Effect of ion bombardment on the a-Si:H based surface passivation of *c*-Si surfaces

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(Received 28 November 2010; accepted 31 May 2011; published online 17 June 2011)

We have found that controlled Ar ion bombardment enhances the degradation of a-Si:H based surface passivation of *c*-Si surfaces. The decrease in the level of surface passivation is found to be independent on the ion kinetic energy (7–70 eV), but linearly proportional to the ion flux $(6 \times 10^{14}-6 \times 10^{15} \text{ ions cm}^{-2} \text{ s}^{-1})$. This result suggests that the ion flux determines the generation rate of electron–hole pairs in a-Si:H films, by which metastable defects are created at the H/a-Si:*c*-Si interface. Possible mechanisms for the ion induced generation of electron–hole pairs are discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3601485]

With the present trend toward higher efficiency and thinner *c*-Si solar cells, thin (5–50 nm) a-Si:H films are deposited on *c*-Si wafers to chemically passivate the defects of the crystal surface.¹ Excellent passivation of defects at the a-Si:H/*c*-Si interface is achieved by the development of mobile H in the a-Si:H layer, during film deposition or post-deposition annealing, which terminates the unpassivated dangling bonds on the surface of *c*-Si wafers.² Light soaking of thin (50 nm) a-Si:H films deposited on *c*-Si surfaces induces the creation of dangling bonds at the a-Si:H/*c*-Si interface of a very short time scale (~s), resulting in a lower level of surface passivation.^{3,4}

Besides light exposure, ion bombardment can also create defects in the Si network, possibly deteriorating the surface passivation.⁵ Although the detrimental role of ion bombardment in surface passivation is still under debate, the investigation of the ion induced defects is typically limited to the transfer of ion kinetic energy to the Si network.^{6,7} Following this approach, energetic ions can induce Si atoms displacement, through ion-Si atoms collisions, which accounts for the defects generation along the ion penetration path in the film.⁸ Based on this mechanism, the level of surface passivation can degrade due to the presence of energetic ions already during the deposition of a-Si:H or postdeposition processing of c-Si wafers, when passivated by very thin $(\sim 5 \text{ nm})$ a-Si:H films as in heterojunction solar cells. In this letter we show that Ar ion bombardment, with a well defined ion energy, enhances the degradation of a-Si:H surface passivation, irrespective of the value of ion kinetic energy (7–70 eV). Moreover, we observed that the degradation scales linearly with the ion flux in the range 6×10^{14} -6 $\times 10^{15}$ ions cm⁻² s⁻¹.

Thin a-Si:H films have been deposited by the remote expanding thermal plasma technique on both sides of low resistivity (1–3 Ω cm) p-type FZ *c*-Si (100) wafers.⁹ We have chosen a film thickness (~50 nm), thicker than the ions penetration depth in a-Si:H films, so that a direct damage of the a-Si:H/*c*-Si interface by ions can be excluded.⁵

Before a-Si:H deposition, the wafers were cleaned with standard RCA1 and RCA2 procedure and subsequently immersed in a 2% HF solution for 1 min. Due to the use of a remote plasma, only low energy (< 2 eV) ions impinge on the substrate during film deposition.¹⁰ After a-Si:H deposition, the front side of c-Si wafers has been exposed to a remote pulsed biased Ar plasma.¹¹ An external pulsed bias scheme has been applied which delivers a narrow, almost monoenergetic ion energy distribution (width of $\sim 2 \text{ eV}$) and a separate control of the ion flux onto the substrate. Minority charge carrier lifetime has been measured for as deposited a-Si:H films and after different exposure times of the same passivated wafer to Ar plasma, by using a Sinton Consulting WCT-100 tester in both quasisteady-state and transient mode. The value of lifetime and surface recombination velocity at the front side of the wafers has been extracted from the measured lifetime, as reported in Ref. 12 by assuming an infinite bulk c-Si lifetime. The defects in the a-Si:H bulk does not affect the lifetime measurements, since the transport of excess carriers from the c-Si wafer to the a-Si:H film is blocked by the large band edge offsets from c-Si to a-Si:H.⁴ In this letter we report the values of lifetime, surface recombination velocity after exposure to Ar plasma [S(t)] and for as deposited a-Si:H (S_0), at an injection level of 10^{15} cm⁻³. Typically for the experiments presented here a lifetime value of 2 ms has been measured for as deposited a-Si:H films, similar to the results reported before.^{13,14}

Light-induced degradation of surface passivation has been measured by covering the front side of passivated *c*-Si with a glass plate and exposing it to the described biased remote Ar plasma. Glass prevents the ion bombardment of the a-Si:H film and absorbs photons emitted by the remote Ar plasma for energies larger than 7 eV. As reported in Fig. 1, the surface recombination velocity increases already after a short exposure of 10 s, due to light-induced creation of fast metastable defects at the a-Si:H/*c*-Si interface, according to Ref. 3. With increasing exposure time, the surface recombination velocity reaches a saturation value, which still corresponds to an excellent level of surface passivation, as also reported in Ref. 3 and 4. This result seems to indicate that a lower density of light induced defects can be created at the

0003-6951/2011/98(24)/242115/3/\$30.00

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FIG. 1. (Color online) Variation in the value of surface recombination velocity for a-Si:H passivated *c*-Si wafers covered by glass while exposed to Ar plasma, without any external biasing, and biased with a voltage of -50 V without glass. An ion flux of 6×10^{14} ions/s cm² is set.

a-Si:H/c-Si interface, as compared to the a-Si:H bulk, possibly justifying the lower degradation of microcrystalline Si materials under light exposure.¹⁵ When the glass plate is removed and an external bias potential of 50 V is applied to the substrate at constant ion flux, the level of surface passivation sharply deteriorates as a function of the exposure time.

