한국신·재생에너지학회 2006년도 춘계학술대회논문집 pp.145~148

프로터결정 실리콘 다층막 태양전지의 특성 연구

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Characterization of the protocrystalline silicon multilayer solar cells

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Key words : solar cells(태양전지), amorphous silicon(비정질 실리콘), prortocrystalline silicon (프로터결정 실리콘), light-soaking behavior(열화특성)

Abstract : The protocrystalline silicon (pc-Si:H) multilayer solar cell is very promising owing to its fast stabilization with low degradation against light irradiation. However, the pc-Si:H multilayers have not extensively been investigated in detail on its material characteristics yet. We present the material characteristics of pc-Si:H multilayer using a transmission electron micorscopy (TEM), and Raman spectroscopy. In addition, we present the superior light-soaking behavior of the pc-Si:H multilayer solar cell. A TEM micrograph shows that a pc-Si:H multilayer has a repeatedly layered structure and crystalline-like objects in a-Si:H matrix. A Raman spectra introduces improved short-range-order and medium-range-order in pc-Si:H multilayer. As a result, the excellent metastability of the pc-Si:H multilayer solar cell is primarily due to the repeatedly layered structure that improves a structural order in absorber layer.

1. Introduction

Conventional hydrogenated amorphous silicon (a-Si:H) materials are known to be seriously degraded against light illumination(1), and thus a great amount of efforts have been undertaken to enhance stabilized efficiency of a-Si:H based solar cells. We have developed hydrogenated protocrystalline silicon (pc-Si:H) multilayer solar cells fabricated by employing alternate hydrogen (H_2) dilution(2-4). The fabrication technique of the pc-Si:H multilayer is partially similar to an 'uninterrupted/annealing' method(5). However, difference on our concept are that device-quality of the pc-Si:H multilayer varies in a great extent by changing sublayer deposition conditions. We may optimize the device quality and the stability by tailoring the sublayers. It should be noted that the conversion efficiency of the pc-Si:H multilayer solar cell rapidly reaches a stabilized value in 12 h under standard 1-sun illumination(2-4). Although we achieved a stabilized efficiency of 9.0%(3,4), the material characteristics of the pc-Si:H multilayer is not fully understood yet. In this work, we investigate material characteristics of the pc-Si:H multilayers by means of a transmission electron microscopy (TEM), and Raman spectroscopy. In addition, we present a long-term light-soaking behavior and annealing behavior of the pc-Si:H multilayer solar cell.

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2. Experimental

2.1 Film preparation

Figure 1 shows a schematic diagram of the alternate H_2 dilution method together with a modulation of the chamber pressure during the deposition. The pc-Si:H multilayer consists of low H_2-diluted a-Si:H sublayer (S_L's) and highly H_2-diluted a-Si:H sublayer (S_H's). We deposited pc-Si:H multilayer by just toggling the gas flow control of H_2/SiH_4 between 0 (for the deposition of S_L) and 19 (for the deposition of S_H) under continuous UV irradiation at a substrate temperature and Hg bath temperature of 250 and 20 ℃, respectively. For the deposition of S_L, we flowed 18 sccm of SiH_4 into the chamber for 1 min. In case of S_H, we fed 20 sccm of mixed gas (H_2+SiH_4) for 5 min. We kept the thickness at ~ 550 nm. Although we cut off the H_2 gas flow during the deposition of S_L, S_L indeed is not an undiluted sublayer but a low H_2-diluted one because of remaining H_2 gas in the reaction chamber. The variation of chamber pressure in Fig. 1 is ascribed to the existence of remaining gas during the modulation of H_2 dilution. For clarity, we fabricatied an undiluted a-Si:H film under the SiH_4 gas flow rate and chamber pressure of 12 sccm and 0.24 Torr, respectively.

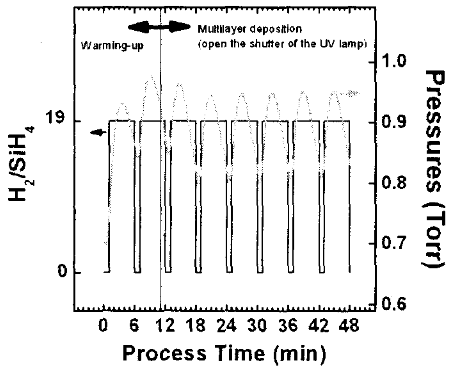

Fig. 1. Schematic diagram of alternate H_2 dilution method and an actual change of the chamber pressure during a pc-Si:H multilayer

