

The negatively charged insulator-semiconductor structure: Concepts, technological considerations and applications

D. König, G. Ebest

Department of Electronic Devices, Technical University of Chemnitz,
09107 Chemnitz, Germany, *e-mail: dirk.koenig@e-technik.tu-chemnitz.de*

Abstract

The use of possibly uncharged and therefore passivated Insulator-Semiconductor structures (IS-structures) in conventional semiconductor devices as MISFETs is well known and has been an issue of many research papers. For drift field generation IS structures with a fixed positive interface charge in the insulator were developed in the 80's and employed mainly as a part of 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. In this paper we introduce theoretical considerations and qualitative models how such a structure would look and work like. Furthermore we consider technological aspects of producing a negatively biased IS structure. Possible applications are discussed as well.

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1. Introduction

Insulator-Semiconductor (IS) structures are widely used in electronic devices. Normally one strives for a minimum interface charge density as it shifts the flat band voltage towards zero bias, resulting in improved sensibility of active semiconductor devices like MOSFETs. On the other hand there are certain applications of positively biased IS structures as field effect solar cells [1], [2]. Those positively charged IS structures have been investigated thoroughly in the 80's [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 work has been carried out concerning a negatively charged IS structure. If it occurred at all the fixed negative charge of such a structure was seen as an inevitable side effect [5].

In this paper we discuss how such an IS structure with a high density of fixed negative interface charges - we call it Γ S structure - could look like, i. e. the resulting qualitative model. This is done in section 1. Section 2 deals with technological considerations and possible ways how to produce these structures. Application examples are represented in section 3, while section 4 draws a conclusion of the Γ S structure introduced.

2. Concepts of the Γ S structure

As the fixed negative charge shall have an impact on a semiconductor we chose a Boron doped ($1 \Omega\text{cm}$) c-Si wafer to be substrate and active layer of the Γ S structure. In order to avoid a direct contact of the majority carriers with the localized electrons which represent the negative charge an insulating layer which prevents the localized electrons from being emitted into the semiconductor is necessary. By

oxidizing the silicon wafer a very thin thermally grown SiO_2 layer ($d \approx 1.5 \dots 9.0 \text{ nm}$) separates the negative charge from the active layer. On this layer arrangement a material X must be deposited this way that there exists a high number of localized electrons at the interface material X || SiO_2 or within material X near the interface.

The basic layer arrangement is given by Fig. 1.

2.1 Localizing electrons - creating a fixed negative interface charge

For localizing electrons at or near the interface material X || SiO_2 those materials have to possess a large band gap. Thus electrons can be captured in local acceptor-like states under ionization of the latter.

Through the large band gaps of material X and SiO_2 an escape of the electron from its orbit around this acceptor-like state is possible only at excitation energies of several electron volts (eV), i. e. of the range of the band gap energy. Hence an excitation of these electrons away from their potential wells is possible only with photons of an energy within the X-ray spectrum. Due to the required large band gap material X has to be a highly insulating solid.

The second requirement for localizing a large number of electrons is that there is a large number of initially free electrons at or near the considered interface. Supplying electrons which can occupy acceptor-like states in an insulator can be done in two ways:

- by an anion which has a very high electron affinity so that it can attract additional electrons - see subsection 2.2.
- by employing an external electron source which can donate free electrons to the material X layer - see subsection 2.3.

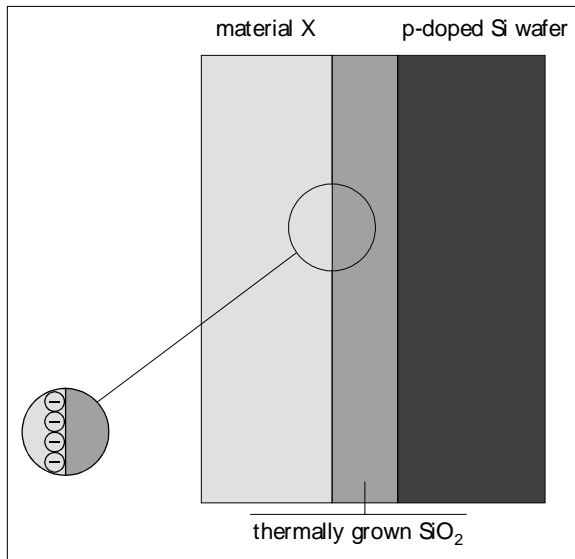


Fig. 1: basic physical arrangement of an IS structure

Finally the material X has to possess a large number of acceptor-like states (i. e. bonds which can capture and localize at least one electron). We see two ways how this could be done:

- by employing a cation with several valence electrons which can leave "their" cation relatively easy - see subsection 2.2.
- by doping the material X with shallow acceptors (i. e. acceptors with an energy level very near the valence band edge) - see subsection 2.3.

