Analysis of the Surface Passivation Mechanisms of p-Doped Crystalline Silicon by Two Different Al₂O₃ Coatings via Transient Photo-Conductance Measurements

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Received 14 September 2015; accepted 1 February 2016; published 6 February 2016

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Abstract

In this paper, contactless transient photo-conductance measurements are applied to p-doped mono-crystalline Silicon (p-Si) coated by two different kinds of aluminum oxide (Al₂O₃) layers in order to study alternative routes to the standard atomic layer deposition (ALD). The aluminum oxides layers were deposited by either spin coating or ion layer gas reaction (ILGAR®). For both coatings an increase of the charge carrier life time is observed indicating a passivation of the p-Si surface. This study shows alternative deposition methods and the potential of transient photoconductance measurements for the elucidation of the origin of the passivation. We show that the passivation induced by coating deposited via ILGAR is at least partially due to charge carrier trapping and storage at the interface. It was also surprisingly found that for those coatings, annealing at 425°C leads to a decrease of the life time. This points to temperature instability for both coatings.

Keywords

Photo-Conductance, Passivation, Aluminum Oxide, Silicon

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1. Introduction

For the study of the electrical passivation of semiconductor surfaces, a reliable analysis of these surfaces is required. In this work we present an analysis of charge carrier dynamics at the interface between p-doped monocrystalline silicon (p-Si) and two different kinds of aluminum oxide (Al₂O₃) layers, measured by contactless transient photo-conductance measurements. Aluminum oxide is an interesting alternative to silicon nitride (Si₃N₄) and silicon oxide (SiO₂) for electrical passivation of the silicon surface for photovoltaic cells [1]. The drawback of silicon nitride on p-type silicon is the parasitic shunting induced by the positive fixed charge [2]. Unlike Si₃N₄, a fixed negative charge in Al₂O₃ coatings on silicon is reported [3]-[5]. Consequently in the Al₂O₃/p-Si interface an accumulation region is formed and a very good passivation is reported comparable to the Si₃N₄/n-Si interface [6] [7]. The best results were obtained with Al₂O₃ layers deposited by atomic layer deposition. However, ALD suffers from its low deposition rate and alternative deposition methods can be of great interest. In the present work the electrical passivation process induced by two different Al₂O₃ coatings will be studied. One produced by spin coating (SC-Al₂O₃) and the other one deposited by ion layer gas reaction (ILGAR-Al₂O₃). Also the influence of annealing at 425°C on the charge carrier decay behavior as monitored by TRMC measurements is investigated. For ALD layers an improvement of the passivation was reported after annealing at 425°C [8] [9].

2. Experimental Details

2.1. Preparation

Aluminum oxide (Al₂O₃) layers were deposited on p-type mono-crystalline silicon (CZ, 130 Ohm.cm; 350 μm thick, 25 × 15 mm in size). The substrates were first cleaned in acetone then ethanol in an ultra-sonic bath, then oxidized in a solution of H₂O₂ (30%)/H₂SO₄ (97%), ratio 1:1 and prior to the deposition, the oxide surface layer was etched in 1% HF. Two kinds of coatings were deposited: Al₂O₃ nanoparticles deposited by spin coating (SC-Al₂O₃) and Al₂O₃ deposited by ion layer gas reaction (ILGAR-Al₂O₃). The spin coating process used an Al₂O₃ nanoparticles (<50 nm) solution diluted 5 times in Isopropyl alcohol. 200 μl were deposited on the substrate and the process was performed at 5000 rpm during 30 seconds. Information about the ILGAR process can be found in ref. [10]. During the process, the substrate was heated up until 500°C, a 20 mM Aluminum acetylacetonate Al(acac)₃ in Ethanol with 5% milli-Q water solution was used as a precursor solution. Time of deposition was 15 minutes. For practical and technical reasons, the depositions were performed on one side. The rear sides were scratched with sandpaper in order to have a recombination sink for excess charge carriers. Back illumination of the substrate shows a very fast decay of the TRMC signal identifying the rear sides as infinite sinks for electron-hole pairs [11] (cf 2.2 Method).

