Accelerated deactivation of the boron–oxygen-related recombination centre in crystalline silicon

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Abstract

A significant acceleration of the permanent deactivation of the boron–oxygen-related recombination centre in crystalline silicon is observed if the samples are exposed to the plasma during plasma-enhanced chemical vapour deposition (PECVD) of a hydrogen-rich silicon nitride (SiN_x) layer. Similar deactivation rate constants are measured in samples passivated with hydrogen-rich SiN_x deposited without plasma exposure and hydrogen-lean aluminium oxide (Al_2O_3) deposited with plasma-assisted atomic layer deposition, suggesting that the critical parameter responsible for the acceleration is not the hydrogen content in the dielectric layer. Instead, we propose increased in-diffusion of hydrogen during or after the deposition of the PECVD SiN_x layer, for example due to surface damage caused by plasma exposure, as the cause for the acceleration.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The permanent deactivation of the boron–oxygen-related recombination centre in B-doped p-type Czochralski-grown silicon (Cz-Si) by illumination at elevated temperatures was first reported by Herguth *et al* [1, 2]. The deactivation process was already found to be influenced by a phosphorus diffusion step [3], the doping concentration p_0 [4], as well as the interstitial oxygen concentration $[O_i]$ [5]. In addition, it was recently reported that the permanent deactivation of the defect could only be observed on solar cells which were coated with hydrogen-rich silicon nitride (SiN_x) films [6]. Silicon nitride is commonly used in crystalline silicon solar cell production as an anti-reflective coating on the front side of the cell. The standard deposition technique is plasma-enhanced chemical vapour deposition (PECVD) at temperatures between 400 and 500 °C. Apart from its optical properties, the SiN_x coating is also known to have beneficial effects on the bulk lifetime of multicrystalline silicon due to the so-called hydrogen passivation: PECVD SiN_x contains large amounts of hydrogen (∼16–18 at.% H [7–9]). During firing of the screen-printed metal contacts at around 850 °C, the hydrogen in the SiN_x becomes mobile and partly diffuses into the

bulk, passivating defects and grain boundaries. In this work, the impact of deposition conditions during the deposition of a dielectric passivation layer on the permanent deactivation process is investigated via lifetime measurements on 0.9 Ω cm B-doped Cz-Si surface passivated with either PECVD SiN_x or plasma-assisted atomic layer deposited (PA-ALD) aluminium oxide (Al_2O_3). PA-ALD Al_2O_3 contains very little hydrogen (∼3 at.% H [10]) and has recently been found to be extremely effective in passivating p-type silicon surfaces [11–13]. By comparing two different PECVD systems, it is found that exposure to the plasma during PECVD increases the deactivation rate constant by one order of magnitude.

2. Experimental details

Sample preparation included acidic damage etching, RCA cleaning and phosphorus diffusion in a quartz tube furnace using $POCl_3$. The resulting sheet resistance was 90 Ω sq^{-1}. The n$^+$-layers on both sides of the wafer were removed by a second acidic etching step before the samples were RCA cleaned again. Subsequently, the samples were split into three groups: (1) surface passivation with PECVD SiN_x using an
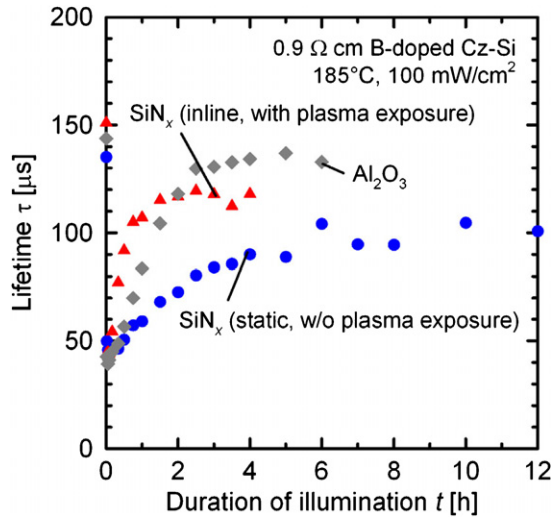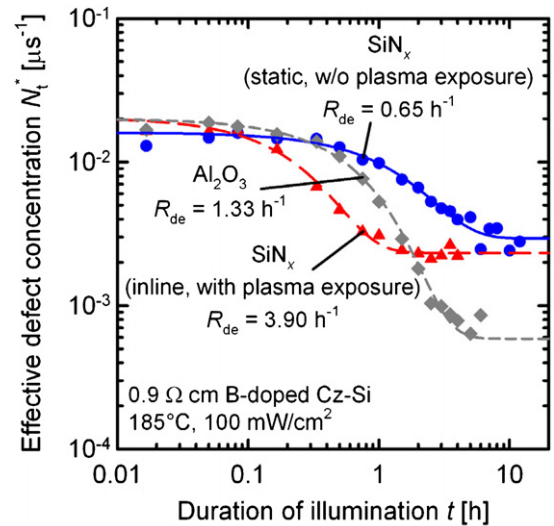
Figure 1. Lifetime τ as a function of the duration of illumination t at 185 °C and 100 mW cm^{-2} light intensity (halogen lamp) of three 0.9 Ω cm B-doped Cz-Si samples. Two of the samples are passivated with PECVD SiN$_x$ deposited in two different types of reactors, while the third sample is passivated with ALD Al$_2$O$_3$.

