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Modeling optical second harmonic generation for oxide/semiconductor interface characterization☆,☆☆

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ABSTRACT

In this work, we present physics-based numerical modeling of experimental time-dependent optical second harmonic generation data from an oxide/semiconductor (SiO_2/Si) interface. A comprehensive numerical solution to the Poisson–Boltzmann equation has been developed here, using the Newton–Raphson method at different time instances. It incorporates the trapping behavior of photo-excited charge carriers at the silicon dioxide/silicon (SiO_2/Si) interface, within the silicon dioxide (SiO_2) and at the SiO_2 surface, in order to model the second harmonic photon count data obtained from our in-house experimental setup. This yields a quantitative analysis of the SiO_2/Si interface, oxide, and surface charge densities, and provides a contact-less and non-invasive optical technique for oxide/semiconductor interface characterization.

1. Introduction

Contactless and non-invasive characterization of insulator/semiconductor interface can facilitate the development of a range of important semiconductor devices. Optical second-harmonic generation (SHG) is a sensitive technique well suited for characterizing such layered structures. The dependency of SHG on the doping concentration in silicon (Si) [1], silicon dioxide (SiO_2) thickness [2], and measuring conduction band offset at the Si/SiO_2 interface [2] has demonstrated its potential and advantages over traditional capacitance/conductance as well as X-ray Photoemission Spectroscopy (XPS) and Internal Photoemission (IPE) methods for in-situ characterization. Mapping of carrier dynamics [3] and trapped charge [4–6] have also been demonstrated using this technique. While SHG based semiconductor/dielectric interface, specifically Si/SiO_2, characterization has been under development [7–11], the method is still not standardized enough to allow easy extraction of quantitative interface characteristics. This is due in part to the absence of models that are handy yet comprehensive. The pioneering effort by Mihaychuk et al. [7], uses an elementary surface charge model. Neither this, nor the following efforts from Damianos et al. [12] and Ionica et al. [13], include interface charge density, or the spatio-temporal dependency of the oxide trapped charge, which are seen to be significant in our experimental samples. The latter two analyses [12,13] are based on matching the time variation of SHG with that of the square root of the interface electric field. Hence, these models lack a direct correlation of the SHG with the trapped charges. Here we present a comprehensive numerical model that solves the Poisson–Boltzmann equation using the Newton–Raphson method in a time stepped iterative approach to mimic the time-dependent second harmonic data obtained from our in-house experimental setup. It enables us to analyze the spatio-temporal profile of the interface charge density at SiO_2/Si interface along with the SiO_2 surface and oxide charge density.

The SHG process involves doubling the frequency of incident light, as a nonlinear or non-centrosymmetric medium converts the cumulative energy of two photons of the incident beam into a single photon [14,15]. Silicon is a centrosymmetric material. The nonlinearity or non-centrosymmetric nature arises due to the broken symmetry at the surface of silicon and at the interface with SiO_2 [5,7].

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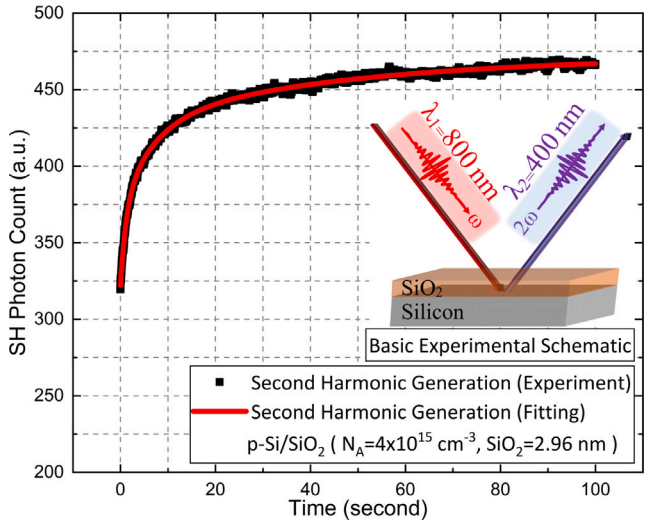

Fig. 1. Time dependent second harmonic (SH) photon counts from experiment, fitting of semi-empirical Eq. (1) to extract various trapping time constants. The schematic of SHG characterization technique captured in the inset.

