

Antipolar Counterpart to the Positively Charged SiO_xN_y Layer for Improvement of Field Effect Solar Cells

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ABSTRACT: For drift field generation IS structures with a fixed positive interface charge in an insulator compound as CsCl-dyed SiO_xN_y 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 I^- S structure - could look like and can be prepared. Empirical data are represented in section 4. In section 5 a brief discussion of empirical data and phenomena encountered is given, while section 6 draws a conclusion of the I^- S structure introduced herein.

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 draw backs:

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^+ 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_2) of Si is difficult due to the high doping density at the rear surface.
4. When insulation layers are used for the I^- S structure the cell can also be illuminated from the rear surface as it is transparent for sunlight.

All draw backs mentioned above have an increasing deteriorating effect on device efficiency with decreasing Si substrate/film thickness. So by creating an I^- S 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 I^- S STRUCTURE

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

A positively doped (1 Ωcm, Boron) c-Si wafer is chosen to be substrate and active layer of the I^- S 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_2 layer separates the negative charge from the active layer and passivates the Si surface.

For localizing electrons at or near the interface (||) material $X||\text{SiO}_2$ 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 (AlF_3) 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 $\Gamma\text{-S}$ structure with AlF_3 .

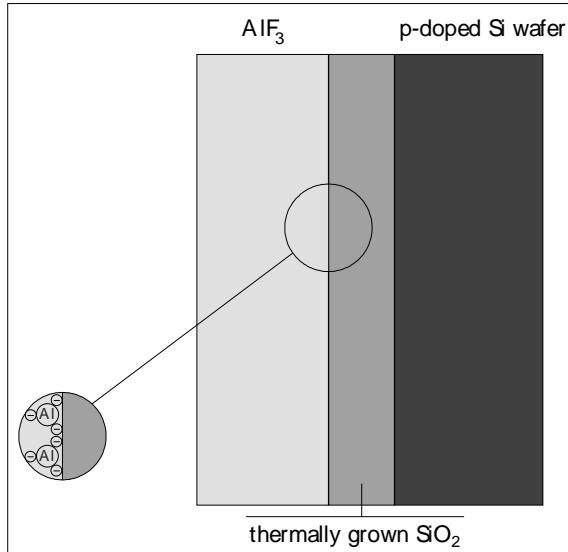


Fig. 1: physical shape of an $\Gamma\text{-S}$ structure with AlF_3

The global charge neutrality within the bulk region of the AlF_3 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 SiO_2 . 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 $\Gamma\text{-S}$ layer arrangement $\text{AlF}_3\text{||thermal SiO}_2\text{||p-Si}$.

Thermally deposited SiO_2 layers on Si have a fixed total charge density of $Q_{\text{Ox||Si}} \approx +1 \dots 3 \times 10^{10} \text{ cm}^{-2}$ so that there is a field component which weakens the negative drift field caused by the negative interface charge. The field caused by $Q_{\text{Ox||Si}}$ is

$$(1) \quad \mathbf{F}_{\text{Ox}} = \frac{q \cdot Q_{\text{Ox||Si}}}{\epsilon_0 \cdot \epsilon_{\text{Si}}}$$

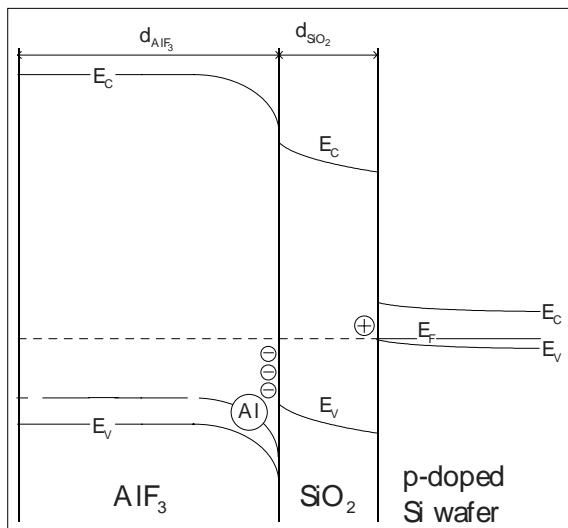


Fig. 2: energy bands and levels for the $\text{AlF}_3\text{-S}$ structure

The Field caused by the fixed negative interface charge Q_{IS} at the transition thermal $\text{SiO}_2\text{||p-Si}$ is

