Surface Passivation of Crystalline Silicon by Micro Crystalline Silicon Deposition Followed by High-Pressure H₂O Vapor Heat Treatment

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Abstract. We report passivation of the crystalline silicon surface by deposition of undoped microcrystalline silicon (μc-Si) followed by high-pressure H_2O vapor heat treatment. 25-nm-thick undoped μc-Si films were formed to the surface of 500-μm-thick *n* and *p*-type silicon substrates using inductively coupled plasma chemical vapor deposition (ICP-CVD) at 150 ^oC. Samples were heated at 180 and 260^oC with 1×10^6-Pa-H_2O vapor for 3h. The effective minority carrier lifetime τ_{eff} was measured by 9.35-GHz microwave absorption system in order to evaluate surface passivation effect. High τ_{eff} were achieved as 1.8×10^{-4} and 5.8×10^{-5} s, respectively, by formation the μc-Si films on the *n* and *p*-type silicon surfaces, respectively. Moreover, τ_{eff} were further increased to 1.4×10^{-3} and 3.4×10^{-4} s, respectively, by subsequent high-pressure H_2O vapor heat treatment at 260 ^oC for *n* and *p*-type silicon samples.

Introduction

Microcrystalline silicon (μc-Si) films can be formed at low temperatures between 100 and 500 ^oC by plasma-enhanced-chemical-vapor deposition (PE-CVD). Taguchi et al. reported capability of surface passivation using μc-Si films [1]. SiN_x and SiO_x insulating layer have been widely applied to surface passivation for crystalline silicon (c-Si) solar cells. Passivation of metal silicon interface is also important to effectively transporting photo-induced carriers because direct deposition of metal electrodes to the c-Si surface, markedly increases carrier recombination velocity and decrease the conversion efficiency of solar cells. SiN_x and SiO_x insulating thick films cannot be used. The other hand, μc-Si has low band gap energy and high conductivity compared with SiO_x or SiN_x. Therefore, μc-Si films will be suitable for the conductive passivation between metal electrodes and c-Si substrates. Moreover, μc-Si films have high impurity activation property compared with amorphous silicon. Therefore, doped-μc-Si will be useful for fabrication of high performance crystalline silicon solar cells, such as Hetero-Junction with Intrinsic Type Silicon Solar Cells [2]. However, there has been still a problem of the plasma damage by PECVD.

In this paper, we report surface passivation of μc-Si film deposition followed by high-pressure H_2O vapor heat treatment. We have reported that high-pressure H_2O vapor heat treatment eliminates plasma damage and the defects in amorphous silicon (a-Si) films and at

polycrystalline grain boundaries [3,4]. We report that high-pressure H_2O vapor heat treatment effectively decreases the carrier recombination velocity at the μc-Si /c-Si interface.

Experiment

We prepared *n* and *p*-type (1 0 0) oriented *CZ*-silicon substrates with a thickness of 500 μm coated with 100-nm-thick thermally grown SiO_2 layers (initial samples). The resistivity of *n* and *p*-type silicon substrates was 35 and 25 Ωcm, respectively. The SiO_2 layers at the top surface were then removed using 5%-diluted hydrofluoric acid. We kept the samples for three days to form the native oxide layer at the top surfaces in air atmosphere at room temperature [5] to prevent epitaxial growth of crystalline silicon during PECVD. Optical reflectivity

Fig.1 : Schematic of microwave absorption system

measurement revealed that the average thickness of native oxide layers was thin about 1 nm, which was enough tunneling quantum electrical conduction. Undoped μc-Si films with a thickness of 25 and 3 nm were deposited at the top surfaces at 150°C by ICP-CVD at 0.5 Pa with mixed gases with SiH_4 at a flow rate of 50 Sccm and H_2 at 25 Sccm [6]. For comparison, we formed 25-nm-thick μc-Si films immediately after 5%-diluted-hydrofluoric-acid treatment. The Samples were subsequently heated in 1×10^6-Pa-H_2O vapor at 180 and 260°C for 3h.