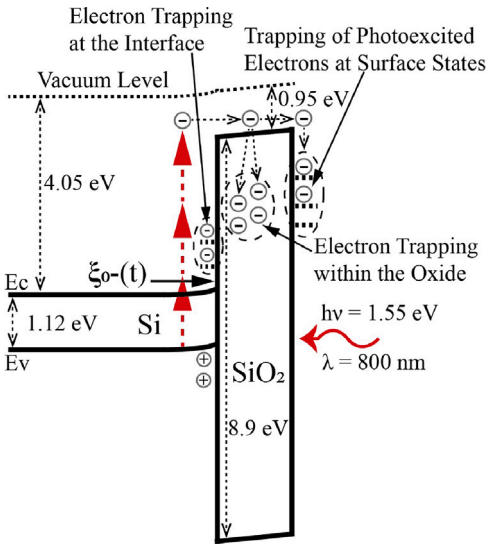

Fig. 2. Schematic representation of the trapping of electrons excited through the multiphoton process that has been simulated here.

2. Basic experiment and observations

An RCA cleaned 1∼5 Ω-cm ($N_A \approx 4 \times 10^{15}$ cm^{-3}) p-silicon (100) substrate is used for thermal oxidation (dry oxidation at 850 °C for 10 s using rapid thermal process) to grow ∼2.96 nm SiO_2 (measured using ellipsometer). An ultrafast laser beam (λ = 800 nm, average power = 100 mW, pulse width ≈ 120 fs, pulse repetition rate = 1 kHz, spot diameter = 1 mm) is focused on the grown SiO_2/Si sample with an incident angle of 45° (schematically shown inset of Fig. 1). The generated second harmonic of the incident ultrafast pulses is recorded over time (shown in Fig. 1 Second Harmonic Generation (Experiment)). The entire experimental setup is designed and developed by us within our laboratory and will be discussed in detail elsewhere [16].

A trend of gradually increasing optical second harmonic intensity $I^{(2\omega)}(t)$ from the sample has been observed (Fig. 1). The generated second harmonic intensity from the SiO_2/Si interface, tends to saturate over time. The explanation for the time varying signature of the second harmonic photon counts is provide in the following section.

3. Explanation

A phenomenological explanation for the time dependent second harmonic generation is depicted through Fig. 2 and described as follows: As the ultrashort pulses irradiate the sample, the carries (electrons) close to the SiO_2/Si interface get excited through multi-photon process (depicted using red dashed arrows in Fig. 2). Within a short duration of time (corresponds to the time constant τ_1 = 0.98 s in Eq. (1)), some of these photo-excited electrons are getting trapped at the SiO_2/Si interface states (depicted in Fig. 2 through 'Electron Trapping at the Interface'). The continuous irradiation generates the exited carriers throughout the experiment and as the trap levels are filled at the SiO_2/Si interface few of these electrons surmount the SiO_2 conduction band barrier and get trapped into the available trap states inside the oxide and SiO_2 surface (corresponds to the time constants τ_2 = 7.81 s and τ_3 = 85.61 s accordingly in Eq. (1) and depicted in Fig. 2 as 'Electron Trapping within the Oxide' and 'Trapping of Photoexcited Electrons at Surface States' respectively). Continuous trapping of photo excited electrons at the SiO_2/Si interface, within the SiO_2 and at the SiO_2 surface creates a time dependent electric field in the direction of the SiO_2 surface from SiO_2/Si interface, described as $\xi_{0-}(t)$ in Fig. 2. The electric field $\xi_{0-}(t)$ increases over time due to the charge separation as the photo-excited electrons further getting trapped. The rise in the electric field $\xi_{0-}(t)$ results in an increase in the second harmonic photon counts (shown in experimental SHG in Fig. 1). The phenomena is called electric field induced second harmonic generation (EFISHG). Over time the electric field $\xi_{0-}(t)$ and the EFISHG starts to saturate as the available states are getting filled by the excited electrons. A semi-empirical equation of the form:

$$I^{(2\omega)}(t) = A_0 + A_1 exp\left(\frac{-t}{\tau_1}\right) + A_2 exp\left(\frac{-t}{\tau_2}\right) + A_3 exp\left(\frac{-t}{\tau_3}\right) \quad (1)$$

is first used to fit the experimental time-dependent SH intensity data, where the parameters τ_1, τ_2 and τ_3 are understood to represent the trapping time constants for the time dependent trapped charges at the SiO_2/Si interface $\left(Q_{it}^{Trapped}(t)\right)$, within the oxide $\left(Q_{ox}^{Trapped}(t)\right)$, and at the surface of SiO_2 $\left(Q_{st}^{Trapped}(t)\right)$ respectively. Their values signify the time taken to fill a portion (63%) of the available trap states at various positions mentioned above. The time constants are fed into the numerical solver described in the following section, to calculate the time-dependent trapped charge and electric field $\xi_{0-}(t)$.

4. Numerical modeling and discussion

We have developed an algorithm to solve the Poisson–Boltzmann equation using the Newton–Raphson method at different time instances with the aforementioned trapped charges at that time instant. The algorithm is depicted through the flowchart shown in Fig. 3.

The upper half of the flowchart provides us with an initial solution to the Poisson–Boltzmann equation and the electric field at the interface at t = 0 s or before laser irradiation. The lower half begins with discretization of the entire (experiment or simulation) time window in steps (Δt), and by defining the trapping probabilities, and calculating the spatio-temporal profile of the trapped charges from rate equations. Then the Poisson–Boltzmann equation is solved with the time dependent trapped charges at each time instance.

We note that the instantaneous distribution of the photo-generated carriers inside the silicon is not considered here, as the 1 kHz pulse repetition rate and 120 fs pulse width in our case ensure a time delay of 0.99999999988 ms between two consecutive pulses. This is much larger than the lifetime of photo-generated carriers in the silicon region. Trapped charges have much larger lifetime or detrapping time, and are therefore the only contributor to the EFISHG here. These charges obviously create a difference in quasi-Fermi levels between the

