Supplementary Information

Simultaneous Specimen Current and Time-Dependent Cathodoluminescence Measurements on Gallium Nitride.

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1.- Deep Level- time based scans

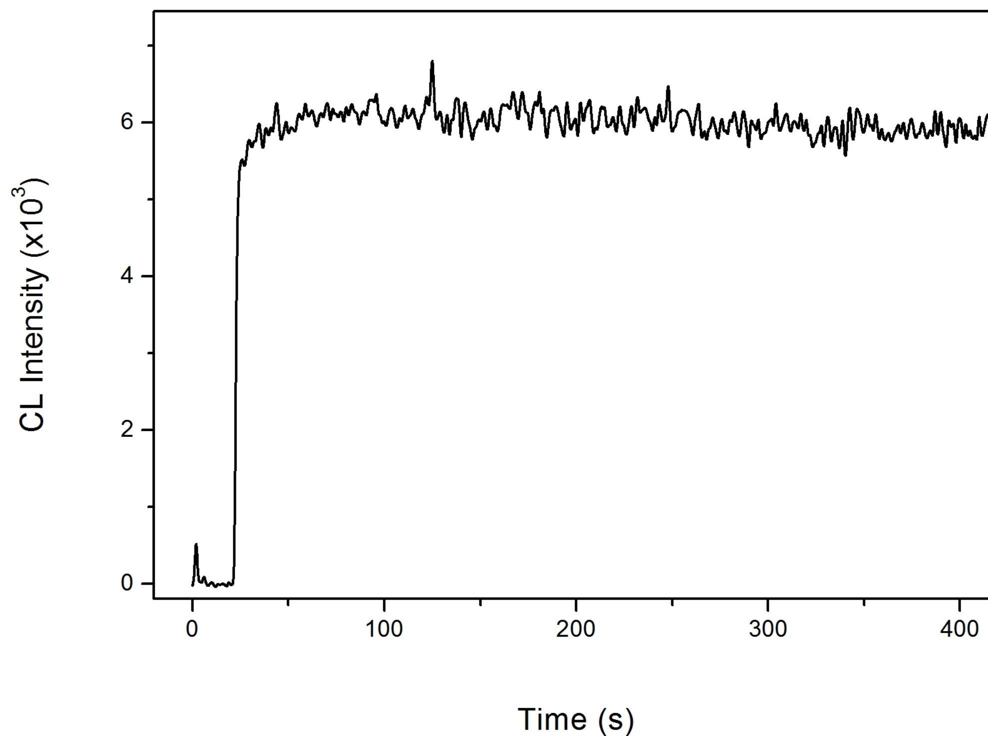


FIG S1. Time based scan of DL emission at 60kx magnification and beam settings 20 keV and 35 nA.

2- Revised Song's method for measuring injected charge.

A variety of methods have been proposed in the last few decades to measure charge injection in insulators during electron beam irradiation, like the scanning electron microscope mirror method (SEMM).[1] On those lines, Elsafi *et al.* adjusted the SEMM method to allow for a dynamic analysis of charging mechanisms. Typically, in SEMM measurements a target sample is implanted with charge using a high energy electron beam (a few tens of kilovolts) until saturation is reached and then SEM is performed at much lower beam energies (a few thousand electron volts). Built up potential from the injected charge causes distortion in the images acquired by SEM and this is used to calculate the total stored charge. Elsafi modified this experiment to capture SEM images every 50 ms for different injection times and beam energies, typically samples were irradiated in SEM for 150 s, providing a time-evolved mechanism of charge dynamics.[1] However, following this method, multiple charge distributions could lead to the same surface potential in one pixel, which frustrated the identification of charge trapping mechanisms.

Later, Fakhfakh et al[2], designed an experiment that identifies leakage and displacement current separately. In this scheme, stored charge was calculated using a relationship between electrostatic influence factor and displacement current; $I_d = \frac{KdQ_s}{dt}$ (K is electrostatic influence factor, and Q_s is stored charge) upon beam off, for a range of primary beam energies and beam currents. Finally, Cazaux monitored time-evolved SE emissions using a kilo electron-volt probe by applying electrostatics arguments.[3] Gauss' Theorem and Maxwell's equations were used to describe distribution of charge in a sample by the total yield approach; which allowed for the analysis of detrapping events.

