

# Modeling pyramidal silicon nanopores with effective ion transport

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## Abstract

While the electrical models of the membrane-based solid-state nanopores have been well established, silicon-based pyramidal nanopores cannot apply these models due to two distinctive features. One is its  $35.3^\circ$  half cone angle, which brings additional resistance to the moving ions inside the nanopore. The other is its rectangular entrance, which makes calculating the access conductance challenging. Here, we proposed and validated an effective transport model (ETM) for silicon-based pyramidal nanopores by introducing effective conductivity. The impact of half cone angle can be described equivalently using a reduced diffusion coefficient (effective diffusion coefficient). Because the decrease of diffusion coefficient results in a smaller conductivity, effective conductivity is used for the calculation of bulk conductance in ETM. In the classical model, intrinsic conductivity is used. We used the top-down fabrication method for generating the pyramidal silicon nanopores to test the proposed model. Compared with the large error ( $\geq 25\%$  in most cases) when using the classical model, the error of ETM in predicting conductance is less than 15%. We also found that the ETM is applicable when the ratio of excess ion concentration and bulk ion concentration is smaller than 0.2. At last, it is proved that ETM can estimate the tip size of pyramidal silicon nanopore. We believe the ETM would provide an improved method for evaluating the pyramidal silicon nanopores.

Supplementary material for this article is available [online](#)

Keywords: pyramidal silicon nanopore, cone angle, effective diffusion coefficient, effective conductivity, concentration limit, size estimation

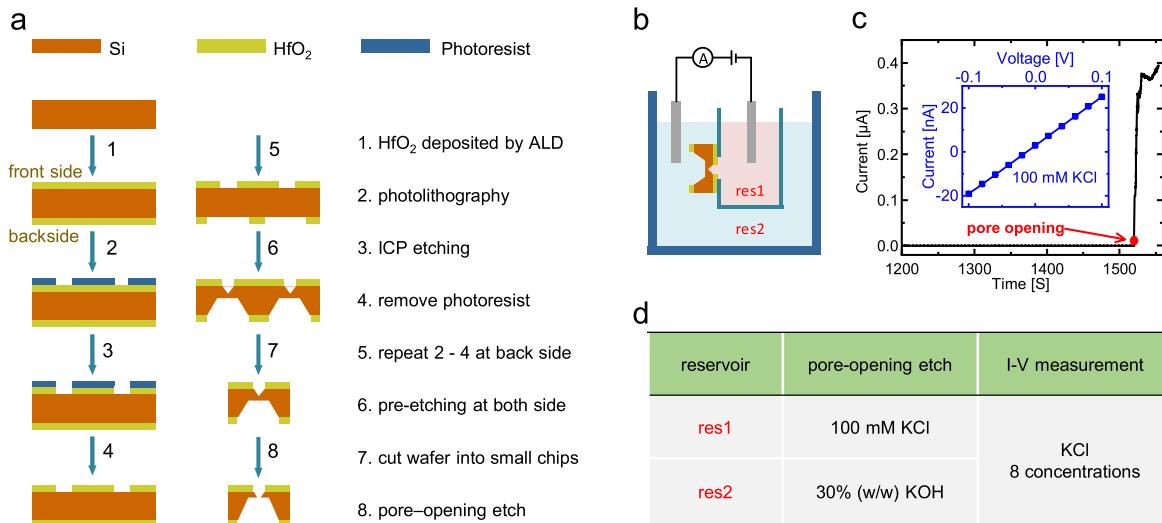
(Some figures may appear in colour only in the online journal)

## 1. Introduction

Attributed to high throughput, label-free and adjustable size, solid-state nanopore sensors have become a type of novel analysis tool for ions [1, 2], DNA [3–5], protein [6–9], and nanoparticles [10, 11]. At present, the widely used methods of nanopore fabrication include focused electron/ion beam [7, 12],

laser-assisted pulling [6, 13], tracked etching [14, 15] and controlled breakdown [16, 17]. However, these methods have the main disadvantages of low efficiency or poor size uniformity. Compared with nanopores fabricated in these ways, pyramidal silicon nanopore [8, 18–20] is based on the traditional semiconductor processes. Therefore, pyramidal silicon nanopore has the potential for large-scale and batch production. Based on the coulter principle, when a molecule passes through a pyramidal silicon nanopore, the current will drop to generate a pulse. The

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**Figure 1.** The fabrication and electrical measurement of the pyramidal silicon nanopores. (a) The fabrication process of a pyramidal silicon nanopore. In step 6, the wafer is immersed into the KOH solution for pre-etching on both sides. (b) The system for the pore-opening etch and the current–voltage ( $I$ – $V$ ) measurement. ‘res1’ and ‘res2’ represent two reservoirs in the system. The electrodes are Pt in the pore-opening etching and Ag/AgCl in the  $I$ – $V$  measurement. (c) The current trace when nanopore opening. Inset:  $I$ – $V$  curve of a pyramidal silicon nanopore (100 mM KCl). (d) The solutions in two reservoirs of (b) are dependent on the applications. KCl solution with 8 different concentrations (100 mM and 16 mM to 1000 mM with gradient) is used for  $I$ – $V$  measurement.

shape of the pulse can reflect the information of the target molecule [8, 10, 11]. Hence, knowledge of its electrochemical properties is required for the applications of pyramidal silicon nanopores. The transport of ions in a nanopore system is influenced by bulk, entrance and surface. The three parts correspond to bulk conductance, access conductance (i.e. access resistance) and surface conductance [21]. And the series and parallel connections of three conductance constitute the total nanopore conductance [22].