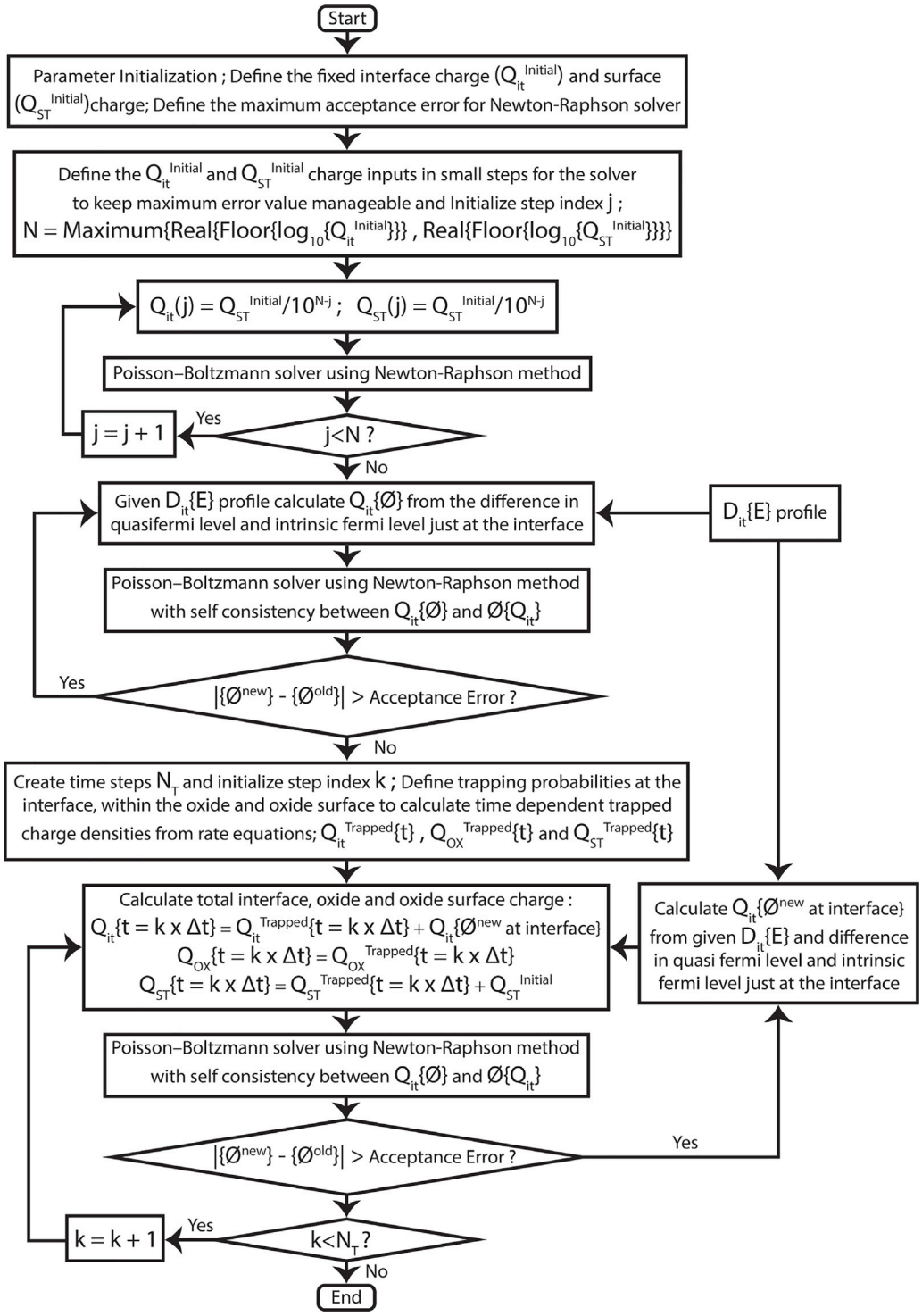

Fig. 3. Flowchart of the time stepped numerical solver that captures the time dependent trapping of photo excited electrons at the SiO_2/Si interface, within the oxide and at the surface states of SiO_2.

bulk silicon region and oxide surface. Based on the aforementioned timescales, a Boltzmann distribution for the carriers with quasi-Fermi levels solves the Poisson–Boltzmann equation in between the laser pulses. In contrast to this, the 80 MHz pulse repetition rate that has been used in the previously reported literature demands consideration of transient carrier distributions.

Now, in terms of validation of the numerical solver by benchmarking to standard TCAD software, the available possibility was a steady-state comparison with predefined fixed interface and oxide charges. A side by side comparison of the results using our technique with the result from 'Sentaurus TCAD' is shown in Fig. 4. The interface charge $Q_{it}\{\phi\}$ and potential profile $\phi\{Q_{it}\}$ in our model are intertwined in a self-consistent manner to capture the occupation probability of the interface states at different time instances. We have considered an interface trap state distribution similar to Thoan et al. [17] because of the similarity of their fabrication process to ours.

The Poisson–Boltzmann solver yields time evolution of the electric field $\xi_{0-}(t)$ and eventually the electric field induced second harmonic

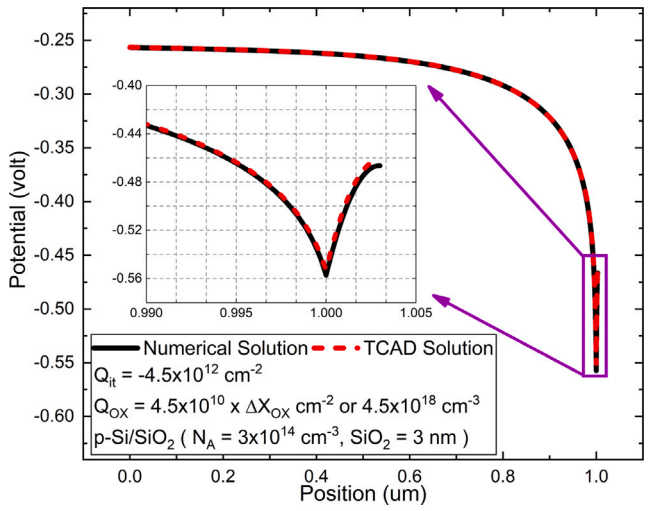

Fig. 4. Comparison of simulation outcomes from Synopsys TCAD (Sentaurus Device) and our numerical solver for the validation of our solver.

