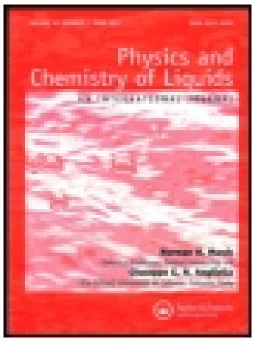

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Investigation of the effect of finite-sized ions on the nanowire field-effect transistor in electrolyte concentration using a modified Poisson–Boltzmann model

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ABSTRACT

One-dimensional (1D) nanowire field-effect transistors (FETs) have recently played a major role in sensing applications. Due to charging of the surface functional chemical groups with protonation and deprotonation, the transport properties of these nanowire transistors affect the aqueous environment, altering the electrical double layer (EDL) potential drops and charge distributions in the electrolyte concentration. In this work, we have implemented the simple modified Poisson–Boltzmann (MPB) theory in a 1D silicon nanowire FET, and the effect of the various finite sizes of ions in z:z symmetric electrolyte concentration was investigated. For a given ionic concentration and surface charge, the EDL potential drop, accumulation of charges and the charge distributions of NaCl and CsCl ions were studied. From the MPB model results with the nanowire FET, it was observed that the potential drop of the EDL depends on the size of the ions in the electrolyte. The study of various electrostatic investigations of finite-sized ions was successfully done by implementing the MPB model on a silicon nanowire FET. It can be used in both chemical and biological sensors.

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Nanowire FET; ionic size effect; MPB model; electrical double layer

1. Introduction

One-dimensional (1D) nanostructures, such as silicon (Si) nanowires [1–3] and carbon nanotubes [4], are excellent building blocks in nanoscale devices. Due to nanoscale confinement, nanowire field-effect transistors (FETs) show higher sensitivity [5]. This higher sensitivity arises due to the drastic increase in the surface-to-volume ratio when the diameter of the nanowire decreases to the nanometre scale [6]. The importance and applications of Si nanowire FETs in areas such as chemical and biological sensors are reported by Cui *et al.* [7].

The dopant-free Si nanowire, and the metallic nanowire on Schottky barrier FET, has a higher on–off ratio [8,9]. Nanowire Schottky barrier FETs can be used for both chemical and biological sensors to sense the change of electrical signals with respect to the gate areas and local charges [10,11]. Multiscale modelling of nanowire-based Schottky barrier FETs, and the application in liquid environments, was developed by Nozaki *et al.* for sensors [12,13].

Modifications of surface charges, and alteration of ions in the solution, vary the conduction of electric current in the nanowire FET. This variation can be measured by chemical and biological sensors. The airfoil of the nanowire FET in electrolyte concentration can be charged via protonation and deprotonation of the surface functional chemical groups. This charged surface works as an additional local gate. Hence, the surface charges affect the potential profile in the nanowire

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FET. Due to formation of an electrical double layer (EDL) at the solid–liquid interface, the surface potential is exponentially reduced due to the screening effect produced by the counterion's surface charges. This affects the local and back gate fields of the nanowire FET. The transport properties of the nanowire FET are affected strongly by the formation of the EDL [14,15].

The Poisson–Boltzmann approach is one of the most widely used analytical methods to explain the electrolyte concentration at the solid–liquid interface. Even so, it does not account for the finite size of ions, as it assumes that they have no size, i.e. they are point-like charges, and so it does not accurately represent the steric effects. The Poisson–Boltzmann model cannot be applied to high electric fields and electrolyte concentration. The modified Poisson–Boltzmann (MPB) is one of the main models used to analyse the ionic effects in the electrolyte concentration.

The conventional and traditional MPB formalism in the literature is the approach developed by Outhwaite and co-workers, among others [16]. The formalism consists of solving a non-linear integro-differential equation, which takes into account inter-ionic correlations and exclusion volume effects. To date, this approach has been one of the most successful theories in describing the structure and thermodynamics of EDLs in the electrolyte solution regime. In this study, however, we will be exploring a more recent theory formulated by Borukhov *et al.* [17]. This latter, also called an MPB theory, essentially tags an exclusion volume component on to the non-linear Poisson–Boltzmann equation. This MPB theory provides more support for higher electric fields and ionic concentrations [18–20]. Various MPB methods, and the importance of simple MPB equations, are elaborately reviewed by Hamou *et al.* [21]. High concentration and high surface charge studies were done by implementing a conventional simple MPB model in the z:z electrolyte concentration. This was done for various finite volume sizes of ion effect. It produces results which are in good agreement with the Montecarlo simulation results reported by Ping Lou *et al.* [22].