$$(2) \quad \mathbf{F}_{\text{IS}} = \frac{q \cdot Q_{\text{IS}}}{\epsilon_0 \cdot \epsilon_{\text{Ox}}} \cdot \frac{\epsilon_{\text{Ox}}}{\epsilon_{\text{Si}}} = \frac{q \cdot Q_{\text{IS}}}{\epsilon_0 \cdot \epsilon_{\text{Si}}}$$

with $\epsilon_{\text{rel}} = \epsilon_{\text{Ox}}$ since the field has to penetrate through the SiO_2 layer before reaching the Si wafer. The resulting field which has an impact on the Si wafer is the sum of the different field components:

$$(3) \quad \mathbf{F}_{\text{tot}} = \mathbf{F}_{\text{IS}} - \mathbf{F}_{\text{Ox}} = \frac{q \cdot (Q_{\text{IS}} - Q_{\text{Ox||Si}})}{\epsilon_0 \cdot \epsilon_{\text{Si}}}$$

Concerning preparation the concept does not require special process steps nor does it represent any technological handicaps. On the SiO_2 the AlF_3 layer is deposited by a low energy process at 250 °C substrate temperature. The deposition can be carried out in batch mode [10].

3. EMPIRICAL DATA & MEASUREMENTS

The estimation of the surface states between the c-Si wafer and the AlF_3 layer was realized by Hg-C/V. A 49 point wafer map was carried out on all samples. For further details of measurement see [11].

The bulk oxide charge is $Q_{\text{SiO}_2} = 2.2 \times 10^{10} \text{ cm}^{-2}$. The calculated effective interface charge is the sum of the fixed oxide charge, the interface charge at $\text{SiO}_2\text{||Si}$, and the fixed interface charge at $\text{AlF}_3\text{||SiO}_2$ referring to $\text{SiO}_2\text{||Si}$:

$$(1) \quad N_{\text{eff}} = Q_{\text{AlF}_3\text{||SiO}_2} + Q_{\text{SiO}_2} + D_{\text{it SiO}_2\text{||Si}}$$

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

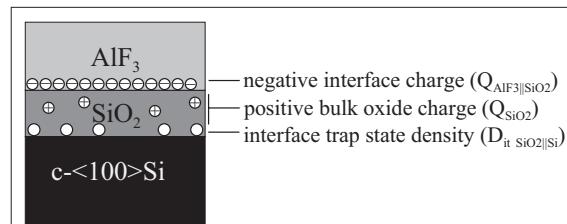


Fig. 2: on the charge of the structure $\text{AlF}_3\text{||SiO}_2\text{||Si}$

In order to preclude that F may falsify the C/V measurements due to diffusion though SiO_2 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.

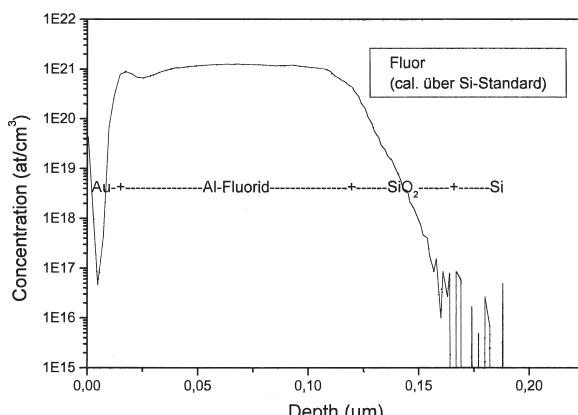


Fig. 3: SIMS profile of the Fluorine content within the layer compound (sample 1); SiO_2 range stretched due to different sputter rates of materials

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 AlF₃ 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 AlF₃||SiO₂ dominate the resulting effective interface charge N_{eff}. The oxide charge Q_{SiO2} ≈ 2×10¹⁰ cm⁻² is completely compensated as shown in table 1.

