TCAD simulation of tunneling leakage current in CaF$_2$/Si(111) MIS structures

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1. Introduction

Calcium fluoride (CaF$_2$) is a crystalline insulator with high dielectric constant and wide bandgap (Table 1). Due to the proximity of its lattice constant to that of Silicon, it can be epitaxially grown on Si(111) substrates, potentially enabling creation of multi-layer device systems. Nevertheless, for a long time CaF$_2$ has been considered an exotic material, not to mention that decades of work were necessary to overcome growth problems related to the formation of pinholes and other issues. Fortunately considerable progress in understanding the growth processes and electrophysical properties of fluoride has been made within the last years [1,2], which today is close to reaching device-relevant quality. Thus, thin fluoride films are now considered for practical applications as the insulating barrier layers in silicon solid state devices such as Resonant-Tunneling Diodes (RTDs) and super-lattices employing Si [3], CdF$_2$ [4] or Fe$_3$Si [5] quantum wells. At the same time, the idea of employing thin fluoride layers as a gate dielectric in the Field-Effect Transistors (FETs) [6] is now being reconsidered.

Along with a necessity for further film growth optimization, there appears a demand for more robust simulations of the main characteristics of fluoride-based structures. Recently we have demonstrated the possibility to reproduce the current–voltage (IV-) characteristics of CaF$_2$-based tunnel Metal-Insulator-Semiconductor (MIS) capacitors without fitting any parameters [7,8]. The next task in this direction is to use this model in TCAD simulators to predict the behavior of devices with thin calcium fluoride films in different operation modes. In this work we simulate the tunnel currents through thin fluoride layers in MIS systems using the TCAD tools Minimos-NT [9] and ViennaSHE [10], which so far has been applied only for the devices with SiO$_2$ and high-k oxides. Beyond the simulation of the usual quasi-equilibrium IV-characteristics we will perform an analysis of the effect of non-equilibrium hot carriers on tunnel charge transport in the mentioned devices.

The central place in the paper will be devoted to the question on how to adapt these TCAD simulators to the case of fluoride. This presumes the physics-based optimization of the tunneling probability formulas and consideration of both electron and hole current components. The theoretical results obtained in this study will be compared to experimental results for Au/CaF$_2$/pSi(111) structures obtained previously [11]. The CaF$_2$ film thickness under consideration will range from about 1.0 to 2.5 nm; it is dictated by a practical relevance, because the ultrathin (<2 nm) fluoride layers are of special interest in the context of applications in RTDs, FETs and most other devices.
2. Tunneling probability for the CaF$_2$/Si system

As of today, the values of Si/CaF$_2$ barrier parameters are rather well known [12] (Table 1). Particularly, the effective carrier mass for both allowed bands of the fluoride is $m_e = m_0 = 1.0$ $m_0$ within a parabolic law (adopted further) or $m_T = 1.2$ $m_0$ with a Franz law.

The barrier height at the Au/CaF$_2$ interface $\chi_m = 2.63$ eV. This value relies on our experience in fabrication and characterization of MIS structures with calcium fluoride. The band diagrams calculated for Au/CaF$_2$/p-Si structure using Minimos-NT [9] are given in Fig. 1. Taking into account the barrier asymmetry and the wide band gap of fluoride one assumes that in all cases tunneling will take place through evanescent states derived from the CaF$_2$ conduction band (i.e. through the “top” barrier).

In the WKB approximation, the tunneling probability is

$$T(E, k_z^2) = \exp \left[ -2\hbar^{-1} \int \sqrt{2m_e (E_{cl}(z) - E + \hbar^2 k_z^2 / 2m_e)} \, dz \right]$$

(1)

where $E$ is carrier energy (with zero at $E_F$, s. right Fig. 1), $k_z$ - transverse momentum component and $E_{cl}$ - coordinate-dependent energy of CaF$_2$ conduction band edge. Eq. (1) is also used for the case of carrier transport between the metal and Silicon valence band.