Among the many ion-sensing nanowire FETs [23,24] developed, however, finite-size ionic effects on the Si nanowire FET in the electrolyte concentration, using a MPB model, have not been clearly defined until now.

In this work, we focused on investigating the effect of various finite volume size ions. This was done by computing the EDL potentials and charge distributions using the Borukhov *et al.* MPB model, on the Schottky barrier nanowire FET, and for a given z:z electrolyte concentration and surface charge distribution. The simple MPB equation is implemented on the airfoil of the nanowire FET to determine the electric potential drop and charge distribution of various sizes of finite volume ions. For the sake of clarity in this study, we concentrated more on ionic excluded volume effects. The results substantiate the hypothesis that the EDL potential drop and charge distribution depend on the finite sizes of the ions in the electrolyte concentration. The change in the EDL potential drop and charge distributions, with the implementation of simple MPB, can be used to find various ions in chemical and biological detectors.

2. MPB model

The Poisson–Boltzmann equation is one of the generalised solutions used to deal with the solid–liquid interface and the interaction of molecules of various ionic strengths. In the equation, each ion concentration distribution, $c_i(r)$ (mol/lit) is given by the Boltzmann distribution,

$$c_i(r) = c_i^{\infty} \exp(-\frac{z_i e(\psi(r) - \psi_0)}{kT}). \tag{1}$$

In Equation (1), $\psi(r)$ is the electric potential forces that act on each ion, c_i^{∞} is the bulk concentration of the ion 'i', z_i is the valence number of ion 'i', e is the proton charge (1.6×10^{-19} C), T is the temperature (°K) and k is the Boltzmann constant (1.38×10^{-23} J/°K). ψ_0 is the liquid electrode potential which is set to be 0 V, and is neglected in this work. The molar ionic concentrations, M_i, are expressed as $M_i = c_i^{\infty}\ 10^{-3}/\mathrm{N_A}$, where N_A is the Avogadro constant

(6.022×10^{23}). The volume-free charge distribution of each ion is given by

$$q_i(r) = z_i e c_i(r). \tag{2}$$

From Equation (2), the total free charge density is given by

$$q(r) = \sum\nolimits_i q_i(r) = \sum\nolimits_i z_i e c_i(r). \tag{3}$$

The potential distribution, and charges linking with the Poisson equation, is defined as

$$\nabla.(-\varepsilon \nabla \psi(r)) = q(r) \tag{4}$$

where $\varepsilon = \varepsilon_0 \varepsilon_r$, ε_r is the relative permittivity of the solution and ε_0 is the dielectric constant of the vacuum. The relative permittivity for water, Si and SiO_2, is 80, 12.1 and 4.2, respectively. The non-linear Poisson–Boltzmann equation has taken shape by combining the charge distribution and electrostatic potential distribution, and is expressed as

$$-\varepsilon \nabla^2 \psi(r) = \sum\nolimits_i z_i e c_i^{\infty} \exp(-\frac{z_i e \psi(r)}{kT}). \tag{5}$$

However, the Poisson–Boltzmann equation assumes that ions with no size can be treated as point charges, and is not possible to apply high electric fields and higher electrolyte concentration. Borukhov *et al.* suggested a MPB, which takes into account the finite volume of ions and includes steric effects. It bears up for larger electric potential and higher electrolyte ionic concentration.