2.2 Solar cell fabrication

To investigate on performance of solar cell, we fabricated *pin*-type solar cell with a structure of glass/SnO_2/p-a-SiC:H/buffer/i-pc-Si:H multilayer (~600nm) /n- μ c-Si:H/Al (cell area: 0.09cm^2). We grew the widely used p-a-SiC:H window by a direct photo-CVD technique with a mixture of Si_2H_6, B_2H_6, and C_2H_4 reactant gases. The buffer layer was prepared with a Hg-sensitized decomposition of a mixture of SiH_4, H_2, B_2H_6 reactant gases. As mentioned in section 2.1, the i-pc-Si:H multilayer was prepared by alternate H_2 dilution. The n-layer was deposited with a Hg-sensitized decomposition of a mixture of SiH_4, H_2, PH_3 reactant gases.

3. Result and Discussion

3.1 Material characteristics

Figure 2 shows a cross-sectional TEM (XTEM) images of a six-cycled pc-Si:H multilayer. We provided dotted lines to emphasize sharp horizontal strips, which have periodicity in the XTEM image. There is no distinct boundary between S_L and S_H because all interfaces are graded by H_2 gas. The horizontal strip may originate from the low deposition rate of S_H. Since the chamber pressure was not stabilized at the first cycle, the thickness as a result of the first deposition cycle is thicker than other deposition cycles. We should note that the alternate H_2 dilution method for the multilayer deposition leads to the repeatedly layered structure.

Figure 3 displays the planar TEM micrograph of 1 cycle prepared pc-Si:H multilayer in high magnification. It should be noted that the embedded CLO (crystalline-like objects) in a-Si:H matrix is shown in this micrograph. These CLO have diameters of 3 -5 nm. Actually, we have expected the existence of the embedded CLO in a-Si:H matrix from photoluminescence (PL) spectra[6]. The PL spectra of the pc-Si:H multilayer arises from the quantum-size-effect (QSE) of CLO in the S_H sublayer, which are confined by their neighboring S_L sublayer along the sample growth direction. Compared to the undiluted a-Si:H, we have also found many chain-like objects in a-Si:H matrix of the pc-Si:H multilayer. The structural order was improved by these chain-like objects and CLO.

Figure 4 exhibits the Raman spectra of the pc-Si:H multilayers. There is no distinct fraction of μ c-Si:H because the continuous deposition interrupts crystalline growth. Therefore, both the undiluted a-Si:H and pc-Si:H multilayer present similar Raman spectra.

These spectra can be deconvoluted to four Gaussian peaks centered near 150, 310, 420, and 480 cm^{-1}, corresponding to the transverse-acoustic (TA), longitudinal-acoustic (LA), longitudinal-optic (LO), and transverse-optic (TO) modes for a-Si:H, respectively. The TO bandwidth (Γ_{TO}) values for the undiluted a-Si:H and pc-Si:H multilayer are 53.6 and 49.5 cm^{-1}, reflecting an improved short-range-order (SRO) in the a-Si:H matrix via the alternate H_2 dilution. Especially, the ratio of the intensities of TA and TO peaks (I_{TA}/I_{TO}) is 0.654 for the undiluted a-Si:H, while that is 0.460 for pc-Si:H multilayer. These results indicate a considerable improvement of medium-range-order (MRO) in the pc-Si:H multilayer[7]. We conclude that the origin of enhanced MRO and SRO is ascribed to the embedded CLOs in well-ordered a-Si:H matrix.

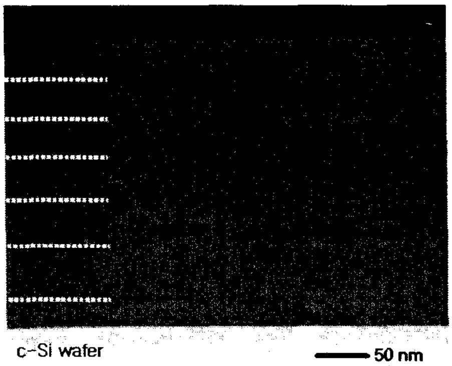

Fig. 2. Cross-sectional TEM image of a six-cycled pc-Si:H multilayer. Prior to the multilayer deposition, a 20 nm tick undiluted a-Si:H was deposited on a c-Si substrate.

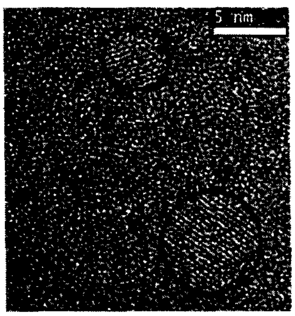

Fig. 3. Planar TEM image of a one-cycled pc-Si:H multilayer.