In summary, many approaches are available to assess charge storage in semiconducting and insulating devices, each with their merits and drawbacks. In addition, severe sample damage is also a possible consequence from beam bombardment, along with species migration.[4] With all, few proposed methods are applicable to coated and grounded insulators, which describe a typical electron beam irradiation experiment in a SEM.[3] The method proposed by Song *et al.* allows for measurements of stored charge in insulators during electron-beam bombardment in a SEM, and in this work, the original equations have been modified to enable the analysis of a coated and grounded sample.[5] In this instance, grounding of the sample surface will contain the evolving electric field in the bulk GaN, minimizing changes to surface potential and leaving zero electric field above the sample surface.[6] As a result, the deflection of the incoming beam will be minimized. However, coated and grounded samples

have been shown to exhibit sub-surface charging, thereby modifying the localized space charge region at the irradiation point.[3]

Indeed, it is important to note that when an irradiated insulator has a coated and grounded surface, internal charging can affect penetration depth,[7] but cannot affect the incident electron beam energy itself, by way of additional acceleration or deceleration as a consequence of a surficial charge. In this scheme, the coating shields the developing internal electric fields, in such a way that an incident electron beam interacts with the electric field only after impinging on the sample.

The model for injected charge determination proposed by Song et al.[5] considers the equation for charge conservation, with incident current i_o, specimen current i_{sc} and backscattered and secondary electron currents i_{bs};

(S1) $$i_o = i_{sc} + i_{bs}$$

There are two contributions to specimen current, the displacement current i_d and the leakage current i_l , which can be expressed as:

(S2) $$i_{sc} = \frac{dQ(t)}{dt} + \frac{g_i}{e_o e_r} Q(t)$$

Solution of the differential equation led to

(S3) $$Q(t) = Q(¥)(1 - e^{-t/t'})$$

Substituting the solution for Q(t) into Eq. (3) yields

(S4) $$i_{sc} = \frac{Q(¥)}{t'} e^{-t/t'} + \frac{g_i}{e_o e_r} Q(¥)(1 - e^{-t/t'})$$

where the first term of Eq. (A4) is the displacement current and the second term is the leakage current. For t → ∞, $i_{sc}(t)$ → $i_l(t)$ → i_l*, the steady state leakage current,

(S5) $$i_l^* = \frac{g_i}{e_o e_r} Q(¥)$$

However, the component of the specimen current related to the trapped charge Q(t) is the displacement current i_d,

$$\text{(S6)} \qquad Q(\infty) = \int_0^{\infty} i_d(t)dt = \int_0^{\infty} \frac{Q(\infty)}{\tau'} e^{-t/\tau'} dt$$

The proposed model is a dynamic description of phenomena in the material during electron beam bombardment. In this scheme, a displacement current is generated by variation of stored charge in the material during irradiation, and a leakage current is current due to electron detrapping. BSE and SE emission is also time-dependent.

Since the time constant τ' is difficult to measure directly,[5] a graphic technique will be used to calculate stored charge avoiding calculation or measurement of parameters like τ' or g_i.

Backscattered and secondary electron current is a function of effective backscattered and secondary electron coefficient σ, which is equal to the sum of backscattered coefficient η and secondary coefficient δ.[8] There are two contributions to the effective coefficient σ. One contribution is the coefficient σ_{uo} in absence of charging in the irradiated material, the other describes effect of charging on emission of backscattered and secondary electrons. This last contribution can be extrapolated as a function of BSE and SE coefficient when there are no charging mechanisms in the solid $\sigma_{uo,}$ and as a function of electron beam voltage U_o as

$$\text{(S7)}\, i_{bs} = \sigma i_o = \left[\sigma_{uo} + \frac{(1-\sigma_{uo})V_C}{(U_o - U_{c2})}\right] i_o$$

where U_{c2} is the secondary critical voltage where $\sigma_{u,o}$ equals unity, and V_C for the case of an *uncoated* sample, is the electrostatic potential at the sample surface created by the charge Q(t) injected at a depth R. This localized field might result in charge-migration and modification of electrical and chemical characteristics in the irradiated region.[6]

Leakage current is described in terms of stored charge Q(t) and relaxation time of trapped charge in the insulator, τ'

$$\text{(S8)}\, i_l = \frac{Q(t)}{\tau} = \frac{g_i Q(t)}{\varepsilon_o \varepsilon_r}$$