τ_{eff} was measured by 9.35-GHz microwave absorption system, as shown in Fig. 1 [7,8]. The sample substrates were put in a gap of wave-guide tubes. Microwave transmittance signals of the samples were measured when continuous wave or periodically pulsed light with 620 nm-wave length was illuminated to the top surfaces of samples at 1.5 mW/cm^2. Moreover, the signals were coincidentally integrated with time during light *ON* to reduce the noise level. τ_{eff} was estimated using the carrier diffusion and annihilation theory. The surface recombination velocity at the top surfaces S_{top} was estimated from τ_{eff} using equation (1) based on the carrier diffusion and annihilation theory with the minority carrier diffusion coefficient D and the thickness of substrate d. We assumed that bulk lifetime τ_b in the c-Si substrates was very long at 1 s and the recombination velocity at the rear surface S_{rear} for *n* and *p*-type samples kept the same initial value of 17 and 100 cm/s obtained from initial τ_{eff} of 1.5×10^{-4} and 2.5×10^{-4} s, respectively. The optical penetration depth for c-Si at 620-nm-wave length was about 2.2 μm, which was much lower than the substrate thickness. Therefore, we assumed that carrier generation was limited in the top surface region.
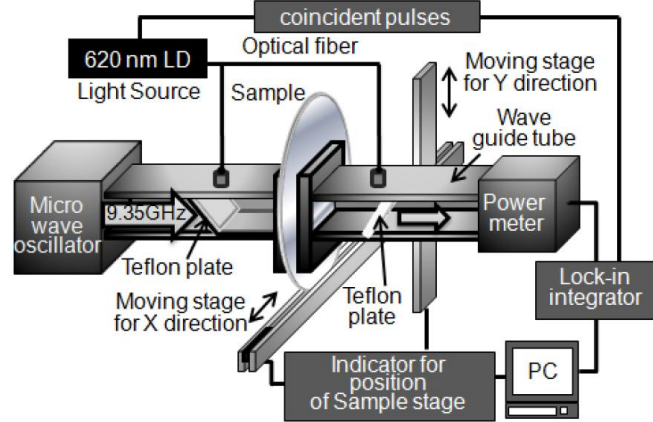
$$\tau_{eff} = \tau_b \frac{\sqrt{\frac{D}{\tau_b}}\left(1 - \exp\left(-\frac{d}{\sqrt{D\tau_b}}\right)\right)\left(\sqrt{\frac{D}{\tau_b}} + S_{rear} + \left(\sqrt{\frac{D}{\tau_b}} - S_{rear}\right)\exp\left(-\frac{d}{\sqrt{D\tau_b}}\right)\right)}{\left(\sqrt{\frac{D}{\tau_b}} + S_{rear}\right)\left(\sqrt{\frac{D}{\tau_b}} + S_{top}\right) - \left(\sqrt{\frac{D}{\tau_b}} - S_{top}\right)\left(\sqrt{\frac{D}{\tau_b}} - S_{rear}\right)\exp\left(-\frac{2d}{\sqrt{D\tau_b}}\right)} \qquad (1)$$