In fact, to obtain a better signal-to-noise ratio [23–25], most molecular analysis experiments such as DNA diagnosis [3, 5] and characterization of protein [7, 26], are performed under high electrolyte concentration. At this time, the surface conductance can be neglected [27]. Based on this premise, many classical models only considering bulk and access have been proposed to describe the electrical behavior of kinds of nanopores [16, 21, 28, 29]. In these models, intrinsic conductivity is used for the calculation of bulk conductance. Taking into account the shape of the nanopore entrances, equipotential disks are applied for calculating access conductance [21]. However, these methods are not suitable for pyramidal silicon nanopores. First, when particles pass through a non-columnar channel, the diffusion coefficient decreases. The magnitude of the decrease is related to the half cone angle of the channel [30]. The reduction in the diffusion coefficient will result in a smaller conductivity, according to the definition of conductivity [21]. The half cone angle of pyramidal silicon nanopore is  $35.3^\circ$  [8]. Thus, it is necessary to consider the influence of smaller conductivity on bulk conductance. Secondly, the shape of the entrance of the pyramidal silicon nanopore is rectangular or square [8, 20], which means that the calculation of the access also needs to be modified. Previously, Wen *et al* [31, 32] proposed an analytical model based on the distribution of electrical fields, but it is only applicable to that

pyramidal silicon nanopore with a square entrance. Therefore, from the point of view of ion transport, a more comprehensive model is necessary for the pyramidal silicon nanopore.

In this work, we establish a new electrical model—effective transport model (ETM). The model can describe the electrical behavior of the pyramidal silicon nanopore with rectangular entrances. After considering the impact of  $35.3^\circ$  half cone angle, an effective diffusion coefficient [30] is used inside the pyramidal silicon nanopore. Correspondingly, the conductivity is also scaled based on the relationship between intrinsic diffusion coefficient and effective diffusion coefficient. On the other hand, two rectangular disks are used to calculate the access conductance at both entrances. The model is validated by experiments. The impact of the effective diffusion coefficient and the access effect is demonstrated by the comparison between comparing three different models—bulk conductance model (BCM), classical model and ETM. Besides, the concentration limit of ETM is discussed. At last, it is proved that the model can be used for the estimation of the tip size of the pyramidal silicon nanopore.

## 2. Experimental section

### 2.1. Nanopore fabrication

Pyramidal silicon nanopores are fabricated in a  $200\ \mu\text{m}$  thick N-type  $<100>$  silicon wafer (Rdmicro Corp, Suzhou, China). The process of nanopore fabrication is shown in figure 1(a). In step 1, 50 nm thick hafnium oxide ( $\text{HfO}_2$ ) is grown on both sides of the wafer through atomic layer deposition. An array (10 or  $20\ \mu\text{m}$  square,  $5 \times 5$ ) is transferred to the front side of the silicon wafer by photolithography (step 2) and ICP etching (step 3). The  $\text{HfO}_2$  in windows is etched in step 3 and the residual photoresist is removed in step 4. Another array

with larger windows (320  $\mu\text{m}$  square, 5  $\times$  5) is transferred to the backside of the silicon wafer through step 5. The arrays on the front side and back side are aligned by lithography. Next, the exposed silicon of both sides is etched with 30% (w/w) potassium hydroxide (KOH) at 70  $^{\circ}\text{C}$  (pre-etching in step 6). The etching depth can be inferred through the size of inverted pyramids on both sides. When the thickness of the remaining silicon is about 10  $\mu\text{m}$ , the etching process is stopped and the wafer is cut into small chips (step 7). In the pore-opening etch (step 8), a small chip is fixed on a polytetrafluoroethylene (PTFE) reservoir by Polydimethylsiloxane (PDMS) and Apiezon W. The system for pore-opening etch is shown in figure 1(b). The solutions in reservoirs are introduced in figure 1(d). The backside is etched by 30% (w/w) KOH (40  $^{\circ}\text{C}$ ). The front side includes an inverted pyramid with a sharp tip, and the side contacts with 100 mM potassium chloride (KCl) solution. The leakage current is monitored by Keithley 2636B (Tektronix, USA) and a pair of platinum (Pt) electrodes. The current will increase rapidly when the pore forms, as shown in figure 1(c). At this time, the etching process is stopped in deionized water.

## 2.2. Nanopore characterization with scanning electron microscope (SEM) and I-V

The characterization of pyramidal silicon nanopore is performed by SEM imaging and electrical (I-V) measurement. For SEM imaging, the images are acquired using SUPRA 55 SAPPHIRE (Carl Zeiss, Germany). The SEM image of the front side (bottom side) of a pyramidal silicon nanopore is shown in figure 2(b). And figure 2(c) presents the image of the backside (tip side).

In the I-V measurement, the pyramidal silicon nanopore is fixed on the PTFE reservoir by PDMS (figure 1(b)), similar to the system for pore-opening etch. As introduced in figure 1(d), the I-V measurements are performed in 8 different concentrations of KCl solution (100 mM and 16 mM to 1000 mM with gradient), respectively. The KCl solutions from 16 to 500 mM are obtained from gradient dilution of 1000 mM KCl solution. From -0.1 to 0.1 V bias (step: 0.02 V), the bias voltage is applied by Keithley 2636B. A pair of silver/silver chloride (Ag/AgCl) electrodes is used to monitor the current. A typical I-V curve of a pyramidal silicon nanopore is shown in the inset of figure 1(c).

