ABSTRACT: For drift field generation IS structures with a fixed positive interface charge in an insulator compound as CsCl-dyed SiO\textsubscript{N}, layer compounds were developed in the 80’s and employed mainly on field effect solar cells. While there has been a large number of publications about the positively biased IS structure there has been very little interest in its antipolar counterpart - the negatively biased IS structure - so far.

We report on a novel insulation layer compound which inhabits a high density of fixed negative charges on crystalline silicon and represent experimental data for the first time. Interpretations of the phenomena encountered are given. Furthermore we briefly consider technological aspects of producing a negatively biased IS structure. The application to silicon solar cells is discussed as well.

Keywords: field effect – 1: thin film - 2: fundamentals - 3: devices - 4

1. INTRODUCTION

Insulator-Semiconductor (IS) structures are widely used in electronic devices. Positively biased IS structures are mainly applied at field effect solar cells [1, 2]. Those positively charged IS structures where investigated thoroughly in the 80s [3] and their positive fixed interface charge density was increased [4].

While this positively charged IS structure is employed on an industrial scale for producing MIS solar cells it seems that hardly any works have been published concerning a negatively charged IS structure [5]. However, employing a negatively charged structure to the rear surface of MIS solar cells could replace the conventional Back Surface Field (BSF) produced by thermal diffusion of Aluminum (Al).

We think that this replacement will improve device efficiency for a number of reasons as briefly outlined in section 2. In section 3 we give a brief description of the possible way how such a negatively charged IS structure - we call it IS structure - could look like and can be prepared. Empirical data are represented in section 4.

2. CONCEPT OF THE ISI-SOLAR CELL

ISI (Insulator-Semiconductor-Insulator) stands for a unipolar field effect solar cell with two antipolar IS structures at respective surfaces.

The preparation of the BSF at silicon (Si) solar cells is done by Rapid Thermal Diffusion (RTD) of Al into the p-Si substrate. Improvement of efficiency thereby is evident, but owing to ultra high doping there are several drawbacks:

1. At high doping levels, bulk and surface defect density rise tremendously due to perturbed Si lattice (thermally inactive dopants at interstitial sites, stretched/tilted/broken bonds), leading to a much increased bulk and surface recombination

2. The field strength from a p\textsuperscript{+} layer at the rear surface is significantly lower compared to a layer system with a high negative charge as an external drift field source [6]; that is especially valid for carrier separation at significant currents. Then the screening of the negative charge is incomplete due to continuous recombination of attracted holes with injected electrons from the rear contact, leading to an increased total drift field within the bulk as both fixed antipolar charges add up their field strength.

3. If a BSF is created by RTD a proper surface passivation (SiO\textsubscript{2}) of Si is difficult due to the high doping density at the rear surface.

4. When insulation layers are used for the IS structure the cell can also be illuminated from the rear surface as it is transparent for sunlight.

All drawbacks mentioned above have an increasing deteriorating effect on device efficiency with decreasing Si substrate/film thickness. So by creating an IS structure at the rear surface device efficiency can be improved significantly which becomes especially useful for thin substrates and films [7]. Another supporting fact is that solar cell manufacturers are striving for thin active layers for obvious reasons not further mentioned here.

3. CONCEPT OF THE IS STRUCTURE

There are two ways of creating an IS structure [8]. One of them is represented herein and its qualitative model is briefly described.

A positively doped (1 Ω\textsubscript{cm}, Boron) c-Si wafer is chosen to be substrate and active layer of the IS structure. In order to avoid a direct contact of the majorities with the localized electrons which represent the negative charge an insulator layer which prevents localized electrons from being emitted into the Si is necessary. By oxidizing the Si wafer a very thin thermal SiO\textsubscript{2} layer separates the negative charge from the active layer and passivates the Si surface.

For localizing electrons at or near the interface (||) material X||SiO\textsubscript{2} the material X has to possess a large band gap, thus has to be a highly insulating solid. Then electrons can be confined in deep local states which lie still above the valence band edge, thereby ionizing them.

The second requirement is that a large number of electrons which can be delocalized easily is at or near the considered interface. That can be realized by employing an atom with a low ionization energy and several valence electrons (a cation like Al).

Finally material X has to possess a large number of deep trap states with a maximum electronegativity which calls for the halogen Fluorine (F).
Hence we used Aluminiumfluoride (AlF₃) as material X. The Fluorine atoms attract valence electrons of the Aluminium in the highly ionic bond that strong that they are practically attached to the Fluorine. The band gap energy of F is $E_{\text{Gap}}(\text{AlF}_3) = 10.7 \text{ eV}$ [9]. Fig. 1 shows the physical shape of an I - Si structure with AlF₃.