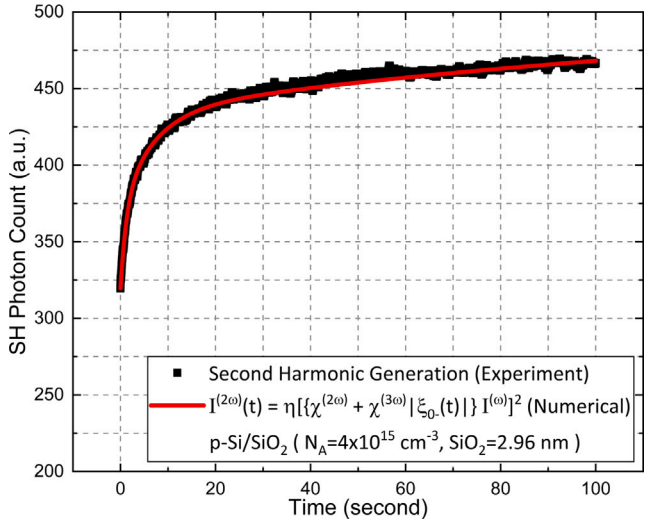

Fig. 5. Comparison of experimental time dependent second harmonic photon counts and prediction from simulation result using our time stepped numerical solver.

Table 1
Extracted interface, oxide and surface charge densities.

Time (s)	Q_{it} (cm^{-2})	Q_{ox} (cm^{-2})	Q_{st} (cm^{-2})
t = 0	1.7802×10^{11}	2.0×10^{11}	-1.2902×10^{12}
t = 100	4.1414×10^{11}	0.7278×10^{11}	-1.3335×10^{12}

The parameter values and spatio-temporal profiles of trapped charge density may be obtained by sending an email request to the corresponding author.

generation (EFISHG) intensity (shown in Fig. 5) by using the following in Eq. (2):

$$I^{(2\omega)}(t) = \eta \left[\left\{ \chi^{(2\omega)} + \chi^{(3\omega)} \left| \xi_{0-}(t) \right| \right\} I^{(\omega)}(t) \right]^2 \quad (2)$$

where $\chi^{(2\omega)}$ and $\chi^{(3\omega)}$ denotes the second order surface dipole and third order bulk dipole susceptibility respectively at SiO_2/Si interface.

The initial values of charge density used in the simulator, and the charge densities at a final later time, are presented in Table 1. In the table, t = 0 s and t = 100 s conditions accordingly represent the charge densities before laser pulse irradiation, and charge densities with the photo excited trapped charges after 100 s of irradiation.

5. Conclusion

In summary, our developed numerical model successfully correlates the experimental SHG results with a quantitative analysis of the SiO_2/Si interface charge, the spatio-temporal profile of the oxide trapped charge, and the SiO_2 surface charge densities. Quantitative analysis of these trapped charge densities could pave the way for the development of a contactless and non-invasive optical second harmonic based oxide/semiconductor interface characterization tool for this and other material systems of interest. Our own efforts on a high-k/Si will be presented elsewhere [16]. Alongside the quantitative analysis of charge densities, through our model and experimental data, we can determine the direction of band bending at an oxide/semiconductor interface on a contactless sample.

CRediT authorship contribution statement

Binit Mallick: Planning of the study, Development of the experimental setup, Performing the experiment, Interpreting the results, Algorithm development, Coding of the numerical solver, Writing of the manuscript. **Dipankar Saha:** Planning of the study, Development of the numerical solver. **Anindya Datta:** Planning of the study, Development of the experimental technique. **Swaroop Ganguly:** Planning of the study, Interpretation of the results, Development of the numerical solver, Writing of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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