**Figure 2.** Effective defect concentration $N_t^*= \tau^{-1}(t) - \tau_0^{-1}$, derived from the lifetime data in figure 1, as a function of duration of illumination t. The data can be fitted by an exponential function (indicated by the lines), which yields the deactivation rate constant R_{de}.

Oxford Instruments Plasmalab 80 Plus reactor. This static setup uses a remote plasma excited in a microwave cavity outside the deposition chamber. The used process gases are silane (SiH$_4$), ammonia (NH$_3$) and nitrogen (N$_2$). (2) Surface passivation with PECVD SiN$_x$ using a Roth & Rau SiNA system. The SiNA is an inline deposition system which works with a remote plasma that is excited by a linear microwave antenna which is located directly above the silicon wafers. In contrast to the static reactor, the wafers are thus exposed to the plasma during deposition in the SiNA system. This may cause some plasma damage at the surface of the samples. The process gases are SiH$_4$, NH$_3$, N$_2$ and hydrogen (H$_2$). (3) Surface passivation with PA-ALD Al$_2$O$_3$ using an Oxford Instruments FlexAL^{TM} reactor. Atomic layer deposition is done with a remote plasma excited by inductive coupling in a cavity and trimethylaluminium (Al$_2$(CH$_3$)$_6$) and oxygen (O$_2$) as process gases. The sample temperature during SiN$_x$ deposition was 400 °C. The thickness of the SiN$_x$ layer was 70 nm with a refractive index of 2.4. During atomic layer deposition, the substrate temperature was set at 200 °C. The Al$_2$O$_3$ layer had a thickness of 30 nm and subsequent to the deposition the samples were annealed at 425 °C for 15 min to activate the surface passivation [13].

3. Results

Figure 1 depicts the typical deactivation behaviour of the boron–oxygen-related recombination centre in three 0.9 Ω cm B-doped Cz-Si samples, one from each group. The lifetime τ, measured at a fixed injection density of $\Delta n = 1.8 \times 10^{15}$ cm^{-3} at room temperature using the quasi-steady-state photoconductance decay technique [14], is shown as a function of time t under illumination at 185 °C and a light intensity of 100 mW cm^{-2} (halogen lamp). Before $t = 0$, the boron–oxygen-related recombination centre had

been fully annihilated by a 10 min anneal at 200 °C in darkness, resulting in comparable lifetimes of 130–150 μs for all three samples. Subsequently, the lifetime drastically decreases due to the accelerated activation of the BO recombination centre at higher temperature. After 5 min, however, the lifetime starts to increase again until it saturates after a few hours. In figure 1, the difference between the three passivation techniques is clearly discernible: the lifetime of the sample that was passivated with SiN$_x$ using the SiNA inline system with plasma exposure (triangles) saturates after 2 h, whereas the lifetime of the sample that was passivated with SiN$_x$ using the static Plasmalab 80 reactor without plasma exposure (circles) saturates after 10 h.

This difference becomes even more obvious in the deactivation rate constants R_{de}, which are extracted in figure 2 by fitting the time dependence of the effective defect concentration N_t^* by an exponential function of the form $y = y_0 + a \exp(-R_{de}t)$. Here, the effective defect concentration N_t^* is defined as the difference between the inverse lifetime at time t and the inverse lifetime after complete annihilation of the boron–oxygen-related defect, i.e. $N_t^* = \tau^{-1}(t) - \tau_0^{-1}$. Through this, $R_{de} = 0.65$ h^{-1} is obtained for the sample that was not exposed to the plasma during PECVD SiN$_x$ deposition (circles), while $R_{de} = 3.90$ h^{-1} is obtained for the sample that was exposed to the plasma during PECVD SiN$_x$ deposition (triangles).