The modified part of the Boltzmann distribution in the MPB equation of co-ions is given by,

$$c_i^-(r) = \frac{c_i^{\infty} \exp(-\frac{z_i e \psi(r)}{kT})}{1 + 2v \sinh^2(\frac{z_i e \psi(r)}{2kT})}. \tag{6}$$

For counterions,

$$c_i^+(r) = \frac{c_i^{\infty} \exp(\frac{z_i e \psi(r)}{kT})}{1 + 2v \sinh^2(\frac{z_i e \psi(r)}{2kT})}. \tag{7}$$

In Equations (6) and (7), $v = (z+1)a^3 c^{\infty}$ is the total volume fraction of the positive and negative ions (called the packing parameter) and a is the effective ion size. We consider a binary symmetric electrolyte and assume that the planar electrode has a negative charge. Thus, we have $z = |z_+| = |z_-|$ and $c^{\infty} = c_+^{\infty} = c_-^{\infty}$, so the MPB equation can be rewritten as

$$-\varepsilon \nabla^2 \psi(r) = -zec^{\infty} \frac{2 \sinh\left(\frac{z_i e \psi(r)}{2kT}\right)}{1 + 2v \sinh^2\left(\frac{z_i e \psi(r)}{2kT}\right)}. \tag{8}$$

From Equation (8), we can see that by changing the value of effective ion size a, the packing parameter is changed, and it can affect the EDL potential distribution and charge distributions. Here, we have analysed the change of electric potential drop and charge distribution of various ions in electrolyte concentration.

3. Nanowire FET model

To estimate the change in electric potential for the alteration in various ions in the electrolyte concentration, we have designed a simulation model using the COMSOL TCAD software. The model shows the 3D and 2D view of the Si nanowire FET design visualised in Figures 1(a,b). We have used five domains: bottom SiO_2 layer (1000 μm length), 20 nm diameter Si nanowire, 100 nm electrodes

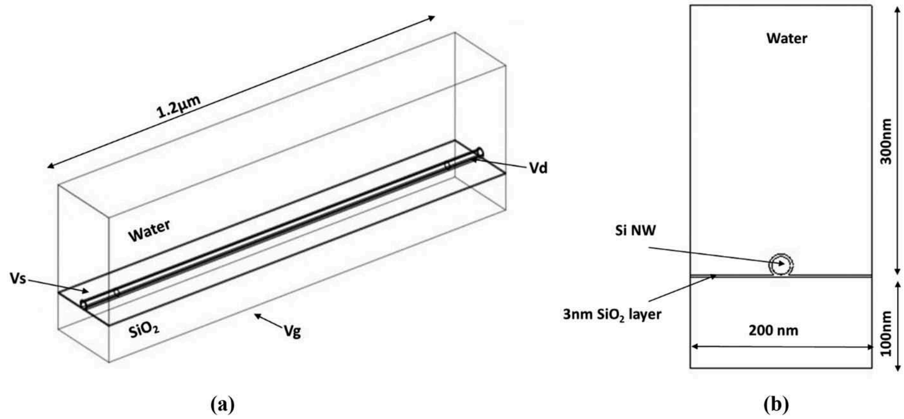

Figure 1. (a) 3D view of nanowire FET model. (b) 2D view of nanowire FET model.

for drain and source contacts, 3 nm SiO_2 layer and the meridian of the layer which is constructed of the aqueous environment to provide the electrolyte concentration. Here, we have implemented a MPB model in an aqueous environment to determine the electric potential $\psi(r)$. In the solid–liquid interface, the surface charge density is applied in between the Si nanowire and the electrolyte