With the premisses listed above we developed two qualitative models how to create a large number of strongly localized electrons and thus a high density of fixed negative interface charges.

2.2 Using a highly ionic solid as material X for creating a fixed negative interface charge

By employing a highly ionic solid for the material X an IS structure can be produced. The anion should have a maximum electronegativity which calls for an element of the halogen group (chemical main group VII). Those elements attract surplus electrons from the cations involved in the ionic compound. The cations on the other hand should possess several valence electrons to be given away to the anions. A suitable candidate for such a material is Aluminiumfluoride (AlF_3). The Fluorine atoms attract the three valence electrons of the Aluminium in the highly ionic bond that strong that they are practically attached to the Fluorine. For that reason the Aluminium atoms are ionized and represent acceptor-like states. The band gap energy of Aluminiumfluoride is $E_{\text{Gap}}(\text{AlF}_3) = 10.8 \text{ eV}$ [6].

The global charge neutrality within the bulk region of the AlF_3 layer is maintained by the Fluorine atoms which screen the Aluminium 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 Fluorine cores and were acquired from Aluminium cores within the bulk region. A similar behaviour is known from Alumina (Al_2O_3) deposited onto silicon with a very thin native oxide layer [5]. Within that compound the oxygen donates electrons which were attracted from Aluminium cores within the bulk region before to dangling Aluminium bonds at the interface $\text{Al}_2\text{O}_3 \parallel$ native SiO_2 . The fixed negative interface charge of $Q_{\text{IS}} = -1 \times 10^{11} \text{ cm}^{-2}$ is seen as a side effect [5].

The thickness of the thermal SiO_2 layer is on the order of $d_{\text{Ox}} \approx 5 \text{ nm}$, the AlF_3 layer has a thickness of $d_{\text{AlF}_3} \approx 100 \text{ nm}$. Starting from the considerations about this IS structure a qualitative model of the band structure of the layer stack $\text{AlF}_3 \parallel$ thermal $\text{SiO}_2 \parallel$ p-Si is proposed.

Fig. 2 shows the physical shape of an IS structure with AlF_3 .

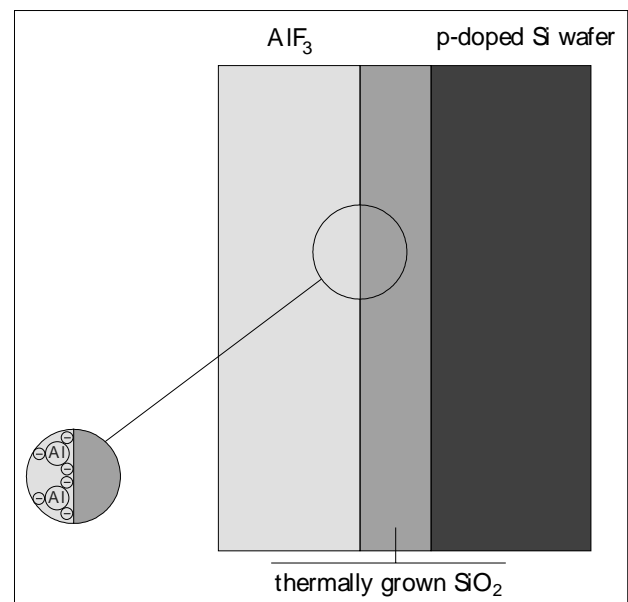


Fig. 2: physical shape of an IS structure with AlF_3

As already mentioned above a large number of electrons are located at Aluminium vacancies at the interface $\text{AlF}_3 \parallel$ thermal SiO_2 so that there is an electron deficiency within the bulk region of AlF_3 .