2.2. Method

The kinetics of excess charge carriers was measured by the Time Resolved Microwave Conductivity (TRMC) method. TRMC is a non-destructive, contact-less photo-conductance measurement method. The sample is continuously irradiated by a 10 GHz microwave and the photo-conductance is induced by a 10 ns (FWHM) pulse of a Nd:YAG laser at 532 nm. The repetition rate of the laser pulse is 10 Hz. The intensity of the laser light can be modified by filters with different optical densities (OD). During the illumination the conductance increases due to the generation of excess charge carriers and will modify the microwave power absorbed by the sample. This (transient) change is then measured by a point contact diode connected to a transient recorder. The normalized modification of the reflected power (the TRMC signal) is given by [12]:

\[
\frac{\Delta P}{P} = B \times \Delta S = B \times e \times (\Delta n \times \mu_n + \Delta p \times \mu_p) \tag{1}
\]

where \(B\) is a proportionality constant, \(e\) the elementary charge, \(\Delta S\) the photo-conductance, \(\Delta n\) (\(\Delta p\)) the excess electron (hole) carrier concentration per unit surface integrated over the whole thickness of the sample (cm\(^{-2}\)) and \(\mu_n\) (\(\mu_p\)) the mobility of electrons (holes).

The absorption coefficient of silicon for the wavelength used (532 nm) is \(11.2 \times 10^3\) cm\(^{-1}\) [13]. So according to Beers law, the major part of the incoming light is absorbed within the first μm and the excitation by 532 nm light can be considered as surface excitation. Charge carrier decay is determined by volume decay characterized by the decay time \(\tau_v\), and surface decay at both surfaces characterized by the decay time \(\tau_s(t)\) in general depend-
ing on time. Volume decay in state of the art crystalline silicon wafers occurs in the 100 \(\mu s\) up to ms time range and is in general much slower than surface decay processes except for very well passivated surfaces.

Excess charge carrier kinetics in silicon is described by ambipolar diffusion as long as other processes than diffusion and recombination can be neglected. Ambipolar diffusion indicates the combined diffusion of electron-hole pairs with the ambipolar diffusion constant \[14\]. Consequently under these conditions \(\Delta n(t) = \Delta p(t)\)

This leads to a simplification of Equation (1):

\[
\frac{\Delta P(t)}{P} = B \cdot e \cdot \Delta n(t) \cdot \left(\mu_n + \mu_p\right) = B \cdot e \cdot \Delta p(t) \cdot \left(\mu_n + \mu_p\right)
\]

(2)

This implies that the decay of the TRMC signal reflects the decay of the excess charge carriers and excess carrier life times can be determined from its decay. Because low injection is warranted for the present measurements, this reduces ambipolar to minority carrier (here electron) diffusion \[14\]. For the present work some useful conclusions from the solution of the minority carrier diffusion equation will be summarized. A more elaborate discussion can be found in the literature \[15\].

The decay of the excess charge carrier population before a considerable number of excess charge carriers attains the non-illuminated surface is extended, \(i.e.\) the decay rate decreases with time. In the extreme case that the illuminated surface can be considered as an infinite sink for excess charge carrier pairs the decay due to surface recombination before a considerable number of excess charge carriers arrives at the non-illuminated surface is characterized by \(t^0.5\) as it has been observed for the uncovered (rear) faces of the present samples \[11\]. Finally a stationary (the so called principal mode) distribution is obtained characterized by an exponential decay \[16\] and \(\tau_s\) will be independent of time. The onset of the principal mode is characterized by a transition to a decay characterized by a constant decay time: \(i.e.\) a much faster decrease of the signal in a double logarithmic representation and an exponential decrease (a straight line) in a semi-logarithmic representation.