Relaxation time of trapped charge is inversely proportional to bombardment induced conductivity g_i. Sullivan[9] found experimentally that irradiation-induced conductivity in units of $\Omega^{-1}m^{-1}$ could be expressed as:

$$\text{(S9)} \qquad \gamma_i = \varepsilon_o \varepsilon_r R \gamma_o \left(\frac{i_o \left(U_o - V_C\right) \times 10^5}{a R \rho} \right)^m$$

Where, g_o is conductivity in absence of radiation or bombardment, ρ is density, i_0 is incident beam current, U_0 is beam energy, a is irradiated area, R penetration depth of the beam and m a constant related to trap distribution in the bandgap. By virtue of a coated and grounded surface, and in agreement with the discussion above, Vc in this equation can be omitted. This is the only modification that our system imposes on the initial model, that would not affect the development of the upcoming equations.

By solving the differential equation of Q(t) for the displacement current, as shown earlier, charge as a function of time can be expressed by:

$$\text{(S10)} \qquad Q(t) = Q(\infty)\left(1 - e^{-\frac{t}{\tau'}}\right)$$

where:

$$\text{(S11)} \qquad \tau' = \left[\frac{\left(1 - \sigma_{uo}\right) i_o}{\left(U_o - U_{c2}\right) \pi \varepsilon_o \left(\varepsilon_r - 1\right) R} + \frac{\gamma_i}{\varepsilon_o \varepsilon_r} \right]^{-1}$$

and

$$\text{(S12)} \qquad Q(\infty) = \frac{i_o\left(1 - \sigma_{uo}\right)}{\frac{\gamma_i}{\varepsilon_i \varepsilon_r} + \frac{\left(1 - \sigma_{uo}\right)}{\left(U_o - U_{c2}\right) \pi \varepsilon_o \left(\varepsilon_r + 1\right) R}}$$

Quantities defined in equations (A11) and (A12) are fundamental for the equation of charge evolution Q(t). It can be shown that the only requirements for Q(t) having the exponential decay form of Eq. (A10) are that

i) The leakage current is proportional to Q(t):

(S13) $$i_l = BQ(t) \quad \text{with} \quad B = \frac{\left(1 - \sigma_{uo}\right) i_o}{\left(U_o - U_{c2}\right) \pi \varepsilon_o \left(\varepsilon_r + 1\right) R}$$

ii) The backscattered current depends on Q(t) as

(S14) $$\sigma(t) = \sigma_0 + AQ(t) \quad \text{with} \quad A = \frac{\gamma_i}{\varepsilon_o \varepsilon_r}$$

iii) The displacement current is the time derivative of Q(t)

A here is dependent on the non-irradiated conductivity of the sample and permittivity, B depends on beam energy and secondary critical voltage (when $\sigma_{uo} = 1$).

For any definitions of A and B, the solution to Eq. (1) is a function of the form

(S15) $$Q(t) = \left[\frac{1 - \sigma_o}{A + B/i_o}\right]\left\{1 - e^{-(i_o A + B)t}\right\}$$

which has the same form of Eq. (S10). Therefore, particular definitions of parameters like electron beam-induced conductivity do not alter the form of the solution. It is worth highlighting there is a good agreement between evolution of stored charge Q(t) in the method by Song[5] and the method by Jbarra.[7]

The resulting expression for the specimen current is:

(S16) $$i_{sc} = \frac{\left(1 - \sigma_{Uo}\right)\gamma_i i_o}{\gamma_i + \dfrac{\varepsilon_r\left(1 - \sigma_{Uo}\right)i_o}{\pi\left(\varepsilon_r + 1\right)R\left(U_o - U_{C_2}\right)}} + \frac{\left(1 - \sigma_{Uo}\right)^2 \dfrac{\varepsilon_r i_o^2}{\pi\left(\varepsilon_r + 1\right)R\left(U_o - U_{C_2}\right)}}{\gamma_i + \dfrac{\varepsilon_r\left(1 - \sigma_{Uo}\right)i_o}{\pi\left(\varepsilon_r + 1\right)R\left(U_o - U_{C_2}\right)}} e^{-\frac{t}{\tau'}}$$

and in terms of A and B:

(S17) $$i_{sc} = \frac{A\left(1 - \sigma_{Uo}\right)i_o}{A + B} + \frac{B\left(1 - \sigma_{Uo}\right)i_o}{A + B} e^{-\frac{t}{\tau'}}$$

