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Characteristics of Heavily Phosphorus-doped Gradient Si-rich Oxide Multilayer Thin Film Structure by Spin-on Method

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Abstract

Phosphorus (P) doping in a super-high density Si quantum dot thin film using a gradient Si-rich oxide multilayer (GSRO-ML) structure is demonstrated by means of spin-on process prepared by sol-gel method. The crystalline and photovoltaic (PV) properties are studied, and the proper drive-in parameters can significantly enhance the PV properties.

1. Introduction

Nano-crystalline Si quantum dot (nc-Si QD) thin films integrated into Si-based solar cells have been widely investigated in recent decades, because the issue of thermalization loss from the high-energy photons can be overcome owing to quantum confinement effect [1]. In order to enhance the poor probability of carrier transport due to the highly-resistive SiO_2 matrix used in Si QD thin films, we had proposed and demonstrated the gradient Si-rich oxide multilayer (GSRO-ML) thin film structure which possesses super-high density Si QDs and provides significant enhancement on crystalline, optical absorption and electrical properties compared with the general [Silicon dioxide/Si-rich oxide] multilayer ([SiO_2/SRO]-ML) thin film structure [2]. To further enhance the photovoltaic (PV) properties for integration with thin film solar cells to achieve high efficiency, it is necessary to increase conductivity and carrier concentration of Si QD thin film by heavily doping [3]. Compared to conventional diffusion method using phosphorus oxychloride ($POCl_3$), the spin-on process with dopant source solution is more easily controllable. The advantages of high throughput, low thermal budget and possible versatility are more suitable for doping in thin film structure [4].

In this study, heavy phosphorus (P)-doping in GSRO-ML thin film is realized by means of spin-on method. The spin-on dopant (SOD), as P dopant source, is coated on annealed GSRO-ML thin film by spin coater. Then, P atoms are diffused into Si QD thin films by the following drive-in process. The effect of heavy P-doping on crystalline, electrical, and PV properties is investigated and discussed.

2. Experiment

A lowly-doped n-type GSRO-ML thin film is deposited on a p-type Si (100) wafer and fused quartz at room temperature by radio-frequency (RF) magnetron sputtering method. The experimental process is described in our previous study [2]. After deposition, the lowly P-doped GSRO-ML thin film samples are annealed at 1100˚C for 1 hour in N_2 ambience to form super-high density Si QDs. The as-deposited and annealed lowly P-doped GSRO-ML thin film structures are shown in Fig. 1(a).

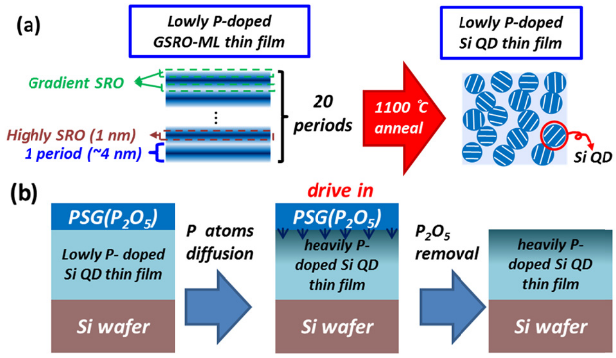

Fig. 1 Illustration of (a) as-deposited and annealed Si QD thin films utilizing GSRO-ML structure, and (b) fabrication process of spin-on dopant and diffusion treatment.

The SOD is SiO_2 solutions containing 2, 8 or 14 percent by weight (wt%) of P_2O_5 prepared under room temperature from tetraethylorthosilicate (TEOS), isopropanol (IPA), hydrochloric acid (HCl), and deionized water (DI water) as precursors for SiO_2 solution and P_2O_5 powders as dopant source. All the mixtures are stirring for 1 hour and followed by aging for 24 hours for complete reaction of hydrolysis and condensation. As Fig. 1(b) shows, the resultant solutions are coated on the annealed GSRO-ML thin film structures to form phosphosilicate glass (PSG) layers by spin coater, and dried at 200˚C for 5 minutes on the hot plate to evaporate the remaining solvent. Subsequently, the diffusion treatments are carried out in a quartz tube furnace at 950˚C for 20 minutes to drive in and activate P atoms. After diffusion, the residual PSG layers are removed by dipping in the diluted HF solution for 80~110 seconds.

3. Results and Discussions

Figure 2 shows the Raman spectra and crystallinity of Si ($f_{c\text{-}Si}$) of heavily P-doped nc-Si QD thin films under different P_2O_5 contents in SOD. The significant peak near 520 cm^{-1} can be observed which represents the formation of nc-Si QDs during annealing. The $f_{c\text{-}si}$ is calculated from the integrated intensity of amorphous- (a-), intermediate- (i-), and nc-Si phases decomposed from the peak. The similar crystalline properties and $f_{c\text{-}si}$ values suggest that the drive-in treatment does not affect the nc-Si QD formation.