Two limiting cases for the decay time of the principal mode by surface recombination, \(\tau_s\), can be calculated \[15\]:

-Both surfaces can be considered as infinite sinks for electron-hole pairs. Then:

\[
\tau_s = \left(\frac{L^2}{D\pi^2}\right)
\]

(3)

where \(L\) is the thickness of the wafer and \(D\) the electron diffusion constant. This corresponds to \(\tau_s = 3.4\ \mu s\) for the wafer used here.

-For one surface an infinite sink and the other one ideally passivated \(i.e.\) no recombination at this surface. Then:

\[
\tau_s = \left(\frac{4L^2}{D\pi^2}\right)
\]

(4)

This corresponds to \(\tau_s = 13.6\ \mu s\) for the wafer used here.

Consequently for the samples studied here, \(i.e.\) one surface is an infinite sink for excess charge carriers, the surface decay time of the principal mode lies between 3.4 \(\mu s\) and 13.6 \(\mu s\).

This reflects only the excess charge carrier decay due to surface recombination. The effect of volume recombination has to be added to account for the total decay. For c-Si this corresponds to the convolution of the decay to surface recombination with an exponential decay due to volume recombination. For state of the art c-Si wafers volume recombination does not have an appreciable influence on the decay in the time range covered in the present work (0 - 100 \(\mu s\)).

The foregoing is valid under the condition that ambipolar diffusion can be assumed. This is not the case if one kind of excess charge carriers (in this case the minority carriers, \(i.e.\) electrons) is trapped or stored in a space charge region \[15\]. So if the decay time of the principal mode exceeds 13.6 \(\mu s\) trapping or storage of excess charge carriers occurs. On the contrary if this decay time is smaller than 3.4 \(\mu s\) volume decay must be taken into account. It must be stressed that these limits concern the principal mode. Before establishment of the principal mode, \(i.e.\) after surface excitation \[11\], the decay can be much faster (see above). So identification of the onset of the principal mode is very important.

3. Results and Discussion

3.1. p-Si/ILGAR-Al2O3 and p-Si/SC-Al2O3 as Deposited

Figure 1 shows the TRMC signal for front illumination of the sample (\(e.g.\) the side covered by the coating) for both samples at different excitation densities in a double logarithmic representation. No decay of the signal is
observed for front illumination during the first few microseconds, indicating an electrical passivation of the covered side. The subsequent decay is faster for the SC-Al$_2$O$_3$ sample. The decay of the signal is due to as well recombination at the p-Si/Al$_2$O$_3$ interface as the recombination of excess charge carriers at the non-covered side of the sample (recombination sink) after arrival of an appreciable number of excess charge carriers at this side.

The onset of the decay is clearly observed for the SC-Al$_2$O$_3$ samples at about 4 $\mu$s. This corresponds approximately to the arrival of excess charge carriers at the uncovered face but this does not unambiguously imply that the subsequent decay is due to recombination at the non-illuminated face. The initial decay times (from 0 to 10 $\mu$s) are given in Table 1.

For the ILGAR-Al$_2$O$_3$ sample the onset is not very clear but tends to be at about the same time as for the other sample. However, the subsequent decay is much slower and involves a much larger part of the signal.

Another representation of the same data is given in Figure 2 in a semi-logarithmic plot. For the SC-Al$_2$O$_3$ sample an approximately exponential decay for more than one decade in signal height is observed giving way to

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**Figure 1.** TRMC signals induced by 532 nm laser pulses (10 ns FWHM) in pieces of a p-Si wafer covered at one side with Al$_2$O$_3$ deposited by spin coating (diamonds) and by spray pyrolysis (line) in a double logarithmic representation. The samples are illuminated at the Al$_2$O$_3$ covered side with laser intensities as indicated in the figure. The onsets are indicated: Black bold line at 4 $\mu$s for the SC coating and black arrows for the ILGAR coating.

**Table 1.** Decay times determined for the initial decay of the TRMC signal for ILGAR-Al$_2$O$_3$ and SC-Al$_2$O$_3$ samples before and after annealing at 425°C at different laser intensities.