The first term in Eq. (A16) describes steady state leakage current, i_l^*, which can be obtained from the experimental data by noting the value of the specimen current at long irradiation times. Subtracting the i_l^* from the i_{sc} curve is equivalent to considering only the second term in Eq. (S16). This term has an exponential time dependence with 1/τ' that can be obtained from experimental data by fitting i_{sc}-i_l^* to the exponential decay described in Eq. (5), section III B, the resulting time constant τ' is associated with the time evolution of the leakage current i_l, as shown in the second term of Eq. (S4). Therefore, two parameters needed to determine i_l can be obtained from the data. Stored charge Q(t) is given by Eq. (S6) as the integral of displacement current over time. Stored charge can therefore be calculated from specimen current data, by subtracting the area below the leakage current from the area below the i_{sc}.

At long irradiation times, the second term in Eq. (S16) is negligible, and i_{sc} measured is the first term in Eq. (S16), which can be fully attributed to the steady state leakage current i_l^* . In the steady state, no net excess charges are being stored in the material because equilibrium is reached between trapping and detrapping. In the experimental set-up of Jbarra et al. [7] specimen current only measures displacement current, which would not allow for the calculations of stored charge. In the present model,[5] an additional step is needed to subtract the leakage current contribution from the specimen current measurement, as shown in Fig. S2.

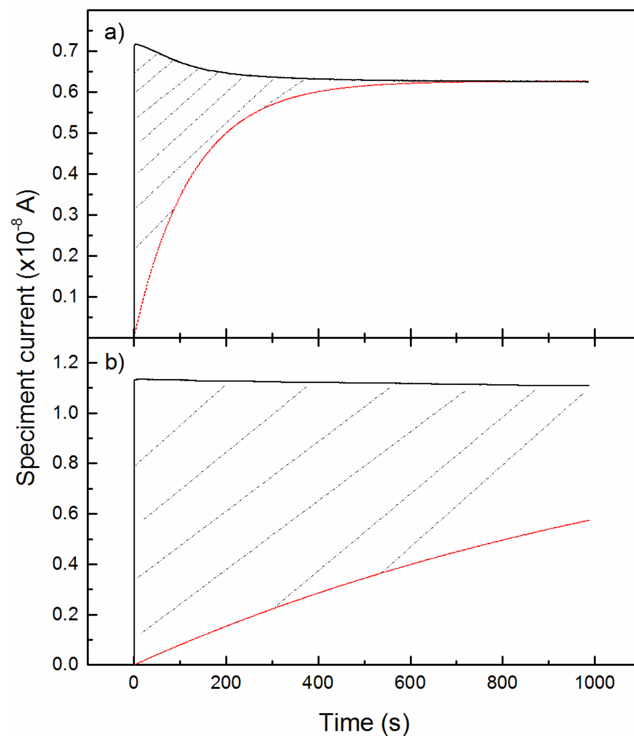
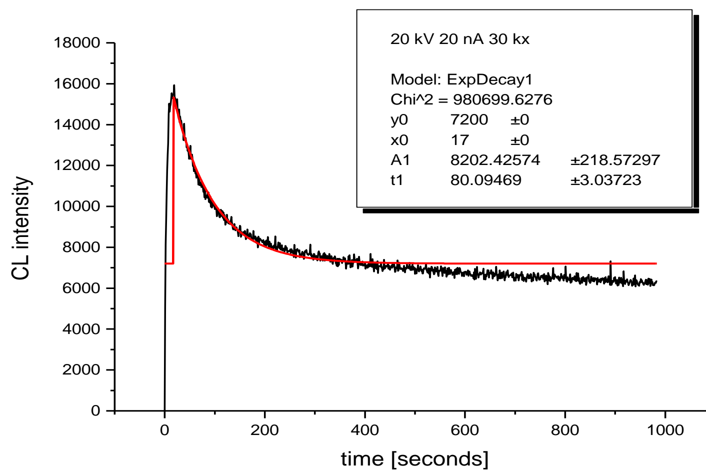


FIG. S2. (a) charge calculation when the steady state was reached during irradiation at 10 keV, 10nA, and 30kx magnification (b) charge calculation of stored charge when the steady state was not reached during irradiation at 20keV, 15 nA, and 60kx magnification.