The Aluminium valence electron of the ionic bond $\text{Al}-\text{F}$ within the bulk region is strongly shifted towards the Fluorine atom because of the high electron affinity of it, so that the Aluminium atom behaves practically like an Acceptor. We assume that - if the Fluorine gives away that electron to a free Aluminium vacancy at the interface $\text{AlF}_3 \parallel$ thermal SiO_2 - the Aluminium atom is still sufficiently screened by the Fluorine atoms surrounding it (i. e.

one of the valence electrons of the Fluorine atom is shifted towards the Aluminium atom, thereby significantly decreasing the ability of the latter one to capture an electron).

Because of the large band gap and strong binding energy of the bond Al—F this charge redistribution process takes place in the immediate surrounding of the interface $\text{AlF}_3 \parallel$ thermal SiO_2 only. The mechanism of charge transport is not clear yet. Probably there exists a kind of electron hopping towards the free Aluminium vacancies at the interface so that those dangling bonds are occupied.

Fig. 3 represents the suggested band structure of the Γ S layer arrangement $\text{AlF}_3 \parallel$ thermal $\text{SiO}_2 \parallel$ p-Si.

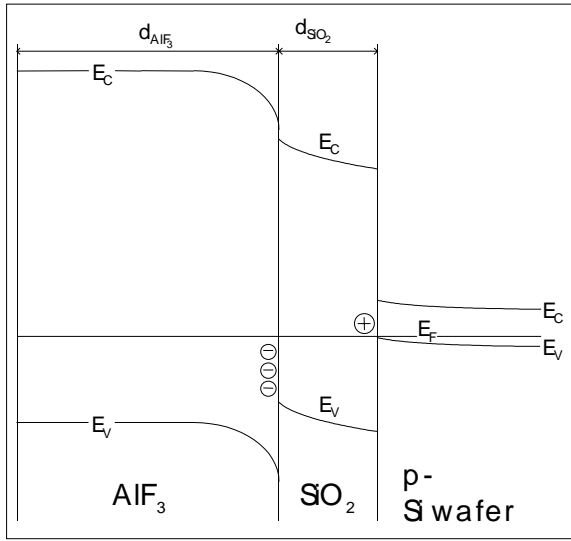


Fig. 3: suggested band structure for the AlF_3 Γ S structure

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

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

The Field caused by the fixed negative interface charge Q_{IS} at the transition thermal $\text{SiO}_2 \parallel$ 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 the specific dielectric constant $\epsilon_{\text{rel}} = \epsilon_{\text{Ox}}$ since the field has to penetrate through the SiO_2 layer before it reaches the Silicon wafer. The ratio of the specific dielectric constants accounts for the change of the field strength depending on the penetrated material. The resulting field which has an impact on the Silicon wafer is the sum of the different field components:

$$(4) \quad \mathbf{F}_{\text{tot}} = \mathbf{F}_{\text{IS}} - \mathbf{F}_{\text{Ox}} = \frac{q \cdot (Q_{\text{IS}} - Q_{\text{Ox}||\text{Si}})}{\epsilon_0 \cdot \epsilon_{\text{Si}}}$$

With the assumed values of $Q_{\text{IS}} \approx -1 \times 10^{12} \text{ cm}^{-2}$ and $Q_{\text{Ox}||\text{Si}} \approx 1 \times 10^{10} \text{ cm}^{-2}$ the resulting drift field strength is on the order of $\mathbf{F}_{\text{drift}} \approx 1.5 \times 10^5 \text{ Vcm}^{-1}$.

2.3 Using an acceptor doped insulating layer as material X with an external electron source
Another way an insulating material can host a large number of electrons is the massive positive doping of this material. In compound with an electron donor those acceptor states can be negatively charged. Again shallow acceptors are needed because their energy level is very near the valence band edge of the insulator. Then a maximum energetical distance from the conduction band edge and therefore a strong binding of the electrons to the acceptors is guaranteed.

Fig. 4 shows the physical shape of that Γ S structure.