<table>
<thead>
<tr>
<th>Laser intensity (μJ)</th>
<th>ILGAR As deposited</th>
<th>ILGAR Annealed</th>
<th>Spin coating As deposited</th>
<th>Spin coating Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>2.85 x 10^{-5}</td>
<td>3.18 x 10^{-5}</td>
<td>1.36 x 10^{-5}</td>
<td>0.78 x 10^{-5}</td>
</tr>
<tr>
<td>14</td>
<td>2.22 x 10^{-5}</td>
<td>2.26 x 10^{-5}</td>
<td>1.36 x 10^{-5}</td>
<td>0.75 x 10^{-5}</td>
</tr>
<tr>
<td>7</td>
<td>1.51 x 10^{-5}</td>
<td>1.36 x 10^{-5}</td>
<td>1.36 x 10^{-5}</td>
<td>0.7 x 10^{-5}</td>
</tr>
<tr>
<td>3.5</td>
<td>1.56 x 10^{-5}</td>
<td>1.45 x 10^{-5}</td>
<td>1.36 x 10^{-5}</td>
<td>0.7 x 10^{-5}</td>
</tr>
<tr>
<td>1.4</td>
<td>1.3 x 10^{-5}</td>
<td>1.34 x 10^{-5}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2. TRMC signals induced by 532 nm laser pulses (10 ns FWHM) in pieces of a p-Si wafer covered at one side with Al₂O₃ deposited by spin coating (diamonds) and by spray pyrolysis (line) in a semi logarithmic representation. The samples are illuminated at the Al₂O₃ covered side with laser intensities as indicated in the figure.

a slower decay. The initial decay times are given in Table 1. For the SC-Al₂O₃ sample these times are independent of the excitation density and reflect the major part of the decay corresponding to the decay of the principal mode. The decay times determined (Table 1), agree with Equation (3) for the present systems. This implies that SC-Al₂O₃ offers a very good passivation of the Si surface and the decay can be attributed to diffusion controlled recombination at the uncovered surface. These experiments indicate that this passivation is satisfactory for high quality pSi-devices, e.g. solar cells, as no appreciable recombination occurs during the transit of electron-hole pairs from one face to the other. On a more quantitative level the experiments show that the interface is characterized by a surface recombination velocity smaller than 50 cm/s.

The small part of the signal (<10%) decaying slower is probably due to charge carrier trapping and/or storage at the SC-Al₂O₃/Si interface and involves only a very small part of the excess charge carriers. The electrical passivation of the p-Si surface by the SC-Al₂O₃ coating is probably due to the negative, fixed charge in the coating as proposed for the effect of an Al₂O₃ layer deposited by Atomic Layer Deposition (ALD) [3] [8]. The accumulation layer so induced in p-Si leads to electrical passivation of p-Si by a field effect [17]. The present measurements show that during the diffusion process to the free surface, charge carrier decay at the passivated surface can be neglected.

For the ILGAR-Al₂O₃ sample the decay is strongly non-exponential: the decay rate becomes slower with time. The initial decay times (Table 1) have only a relative meaning as initially only a small part of the signal decays exponentially (Figure 2): the initial decay time increases with the excitation density. Identification of the principal mode is difficult for this sample because no clear transition is observed. At low excitation densities the initial decay times tend to the value observed for the SC-Al₂O₃/Si (Table 1) and are tentatively attributed to diffusion limited recombination at the uncoated surface (Equation (3)). The subsequent decay in the ILGAR-Al₂O₃ coated sample is much slower than that given by Equation (3). This implies that at least the excess charge carriers involved in this part of the signal do not participate in the diffusion to the uncoated surface and in the recombination there (cf. Section 2.2). It is attributed to trapping and storage of charge carriers at the interface. The increase of the initial decay time with the excitation density (Figure 2) indicates an increase of the relative number of excess charge carriers involved in these trapping and storage processes with the excitation density.
The observation of this storage and trapping processes at the p-Si/ILGAR-Al2O3 does not necessarily imply that the p-Si passivation by this interface is bad and is not convenient for Si-devices. However, this depends on the evolution of these processes under stationary illumination. Preliminary results suggest a stationary state which is characterized by a relatively low surface recombination rate [18] and so this interface offers a useful passivation of the p-Si surface.