In fact, a graphic technique based on Eq. (S16) can be used to calculate the stored charge avoiding the calculation or measure of parameters like τ' or g_i. The first term in Eq. (S16) describes the steady state leakage current, which can be obtained from the experimental data by noting the value of the specimen current at long irradiation times. In Fig. A1a the value of i_{sc} at long irradiation times, or i_l^*, is approximately $0.6x10^{-8}$ A. Subtracting the i_l^* from the i_{sc} curve is equivalent to considering only the second term in Eq. (S16). This term has an exponential time dependence with $1/\tau'$ that can be obtained from the experimental data by fitting i_{sc}-i_l^* to the exponential decay described in Eq. (5) in section III B. The resulting time constant τ' is the time constant associated with the time evolution of the leakage current i_l, as shown in the second term of Eq. (S4). The leakage current is zero at the beginning of the irradiation since charges need to be injected before the leakage process develops. Therefore, the two parameters needed to determine i_l can be obtained from the data, and $i_l(t)$ is plotted in Fig. A1 as red curves. Stored charge Q(t) is given by Eq. (S6) as the integral of the displacement current over time. The stored charge can therefore be calculated from the specimen current data, by subtracting the area below the leakage current from the area below the i_{sc} in Fig. S2. Integration from 0 to infinity would provide the stored charge at steady state. Integration from t=0 to the total irradiation time would provide the stored charge Q(t) built up during the irradiation time t. If the leakage current has reached the steady state during the irradiation time, the stored charge at steady state and the stored charge during irradiation are the same, as for the case shown in Fig. S2a. If the leakage current has not reached the steady state during irradiation time, both the i_{sc} and the leakage current i_l must be extrapolated to longer times. The injected charge during the irradiated period is smaller than the steady state stored charge. Fig. S2b shows an example where the steady state was not reached during irradiation.

3- Time based CL and SC Fits



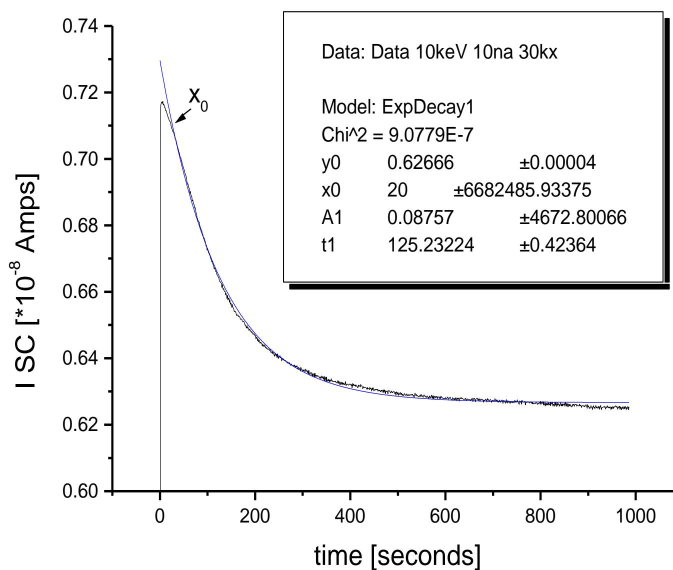


FIG. S3 NBE-time based CL scans are shown by the black curve (Top). Exponential decay fits are shown by the red curves. Results from the fits are shown in the data on the top right corner. CL scan was taken at 20kV 20 nA 30kx.

Specimen current scans are shown by the black curve (Bottom). Exponential decay fits are shown by the blue curves. Results from the fits are shown in the data on the top right corner. Values of χ^2 have been calculated from vales of time larger than x_o, as shown in the figure.

4- Parametric equations for *Time Constants,* τ_{CL}

Indeed, two regions of dynamic behaviour were identified for τ_{CL}, in both 10 and 20 keV an exponential decrease is seen up to 60 kx magnification. Beyond this point τ_{CL} shows variations of less than 10 %. This indicates that a saturation point has been reached at 60 kx whereby increasing current density does not degrade CL emissions efficiently any further. This high systematicty leads to a parametric expression of τ_{CL} as a function of experimental parameters:

$$\tau_{CL} = k_1 E_0 + k_2 E_0^2 e^{-0.08M} \quad (6)$$

With $k_1 = \frac{1.5 \times 10^{15} s}{kg\, m^2}$, and $k_2 = \frac{1.9 \times 10^{31} s^3}{kg^2 m^4}$

where E_0 is the primary beam energy in keV and M is magnification x1,000. It is noted that magnification and beam energy are first order factors in CL evolution, and beam current plays a minor role. This parametric equation is useful for the estimation of CL time constants; allowing to determine when emissions achieve a steady state. However, due to the poor systematicity in τ_{SC}, it was not possible to derive an equation to describe the progression of the SC in terms of time constants at various magnifications, an indication to a lack of causality between CL and direct e-beam charging processes. In the next section, the impact of degradation on the relative change in CL intensity will compared to the corresponding SC measurements.

