	78.4	21.6	N.D.	1.37e^{22}
p(yc-siO)	0	100	N.D.	N.D.	1.68e[illegible]
	0.37	73.9	26.0	N.D.	8.71e[illegible]
	0.54	65.0	35.0	N.D.	7.30e[illegible]

Table 3 Crystallite size and volume fraction of ,uc-Si in p(,8c-SiO) films

Type	CO_2 /(CO_2 + SiH_4)	Crystallite Size(°A)	Volume fraction (%)
P(μc-SiO)	0	298	100(assumed)
	0.37	127	58
	0.54	50	39

3.1.3. IR spectra

From IR spectra, it is observed that p(, (lC-SiO) films also contain oxygen atoms in a form of Si-O-Si, not O-H, which is similar to a-SiO films [6].

3.2. Optical and electrical properties

Fig. 1 shows the relation between the gas ratio of CO_2 to SiH_4[CO_2(SiH_4 +CO_2)} and the absorption coefficient for the p - type , ac-SiO films . As can be Seen From this figure, the absorption coefficient decreases with an increase of the gas ratio due to the incorporation of oxygen into the film. The same result is also observed for the n-type films.

Fig. 2 shows the effect the gas ratio, CO_2/(SiH_4+CO_2) on the optical bandgap (Eopt) dark conductivity (tJd) and photoconductivity ((Tph) f p-type, ac-SiO films. The conductivity decreases with increasing the gas ratio while the bandgap increases due to the incorporation of oxygen into the film. It should be noted here that the conductivities of n-type yc-SiO films are higher than those of p-type ,uc-SiO films.

Fig. 3 shows the dark conductivity and photoconductivity as a function of Eopt for conventional p-type a-SiO and ,ac-SiO films. As can be seen from this figure,the conductivities of p(,u c-SiO) films are about four orders magnitude higher than those of conventional p (a-SiO) films in the optical gap range of 2.15-2.25 eV, showing that the ,ac-SiO film is the promising material for the window layer of a-Si solar cells.

3.3. The deposition of ,ac-SiC film under the same deposition conditions

To compare with p(,ac-SiO) films, we have fabricated some p-type ,uc-SiC films from the gas mixture of SiH_4-C_2H_2-H_2-B_2H_6. We have found that it is difficult to fabricate a-SiC with microcrystalline Si under the same conditions at the substrate temperature of 150° C. This may come from the fact that the substrate temperature was not high enough for the deposition of ,ac-SiC.

3.4. Application tq metal/nip/ito type solar cell.

The above-mentioned p(,ac-SiO) films were applied to the p-layers of metal/ni-p/ITO type solar cells. Inthis type of solar cells, the microcrystalline Si p layers should be normally prepared at the substrate temperature lower than 100°C to achieve high VOC (> 0.85 V) and high performance [7]. However, it will be better for

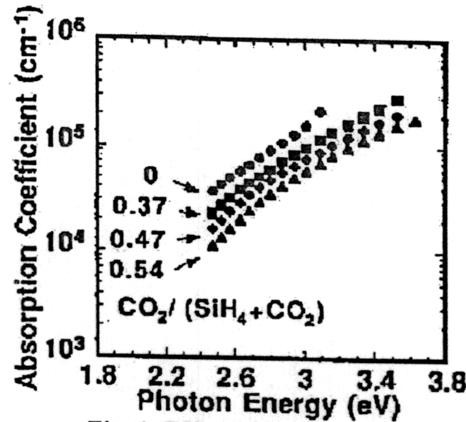

Fig. 1. Effect of the gas ratio, CO_2 /(SiH_4 + CO_2) on the absorption coefficient of p-type ,uc-iO films.

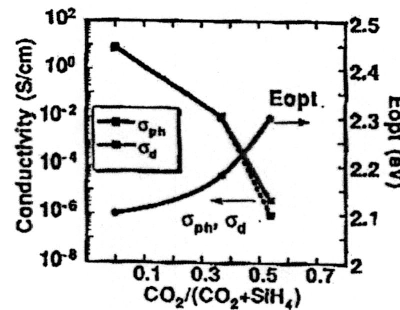

Fig. 2. Effect of the gas ratio, CO_2 /(SiH_4 + CO_2) on the Eopt, dark conductivity and photoconductivity of p-type yc-SiO films.