Results and Discussion

Figure 2 shows Raman scattering spectrum for μc-Si films formed on glass substrates. This spectral curve was analyzed by three Gaussian curves with peak wavenumber of 470, 500, 520 cm^{-1}, associated with bonding vibrations of amorphous, nano-crystalline and crystalline silicon, respectively. The best fitting resulted in a crystalline volume ratio of 0.5 from the ratio area of nano-crystalline and crystalline components to the total area.
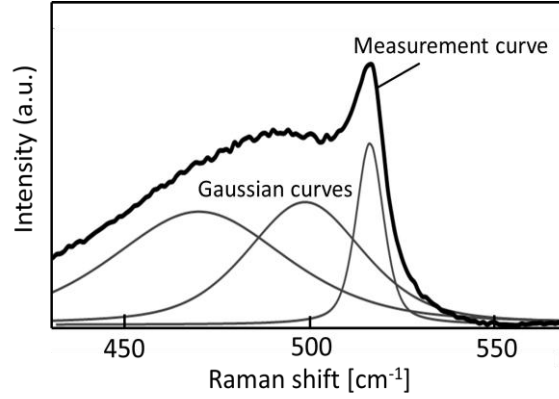
Experimental τ_{eff} are summarized in Fig. 3 (a) and (b) in the cases of 25 and 3-nm-thick μc-Si films, respectively, for n and p-type silicon samples. S_{top} were analyzed from experimental τ_{eff}. They are summarized in Fig. 4 (a) and (b) in the cases of 25 and 3-nm-thick μc-Si films, respectively, for n and p-type silicon samples. The samples with bare top surfaces kept for three days after after 5%-diluted-hydrofluoric -acid treatment had low τ_{eff} of 2.0×10^{-5} and 5×10^{-6} s for n and p-type samples. S_{top} were therefore high of 2500 and 7500 cm/s, respectively. On the other hand, 25-nm-thick μc-Si deposition increased τ_{eff} to 1.8×10^{-4} and 5.8×10^{-5} s for n and p-type samples, respectively, as shown in Fig.3 (a). S_{top} decreased to 260 and 730 cm/s, respectively, as shown in Fig.4 (a). We interpret native oxide does not have stable SiO_2 bonding network and that native oxide/silicon interface is also unstable accompanied with many defects. Moreover, native oxide was spontaneously and inhomogeneously formed on the silicon surface. We believe that there must be some clucks between native oxide domains, which cause carrier recombination sites. We believe that silicon deposition it does not work perfectly passivation of the silicon surface. Silicon deposition was effective to increase τ_{eff} probably because the recombination velocity was decreased at the region cluck
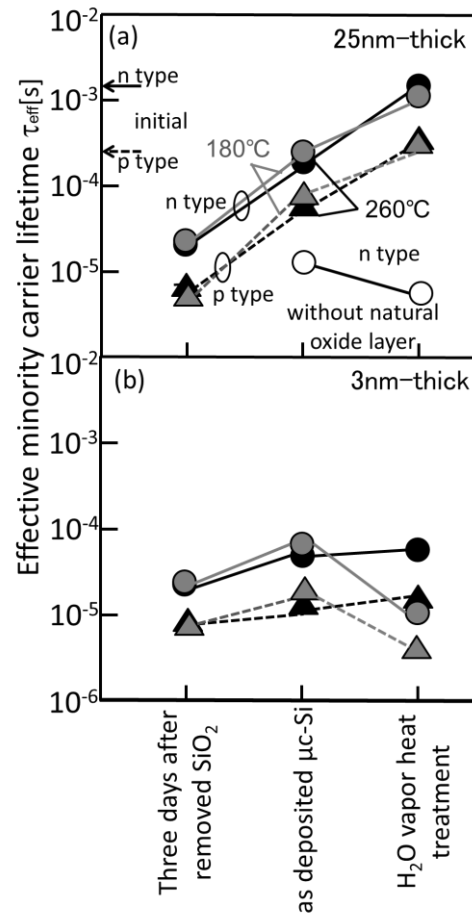

Fig. 2 : Raman scattering spectra for μc-Si

Fig.3 : Minority carrier lifetime τ_{eff} for n (circles) and p-type (triangles) samples with 25(a) and 3(b) nm-thick-μc-Si films at as-top-SiO$_2$ removed, as-μc -Si deposited, and final H$_2$O vapor heat treatment at 180 and 260°C.

regions, in which we believed amorphous silicon was formed just at silicon surface. μc-Si grains grew on the a-Si incubation region. Subsequent 1.0×10^6-Pa H$_2$O vapor heat treatment at 260°C for 3h markedly increased τ_{eff} for n and p-type samples to 1.4×10^{-3} and 3.4×10^{-4} s, respectively. S_{top} decreased to 19 and 51 cm/s, respectively. Those results indicate that

high-pressure H_2O vapor heat treatment effectively decreased the density of recombination sites at a-Si /c-Si [9] and native oxide/c-Si interfaces probably because their interfaces became stable. τ_{eff} for n and p-type samples were finally comparable to values of the initial samples with the both surface coated with 100-nm thermally grown SiO_2 layers. Moreover, 180^oC H_2O vapor heat treatment also increased τ_{eff} for n and p-type samples with 25-nm-thick μc-Si to 1.3×10^{-3} and 3.0×10^{-4} s, respectively. The results of long τ_{eff} obtained by 180^oC H_2O vapor heat treatment shows that the combination μc-Si film formation with high pressure H_2O vapor heat treatment is effective for surface passivation at low process temperature.

On the other hand, τ_{eff} was increased to 4.7×10^{-5} and 1.5×10^{-5} s by 3-nm-thick μc-Si deposition for n and p-type samples, as shown in Fig. 3(b). However, high pressure H_2O vapor heat treatment was not effective to further increase τ_{eff}. They were 5.6×10^{-5} and 1.7×10^{-5} s for n and p-type samples, respectively when 1.0×10^{6}-Pa H_2O vapor heat treatment at 260^oC for 3h was carried out. We interpret that the surface 3-nm-thick μc-Si was not enough to completely cover the c-Si surfaces.

Moreover, τ_{eff} of the n-type silicon sample coated with 25-nm-thick μc-Si immediately after 5%-diluted-hydrofluoric -acid treatment had a low value about 1.3×10^{-5} s. High-pressure H_2O vapor heat treatment at 260 ^oC did not increase τ_{eff}. This result indicated that Pre-formed thin oxide layers before μc-Si deposition was important to formed high quality μc-Si/c-Si interfaces. We probably thought that the native oxide layer protected c-Si surface from plasma damage.