Exposure to the plasma during deposition thus increases the deactivation rate constant by almost one order of magnitude. Interestingly, the deactivation rate constant R_{de} of the PA-ALD Al$_2$O$_3$-passivated sample is 1.33 h^{-1} (diamonds), which is slightly higher than that of the PECVD SiN$_x$-coated sample not exposed to the plasma. Given that the hydrogen content in PA-ALD Al$_2$O$_3$ is significantly lower than in PECVD SiN$_x$ ($\sim$3 at.% H in Al$_2$O$_3$ compared to $\sim$16–18 at.% H in SiN$_x$), this finding suggests that the hydrogen content
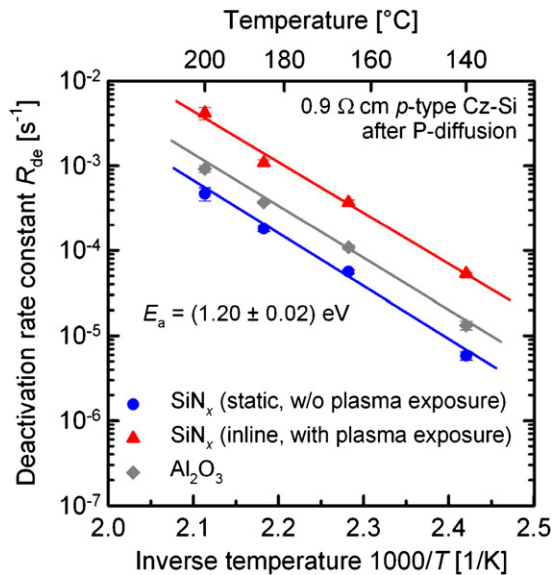
Figure 3. Arrhenius plot of the deactivation rate constants R_{de} determined in the three groups of samples. The activation energy $E_a = (1.20 \pm 0.02)$ eV is the same for all samples. The deactivation rate constants measured in the SiN$_x$-coated samples with plasma exposure (triangles), however, are one order of magnitude greater than those measured in the samples without plasma exposure (circles).

in the dielectric layer does not play a crucial role in the deactivation process by itself. In addition to the experiments shown in figures 1 and 2, the deactivation rate constants R_{de} were also determined at 140, 165 and 200 °C. In figure 3, these deactivation rate constants are plotted versus the inverse temperature $1000/T$ in an Arrhenius plot. For all investigated temperatures, the deactivation rate constant of samples that were exposed to the plasma during SiN$_x$ deposition (triangles) is one order of magnitude higher than that of the samples not exposed to the plasma (circles), confirming the result presented in figure 2. The activation energy $E_a = (1.20 \pm 0.02)$ eV is the same for all samples.

4. Conclusion

In this work, we have investigated how the deposition of a passivating dielectric layer affects the permanent deactivation of the boron–oxygen defect in boron-doped silicon. By comparing samples which were passivated with hydrogen-lean aluminium oxide (Al$_2$O$_3$) deposited via plasma-assisted atomic layer deposition (PA-ALD) with hydrogen-rich silicon nitride (SiN$_x$), which was deposited using plasma-enhanced chemical vapour deposition (PECVD), no significant difference was observed as long as the samples were not exposed to the plasma during deposition. This suggests that the hydrogen content in the dielectric layer does not play a crucial role in the deactivation process by itself. On the other hand, exposure to the plasma during deposition

was found to increase the deactivation rate constant by one order of magnitude. The results presented in this work can also consistently explain the results presented in [6], where solar cells coated with hydrogen-free silicon nitride deposited via low-pressure chemical vapour deposition (LPCVD) were compared to solar cells coated with hydrogen-rich silicon nitride deposited via PECVD. Since deactivation could only be observed in the solar cells that were coated with hydrogen-rich PECVD SiN$_x$, it was concluded that hydrogen was vital for the deactivation process. However, in light of the findings presented in this work, it seems more likely that the different deposition techniques are the reason for the different deactivation behaviour since LPCVD, in contrast to the deposition techniques used in this work (i.e. PECVD and PA-ALD), is not a plasma process. This conclusion in turn suggests that a precursor for the deactivation process is created in the presence of a plasma. Exposure to the plasma during deposition could then either increase the amount of this precursor or facilitate the in-diffusion of the precursor into the silicon bulk. A possible candidate for this precursor is some form of hydrogen. Hydrogen is present both during PA-ALD of Al$_2$O$_3$ and PECVD of SiN$_x$ and it is known that surface damage caused by a PECVD passivation process can increase in-diffusion of hydrogen into silicon [15]. In addition, it was recently reported that the amount of hydrogen that diffuses from a SiN$_x$:H layer into the silicon bulk is sensitive to the deposition conditions [16].

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