## 3. Physical model

Pore conductance is related to its geometry [27, 28, 33]. The schematic diagram of a typical pyramidal silicon nanopore is demonstrated in figure 2(a).  $h$  represents the thickness of the supporting layer, in other words, the length of the nanopore in the axial direction ( $z$ -axis). Attributed to the manufacturing errors of the masks and defects of the wafer, the shape of the pore tip is usually a rectangle instead of a standard square [20], and the phenomenon is confirmed by SEM images (figures 2(b) and (c)). Two adjacent sides of the pore tip are denoted by  $a$  and  $b$ , which can be measured by SEM. Here,

we call the longer side  $a$ . And two adjacent sides of the pore bottom are represented by  $L_a$  and  $L_b$ . Because the bottom window size is very large in this work, the impact of manufacturing errors on window size can be neglected. So  $L_a$  is almost equal to  $L_b$ . The sloped angle ( $\beta$ ) is 54.7° resulting from the orientation selectivity of KOH wet etching. Thus, the half of the cone angle ( $\alpha$ ) is 35.3°.

The conductance of a nanopore is contributed by three parts: (a) bulk: ions of the bulk solution inside the nanopore [21]; (b) access: the convergence effect of electric field lines from the reservoir to the entrances of the nanopore [34, 35]; (c) surface: excess ions neutralizing the fixed charges located in the pore sidewalls [36]. Here, we only consider the pyramidal silicon nanopore conductance under high electrolyte concentration. In this situation, the excess ion concentration is much smaller than the bulk ion concentration. Therefore, the surface conductance is neglected. And the total conductance ( $G_t$ ) is equal to the series connection of the bulk conductance ( $G_b$ ) and the access conductance ( $G_a$ ). The ions are considered to be in equilibrium, i.e. the ion concentration is uniform in the whole system. In the classical model for calculating nanopore conductance, the conductivity of the system is considered to be equal to the intrinsic conductivity of the electrolyte solution [21].

However, according to Zwanzig's work [30], when passing through a non-columnar channel, particles (e.g. ions) need extra time to find their way out of the cross-section. This effect will lead to a reduction in the diffusion coefficient ( $D_i$ ). The smaller diffusion coefficient can be expressed as effective diffusion coefficient ( $D_{i,\text{eff}}$ ). In this work,  $i$  ( $= \text{K}^+, \text{Cl}^-$ ) represents the type of ion. In the channel, the effective diffusion coefficient ( $D_{i,\text{eff}}$ ) [30, 37] is

$$D_{i,\text{eff}}(z) \approx \frac{D_{i,\text{ins}}}{1 + \gamma [L'_z(z)]^2}, \quad (1)$$

where  $D_{i,\text{ins}}$  is the intrinsic diffusion coefficient of  $i$ th ion.  $\gamma$  is a parameter related to the geometry of the channel. In detail,  $\gamma$  is 1/12 for a two-dimensional channel and 1/8 for a conical (three-dimensional) channel [30, 38]. As shown in figure 3(a),  $L_z(z)$  is the  $z$ -dependent channel width

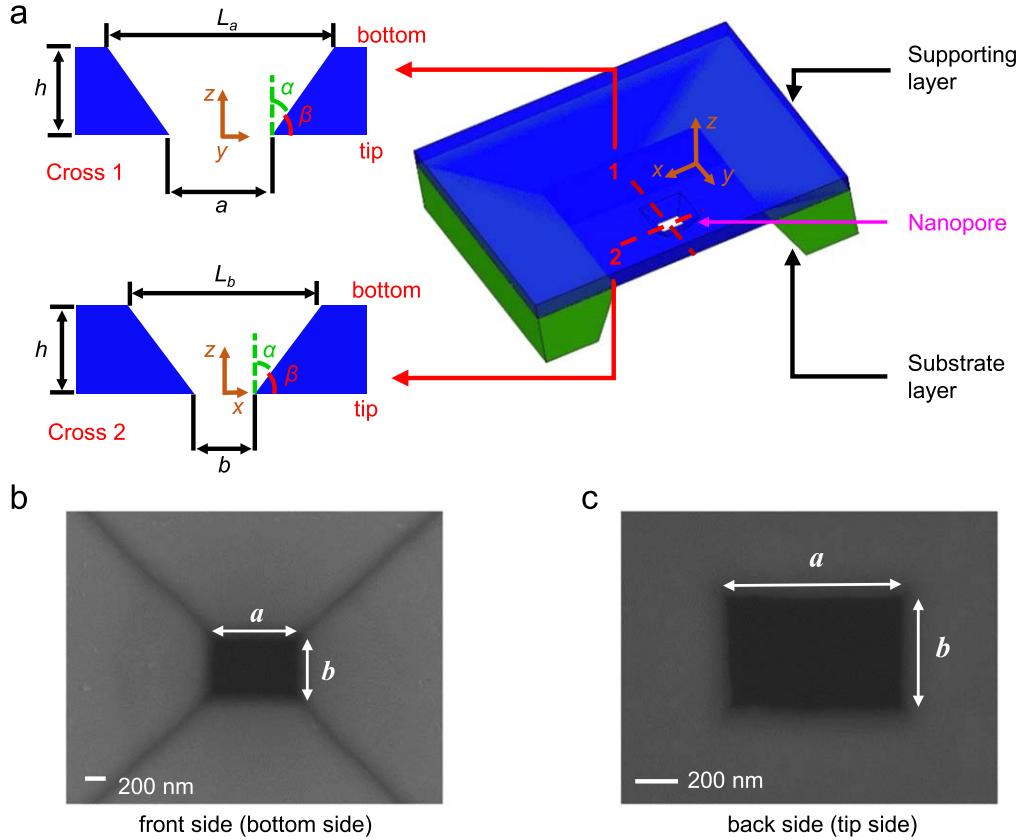
$$L_z(z) = L_0 + z \cdot 2 \tan \alpha, \quad (2)$$

$L_0$  is the width of the tip. The conductivity ( $\sigma$ ) is [21]

$$\sigma = \frac{z_i^2 F^2}{RT} \sum_i D_i c_i, \quad (3)$$

$z_i$  ( $= 1$  for  $\text{K}^+$ ,  $-1$  for  $\text{Cl}^-$ ) is the valence of the  $i$ th ion.  $F$  ( $96\,485 \text{ C mol}^{-1}$ ) is Faraday constant.  $R$  is the universal gas constant.  $T$  is the temperature.  $c_i$  is the concentration of the  $i$ th ion. From equation (3), the decreasing diffusion coefficient will lead to a smaller conductivity.