The effect of ion kinetic energy on the surface passivation has been investigated by applying different bias potentials for a constant ion flux. With increasing ion kinetic energies (E_{ion}) , ions can penetrate as interstitial in the Si network ($E_{ion} \sim 7 \text{ eV}$), displace surface ($E_{ion} > 18 \text{ eV}$) or bulk Si atoms ($E_{ion} > 40$ eV) or sputter them (E_{ion} >50 eV).⁸ As shown in Fig. 2, the increase in surface recombination velocity does not depend on the ion kinetic energy. Moreover, the variation in surface recombination velocity $[\Delta S = S(t)/S(0) - 1]$ increases with exposure time (t) following a trend: $\Delta S \sim Gt^{1/2}$, with G a constant (possibly depending on ion flux), for all the applied bias potentials. A $t^{1/2}$ time dependence has been found typically for the rise of metastable defects density in a-Si:H bulk under pulsed light exposure and recently also for continuous light source, if the total defect density is corrected for the intrinsic defects.^{16,17} As shown in Fig. 3, the decrease in the level of surface passivation is fully reversible by annealing at 300 °C for 10 min. This result indicates that the deterioration of surface



FIG. 3. (Color online) Lifetime value for as deposited a-Si:H film on *c*-Si wafers, after ion bombardment and thermal annealing. Similar results are obtained for wafers biased with different potentials (-15, -50, and -70 V) and fluxes (6×10^{14} , 3×10^{15} , 6×10^{15} ions/s cm²).

passivation is due to the creation of metastable defects at the a-Si:H/c-Si interface.

The effect of ion flux on the creation of metastable defects on the *c*-Si surface has been investigated by exposing passivated *c*-Si wafers to different ion fluxes while being biased with an ion energy of 7 eV. As shown in Fig. 4, the value of the surface recombination velocity increases with ion flux, until a saturation level is reached. For a high ion flux, the increase in the surface recombination velocity reaches a saturation value already at a relatively short exposure time (~100 s). In the inset of Fig. 4, we plot the ratio between the variation in surface recombination velocity and the square root of the exposure time, i.e., $G = \Delta S/t^{1/2}$, as a function of the ion flux.

Since we use relatively thick a-Si:H films, the increase in surface recombination velocity with the ion flux, and not as a function of the ion kinetic energy, indicates that an alternative mechanism occurs at the a-Si:H/c-Si interface. Besides the transfer of kinetic energy by direct impact, ions can create an excess of charge carriers in the a-Si:H film by second-ary electron emission or exciting electron–hole pairs through the ionization energy released in the ion neutralization process (about 15.8 eV in the case of Argon). The latter occurs a few Angstroms from the a-Si:H films surface.^{18,19} Iongenerated charge carriers can enhance the light induced degradation of a-Si:H based surface passivation when nonradia-





FIG. 2. (Color online) Variation in the surface recombination velocity for different values of external bias potential (-7, -15, -50, and -70 V) and same ion flux of 6×10^{14} ions/s cm².

FIG. 4. (Color online) Variation in the surface recombination velocity for different values of Ar ion fluxes and a bias potential of -15 V. In the inset, plot of $G=[S(t)/S_0-1]/t^{0.5}$ vs the ion flux.

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tive recombination processes occur at the a-Si:H/c-Si interface, resulting in emission of mobile H through Si-H bonds breaking on c-Si surface and creation of metastable defects. Following this possible mechanism, the ion flux determines the generation rate of electron-hole pairs, i.e., proportional to G, and therefore the number of metastable defects on the c-Si surface. For the values of ion flux used in our experiments, i.e., $6 \times 10^{14} - 6 \times 10^{15}$ ions cm⁻² s⁻¹, considering that the expected energy per electron-hole pair generation is from 4.3 to 5 eV (Ref. 20) and that about half of the ionizing radiation irradiates toward the film, we can estimate a generation rate of electron-hole pairs of about $10^{15}-10^{16}$ e-h cm⁻² s⁻¹. According to this estimate, the ioninduced creation of metastable defects is found to saturate in a time scale (~ 100 s) longer than the reported light-induced creation of defects (~1 s) at the a-Si:H/c-Si interface,³ for which G is typically in the range from 10^{16} to 10^{21} e-h cm⁻³ s⁻¹.^{21,22}

We have shown that a sharp deterioration of the surface passivation level occurs when a-Si:H passivated *c*-Si wafers are exposed to Ar ion bombardment. The increase in surface recombination velocity is found to vary linearly with the ion flux for short exposure time (<100 s) and being independent on ion kinetic energy. A possible mechanism is proposed, based on ion-induced creation of excess charge carriers in the a-Si:H film.

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