### 3.2. Annealed p-Si/ILGAR-Al2O3 and p-Si/SC-Al2O3

J. Schmidt et al. [8] reported that 425°C annealing of an Al2O3 layer deposited by Atomic layer deposition (ALD) during 10 minutes increased the lifetime of excess charge carrier within the silicon substrate. The same treatment was performed with our samples in order to check the influence of annealing on both kinds of coatings. Both samples were annealed at 425°C during 10 minutes under Argon atmosphere. Comparison with the measurements performed on the samples before annealing is shown in **Figure 3**.

It is clear that for both samples, annealing leads to an acceleration of the decay in contrast to the data from the literature for ALD samples [8] [9]. For the SC-Al2O3 sample mainly the initial decay is accelerated, whereas for the ILGAR-Al2O3 sample mainly the final decay is accelerated.

For the SC-Al2O3 sample the initial decay times (Table 1) are smaller than corresponding to diffusion limited recombination at the uncoated surface (Equation (3)). This indicates that surface recombination at the illuminated SC-Al2O3 coated surface must be taken into account. So annealing deteriorates the passivation of p-Si by a SC-Al2O3 coating. This is explained by a decrease of the fixed, negative charge in this coating, if the initial passivation is due to the interface accumulation field. The effect of annealing on the final decay in this sample is not clear (Figure 3) but in any case not very important.

The influence of annealing on the final decay in the ILGAR-Al2O3 sample indicates a change in the nature and/or the density of the interface traps responsible for the slow decay observed. As the initial decay has not changed, this suggests that the initial decay in this sample is due to recombination at the untreated surface.

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**Figure 3.** TRMC signals induced by 532 nm laser pulses (10 ns FWHM) in pieces of a p-Si wafer covered at one side with Al2O3 deposited by spin coating (hollow circles before annealing—filled circles after annealing) and by ILGAR (dashed lines before annealing—line after annealing) in a double logarithmic representation. Annealing was performed 10 minutes at 425°C. The samples are illuminated at the Al2O3 covered side with laser intensities as indicated in the figure.
D. Klein et al.

4. Conclusions

In this article, we have shown that contactless transient photo-conductance measurements allow a detailed analysis of the p-Si surface. Furthermore, this work indicates that for the characterization of the passivation merits of coatings, there is an advantage to use samples with only one face coated: this enables to distinguish between real passivation, i.e. suppression of charge carrier recombination, and storage at the Si/coating interface (charge carrier storage by trapping and/or field induced storage).

- The present investigations of Al₂O₃ layers deposited by spin coating on p-Si show a satisfactory electrical passivation of the p-Si surface. The influence of trapping and storage at the passivated surface can be neglected. This suggests a stable passivation under stationary illumination.
- This work points out that the density of states at the ILGAR-Al₂O₃ interface has a strong influence on charge carrier kinetics and may hinder its application. A strong influence of the substrate pretreatment cannot be excluded [18].
- The decrease of the degree of passivation by annealing at 425°C indicates that the temperature stability of the SC-Al₂O₃ is unsatisfactory. Improvement seems necessary for a fruitful use of this coating deposited by spin coating or ILGAR for Si-devices.
- Evidently with the coating at both faces, the interface recombination parameters can be determined much more accurately. However, the possibility to observe the influence of recombination at the Si/coating interface during the diffusion of excess charge carriers offers an excellent measure for the efficiency of the coating in Silicon based photonic semiconductor devices. A complete analysis of the coating can be obtained if the measurements presented here are combined with measurements of a sample coated at both faces with and without bias illumination.

References