The conical nanopore widely used, e.g. PET nanopore [39, 40] and glass nanopipette [29], has a small  $\alpha$  (close to 0°).  $D_{i,\text{eff}}$  inside channel is approximate to  $D_{i,\text{ins}}$ . Thus, the classical model applies to these nanopores. Besides, these nanopores usually have another feature: a large aspect ratio. At this time,  $G_a$  is much smaller than  $G_b$ , so the classical model can be simplified into the BCM in which the



**Figure 2.** (a) The schematic diagram of the structure of a top-down fabricated pyramidal silicon nanopore (not in scale). The masking layer ( $\text{HfO}_2$ ) is not shown. It is worth noting that the supporting layer and the substrate layer belong to the same wafer. And two colors are only used to highlight the nanopore and do not represent two different divided materials. The SEM images of a typical pyramidal silicon nanopore are pictured from (b) the front side (bottom side) and (c) the backside (tip side). ‘*a*’ and ‘*b*’ represent the long edge and short edge of the nanopore tip.

total nanopore conductance is approximately equal to bulk conductance.

However, these geometry limits are not met in pyramidal silicon nanopores. First,  $\alpha$  is  $35.3^\circ$ , and so  $L'_z (= 2\tan\alpha)$  is  $\sqrt{2}$ , which means the deviation of diffusion coefficient cannot be neglected. Therefore, it is necessary to re-calculate conductivity inside pyramidal silicon nanopores. On the other hand, although  $h$  ( $10\text{--}20\ \mu\text{m}$ ) is much larger than tip size ( $a$  and  $b$ ,  $<1\ \mu\text{m}$ ), bottom size ( $L_a$  and  $L_b$ ) may exceed  $h$  ( $L_a = a + 2h\tan\alpha$ ). So the contribution of  $G_a$  on  $G_t$  should be evaluated. In order to figure out these questions, three different physical models are established.

### 3.1. Classical model

The equivalent circuit diagram of the classical model is shown in figure 3(b). In this model, the conductivity in the whole system is intrinsic ( $\sigma_{ins}$ ). In other words, we do not consider the impact of decreasing diffusion coefficient. The bulk conductance is represented by  $G_{b,ins}$

$$G_{b,ins} = \sigma_{ins} \left( \int \frac{dz}{s(z)} \right)^{-1}. \quad (4)$$

According to equation (2),  $s(z)$  ( $= [\sqrt{2}z + a]$   $[\sqrt{2}z + b]$ ) is the  $z$ -dependent area of the cross-section distanced from the pore tip along the nanopore axis ( $z$ -axis). It is emphasized that the mathematical expression is different when  $a = b$  and  $a \neq b$ . Considering the factors above, the result is

$$G_{b,ins} =$$

$$\sigma_{ins} \cdot \begin{cases} \sqrt{2} \cdot \text{diff} \cdot \left( \ln\left(\frac{\sqrt{2}h + b}{\sqrt{2}h + a}\right) + \ln\left(\frac{a}{b}\right) \right)^{-1}, & a \neq b \\ \sqrt{2} \left( -\frac{1}{\sqrt{2}h + a} + \frac{1}{a} \right)^{-1}, & a = b \end{cases}, \quad (5)$$

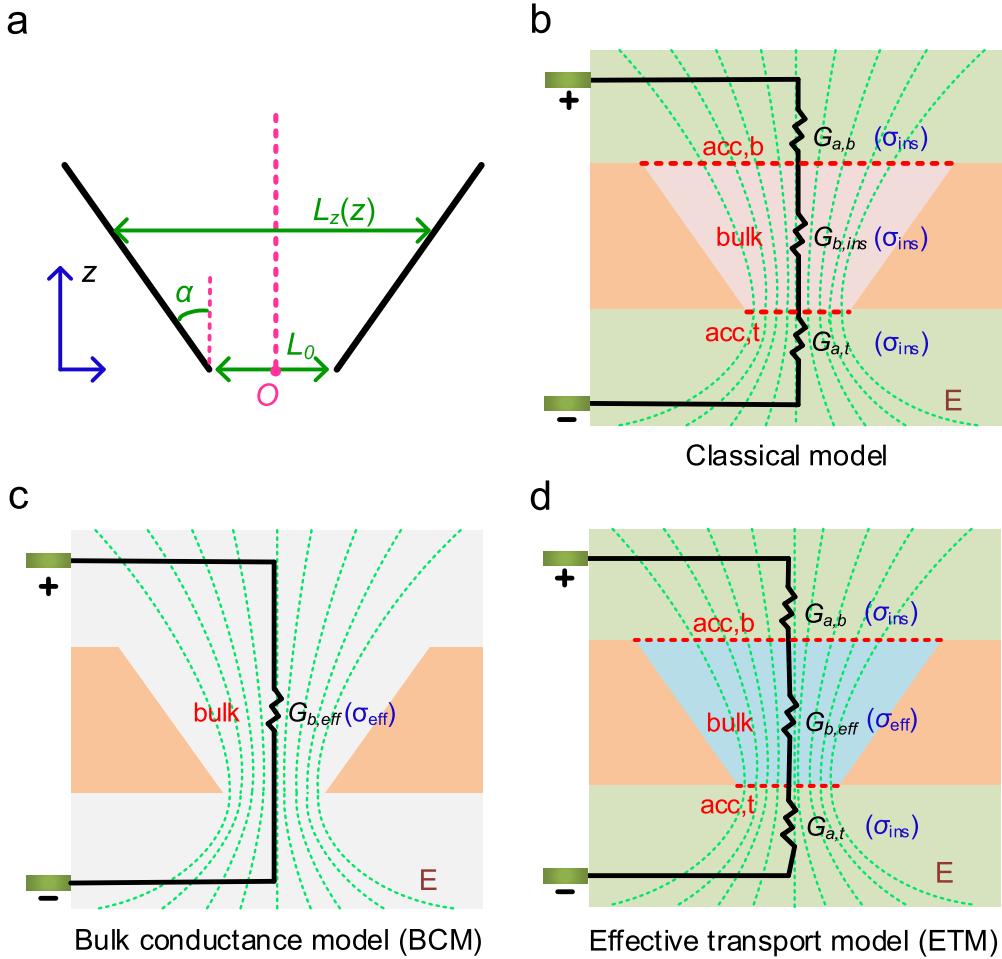
where  $\text{diff} (= a - b)$  is the difference between two adjacent edges of the pore tip.