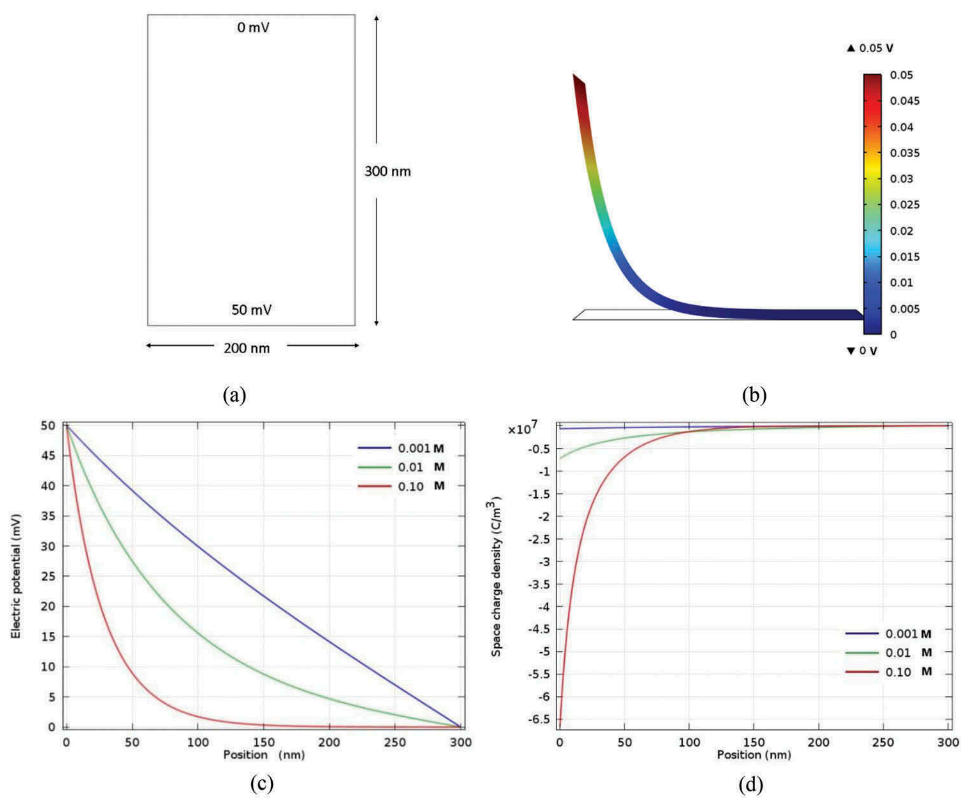

Figure 2. (a) Geometry of MPB applied in 2D model. (b) 2D view of the electric potential profile. (c) EDL potential characteristics with 0.001, 0.01 and 0.1 M, ionic concentrations. (d) Charge distributions with various concentrations.

concentration. Gate, source, and drain, electric potentials are applied to the respective contacts. For all calculations, a gate voltage V_g of 5 V and a drain voltage V_d of 0.5 V is used.

4. Results and discussion

4.1. *Simple 2D model analysis*

To confirm our model results, initially we tested with the simple 2D solid–liquid interface model. The model dimensions were length 300 nm and width 200 nm. Here, we have chosen a bias