Often, attempts are being made toward converting this expression into the form of

$$\tilde{T}(E, E_L) = \exp \left[ -2\hbar^{-1} \int \sqrt{2m_e (E_{cl}(z) - E + m_L m_e^{-1} E_L + m_0 m_e^{-1} \Delta E(E))} \, dz \right]$$

(4)

over all the electron states in the $k$-space (specified by a parameter “$\alpha$”) with the given $[E, E_L]$ pair:

$$\tilde{T}(E, E_L) = \left\langle \tilde{T} \left( E, k_z^2 (E, E_L, \alpha) \right) \right\rangle \alpha .$$

(2)

In the case of tunneling through an amorphous dielectric layer (e.g. SiO$_2$), or carrier transport from the valence band, or Si (100) substrate, Eq. (2) simplifies to

$$\tilde{T} = T(E, 2m_L E_L \hbar^{-2}) ,$$

(3)

where $m_L$ is the electron mass in Si in the surface plane. However, this does not work for the conduction band transport through a crystalline CaF$_2$ film on Si(111) substrate because of the large transverse momentum $k_z$ (“$k_z$-effect”) for the tunneling electrons.

**Table 1**

<table>
<thead>
<tr>
<th>Simulation parameters</th>
<th>Studied Au/CaF$_2$/Si system parameters</th>
<th>Essential Si wafer parameters</th>
</tr>
</thead>
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<tr>
<td>$\epsilon_i$</td>
<td>8.43</td>
<td>$\chi_m$, eV</td>
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<tr>
<td>$E_{GR}$, eV</td>
<td>12.1</td>
<td>$\Gamma_m$, eV</td>
</tr>
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<td>$N_0$, cm$^{-2}$</td>
</tr>
<tr>
<td>$\zeta_i$, eV</td>
<td>1.67</td>
<td>$V_{th}$, V</td>
</tr>
</tbody>
</table>

**Fig. 1.** Band diagrams of a MIS structure with a tunnel-thin fluoride film (in scale).

**Fig. 2.** Determination of the parameter $E_i$ of the simple model for the electron tunneling probability by comparison with the results for the current yielded by the more precise models.
3. Tunneling current model: implementation and results

In this work Minimos-NT device simulator [9] is used for the simulations of near-equilibrium carrier transport and the deterministic Boltzmann transport equation solver ViennaSHE [10] is employed when dealing with hot electrons. Earlier, the simulator Minimos-NT has been successfully applied for simulations of a wide spectrum of different effects encountered in production quality devices, such as time-dependent reliability of nanoscale MOSFETs [13]. The simulator ViennaSHE uses the Spherical Harmonics Expansion (SHE) approach for the solution of the Boltzmann transport equation [14] and has already been successfully applied for the treatment of hot-carrier degradation (HCD) effects in the transistors of traditional architecture with SION films [15,16]. Keeping the application perspectives of calcium fluoride in mind, it seems to be reasonable to employ these simulation tools also for the CaF$_2$-based MIS devices.

The current flowing through the MIS structure with CaF$_2$ is obtained as a sum of the electron and hole components. Note that it would be more correct to formulate the problem in terms of the carrier distribution functions for metal and Si conduction band, or metal and Si valence band, as transport of a hole can be interpreted as transport of an electron in the opposite direction, and vice versa:

$$j = j_e + j_h$$

(6)

It is commonly known that the states of carriers are quantized near the insulator/Si interface, so that discrete levels are formed (the level $E_0$ is shown in the diagrams of Fig. 1). For a physically rigorous approach, this effect has to be considered when modeling the currents. Also, in our own reference physical simulator (RPS) [7,8] one of the components ($j_h$ in the left Fig. 1 or $j_e$ in the right) contains a contribution from the discrete-levels plus the continuum current. The RPS program will be used below for some comparative calculations.

However, in most TCAD simulators such as Minimos-NT and ViennaSHE, the discrete states are only approximately considered by the introduction of quantum corrections to the density of states. Due to these corrections, the surface potential $\phi_S$ (for the given bias $V$) approaches its exact value; otherwise it would have been much lower. This correction function $\xi(E)$ is included also into the formulas for the current:

$$j_{eh} = \frac{4\pi q}{\hbar^2} \int_{E_{min}}^{E_{max}} T^e(E, E_0) dE \int \xi(E) (f_S(E) - f_{eq}(E)) \int T^h(E, E_1) dE_1 dE$$

(7)

Here $f_{eq}$ and $f_S$ are the carrier distribution functions for metal and Si, in the quasi-equilibrium case they are Fermi functions. The integration limits in (7) are $E_{min} = -\infty$, $E_{max} = -E_{gs}$, $E_{max} = -E_{gs} - E$ for the current from the valence band and $E_{min} = 0$, $E_{max} = +\infty$, $E_{max} = -E$ for the current from the conduction band. The correction function $\xi(E)$ for the electron quantum well (right Fig. 1), approaches 0 if $E \to 0$ and is equal to 1 if $E \geq q\phi_S$ or $E < -E_{gs}$. The trends for the hole quantum well are evident.