The access conductance consists of  $G_{a,t}$  and  $G_{a,b}$ , which are the access conductance at the pore tip and the bottom, respectively. Based on the Hall model [21, 41],  $G_{a,t}$  and  $G_{a,b}$  are calculated by

$$G_{a,t} = \sigma_b \cdot C_t / (2\epsilon_r \epsilon_0) \quad (6)$$

$$G_{a,b} = \sigma_b \cdot C_b / (2\epsilon_r \epsilon_0), \quad (7)$$

where  $\epsilon_r$  ( $= 78.5$ ) and  $\epsilon_0$  ( $= 8.85 \times 10^{-12}\ \text{F m}^{-1}$ ) are the relative permittivity of electrolyte solution and the vacuum dielectric constant, respectively.  $C_t$  and  $C_b$  are the capacitances of



**Figure 3.** (a) The schematic diagram of a typical non-columnar channel.  $L_0$  is the length of the tip of the channel.  $O$  is the origin. (b) The classical model. (c) The bulk conductance model (BCM). (d) The effective transport model (ETM). The red dashed lines in (b) and (d) represent the two entrances. In these models, ‘bulk’, ‘acc,b’ and ‘acc,t’ represent three different effects: the drift of bulk ions inside the nanopore, access effect at the bottom and access effect at the tip. ‘E’ represents the electrical field and green lines represent electrical field lines. ‘ $\sigma_{eff}$ ’ and ‘ $\sigma_{ins}$ ’ represent effective conductivity and intrinsic conductivity, respectively.

the equipotential disks representing the tip and the bottom, respectively. Because of the rectangular shape, the two capacitances are [35]

$$C_t = 2\pi\epsilon_r\epsilon_0 a / \ln(4a/b) \quad (8)$$

$$C_b = 2\pi\epsilon_r\epsilon_0 L_a / \ln(4L_a/L_b). \quad (9)$$

As the result,  $G_t$  is

$$G_t = (G_{b,ins}^{-1} + G_{a,t}^{-1} + G_{a,b}^{-1})^{-1}. \quad (10)$$

The length of the pyramidal silicon nanopore can be acquired by  $h = (L_a - a)/(2 \tan \alpha)$  based on equation (2). In this work,  $L_a$  ( $> 10 \mu\text{m}$ ) is much larger than  $a$  ( $< 1 \mu\text{m}$ ). So,  $h$  can be roughly estimated by  $L_a/(2 \cdot \tan \alpha)$ .

### 3.2. Bulk conductance model

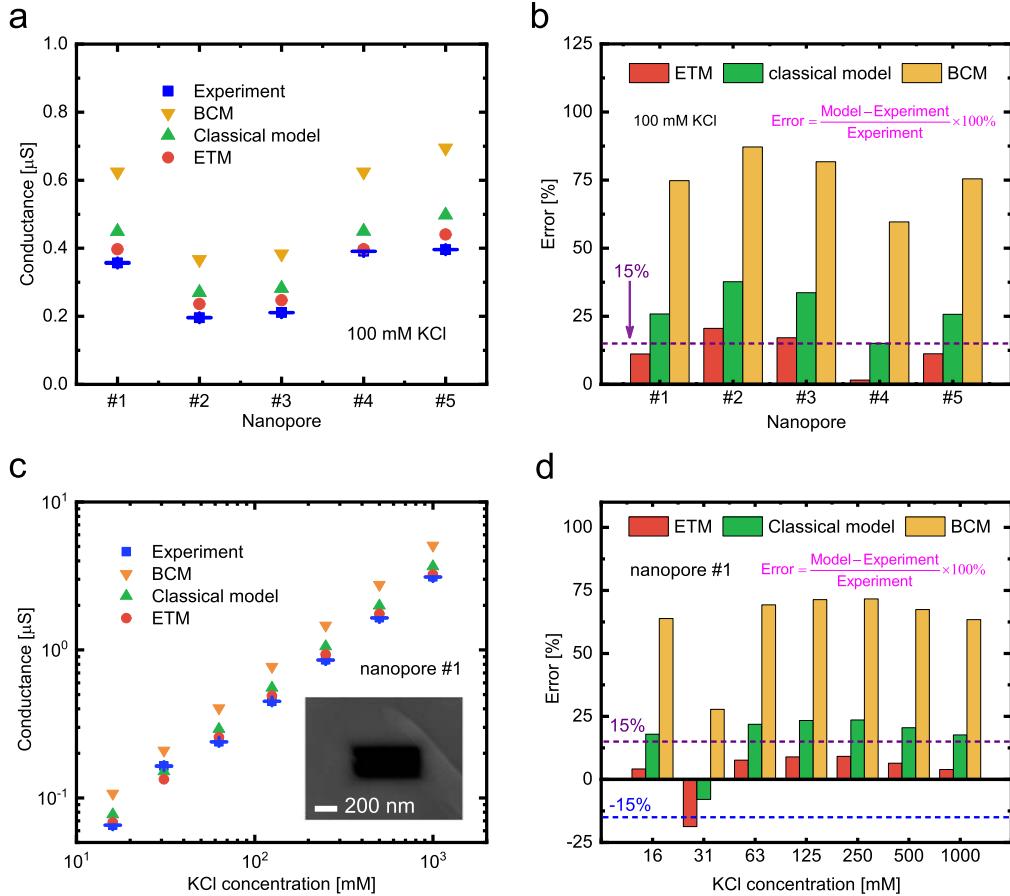
The equivalent circuit diagram of the classical model is shown in figure 3(c). In this model,  $G_t$  is considered equal to the bulk conductance. However, different from the classical model, the decrease in the diffusion coefficient is taken into account. However, the previous research on  $D_{i,eff}$  mainly focused on 2D channels or 3D channels with circular cross-