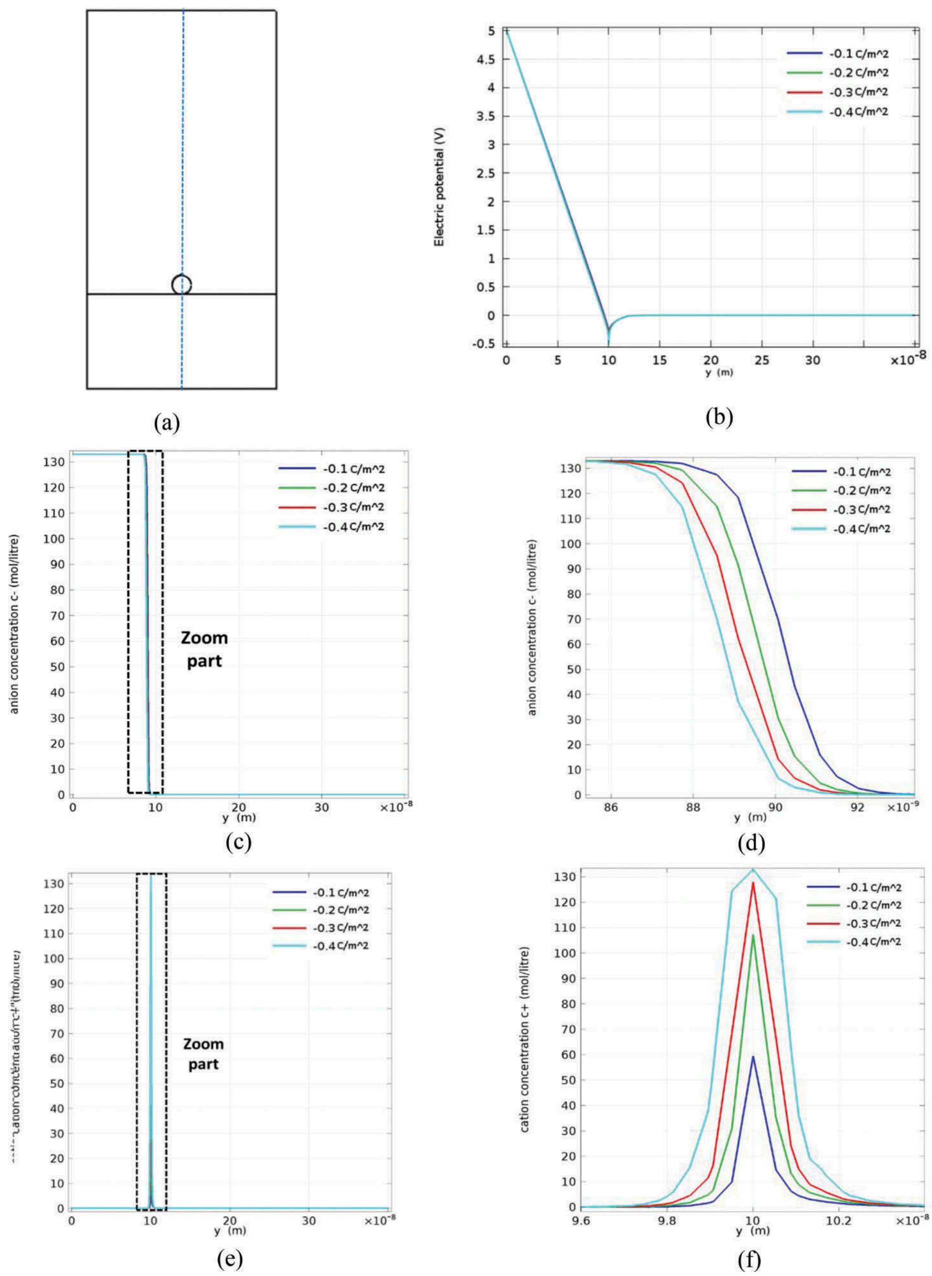

Figure 3. (a) 2D nanowire FET Model with MPB applied. (b) EDL potential characteristics for a range of surface charge distributions (−0.1 to −0.4C/m^2) in 0.001 M NaCl ionic concentrations. (c–f) anion and cation concentrations (mol/litre) and corresponding magnified view for the different charge distributions.

voltage of 50 mV, the dielectric constant of water is 78.5 and the effective ion size is 3×10^{-10} m. The Figure 2(a) shows the basic 2D model and 2(b) shows the electric potential profile of the basic model. Figure 2(c) shows the electric potential distribution, and Figure 2(d) shows the charge distributions, for different ionic concentrations. The EDL potential drop is increased with increasing concentration, and it is reflected in the charge distributions as well. The effects are in good agreement with the model of Nozaki *et al.* [13].

4.2. *2D nanowire FET EDL analysis*

Here, we analysed the 2D model of the nanowire FET with a NaCl 0.001 M electrolyte solution. EDL potential profiles, and anion and cation concentrations, are depicted in Figures 3(b,c–e). From Figure 3(c), we can clearly infer that the cation concentration is higher when the surface charge is increased. From Figure 3(e), we can see that the anion concentration reduced before arriving at the nanowire position, when the surface charge density increases. This confirms that changes in applied surface charges affect the ion distributions. This will be reflected in the EDL potential and charge distribution characteristics.

4.3. *Results of EDL analysis with different finite-size ions in various electrolyte concentrations*

For investigation of electric potential drop between various ions in electrolyte concentration, we have chosen NaCl and CsCl electrolyte solutions. In NaCl, the effective ion size, *a*, of Na is