![Fig. 1: physical shape of an I - Si structure with AlF₃](image)

The global charge neutrality within the bulk region of the AlF₃ layer is maintained by the F atoms which screen the Al cores. At the interface those conditions do not hold anymore as there will be a large number of dangling bonds due to lattice mismatch to the SiO₂. Those bonds can be occupied by electrons which orbit the F cores and were acquired from Al cores within the bulk region.

Fig. 2 represents the suggested band structure of the I - Si layer arrangement AlF₃||thermal SiO₂||p-Si.

The calculated effective interface charge is the sum of the fixed oxide charge $Q_{\text{SiO}_2}$, the interface charge at SiO₂||Si, and the fixed interface charge at AlF₃||SiO₂ referring to SiO₂||Si:

$$N_{\text{eff}} = Q_{\text{AlF}_3||\text{SiO}_2} + Q_{\text{SiO}_2} + D_{\text{it SiO}_2||\text{Si}}$$

For further explanation see also fig. 2 and table 1.

![Fig. 2: on the charge of the structure AlF₃||SiO₂||Si](image)

In order to preclude that F may falsify the C/V measurements due to diffusion though SiO₂ into Si a secondary ion mass spectroscopy (SIMS) measurement was carried out for examining the F content depending on the position within the layer compound.

![Fig. 3: SIMS profile of the Fluorine content within the layer compound (sample 1): SiO₂ range stretched due to different sputter rates of materials](image)
The SIMS profile of the F content in fig. 4 shows that some F penetrates the oxide whereby there is a strong negative gradient within the oxide layer.

The scattered peaks are due to the fact that during primary ion bombardment with Oxygen (O) of AlF<sub>3</sub> some F is gassing out, being subsequently present in the reactor. There was no F detected within the c-Si.

The negative localized states of AlF<sub>3</sub>||SiO<sub>2</sub> dominate the resulting effective interface charge \( N_{\text{eff}} \). The oxide charge \( Q_{\text{SiO}_2} = 2 \times 10^{10} \text{ cm}^{-2} \) is completely compensated as shown in table 1.

<table>
<thead>
<tr>
<th>Wafer No.</th>
<th>d&lt;sub&gt;SiO&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt; [nm]</th>
<th>d&lt;sub&gt;AlF&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt; [nm]</th>
<th>( V_{\text{fb}} ) [V]</th>
<th>( V_{\text{thr}} ) [V]</th>
<th>( N_{\text{eff}} ) [cm&lt;sup&gt;-2&lt;/sup&gt;] x ( 10^{11} )</th>
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</table>

Table 1: sample parameters and results, extracted by 49 point - wafer maps (average mean values); wafer 6 without AlF<sub>3</sub> was added as a reference.

\( N_{\text{eff}} \) increases clearly with decreasing oxide thickness \( d_{\text{SiO}_2} \), due to the positive bulk charge of SiO<sub>2</sub> in compound with the decreasing distance of AlF<sub>3</sub>||SiO<sub>2</sub> from SiO<sub>2</sub>||Si. The reference wafer does not possess any fixed negative charges, obviously due to absence of AlF<sub>3</sub> on SiO<sub>2</sub>. Both facts indicate that the negative charge lies at AlF<sub>3</sub>||SiO<sub>2</sub>.

The negative charge increased by a factor of 1.5 when samples were stored in air at room temperature within the first four weeks after preparation, leveling off at the values shown in table 1 and fig. 5. At the reference sample a negative charge and hence a positive shift of the Hg-C/V curves did not exist.

The mechanism of massive electron localization at the interface AlF<sub>3</sub>||SiO<sub>2</sub> is not clear yet. It is assumed that electrons from the AlF<sub>3</sub> bulk region are drawn towards the interface for refilling the sites which were created by a lattice mismatch between SiO<sub>2</sub> and AlF<sub>3</sub>. F vacancies within AlF<sub>3</sub> play an important role for electron localization.

When depositing AlF<sub>3</sub> films by evaporation the stoichiometric ratio of Al:F = 1:3 is not reached [9]; such AlF<sub>3</sub>
layers consist actually of AlF$_x$ with $x \approx 2.6$ ... 2.9. An imbalanced ratio Al:F appears to have a very strong influence on the density of localized negative charges at vacancies as well. The excess of Al atoms could provide surplus moveable electrons, provided there are negatively charged particles for resaturring the Al core. With the incorporation of $\text{H}_2\text{O}$ at interstitial sites a possibility exists for screening the loss of valence electrons of the Al cores.