sections [30, 38, 42–44]. As far as we know, there is no study of  $D_{i,eff}$  in the pyramidal structure. The reason may be that the non-circular section makes the calculation difficult. Therefore, for simplicity, we apply  $D_{i,eff}$  of the conical channel in the pyramidal silicon nanopore. Because compared with the two-dimensional channel, pyramidal silicon nanopore is closer to the three-dimensional conical channel. In conical structure,  $\gamma$  is 1/8. Because  $\alpha$  is 35.3°,  $D_{i,eff}$  is equal to 0.8 $D_{i,ins}$  according to equation (1). Assuming the concentration is uniform in the system, the effective conductivity ( $\sigma_{eff}$ ) inside the pyramidal silicon nanopore is 0.8 $\sigma_{ins}$ . Therefore, the effective bulk conductance ( $G_{b,eff}$ ) is equal to 0.8 $G_{b,ins}$

$$G_{b,eff} = \sigma_{eff} \left( \int \frac{dz}{s(z)} \right)^{-1} = 0.8\sigma_{ins} \left( \int \frac{dz}{s(z)} \right)^{-1}. \quad (11)$$

### 3.3. Effective transport model

The equivalent circuit diagram of the classical model is shown in figure 3(d). Similar to the classical model,  $G_t$  is equal to the series connection of access conductance and bulk conductance. The



**Figure 4.** The validation of three models using the experiment results. (a) The comparison between theoretical values calculated from BCM, classical model and ETM and measured conductance for 5 different pyramidal silicon nanopores under 100 mM KCl concentration. The sizes of 5 nanopores are introduced in table 1. (b) The relative errors between three models and experiment in (a). (c) The comparison between three models and measured conductance under 7 different KCl concentrations (16–1000 mM with gradient) for nanopore 1. Inset: SEM image of nanopore 1 pictured from tip side. (d) The relative errors between three models and experiment from (c). The error bars shown in (a) and (c) represent a standard deviation from three consecutively measurements. The purple and blue dashed lines in (b) and (d) represent 15% and -15%, respectively.

difference is the decreasing diffusion coefficient is in consideration. Therefore,  $\sigma_{ins}$  is used in the calculation of  $G_{a,t}$  and  $G_{a,b}$ , as shown in equations (6) and (7).  $\sigma_{eff}$  is used in the calculation of  $G_{b,eff}$  as shown in equation (11). In this model,  $G_t$  is

$$G_t = (G_{b,eff}^{-1} + G_{a,t}^{-1} + G_{a,b}^{-1})^{-1}. \quad (12)$$

## 4. Results and discussion

In section 4.1, the ETM was validated using the experimental results of 5 pyramidal silicon nanopores. Since ETM only considers nanopores under high electrolyte concentration, the concentration limit is discussed in section 4.2. Finally, in section 4.3, ETM is used for the size prediction of pyramidal silicon nanopore tip.

### 4.1. Validation of ETM

The conductances of five different pyramidal silicon nanopores (nanopore #1–5) are used to validate the three models.

**Table 1.** The geometry of 5 nanopores for model validation.

Nanopore	$a$ (nm)	$b$ (nm)	$h$ (μm)
#1	600	278	10
#2	375	158	20
#3	385	169	20
#4	758	200	10
#5	724	276	10

The sizes of the 5 nanopores are shown in table 1. The conductances are measured in 100 mM KCl solution ( $\sigma_b = 1.28 \text{ S m}^{-1}$  from table S1). The results are shown in figure 4(a) and the relative errors are shown in figure 4(b). It can be found that compared with experiments, the classical model has a relatively large deviation ( $\geq 25\%$  in most cases). The relative errors in nanopores #2 and #3 even exceed 30%. After considering the decrease of diffusion coefficient, ETM is closer to experiments. On the other hand, there is also a huge deviation between BCM and experiment.

To get a more comprehensive evaluation, based on nanopore #1, the three models are further tested under

different KCl concentrations ranging from 16 to 1000 mM. The predicted nanopore conductance and experimental values are shown in figure 4(c), and the relative errors are shown in figure 4(d). The conductivity of the KCl solution does not increase with concentrations linearly [21, 45], and their relationship is shown in figure S1 (available online at [stacks.iop.org/NANO/33/485503/mmedia](https://stacks.iop.org/NANO/33/485503/mmedia)). The detailed values are shown in table S1. The comparisons and relative errors of nanopores #2–5 are shown in figure S2(a)–(h). Compared with the other two models, the conductance predicted by ETM is closer to experiments. Overall, the relative errors between ETM and measured conductance are within 15%. The results prove that: (1) in non-columnar channels with a large half cone angle, the reduction of diffusion coefficient should be taken into account; (2) the access effect has a great contribution to the conductance of pyramidal silicon nanopores.