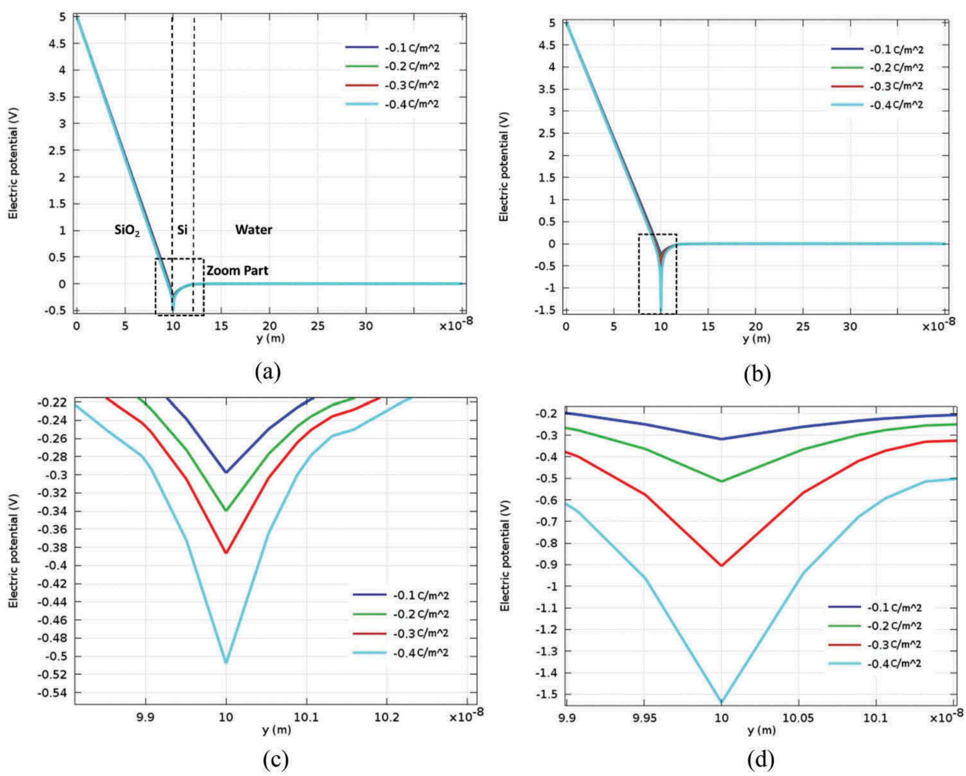

Figure 4. EDL potential distribution of (a) NaCl and (b) CsCl in electrolyte concentration 0.001 M with implementation of MPB model. Here, we have kept all parameters constant, apart from the surface charge which varied negatively from−0.1 to −0.4C/m^2. Parts (c) and (d) show the magnified view of NaCl and CsCl ionic concentration with EDL formation.