Figure 5 shows changes in τ_{eff} as a function of elapse time for n and p-type samples coated with 25-nm-thick μc-Si films treated with 1.0×10^{6}-Pa H_2O vapor heat treatment at 260^oC for 3h, were kept in air atmosphere at room temperature. τ_{eff} kept high values of 1.1×10^{-3} and 2.5×10^{-4} s for n and p-type samples, respectively, in 150 days after high-pressure H_2O vapor heat treatment. Those
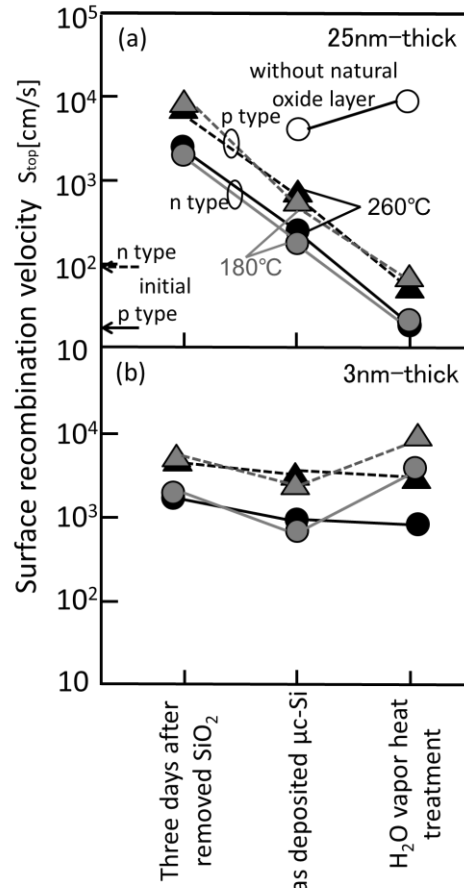

Fig.4 : Surface recombination velocity S_{top} analyzed from experimental τ_{eff} for n and p-type samples with 25(a) and 3(b) nm-thick-μc-Si films at as-top-SiO_2 removed, as-μc -Si deposited, and final H_2O vapor heat treatment at 180 and 260^oC.
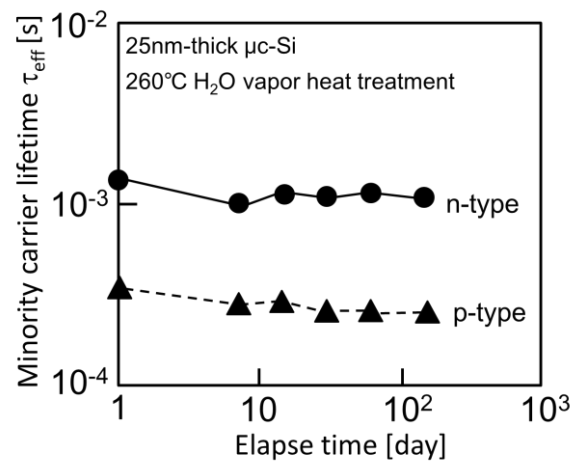

Fig.5 : The change in minority carrier lifetime τ_{eff} for n (circles) and p-type (triangles) as H_2O vapor heat treatment at 260 ^oC samples with elapse time.

results of Figs. 3, 4 and 5 show that the present method of μc-Si film formation followed by high-pressure H_2O vapor heat treatment gives effective and stable passivation of the silicon surfaces.

Summary

Passivation of crystalline silicon surfaces was investigated by μc-Si film formation using ICP-CVD. Long τ_{eff} of 1.4×10^{-3} s and 3.4×10^{-4} s were achieved for 500-μm-thick n and p-type crystalline silicon substrates by 25-nm-thick μc-Si deposition followed by 1×10^6 Pa H_2O vapor heat treatment at 260^oC for 3h. Those τ_{eff} were comparable to the value of 1.5×10^{-3} and 2.5×10^{-4} s for samples coated with 100-nm-thick thermally grown SiO_2 layers. Moreover, 180^oC H_2O vapor heat treatment also increased τ_{eff} for n and p-type samples with 25 nm-thick μc-Si to 1.3×10^{-3} and 3.0×10^{-4} s, respectively. Those results of long τ_{eff} shows that the combination μc-Si film formation with high-pressure H_2O vapor heat treatment is effective for surface passivation at low process temperature.

Acknowledgments

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