Although ETM has a better performance compared with the classical model, the error still exists between the predicted value and the experimental result. It may be originated from the approximation of the diffusion coefficient. The change in channel geometry can affect the effective diffusion coefficient, according to the difference in  $D_{i,eff}$  in 2D channel and 3D conical channel [30]. Similarly, it can be speculated that  $D_{i,eff}$  is also different in the pyramidal structure and the conical channel. Therefore,  $D_{i,eff}$  used is not the real effective diffusion coefficient of the pyramidal silicon nanopore.

#### 4.2. Concentration limit

For a long time, it was believed that when the thickness of the Debye layer is much smaller than the nanopore radius, the effect of surface charge can be ignored [21]. However, recently, Poggioli *et al* [46] and Dal Cengio *et al* [47] proved that the criterion is the ratio between excess ion concentration and bulk ion concentration, which is characterized by Dukhin number ( $Du$ ). At  $z$ -position dependent cross-section, excess ion concentration is

$$X(z) = -\frac{Q_s L_s(z)}{F_s(z)}, \quad (13)$$

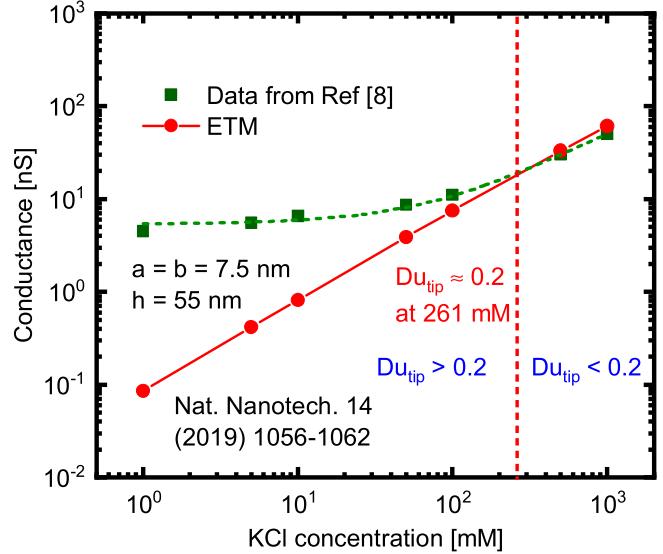
where  $Q_s$  is the surface charge density and set to  $-0.016 \text{ C m}^{-2}$  in pyramidal silicon nanopore [8]. So the excess ion is  $\text{K}^+$ .  $L_s (= 4\sqrt{2}z + 2a + 2b)$  is perimeter of the  $z$ -position dependent cross-section.

According to Donnan equilibrium [48], the co-ion (i.e.  $\text{Cl}^-$ ) concentration is

$$c_{\text{Cl}^-}(z) = -\frac{X(z)}{2} + \sqrt{\left(\frac{X(z)}{2}\right)^2 + c_{\text{res}}^2}, \quad (14)$$

$c_{\text{res}}$  is the electrolyte concentration in the reservoir. The Dukhin number is

$$Du(z) = \frac{X(z)}{2c_{\text{Cl}^-}(z)}. \quad (15)$$



**Figure 5.** The concentration limit of ETM based on the pyramidal silicon nanopore from the [8]:  $a = b = 7.5 \text{ nm}$  and  $h = 55 \text{ nm}$ . Red solid line: predicted conductance as the function of KCl concentration based on ETM. Green dashed line: the fitted curve of measured conductance. Red dashed line: KCl concentration is 261 mM and  $Du_{tip}$  is 0.2 under the concentration.

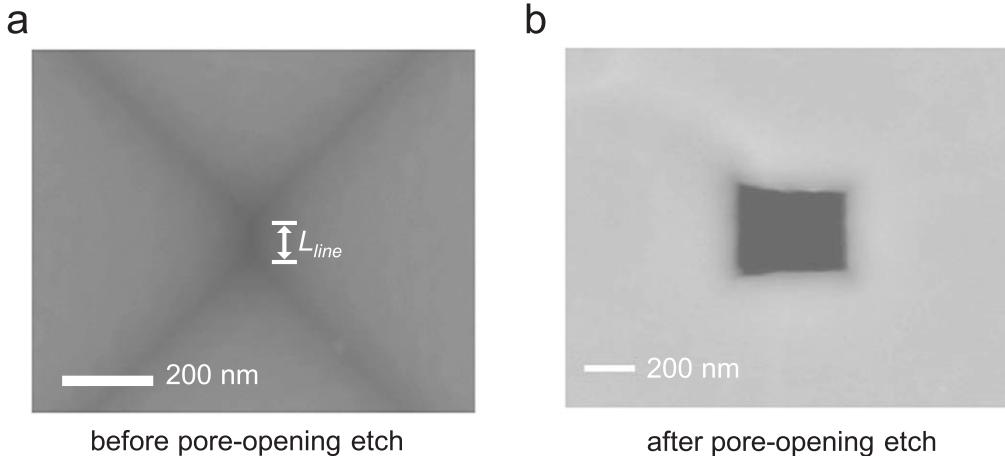
Considering the pore tip is the region with the largest ion selectivity, we focus on the  $Du$  of tip ( $Du_{tip}$ ), i.e.  $z = 0$ .

Figure 5 shows the conductance of a  $7.5 \times 7.5 \text{ nm}$  pyramidal silicon nanopore at varied KCl concentrations from Zeng *et al* [8]. The values predicted by ETM at low concentrations (1–100 mM KCl) are much smaller than the experimental results. And the model is consistent with the experiment at high concentrations (500–1000 mM KCl). It can be found that the ion concentration (261 mM) satisfying  $Du_{tip} = 0.2$  is between 100 and 500 mM. On basis of the result, it can be concluded that ETM can describe the electrical behavior of silicon pyramidal nanopore when  $Du_{tip}$  is smaller than 0.2. The conclusion can also explain why ETM is applicable in our pyramidal silicon nanopores under 16 mM. Taking nanopore #1 as an example, at 16 mM,  $Du_{tip}$  is 0.06, which is still smaller than the limit (0.2).