The IV-characteristics simulated with the simplified model implemented in Minimos-NT for Au/CaF$_2$/p-Si(111) structures with three different insulator thicknesses are summarized in Fig. 3. These curves were obtained within a quasi-equilibrium approach inside the semiconductor for all bias conditions. They have all typical features known from the theory of tunnel MIS structures. Namely, there is an almost exponential increase of the current in the range of rather high voltages at any polarity. Furthermore, the total current $j = j_e + j_h$ (solid lines) depends very strongly on the fluoite thickness. Just left from the zero bias, there is a plateau because this range corresponds to the depletion of the semiconductor where the insulator voltage $U$ does not follow the changes of the terminal bias $V$ (the flat-band bias is $V_{FB} = -0.7$ V).

The dashed lines represent the valence band component $j_h$ alone. In MIS studies it is often assumed that the electron component $j_e$ is dominant while the hole part is neglected. The results shown in Fig. 3 unequivocally demonstrate the importance of the hole current in the CaF$_2$/Si(111) system. The energy of electrons which tunnel between the metal and the near-minima states of the conduction band of silicon is effectively reduced by the value of $\Delta E(E) > E_g$. As a consequence, the barrier for such electrons becomes higher than for the valence-band transport. With an increase in energy $E$, this effect gradually vanishes due to the exponent, cf. Eq. (6). All this means that one needs to deal with a complicated interplay between the two components.

Indeed, when a rather small accumulating bias is applied to the electrode (a little bit left from $V = V_{FB}$ in Fig. 3) the total current is mainly determined by $j_h$ which is blocked while $E_{min}$ lies below $E_{gs}$. At higher negative bias $j_h$ starts to decrease versus $|V|$ because the valence band tunneling occurs through the strengthening top barrier but the total current strongly increases due to a contribution of the electron component $j_e$. This component rapidly increases with increasing $U$ and because the energies $E$ of the involved electrons depart from $E_{gs}$, which reduces the $\Delta E$-effect on the tunneling probability. In the inversion-depletion mode ($V > 0$) the hole current is blocked at low voltages, while $E_{eq}$ is below $E_{Fm}$, while at higher positive voltages $j_h$ comes into play and both components become comparable.
Minimos-NT simulations predict that there is some range (near \( V = 1.5 \) V) where \( j_h \) is even dominant. At higher positive biases \( j_c > j_h \), but the difference is not large enough for \( j_h \) to become negligible.

The results provided in Fig. 3 represent the first successful attempt to capture the essence of a carrier transport in MIS structures with fluoride films using the TCAD simulator. As we have just seen, an analysis of the underlying physics, e.g. of the interrelation between both tunneling current components, became possible. Evidently, a behavior of the total current \( j \) is strongly affected by an impact of the band structure on the electron current component. If the \( k_z \)-effect (\( \Delta E \)-shift) had been neglected, all the values of the current would have been considerably higher. An important application of Minimos-NT is also clear: it potentially enables detailed consideration of a real device design. This is not critical while only the simplest structures are dealt with but will become necessary by even minimal complications of the configuration.

4. Comparison to other simulations and to experiment

In Fig. 4 the results for the structure with \( d = 5 \) ML simulated with Minimos-NT are compared to those obtained using our RPS assuming the accurate (with \( T \) after Eq. (2) for \( j_c \)) and simplified models, cf. Eq. (4). One can see that agreement is rather good. However, a slight difference between the obtained current values is still present which is due to the different models employed. In particular, for the Minimos-NT simulations the typical insulator bias \( U \) is a bit higher than in the RPS (see the inset). Furthermore, the expressions for the tunneling current (both \( j_c \) and \( j_h \)) are quite different: while Minimos-NT uses a continuum Eq. (7), our RPS separately treats also the discrete levels in the near-surface quantum well. In such a case a slight deviation between the results of the two simulators appears to be reasonable. Furthermore, the RPS also cannot be considered as perfect “calibration” tool. It is only important that there is no substantial qualitative and quantitative contradiction between the results of two different approaches. From Fig. 4 one concludes that the magnitude of the typical current difference between Minimos-NT and the RPS is of the same order as the discrepancy between the results of the accurate and simplified versions of the RPS itself.

Noteworthy, due to slightly larger insulator voltages \( U \) within Minimos-NT, the hole current \( j_h \) appears stronger at lower terminal voltages \( V > 0 \) than within the RPS, because the condition \( E_{\text{F0}} > E_{\text{Fm}} \) is satisfied earlier. For this reason we see a hump in the \( j(V) \) curve which is absent in the RPS case. In fact, the values of the CaF\(_2\)/Si barrier heights, although converged in the literature, nevertheless allow some variations. Again, it should be stressed that there is no serious disagreement between the models.