Wafer No.	d _{SiO₂} [nm]	d _{AlF₃} [nm]	V _{fb} [V]	V _{thr} [V]	N _{eff} [cm ⁻²] ×10 ¹¹
1	20	120	0.50	3.22	- 1.7
2	10	120	0.66	3.35	- 2.1
3	1.5	120	3.76	6.86	- 8.6
4	20	20	1.15	2.68	- 11.5
5	10	20	1.46	2.77	- 15.7
6	10	-	- 0.78	- 0.29	0.22

Table 1: sample parameters and results, extracted by 49 point - wafer maps (average mean values); wafer 6 without AlF₃ was added as a reference

N_{eff} increases clearly with decreasing oxide thickness d_{SiO₂}, due to the positive bulk charge of SiO₂ in compound with the decreasing distance of AlF₃||SiO₂ from SiO₂||Si. The reference wafer does not possess any fixed negative charges, obviously due to absence of AlF₃ on SiO₂. Both facts indicate that the negative charge lies at AlF₃||SiO₂.

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.

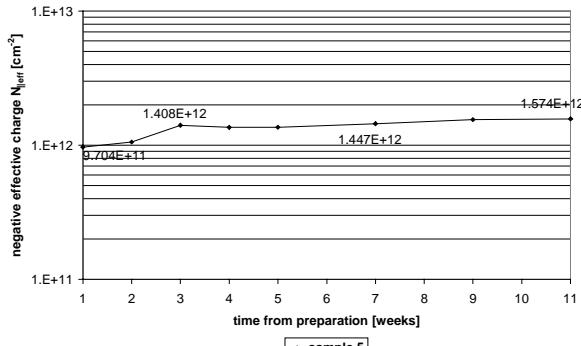


Fig. 5: effective negative interface charge N_{eff} of sample 5 measured by Hg-C/V as a function of time from preparation, extracted by 49 point - wafer maps (average mean values)

Fig. 6 shows the high frequency (HF-) Hg-C/V curve of sample 5, measured eleven weeks after preparation, compared to the reference sample 6. The different maximum capacities C_{max} are due to different total insulation layer thickness.

By electron energy loss spectroscopy (EELS) of the AlF₃ layer O was detected which corresponds well to the incorporation of water (H₂O) [12]. Fig. 7 shows the relevant high energy EELS spectrum range of an AlF₃ layer directly deposited on c-Si.

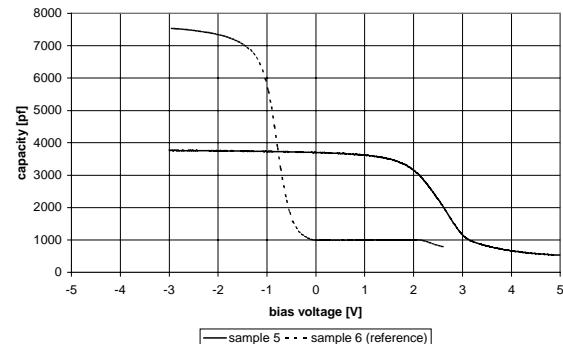


Fig. 6: HF-Hg-C/V curves of sample 5 and reference sample 6

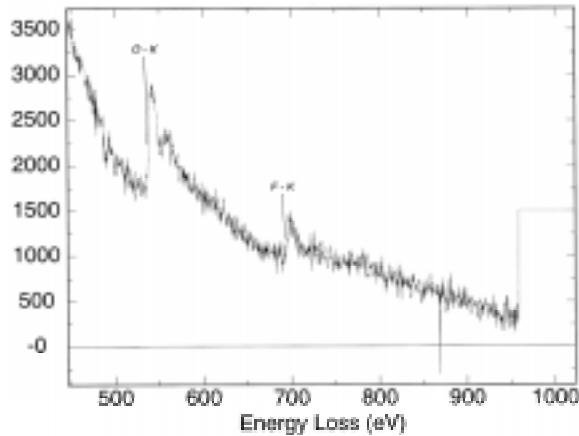


Fig. 7: high energy EELS spectrum of an AlF₃ layer deposited onto c-Si, showing the O peak originating from H₂O at interstitial sites at E_{loss} = 540 eV

Concerning layer orientation and crystallography X-Ray Reflection- (XRR) and X-Ray-Diffraction (XRD) measurements showed that evaporated AlF₃ layers are x-ray amorphous. Fig. 8 shows the XRR curve measured.

