Inclusion of nanosized silicon grains in hydrogenated protocrystalline silicon multilayers and its relation to stability

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Photoluminescence and Fourier transform infrared spectroscopy measured at room temperature produce strong evidence that nanosized silicon (nc-Si) grains embedded in hydrogenated protocrystalline silicon (i-pc-Si:H) multilayers. Thus, we propose the structure of the i-pc-Si:H multilayer possessing isolated nc-Si grains and their wrapping layers with a high hydrogen concentration embedded in highly hydrogen-diluted sublayers. The isolated nc-Si grains may act as radiative recombination centers of photoexcited carriers, and hence suppress the photorecreation of dangling bonds caused by the nonradiative recombination in amorphous silicon matrix. Because of the repeatedly layered structure, the i-pc-Si:H multilayers have a fast light-induced metastability with a low degradation. © 2006 American Institute of Physics. [DOI: 10.1063/1.2179130]

We proposed alternately H2-diluted hydrogenated protocrystalline silicon (pc-Si:H) multilayer absorbers. The pc-Si:H material is an unique H2-diluted hydrogenated amorphous silicon (a-Si:H) material existing just below the threshold of the a-Si:H-to-hydrogenated microcrystalline silicon (μc-Si:H) transition. Since the i-pc-Si:H multilayers exhibit a fast light-induced metastability with a low degradation, we developed the pc-Si:H multilayer solar cell that displayed the degradation ratio lower than 10%. We developed pc-Si:H multilayer solar cells employing H2-diluted hydrogenated boron-doped amorphous silicon-carbide (p-a-SiC:H) buffer layer. Since the p-a-SiC:H buffer layer effectively reduces the recombination loss at the p/i interface, we have achieved a stabilized efficiency of 9.0% (initial efficiency, 10.4%) without using any back reflector after 12 h 1-sun (AM 1.5, 100 mW/cm2) standard light irradiation at 50 °C. However, the origin of the fast light-induced metastability with the low degradation is still unclear. Hereafter, we provide strong evidence that shows the inclusion of nanosized (nc-Si) grains in the i-pc-Si:H multilayers. We also demonstrate the correlation of the nc-Si grains and light-induced metastability of the i-pc-Si:H multilayers.

We prepared alternately H2-diluted i-pc-Si:H multilayers via a photoassisted chemical vapor deposition (photo-CVD) technique. To dissociate the gases, we used a low-pressure Hg lamp with resonance lines of 184.9 and 273.7 nm as an UV light source. The i-pc-Si:H multilayer consists of low H2-diluted a-Si:H sublayers (Sts) and highly H2-diluted a-Si:H sublayers (Shs). This repeatedly layered structure is deposited by just toggling the mass flow control of the hydrogen dilution ratio (H2/SiH4) between 0 (for the deposition of Sts) and R (15–30 for the deposition of Shs) under continuous UV light irradiation. During the deposition, however, the chamber pressure was also slightly toggled with the gas flow control, because we maintained the angle of the throttle valve at a constant value. With an increase in R, both the thickness values for Sts and Shs reduce due to the decreased growth rate by strengthened hydrogen coverage near the growing surface during the continuous process, and thereby N should be increased in order to maintain the total thickness at ~550 nm. The i-pc-Si:H multilayer deposition using the modulation of the hydrogen dilution can be easily realizable via the conventional plasma-enhanced chemical vapor deposition (PECVD) technique.

The Raman spectroscopy was performed using JASCO Corp., NRS-1000 system with an Ar laser (wavelength, 532 nm). The photoluminescence (PL) spectra were obtained at room temperature using an Ar laser (wavelength, 514 nm). We failed to achieve any electron spin resonance (ESR) results of the i-pc-Si:H multilayers, because their density of neutral dangling bonds (DBs) was lower than the detection limit.

Figure 1 shows Raman spectra for the i-pc-Si:H multilayers prepared with different R and a H2-diluted single layer (300 nm) prepared at H2/SiH4=15. We should note that ~550 nm thick multilayers fail to show any distinct fraction of a μc-Si:H phase, while the 300 nm thick single layer indicates a μc-Si:H phase. We can speculate that ~10 nm thick Ss interrupt the columnar growth of μc-Si:H.