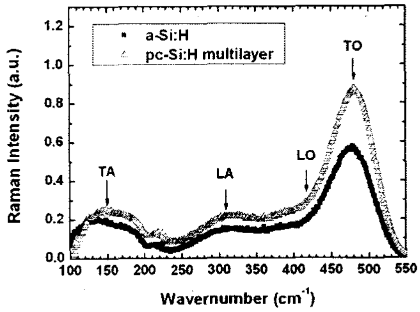

Fig. 4. Raman spectra for the undiluted a-Si:H and pc-Si:H multilayer.

3.2 Solar cell characteristics

Figure 5 shows the initial and 90 h light-soaked current-voltage (J-V) characteristics of pc-Si:H multilayer solar cell. The cell characteristics were measured under 100 mW/cm^2 (AM1.5).

Figure 6 displays the light-soaking behavior of a pc-Si:H multilayer solar cell with 8.81 % initial efficiency. The long-term light illumination is performed in the standard environment (AM 1.5, 1-sun at 50 ℃). The pc-Si:H multilayer solar cell achieved a stabilized efficiency of 8.02 % (V_{oc} = 0.942 V , J_{sc} = 13.4 mA/cm^2, FF = 0.635, degradation rate ~ 10%) after 90 h 1-sun illumination. In general, conventional a-Si:H solar cell have a degradation rate of over 20 % after 20 h 1-sun illumination[4]. In addition, the increase in V_{oc} of pc-Si:H multilayer is introduced as shown in Fig. 5. This interesting phenomena, which sometimes shows in a-Si:H based solar cells prepared at H_2 dilution ratio > 0, is reported by several literatures[8,9].

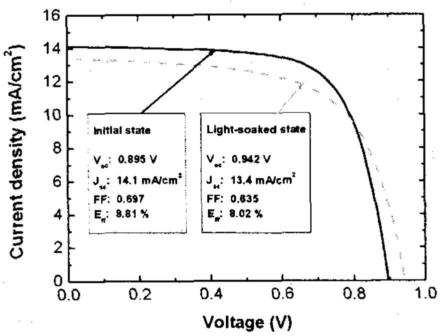

Fig. 5. Initial and 90 h light-soaked current-voltage (J-V) characteristics of pc-Si:H multilayer solar cell.

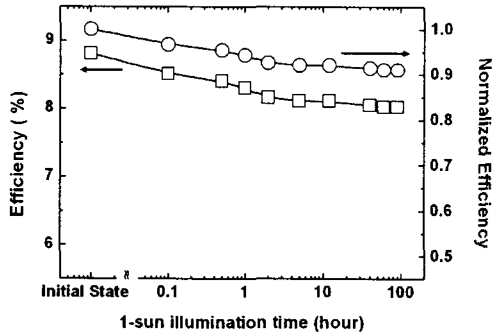

Fig. 6. Long-term light-soaking behavior of pc-Si:H multilayer solar cell.

Recently, Kamei *et al.* reported that photo-exicited carriers generated in a-Si:H matrix can be transferred to the isolated spherical small grains embedded in a-Si:H matrix and then recombine(10). Thus, the isolated small grains may suppresses subsequent dangling bond creation. As a result of TEM analysis, the photo-created dangling bonds of the pc-Si:H multilayer solar cell are the lower than that of a-S:H solar cell since the non-radiative recombination in defective boundary regions disturbs the radiative recombination within the isolated CLO.

In addition, Guha *et al.* introduced that enhanced metastability of intermediate material is due to the improved MRO of a-Si:H matrix and/or increasing volume fraction of a more ordered structure(11). From the result of Raman analysis, pc-Si:H multilayer is well-ordered material. The improved MRO of pc-Si:H multilayer is also ascribed to the superior metastability.

Finally, we emphasize that the origin of the excellent light-induced metastability of the pc-Si:H multilayer comes from the repeatedly layered structure processed through alternate H_2 dilution. The embedded CLO in a-Si:H matrix and improved structural order in this peculiar structure contributes to the fast stabilization with low degradation of the pc-Si:H multilayers against light irradation.

4. Conclusions

We have investigated characteristics of the pc-Si:H multilayers using TEM, Raman spectroscopy. The TEM micrograph shows repeatedly layered structure of the pc-Si:H multilayer and the Raman spectra present the improved SRO and MRO in pc-Si:H multilayer. We have also studied the long-term light-soaking behavior of the pc-Si:H multilayer solar cell. We have achieved the stabilized efficiency of 8.02 %, and the degradation rate of ~ 10 %.

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