The failure of ETM at low concentrations is mainly due to the effect of surface charge. In ETM, surface conductance is neglected. However, under low concentrations, the ions in the nanopore are mainly excess ions [27, 36]. At this time, surface conductance dominates the conductance inside the nanopore. Therefore, ETM is not suitable for nanopores at low concentrations.

#### 4.3. Size estimation

Estimating nanopore size through the measured conductance has been widely used, especially for the nanopores fabricated in a liquid environment [14, 16, 17], because of the negative effects from the electron microscope [49–51] and corresponding pre-treatment. The SEM images of a typical pyramidal silicon nanopore before and after pore-opening etch are shown in figures 6(a) and (b), respectively. Figure 6(a) shows  $L_{line}$  is the length of the line located at the tip of the inverted



**Figure 6.** The SEM images of a typical pyramidal silicon nanopore (a) before and (b) after pore-opening etch.  $L_{line}$  is the length of the line at the tip of the inverted pyramid.

**Table 2.** The comparison between predicted size from ETM and measured size (100 mM KCl).

Nanopore	$G_m \pm \delta (\times 10^{-8} \text{ S})^a$	$L_{line}$ (nm) <sup>b</sup>	$h$ ( $\mu\text{m}$ )	$a_p \times b_p$ (nm) <sup>c</sup>	$diff_m$ (nm) <sup>d</sup>	$a_m \times b_m$ (nm) <sup>e</sup>
#1	$35.75 \pm 0.12$	312	10	$561 \times 249$	322	$600 \times 278$
#2	$19.63 \pm 0.07$	222	20	$340 \times 118$	217	$375 \times 158$
#3	$21.15 \pm 0.02$	221	20	$354 \times 133$	216	$385 \times 169$
#4	$39.10 \pm 0.03$	553	10	$755 \times 202$	558	$758 \times 200$
#5	$39.62 \pm 0.03$	463	10	$695 \times 232$	448	$724 \times 276$
#6	$28.81 \pm 0.68$	51	12	$329 \times 278$	90	$412 \times 322$
#7	$54.18 \pm 0.43$	394	10	$802 \times 408$	398	$798 \times 400$

<sup>a</sup> Average measured conductance and the uncertainty ( $\delta$ ) expressed by a standard deviation based on three continuously measured conductances.

<sup>b</sup> Measured length of line located in the tip of the inverted pyramid, as shown in figure 6(a).

<sup>c</sup> Predicted pore size from ETM using  $G_m$ . Only  $G_m$  is used because the standard deviation is too small.

<sup>d</sup> Calculated  $diff$  from  $a_m - b_m$ .

<sup>e</sup> Measured pore size from SEM image.

pyramid before the pore-opening etch, which is considered to be equal to  $diff$ . According to equation (2),  $h$  can be estimated from  $L_a$ . When these parameters are known, the size of pore tip ( $a$  and  $b$ ) can be inferred from the measured conductance based on equation (12).

The conductance is measured in 100 mM KCl solution. Table 2 shows the comparisons between the predicted size and measured size of 7 different pyramidal silicon nanopores, including 5 samples (nanopore #1–5) in figure 4(a). It can be found that the size of most nanopores can be predicted accurately. The deviations between predicted values and measured values of these pyramidal silicon nanopores can be attributed to three reasons: (1) imperfect geometry of tip deviating from the ideal rectangle; (2) the difference between  $diff$  and  $L_{line}$ ; (3) the error between experiments and ETM introduced in section 4.1.

Besides our work, the ability of size estimation of ETM is also evaluated by other samples from references. Because SEM images of these pyramidal silicon nanopores before pore-opening etch are unknown,  $diff$  is directly equal to the difference between  $a$  and  $b$ .  $diff$ ,  $h$  and  $G_t$  of the first example [20] are 23 nm, 21  $\mu\text{m}$  (estimated from the size of the front window) and 167 nS (1 M KCl), respectively. The estimated

value is 12 nm  $\times$  35 nm and the measured value is 15 nm  $\times$  38 nm. The parameters of the second sample [8] are shown in figure 5. The conductance is about 50 nS (1 M KCl) estimated from the conductance-conductivity plot. Based on this value, the predicted size is 6.2 nm  $\times$  6.2 nm, which is close to the actual value—7.5 nm  $\times$  7.5 nm. Hence, it is concluded that ETM can be applied in the size estimation of the pyramidal silicon nanopore.

## 5. Conclusion

In summary, we proposed a new model—ETM—to describe the relationship between the conductance and the geometry of the pyramidal silicon nanopore. Different from other types of nanopores, a large half cone angle (35.3°) leads to additional resistance on ion movement, which is appeared as the decrease of diffusion coefficient. As the result, the conductivity will be smaller. After considering the effect, effective conductivity instead of intrinsic conductivity is used in the calculation of bulk conductance. Besides, equipotential rectangular disks are used for calculating access conductance due to the rectangular entrances. Compared with the

experimental results, the error of conductance predicted by ETM is less than 15%, which is better than the classical model ( $\geq 25\%$  in most cases). ETM is applicable when  $Du_{tip}$  is smaller than 0.2. At last, it is proved that ETM can predict the size of the pyramidal silicon nanopore. In addition to providing a new model, this work also points out that the decreasing diffusion coefficient needs to be noticed in other types of non-columnar channels.

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## Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

## Conflict of interest statement

The authors declare no competing financial interest.

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