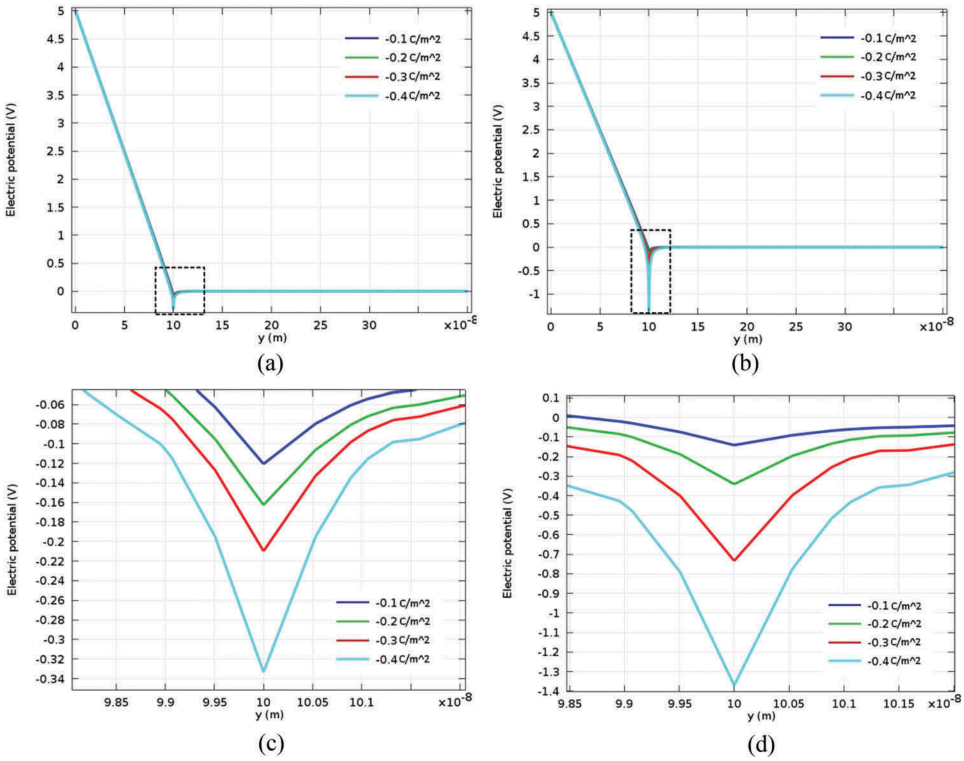

Figure 5. EDL of 1 μM NaCl (a) and CsCl (b) ionic concentration, with enlarged views in (c) and (d).

2.32×10^{-10} m and in CsCl *a* of Cs is 3.2×10^{-10} m .When the charge density is larger than 0.1 C/m^2, the ionic size effect is more important in electrolyte concentration. Here, we have studied the surface charge density in the range between −0.1 to −0.4 C/m^2.

Figures 4(a,b) show the EDL potential drop of the NaCl and the CsCl ions with 0.001 M ionic concentration. In Figures 4(c,d), an enlarged view of the EDL potential drop of the NaCl and CsCl ions is shown. From this expanded view of the image, we note that the larger the size of Cs ion, the higher is the negative potential drop, compared with the Na ions. Even for a surface charge of −0.1 C/m^2, the ions approach their closest value, whereas an increase in the surface charge distribution causes a difference in potential drops between the two ionic concentrations.

Figures 5(a,b) show the EDL potential drop at 1 μM ionic concentrations. Figures 5(c,d) show the magnified view of the EDL of NaCl and CsCl ionic concentration. Increasing ionic concentrations reduce the possible fall in the EDL. For constant surface charge density, the higher (0.001 M) ionic concentration results in a lower potential drop compared with (1 μM) the lower concentration due to the potential drop across the diffuse layer. The difference in the electric potential drop is caused only by the change of ions, since we maintained all parameters constant except the ion size.

4.4. *3D nanowire FET charge accumulation and distribution analysis*

Figures 6(a,b) show the 3D perspective of the accumulated charges on the nanowire surface at the solid–liquid interface for $Vds = 0$ V and $Vds = 0.5$ V bias voltage, at $Vg = 5$ V. Figures 7(a,b) show the NaCl finite-size ion effects on charge distributions with various surface charge distributions in

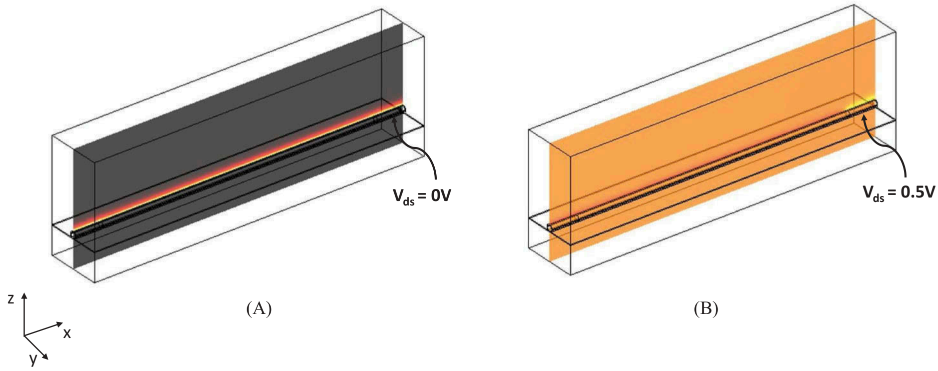

Figure 6. 3D view of accumulated charges on the nanowire surface at solid–liquid interface for (a) *Vds* = 0V, and (b) *Vds* = 0.5V bias voltage. *Vg* = 5V at 0.001 M NaCl electrolyte concentration with surface charge density of 0.1 mC/m^2.