Next, we compare the theoretical results against experimental data measured on our MIS capacitor samples (Fig. 5). The curves (left from \( -0.7 \) V) correspond to accumulation mode which is more suitable for an analysis. (Under the reverse polarity, due to the minority carrier deficit in the two-electrode capacitors, the current relies rather on the thermal generation rate than on any insulator barrier properties; this complicates interpretation.) As a technical remark it has to be mentioned that such measurements slightly suffer from sample degradation, which results in a gradual decrease of the current especially in the high-bias range (arrows in Fig. 5). Qualitatively, the form of the characteristics agrees with expectations. However, for a purpose of quantitative comparison we should account for thickness fluctuation always occurring in practical samples. The fluctuations are usually measured by atomic-force microscope and obey the normal (Gaussian) distribution with a nominal value \( d_0 \) and standard deviation \( \sigma_d \) (provided directly in Fig. 5).

Due to non-zero \( \sigma_d \) values for the measured films (Fig. 5), the results shown in Figs. 3 and 4 cannot be used for verification and should be re-generated. The fairest way would be to weight the current \( j(d) \) with a Gaussian distribution. This is an elementary action but, to save computational resources, it is more convenient to employ an effective uniform thickness \( d_{\text{eff}} \). The latter is introduced as \( d_{\text{eff}} = d_0 - \eta \sigma_d \), like it was earlier performed for SiO\(_2\). This approach is based on the assumption \( j(d) \sim \exp(-2\chi) \) \( (\chi = (2m_e^{-1})^{1/2}h^{-1}) \) for the local current density, with the “effective” barrier height \( \chi \sim 3-3.5 \) eV; such a density is then Gaussian-weighted. When \( d_0 \) and \( \sigma_d \) are expressed in angstroms (\( \text{Å} \)), the value of \( \eta \) for CaF\(_2\) can be estimated as 1.0.

The IV-characteristics simulated with the properly asserted fluoride thicknesses \( d_{\text{eff}} \) are included into Fig. 5. The simulations were performed using Minimos-NT and supported also by the RPS tool; the latter gives nearly the same curve for both the accurate and the simplified variant. In general, for each of the two nominal fluoride thicknesses, an agreement can be estimated as satisfactory, especially for the 5 ML sample. The most obvious discrepancy,

![Fig. 4. IV-characteristics of the Au/CaF\(_2\)/p-Si(111) structure simulated with Minimos-NT and with the reference physical simulator (RPS) program assuming accurate or simplified tunnel probability models.](image)

![Fig. 5. IV-characteristics simulated using Minimos-NT under the assumption of thickness fluctuations compared to the experimental data and similar results obtained using the RPS program. Effective thickness model is used. Capacitance-voltage characteristics are given in the inset. Line styles correspond to those in Fig. 4.](image)
occurring also for the RPS, is in the slope of the characteristic for $d_n = 7$ ML, although even in that case the simulated current values are close to the measured data. This discrepancy arises from the use of $d_{et}$ and has been seen previously in similar studies of SiO$_2$ structures, if $d_{et}$ is relatively large. We have checked (not shown) that a Gaussian integration applied to the present simulation of Au/CaF$_2$/p-Si(111) structures yields better agreement for $d_n = 7$ ML. Furthermore, certain underestimation of the currents at highest $V$ in Fig. 5 might be related to a degradation trend mentioned above. The inset to Fig. 5 shows the capacitance—voltage curves for the same samples (the range of accumulating bias). Otherwise than on the current, $k_x$ conservation has no impact on the capacitance; it was calculated like for the structures with SiO$_2$.

The progress in this work consisted in implementation of the appropriate tunneling model for the CaF$_2$/Si(111) case, where the old relatively simple approaches like the known Tsu-Esaki or the Fowler-Nordheim models would completely fail because of ignoring the $k_x$-effect (Section 2). Such kind simple approaches have been long ago implemented into Minimos-NT and many other simulators, enabling quite successful calculation of currents in MIS structures with amorphous oxides. A comparison of the predicted (using RPS) tunneling currents through CaF$_2$ and SiO$_2$, HfO$_2$, La$_2$O$_3$ was presented in our earlier work [17].