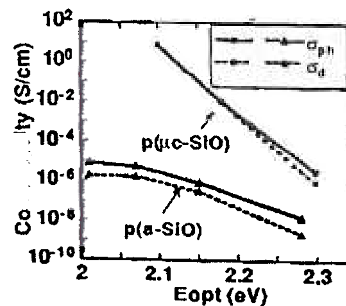

Fig. 3. The dark conductivity and photoconductivity as a function of Eopt for conventional p(a-SiO) and p(,u c-SiO) films

mass production if the p-layer can be deposited at a temperature as high as those of other layers.

We have investigated the effect of CO_2 gas ratio to the performance of the cell with p (,ac-SiO) films and its result is shown in Fig . 4. Here, p(,uc-SiO) layer was deposited at 150°C directly on the i-layer without any interface layer at p/I interface. The result obtained with the conventional microcrystalline Si p-layer prepared at 100°C is also shown in this figure for comparison. As can be seen from this figure, higher performance with higher VOC (> 0.92 V) and Jsc are obtained with p (,LtC-SiO) layer. It should be also noted here that its performance is better than the one with conventional ,ac-Si p-layer, even though the p(,uc-SiO) layer was deposited at 150°C.

Fig. 5 shows the effect of gas ratio to the collection efficiency. As seen from this figure, the response at short wavelength increases with an increase of oxygen due to the wider bandgap of the p-layer. Furthermore, it is confirmed that the cells with p(,ac-SiO) layer have better performance (higher VOC and Jsc) than the cells using conventional a-SiO layer as the p- and p/i interface layers. Up to now, an efficiency of 9.1% (VOC = 0.913 V, Jsc = 15.8 mA/cm2, FF = 0.632) was achieved for 1 cm2 area cell. It is expected that higher performance can be obtained by slightly boron-doping into the i-layer and by optimizing the p-layer thickness and the properties of p/i and ITO/p interfaces.

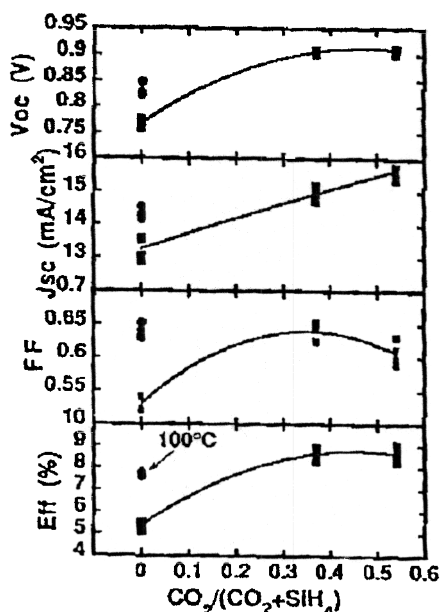

Fig. 4. Effect of the gas ratio, CO_2 /(SiH_4 + CO_2) on the cell performance of metal/n-i-p/ITO havingp(,gc-SiO) film as the p-layer.

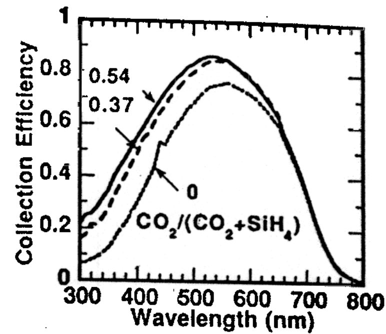

Fig. 5. Effect of the gas ratio, CO2/(SiH4+CO2) on the collection efficiency of metal/n-i-p/ITO having p(,u c-SiO) film as the p-layer.

4. Summary

We have found that a-SiO films with a microcrystalline Si phase can be easily fabricated by introducing an amount of CO_2 gas to the gas mixture of SiH_4 under the deposition condition of microcrystalline Si films. These films have lower absorption coefficients than conventional a-SiO films because of larger oxygen contents and some microcrystalline Si phase. However, their conductivities are still high since they contained some microcrystalline phase. By applying these films to the p-layer of metal/nip/ITO type cells, it was confirmed that higher perfor mance was obtained with this p (,uc-SiO) layer, comparing to the cells with conventional microcrystalline and conventional a-SiO p-layers. From these results, we consider that this novel ,ac-SiO film is a promising material for the window layer of a-Si solar cells.

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