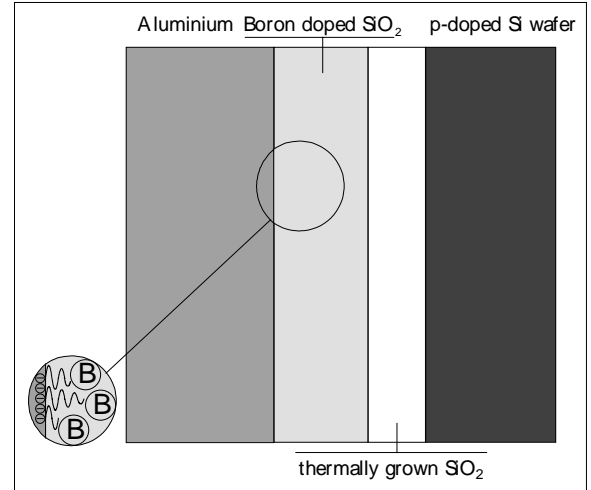


Fig. 4: Γ S structure with doped SiO_2 and Al layer

Although hopping conduction may occur at very high doping levels the doped insulator layer has to be very thin so that penetrating electrons can occupy the majority of acceptors. At lower doping levels an occupation can take place by indirect (i. e. Fowler-Nordheim) tunneling. In our model we employed Boron -doped SiO_2 for the doped insulator layer. Its thickness is $d_{\text{p-Ox}} \approx 10 \text{ nm}$, the doping density is $N_{\text{A}} \approx 1 \times 10^{20} \text{ cm}^{-3}$. As an electron donor Aluminium is a good candidate.

The occupation of acceptor states in Boron doped Spin-On-Glass (SOG; Filmtronics B 405) layers, annealed at $450 \text{ }^\circ\text{C}$ for 1h in N_2 ambient with $d_{\text{p-Ox}} = 50 \text{ nm}$, by electrons coming from an Aluminium layer failed to generate a negative interface charge [7]. This was due to a very low tunneling probability which becomes obvious since 50 nm of SiO_2 represent a

formidable tunneling barrier. So a maximum thickness of $d_{p-Ox} \approx 10$ nm is essential for the function of the doped SiO_2 layer in an Γ S layer compound.

In Fig. 5 the assumed band structure of the doped oxide Γ S structure is shown.

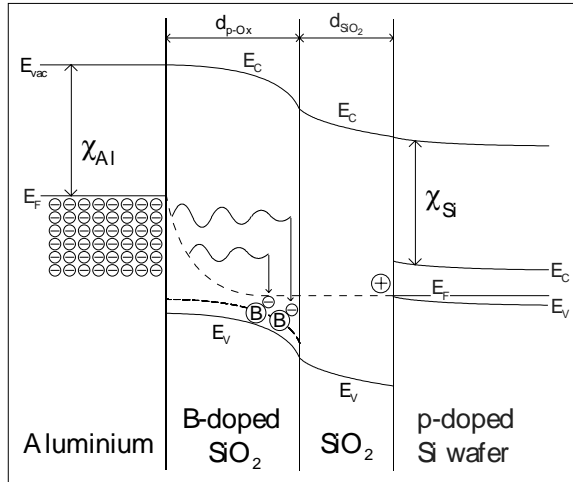


Fig. 5: assumed energy band structure of the Γ S structure with Boron doped SiO_2 and Al as electron donor

Aluminium possesses a high density of free electrons of $\rho_e \approx 1.8 \times 10^{23} \text{ cm}^{-3}$ [8] and a low electron work function ($\chi_{Al} = 4.2 \text{ eV}$ [9]) so that a large number of electrons can leave the metal relatively easy, tunneling to the acceptor states within the SiO_2 layer. The electron deficiency within the Aluminium may result in a slight increase of the electron work function although the electron density of Aluminium is larger than the doping density of the SiO_2 by a factor of about 1.8×10^3 . So the electron attractive field of the Aluminium is somewhat low. Therefore the Aluminium layer must have a minimum thickness of $d_{Al} = 200$ nm so that it can provide enough electrons without increasing its electron work function and electron attractive field significantly.

With the values of $N_A \approx 1 \times 10^{20} \text{ cm}^{-3}$, $d_{p-Ox} \leq 10$ nm and a nearly complete occupation of all acceptors the resulting surface charge of the Boron doped SiO_2 layer is $Q_{p-Ox} \leq -1 \times 10^{13} \text{ cm}^{-2}$.