5. CL and SC Evolution to Steady State

In this section, the extent of variations in CL during irradiation will be compared with the extent of variations in SC to assess correlation between optical and electrical phenomena. To this end, maximum to steady state ratios of CL emissions, I_{CLss} and specimen currents I_{SCss} were estimated as a percentage change, and are shown in Fig.4. At 10 keV and 10 nA, I_{CLss} dropped from 25% to 18 % from 15 kx to 30 kx magnification, remaining at 20 % for magnifications up to 120 kx. I_{CLss} under 20 keV, showed very similar behaviour for all beam currents investigated. Steady state values, at 20 keV, fell from 50 % to 40 % between 15 kx to 30 kx magnification and then decreased slightly to 38% at 60 kx and 120

kx. Similar to the trends observed in τ_{CL}, evolution of I_{CLSS} for both energies showed an overall decrease with increasing magnification up to 60kx, where it plateaus.

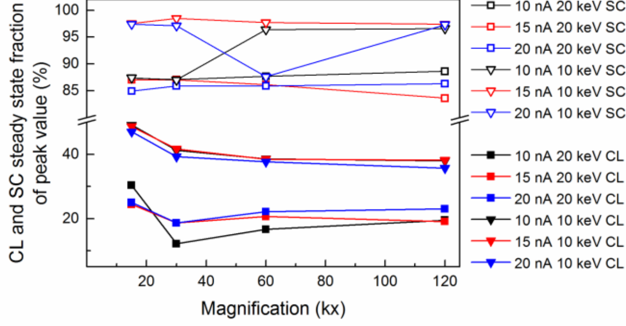


FIG. S4. Graph of the Percentage Change in CL and SC Values from Peak to Steady State Ratio. CL is shown in full symbols and lines, SC shown in open symbols and dashed lines. Square symbols show measurements at 10 keV and triangles those at 20 keV.

From analysis of exponential fits of change in CL intensity, an expression can be derived to describe I_{CLSS} in terms of beam energy and magnification settings, i.*e.* an equation to predict the steady state CL emission was found such that:

$$I_{CL_{SS}} = k_3 E_0 + 4\, e^{-M/_{18}} \tag{7}$$

With $k_3 = \frac{10^{16} s^2}{kgm^2}$

where $I_{CL_{SS}}$ is the change in CL to steady state as a percentage and M is magnification x 1,000 times.

Similarly, SC steady state was investigated, as seen in Fig.4. At 10 keV, all currents investigated did not diverge by more than 10 % at all magnifications, with all steady state values falling within 83 % and 90 %. At 20 keV the dynamics were much more complicated with all current values remaining constant from 15 kx to 30 kx. At 30 kx the dynamics diverge, with 10 nA current showing an increase in final percentage, 15 nA remaining constant and 20 nA decreasing. It is interesting to note that, all values converge at 120 kx magnification at 95 % of the peak current. At saturation, traps in the sample are filled and injection rate will be decreased. At higher beam energies there is a greater capacity to trap charges because a larger volume is affected as penetration depth increases. Causes of these irregularities are unclear but point to there being a multiplicity of events, possibly including dielectric breakdown as a factor in SC progression.

Summarizing from section 1 and 2, neither the time constants nor the amount of degradation seem comparable in CL and SC measurements, suggesting that direct effects from electron beam bombardment such as influence on electron hole generation and recombination efficiency as a result of a nascent space charge region, do not seem likely. Amongst other, the generation of additional intrinsic defects (V_{Ga} or V_N) is also unlikely under the low energy beam used here,[10] all suggesting direct electron beam effects are not primary actors in NBE CL degradation. The following section discusses charge trapping, its quantification as well as a likely degradation model, where the activation of existing V_{Ga} dominate charge trapping and primarily modulates NBE CL.

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