We performed the PL and Fourier transform infrared (FTIR) spectroscopy for the i-pc-Si:H multilayers prepared on c-Si wafers. To reduce the effect of substrates, we grew a 10 nm thick SiO2 layer on c-Si via thermal oxidation. Figure 2 exhibits the PL spectra for the i-pc-Si:H multilayers measured at room temperature. Broad and small peaks centered at ~690–700 nm were detected. As both the bulk μc-Si:H...
and $a$-Si:H films exhibit no visible PL at room temperature, we suggest that PL of multilayers arises from the nanocrystallites embedded in $S_{96}$.$^3$ From transmission electron micrographs (TEM), it is found that 3–5 nm sized spherical nc-Si grains are embedded in $i$-pc-Si:H multilayers prepared at $R=20$.$^9$

Figure 3(a) depicts FTIR spectra for an undiluted $i$-$a$-Si:H film and the $i$-pc-Si:H multilayers. The undiluted $i$-$a$-Si:H film possesses absorption peaks centered at 631, 712, 880, and 1990 cm$^{-1}$. We attribute the weak absorption band at 712 cm$^{-1}$ (multilayer, $\sim$714 cm$^{-1}$) to Si-O-Si symmetric stretching,$^{10}$ which is caused by the SiO$_2$ bottom layer. With an increase in $R$, the main Si–H wagging vibrational mode typical for $a$-Si:H gradually shifts downward to $\sim$612 cm$^{-1}$, which can be assigned to monohydride (SiH) bonding on c-Si(100) surfaces.$^{13,12}$ Thus, this frequency shift can be attributed to the inclusion of crystallites in $S_{96}$. In the case of the multilayers, the Si–H stretching vibrational mode of $a$-Si:H centered at 1990 cm$^{-1}$ shifts upward to 2000 cm$^{-1}$ and a new component centered at $\sim$2080 cm$^{-1}$ emerges. Because we failed to detect any microvoids by small-angle x-ray scattering (SAXS) for our pc-Si:H samples, the latter peak can be attributed to the stretching vibrational mode of dihydride (SiH$_2$) bonding groups$^{13}$ or clustered SiH bonds in the grain-boundary region.$^{14,15}$ We assign the absorption peak at $\sim$2080 cm$^{-1}$ of the multilayers to clustered SiH bonds in grain-boundary regions by taking into account the appearance of the peak at $\sim$612 cm$^{-1}$. The enlargement of the doublet centered at 880 cm$^{-1}$ corresponding to the vibrational mode of higher order SiH supports the assignment.$^{12}$ Because the multilayers are more stable than $i$-$a$-Si:H, the appearance of the peaks at $\sim$612 cm$^{-1}$ and $\sim$2080 cm$^{-1}$ can be ascribed to the inclusion of small crystallites in $S_{96}$. From the spectra, we evaluated the microstructure factor, $I_{2080}/(I_{2000}+I_{2080})$, where $I_i$ denotes an integrated intensity of a peak centered at $i$ cm$^{-1}$. In the case of undiluted $i$-$a$-Si:H, $I_{2000}$ is evaluated from the peak centered at 1990 cm$^{-1}$. As shown in Fig. 3(b), the microstructure factor monotonously increases with the increase in $R$.

Based on the PL and FTIR spectroscopy, we propose the structure of the $i$-pc-Si:H multilayers with a nonuniform distribution of hydrogen.$^{11}$ An $i$-pc-Si:H multilayer has a repeatedly layered structure consisting of $S_{96}$ and $S_{98}$. Isolated spherical nc-Si grains are embedded in the $a$-Si:H matrix of $S_{98}$. Each nc-Si grain is wrapped by an hydrogen-rich $a$-Si:H grain-boundary layer.$^{16}$ The grain-boundary layers are the most defective component with the widest optical band gap in the multilayer due to their high hydrogen concentration. $S_{96}$ which hinder the percolation path of $\mu$-Si:H possess a less-ordered $a$-Si:H matrix than that of $S_{98}$. All interfaces are graded by H$_2$. We believe that some photoexcited carriers generated in the $a$-Si:H matrix in all the sublayers can diffuse to grain-boundary layers surrounding nc-Si grains. Because isolated nc-Si grains have a much
light illumination at 50 °C using glass/SnO$_2$·F/H$_2$O$_8$49/constant energy monochromter/multilayer/H$_2$O$_8$49/H$_1$11011/H$_9$262