These qualitative models are a very first attempt to find plausible descriptions of Γ S structures. For that reason distinguished statements and explanations require a preparation and characterization of these Γ S structures and a detailed atomistic consideration and simulation [10], especially regarding the interfaces or layer zones where the localization of electrons occurs. Presently several preparations of the first model ($\text{AlF}_3 \parallel \text{SiO}_2 \parallel \text{p-Si-wafer}$) are in progress at the Technical University of Chemnitz.

3. Technological considerations

After introducing the two concepts some aspects of preparing these Γ S structures shall be discussed.

The first proposed concept (subsection 2.2) does not require special process steps nor does it represent any technological handicaps. By a rapid thermal oxidation (RTO) at $900 \text{ }^\circ\text{C}$ in $\text{N}_2 / \text{O}_2 = 19 / 1$ for 120 sec. thermal SiO_2 with $d_{Ox} = 2$ nm is formed on the Boron doped Silicon wafer. Alternatively a thermal oxidation of the Silicon wafer can be employed to produce an oxide layer of high quality.

On that oxide the AlF_3 layer is deposited at $300 \text{ }^\circ\text{C}$ substrate temperature by electron beam evaporation. This deposition temperature is sufficient for guaranteeing a very compact AlF_3 layer with a minimum number of pores or cavities [11].

Preparing an ultrathin and highly doped SiO_2 layer for the second proposed concept (subsection 2.3) represents a major challenge to process controlability and tolerance ranges of layer properties. As the dopants must not penetrate into the underlying thermal SiO_2 we see the only possibility of preparing a highly doped SiO_2 layer by plasma enhanced chemical vapour deposition (PECVD) with in-situ doping (Boron via Borane: B_2H_6). The preparation of such very thin doped SiO_2 layers is presently possible down to $d_{p-Ox} = 20$ nm [12]. For the desired SiO_2 layer a thickness of $d_{p-Ox} = 10$ nm should not be exceeded. Increasing the thickness of the Boron doped SiO_2 beyond this value results in a tremendous decline of tunneling probability of free electrons from the Aluminium into the doped oxide [7]. For that reason the preparation of an Γ S structure introduced here as a second concept (subsection 2.3) is basically difficult.

4. Applications for Γ S structures

The major purpose of an Γ S structure is to generate a negative drift field which attracts holes and repels electrons, thereby separating free charge carriers in a semiconductor layer.

That property can be made use of in electronic devices which have to separate electrons and holes in a static manner as photo detectors and field effect solar cells [13]. Positively charged IS structures are existent since the 70's [1], [2]. The creation of a drift field source consisting of two antipolar IS-structures mounted on opposite sides of an active semiconducting layer would double the total drift field strength of the $\Gamma^+ \parallel \text{S} \parallel \bar{\Gamma}$ compound. That results in a faster carrier velocity, an increased mean free path for free carriers and thus in a faster carrier separation and significantly decreased bulk recombination rate. The latter is especially interesting for polycrystalline and amorphous semiconductors. In the case of polycrystalline and amorphous solar cells

a significant enhancement of open circuit voltage, an increased short circuit current and therefore an increased device efficiency can be expected. Concerning photo detectors an increased sensibility and faster response to optical excitations is very likely.

5. Conclusions

Two concepts of a negatively charged IS structure (Γ S structure) were represented. The corresponding qualitative models were discussed and resulting energy band structures were shown.

In section 3 we discussed the problems which may occur when preparing such Γ S structures. The first concept ($\text{AlF}_3 \parallel \text{thermal SiO}_2 \parallel \text{p-Si}$) does not seem to cause any severe difficulties in processing. The preparation of an ultrathin Boron doped SiO_2 layer for the second model ($\text{Al} \parallel \text{Boron doped SiO}_2 \parallel \text{thermal SiO}_2 \parallel \text{p-Si}$) is a major challenge to both process controllability and tolerance ranges of layer properties. This is one of the reasons why the first model of an Γ S structure was chosen for preparations and further investigations at the Technical University of Chemnitz.

The applications of Γ S structures to electronic devices are manifold. Especially in the field of photo detectors and solar cells a significant enhancement of device performance can be expected.

The concepts and considerations about the Γ S structure represented herein are merely a first attempt to create and understand such a structure. Much research work still has to be done in order to describe these layer arrangements in more detail and develop a quantitative and empirically founded model.

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