5. Simulation of the hot-electron induced effects

Hot-electron induced effects are rather important in the context of the device reliability. They have been investigated earlier in detail for devices with SiO$_2$ and SiON films [15,16,18]. However their consideration requires application of TCAD device simulators and is impossible with our RPS program. For this reason no attempts to incorporate the hot electron impact on devices with CaF$_2$ have been made so far. Thus, in this work the first attempt to address this issue with respect to the fluoride-based structures will be undertaken.

In the equilibrium case the electron distribution in Si is described by the standard Fermi function which has to be substituted into Eq. (7) instead of $f_f$. However, in the case of channel hot carriers one has to use a non-equilibrium distribution function.

$$f_s(E) = \frac{dn(E)}{dE} = \rho_{3D}(E) - \xi^{-1}(E)$$

where $\rho_{3D}$ is the usual density of states which is known for the Silicon band structure and behaves as $E^{1/2}$ near the conduction band minimum. The energy distribution of electrons $dn/dE$ (cm$^{-3}$ eV$^{-1}$) is taken at the Si/CaF$_2$ interface. Near the equilibrium state Eq. (8) transforms into the standard Fermi function. Note that the term “distribution function” ("DF") is often used with respect to both $dn/dE$ and $f_s$. This should not, however, cause a confusion as the units are evidently different, i.e. cm$^{-3}$ eV$^{-1}$ and dimensionless, respectively.

The physical situation with the hot electrons in a MIS structure can be illustrated for example by monitoring the heating along a MISFET channel, after which the electron leakage into the gate starts to dramatically increase. The magnitude of this leakage is considerably stronger than it would be without the impact of heating. This leads to hot-carrier degradation of the device, which is known to be one of the most important reliability concerns [15].

We next try to capture the essence of HCD for MISFETs with fluorite as a gate insulator. This is done with using ViennaSHE which has successfully been applied for production quality MOS-FETs. The devices similar to imec design with a gate length $L_g = 65$ nm and CaF$_2$ thickness $d = 2.5$ nm corresponding to an effective oxide thickness $EOT = d \times \epsilon_{CaF_2} = \epsilon_{SiO_2} - 1.2$ nm are examined (see the configuration in Fig. 6, inset). The CaF$_2$/Si(111) surface state density $N_s$ was set to $10^{12}$ cm$^{-2}$. The key feature of the simulations is the consideration of electron—electron scattering (EES) effects while calculating the non-equilibrium DFs using the deterministic simulator ViennaSHE [10]. This is of particular importance for ultra-scaled MISFETs and especially in the context of hot-carrier degradation which is very sensitive to high-energy tails of the DF [16,19].

In Fig. 6 the non-equilibrium leakage currents simulated for the devices with CaF$_2$ for $V_g = V_d = 1.8$ V are compared to those a similar device with SiO$_2$ (also $d = 2.5$ nm). One can see that near the source and in the center of the device the gate leakage is substantially lower in the CaF$_2$ based MISFET as compared to that simulated for the device with SiO$_2$. Near the drain, however, the gate current through the CaF$_2$ film appears to be higher. Such a trend is explained as a trade-off of two competing factors. On the one hand, the tunnel probability (calculated with a fixed carrier DF) is substantially suppressed in the CaF$_2$ film due to the higher dielectric permittivity $\epsilon_r$, larger electron effective mass in CaF$_2$ (1.0 $m_0$ compared to 0.42 $m_0$ in SiO$_2$) and also due to the transversal shift $k_{0LL}$. On the other hand, a higher $\epsilon_r$ value for CaF$_2$ leads to a higher electric field in the channel of the CaF$_2$-based transistor, so that the carriers are hotter, as compared to the device with SiO$_2$. The second tendency is further enforced by EES in the case of CaF$_2$ which dramatically increases the gate current near the drain. Note also that at relatively high $V_d$ a substantial fraction of the electrons collected by the gate electrode is injected over the potential barrier. In the case of CaF$_2$, the height of the Si/dielectric barrier $\chi_e$ is lower than for SiO$_2$, which makes the effect even stronger.

6. Conclusion

In this work an attempt to apply the TCAD simulators Minimos-NT, ViennaSHE to model the carrier transport through thin calcium fluoride films has been performed. Real physical barrier parameters have been taken for this. The important point is that a numerical accuracy has been achieved and that the simulation results are in reasonable agreement with the experimental data for the case of equilibrium tunneling through the thin fluoride film. Also, the simulation technique has been tested for the case of hot-electron leakage from the MISFET channel. The presented modeling approach can be used in future to characterize different operational devices employing thin CaF$_2$ layers.
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