Notice that the highest visible PL peak measured at room temperature in the microstructure factor, as shown in Fig. 3, sider that the total number of nc-Si grains increases with the most defective grains. The multilayer prepared at remaining H$_2$ gas in the reaction chamber during the depositions of a-Si:H matrix for $S_{2}$ and $S_{3}$, and that also contributes to the good light-induced metastability. In addition, the isolated nc-Si grains have a considerable vertically regular distribution due to the regular arrangement of $S_{3}$ in the multilayers.

We performed standard 1-sun (AM 1.5, 100 mW/cm$^2$) light illumination at 50 °C using glass/SnO$_2$·F/i-pc-Si:H multilayer ($\sim$550 nm)/Al Schottky diode structures. Using a constant energy monochrometer (light intensity, 50 $\mu$W/cm$^2$), we checked the photogenerated current density at a wavelength ($\lambda$) of 600 nm as a measure of the stability. As shown in Fig. 4, the initial photogenerated current density at 600 nm decreases with the increase in $R$. All the multilayers exhibit fast light-induced stabilization behaviors. Several recent reports have suggested “fast” and “slow” metastable defects in a-Si:H.20 Thus, we speculate that the vertically regular distribution of the isolated nc-Si grains in i-pc-Si:H multilayers reduces “slow” metastable defects. Notice that the highest visible PL peak measured at room temperature is obtained for the most stable multilayer prepared at $R$=20 (thickness ratio of $S_{2}$/$S_{3}$, 10/32 nm/nm).5 Due to the continuous deposition, the average deposition rate of the multilayer (7 nm/min) is comparable to that of conventional undiluted i-a-Si:H (10 nm/min) (Ref. 5) and faster than that of the optimized i-pc-Si:H single layer prepared by the photo-CVD technique.21 Based on the increase in the microstructure factor, as shown in Fig. 3(b), we consider that the total number of nc-Si grains increases with the increase in $R$ due to the increase in the total number of $S_{3}$, and thus the initial photogenerated current density decreases due to the enhanced recombination in the isolated nc-Si grains. The multilayer prepared at $R$=15 has the thickest and most defective a-Si:H matrix in $S_{2}$ due to the lowest remaining H$_2$ gas in the reaction chamber during the depositions of $S_{3}$. The lowest PL intensity among the multilayers reflects that nc-Si grains with the lowest density are formed within $S_{3}$ (see Fig. 2). Thus, this multilayer shows the highest degradation ratio due to the increased photocreation of DBs in the a-Si:H matrix. Meanwhile, the multilayer prepared at $R$=20 shows a remarkable suppression of the photocreation together with the highest PL intensity. It can be attributed to the improved a-Si:H matrix in all the sublayers, the increased density of nc-Si grains, and the reduced thickness of $S_{3}$. Since the recombination in nc-Si grains are elevated by the uniform distribution and high density, the i-pc-Si:H multilayer has the lowest light-induced degradation. For $R$>20, the degradation ratio increases. In this regime, the decline in the PL intensity is mainly due to the increased size of the nc-Si grains. Because of strengthened hydrogen coverage near the growing surface, both the density and size of nc-Si grains increase with the increase in $R$. This in turn increases the volume fraction of defective a-Si:H grain-boundary layers wrapping the nc-Si grains. Owing to the increased nonradiative recombination within the defective grain-boundary layers, the radiative recombination in nc-Si grains is disturbed, and thereby the photocreation of DBs is enhanced.

In summary, due to the vertically regular distribution of the isolated nc-Si grains, the i-pc-Si:H multilayers exhibit the fast light-induced metastability with the low degradation.