Figure 3 shows Hall measurement results of heavily P-doped Si QD thin films under different P_2O_5 contents in

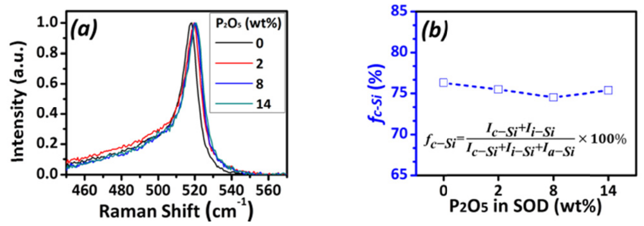

Fig. 2 (a) Raman spectra and (b) the corresponding crystallinity ($f_{c\text{-}Si}$) of P-doped Si QD thin films with different percentages by weight of P_2O_5 in SOD.

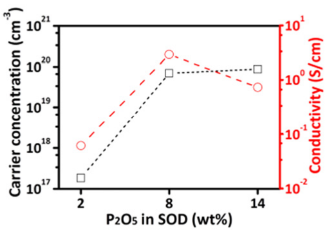

Fig. 3 Carrier concentration (□) and conductivity (○) of the P-doped Si QD thin films under different percentages by weight of P_2O_5 in SOD

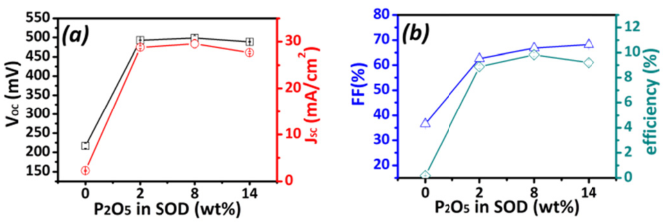

Fig. 4 (a) Open-circuit voltage (□) and short-circuit current density (○), (b) fill factor (Δ) and efficiency (◇) of P-doped Si QD thin film as a function of percentage by weight of P_2O_5 in SOD.

Table I PV properties of P-doped Si QD thin films with 8 wt% P_2O_5 in SOD under drive-in temperatures ranged from 850 ~ 1000°C for 20 minutes.

Drive-in temperature (°C)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	Efficiency (%)
850	403	6.9	21.2	0.6
900	531	31.1	70.7	11.7
950	499	29.5	66.9	9.8
1000	456	20.9	72.8	6.9

SOD. As P_2O_5 content increases, the carrier concentration and conductivity increase drastically and show optimal values when P_2O_5 = 8 wt% owing to the increase in active P atoms. When P_2O_5 > 8 wt%, the carrier concentration becomes saturated and conductivity shows degradation, which may result from the saturation of doped P atoms in the Si QDs thereby inducing defects to form at the interface of Si QD/SiO_2 matrix or inside the SiO_2 matrix [3, 5].

Figure 4 summarizes the PV properties including open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF) and efficiency under air mass (AM) 1.5G illumination. Significant enhancement after heavy P-doping can be observed. The variation trends of V_{OC}, J_{SC} and efficiency show the optimal values when P_2O_5 = 8 wt%, then gradually degrade as P_2O_5 content further increases. According to literatures, the diffusion depth and concentration of doped P atoms are highly dependent on drive-in temperature ($T_{drive\text{-}in}$) and duration. The higher $T_{drive\text{-}in}$ and/or the longer drive-in duration will lead to deeper diffusion depth and/or heavier doping concentration [6]. Therefore, a series of P-doped Si QD thin films coated with 8 wt% P_2O_5 in SOD under $T_{drive\text{-}in}$ ranged from 850 ~ 1000°C for 20 minutes are prepared, and the corresponding PV properties are listed in Table I. Better properties are obtained at $T_{drive\text{-}in}$ = 900°C. The poor PV properties under $T_{drive\text{-}in}$ = 850°C indicate that the temperature is not sufficient to efficiently drive in and activate P atoms. Besides, the PV properties degrade as $T_{drive\text{-}in}$ > 900°C, which may result from the over diffusion of P atoms at the film/wafer interface, thereby weakens the built-in electric field. From these results, the efficiency can be greatly enhanced by heavy P-doping, and drive-in parameters need to be optimized for the GSRO-ML thin film for best PV performance.

4. Conclusions

In summary, we demonstrated heavily P-doped GSRO-ML thin films with enhanced PV properties by means of spin-on method and proper drive-in parameters. After P doping, crystalline properties of Si QD thin films can be maintained. A proper doping condition can enhance the carrier concentration, conductivity, and PV properties efficiently. Therefore, Si thin film solar cells integrated with p-i-n Si QD thin films can be expected employing the GSRO-ML thin film structure in the future.

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