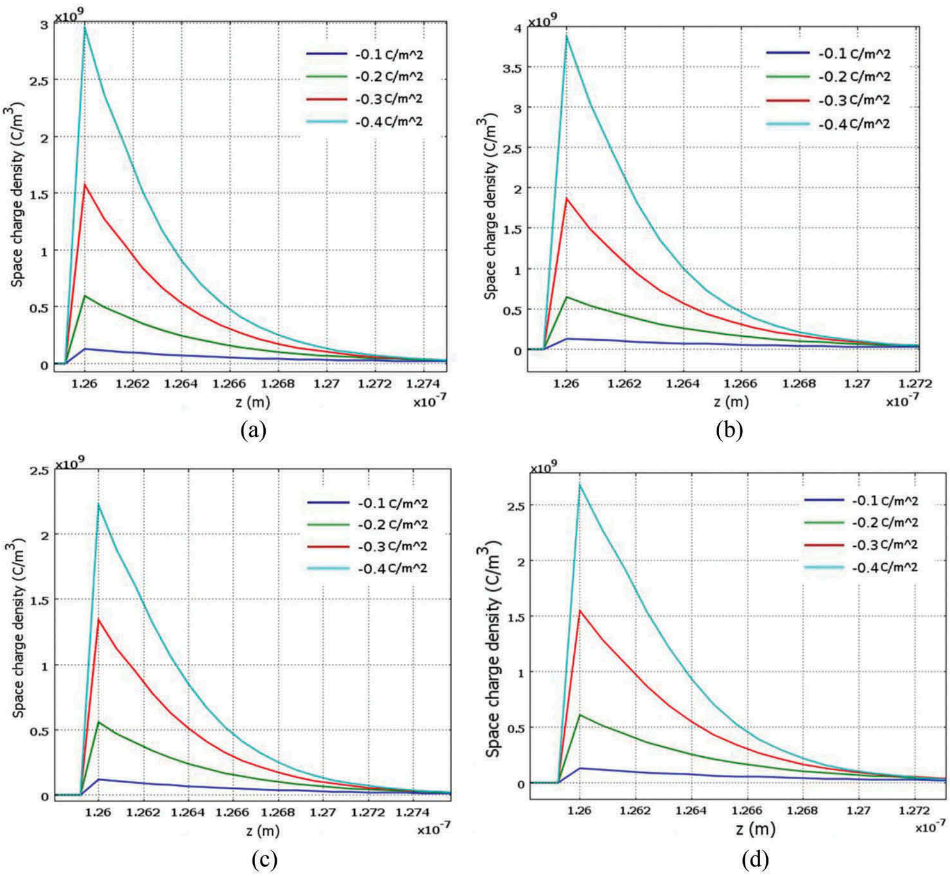

Figure 7. Charge distributions for NaCl ion effect for various surface charge distributions at 1 (a) and 0.001 M (b) ionic concentrations. Charge distributions for CsCl ion effect for the same surface charge distributions at 1 (c) and 0.001 M (d) ionic concentrations.

1 and 0.001 M ionic concentrations, respectively. Figures 7(c,d) show the same result for CsCl finite-size ions. From the figures, we can confirm that when the concentration is decreased, the charge distribution is higher. If the concentration increases, the charge distribution gets reduced

due to the screening effect. The change in charge distribution is high when the surface charge density goes higher than −0.1 C/m^2.

5. Conclusion

We have applied a MPB model in a Si nanowire FET to investigate the various finite size of ions influencing the z:z binary symmetric electrolyte concentration. We selected NaCl and CsCl electrolyte concentration, which is commonly used in chemical and biological sensing area. The simulation describes the EDL formation and the charge distributions at the solid–liquid interface of the Si nanowire FET. The accumulated charge on 3D nanowire FET was also studied. The results of the EDL show the highest potential drop in larger ions, compared with the smaller ion system, for fixed charge distribution and electrolyte concentration. As charge distribution increases in the negative beyond −0.1 C/m^2, the deviation of the EDL potential drop increases with consequences for the sensing element design. From the results, we can conclude that the potential drop deviations in the EDL and the charge distributions depend only on the size of the ions in the electrolyte concentration. The outcomes of this model confirm that it can be used to discover various ions in chemical and biological detectors. It would be interesting to further explore the ionic correlation effect on our nanowire FET model in the electrolyte environment.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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