Once valence electrons of the Al cores are captured by the outer shell of the F atoms their excitation energy for hopping to the next F atom is lower as if they would be confined to Al cores and screened by F atoms. In F compounds hopping conduction of electrons can occur [13]. So if there are unoccupied states at AlF$_3$||SiO$_2$, electrons trapped by F cores could move towards the interface. Therefore a strongly localized negative interface charge probably consists of a surplus of negatively charged F vacancies at AlF$_3$||SiO$_2$.

Another possibility for occupying one of the six 2p electron states of the F core could be provided by electrons from Si tunnelling through SiO$_2$ to AlF$_3$. The 2p electron states of F lie very deep within the valence band so that they are strongly localized there; for that reason further movement under excitation with sunlight is not possible. Thus the increase of $N_{\text{Al}}$ within the first four weeks after preparation could originate from Si electrons tunnelling through SiO$_2$ to very deep localized states with an extremely low tunnelling probability. Therefore the occupation of the 2p states takes quite a long time. The driving force for tunnelling is apparently the Coulomb force of AlF$_3$ near or at AlF$_3$||SiO$_2$.

Another source for electrons forming the fixed negative charge seems to be water ($\text{H}_2\text{O}$) which diffuses into AlF$_3$, being built in at interstitial sites. Due to extremely strong Coulomb forces between Al and F atoms $\text{H}_2\text{O}$ can dissociate so that hydroxide groups (OH') are released. These OH' can occupy F vacancies on screen ionized Al cores. In the latter case the Coulomb field reattracting electrons to the Al core will be deceased significantly. In comparison to F atoms the surplus electron of an OH' is moveable by strong Coulomb fields. It could diffuse further into the AlF$_3$ for occupying F vacancies until a high number of these vacancies are occupied by electrons down to AlF$_3$||SiO$_2$, thereby forming a fixed negative charge. Lattice mismatch between SiO$_2$ and AlF$_3$ (crystallites) at AlF$_3$||SiO$_2$ provides a high density of sites at the interface to be occupied. Still, there is no explanation how the remaining hydrogen ions (H') would react.

An effect which has to be taken into consideration at AlF$_3$||SiO$_2$ is the exchange of O and F between AlF$_3$ and SiO$_2$ according to the F profile of the SIMS measurement. As reported in [14], F atoms can react with O, Al and Si to chemical compounds of the form AlO$_x$F$_y$ and SiO$_x$F$_y$.

The density of the AlF$_3$ film of $\rho_{\text{AlF}} = 2.8 \pm 0.3$ g cm$^{-3}$ at $d_{\text{AlF}} = 120$ nm gave a clue about the composition in respect to the orientation of different basis sets of unit cells as a nanocrystalline structure of ≤ 50 Å is expected [15]. There are three different phases of AlF$_3$:

- Hexagonal $\rho_{\text{AlF}} = 2.815$ g cm$^{-3}$
- Rhombohedral $\rho_{\text{AlF}} = 3.192$ g cm$^{-3}$
- Tetragonal $\rho_{\text{AlF}} = 3.016$ g cm$^{-3}$

Probably the manufactured AlF$_3$ layers are dominated by hexagonally oriented unit cells. Rhombohedrally oriented unit cells do not seem to occur.

Finally it is stated that the total charge of AlF$_3$ on SiO$_2$ has a great potential to serve as a negative drift field source for solar cell applications.

6. CONCLUSIONS

The concept of a negatively charged IS structure (IS structure) and first experimental results were represented. The phenomena encountered were discussed. In summary, the layer compound AlF$_3$–SiO$_2$ on Si represents a very good candidate for the preparation of the ISI solar cell.

The major purpose of an IS structure is to generate a negative drift field which attracts holes and repels electrons, thereby creating a very strong positive band bending. For that reason a very efficient rear surface passivation of field effect solar cells can be expected. That can result in a faster carrier separation and significantly decreased surface and bulk recombination rate. The latter is especially interesting for thin film devices. A strong increase of open circuit voltage, short circuit current and fill factor is very likely.

It shall be emphasized here that for the first time a structure with a high density of fixed negative charges was prepared.

With the measured charges of $N_{\text{ion}} \leq -1.6 \times 10^{12}$ cm$^{-2}$ the resulting drift field strength at SiO$_2$–Si is already up to $F_{\text{drift}} = 2.4 \times 10^5$ V cm$^{-1}$. Further improvement of the IS structure performance can be expected.

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