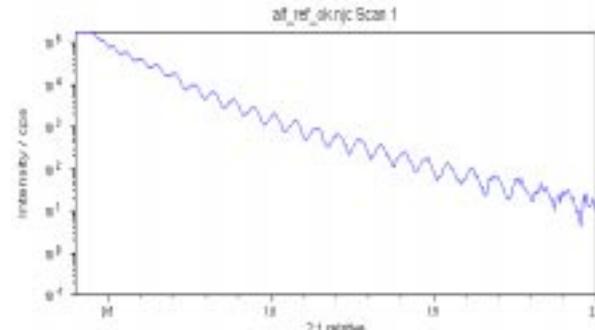


Fig. 8: measured XRR curve of the AlF₃ film, thickness 120 nm, directly deposited onto c-<100>Si

The AlF₃ films possess a very smooth surface. The mass density of ρ_{AlF₃} = 2.8 ± 0.3 g/cm³ estimated by XRR was lower than expected.

4. DISCUSSION OF RESULTS

The mechanism of massive electron localization at the interface AlF₃||SiO₂ is not clear yet. It is assumed that electrons from the AlF₃ bulk region are drawn towards the interface for refilling the sites which were created by a lattice mismatch between SiO₂ and AlF₃. F vacancies within AlF₃ play an important role for electron localization.

When depositing AlF₃ films by evaporation the stoichiometric ratio of Al:F = 1:3 is not reached [9]; such AlF₃

layers consist actually of AlF_x with $x \approx 2.6 \dots 2.9$. 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 resaturating the Al core. With the incorporation of H_2O 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 $\text{AlF}_3||\text{SiO}_2$, 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 $\text{AlF}_3||\text{SiO}_2$.

Another possibility for occupying one of the six 2p electron states of the F cores could be provided by electrons from Si tunnelling through SiO_2 to AlF_x . 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_{eff} 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_x near or at $\text{AlF}_x||\text{SiO}_2$.

Another source for electrons forming the fixed negative charge seems to be water (H_2O) which diffuses into AlF_3 , being built in at interstitial sites. Due to extremely strong Coulomb forces between Al and F atoms H_2O can dissociate so that hydroxide groups (OH^-) are released. These OH^- can occupy F vacancies or screen ionized Al cores. In the latter case the Coulomb field reattracting electrons to the Al core will be decreased 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 $\text{AlF}_3||\text{SiO}_2$, thereby forming a fixed negative charge. Lattice mismatch between SiO_2 and AlF_3 (crystallites) at $\text{AlF}_3||\text{SiO}_2$ 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 $\text{AlF}_3||\text{SiO}_2$ 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_xF_y and SiO_xF_y .

The density of the AlF_3 film of $\rho_{\text{AlF}_3} = 2.8 \pm 0.3 \text{ gcm}^{-3}$ at $d_{\text{AlF}_3} = 120 \text{ nm}$ gave a clue about the composition in respect to the orientation of different basis sets of unit cells as a nanocrystalline structure of $\leq 50 \text{ \AA}$ is expected [15]. There are three different phases of AlF_3 :

Hexagonal	$\rho_{\text{AlF}_3} = 2.815 \text{ gcm}^{-3}$
Rhombohedral	$\rho_{\text{AlF}_3} = 3.192 \text{ gcm}^{-3}$
Tetragonal	$\rho_{\text{AlF}_3} = 3.016 \text{ gcm}^{-3}$

Probably the manufactured AlF_3 layers are dominated by hexagonally orientated unit cells. Rhombohedrally orientated 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 $\text{AlF}_3 - \text{SiO}_2$ 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 $N_{\text{eff}} \leq -1.6 \times 10^{12} \text{ cm}^{-2}$ the resulting drift field strength at $\text{SiO}_2||\text{c-Si}$ is already up to $F_{\text{drift}} \approx 2.4 \times 10^5 \text{ Vcm}^{-1}$. Further improvement of the IS structure performance can be expected.

Acknowledgements

The author would like to thank M. Rennau and M. Henker, TU Chemnitz/Germany for Hg-C/V measurements and J. Heber, FHI for applied Optics and Precision Engineering Jena/Germany for preparation of AlF_3 layers.

The author receives a PhD scholarship of the German Research Society (DFG) within the Post Graduate Research Centre "Renewable energy sources" of the DFG.

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