

# AC impedance studies on metal/nanoporous silicon/p-silicon structures

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## Abstract

Alternating current (AC) impedance measurements have been performed on  $10\mu\text{m} - 15\mu\text{m}$  thick porous silicon layers on a (100) p-type silicon (p(+)-Si) substrate with the aluminium (Al) top electrode in a sandwich configuration in the range of 20 Hz to 1 MHz and in the temperature ranging between 152 K – 292 K. The ac conductivity  $\sigma_{ac}$  was found to increase with frequency  $f$  according to the universal power law:  $\sigma_{ac} = Af^s$  where the exponent  $s$  is a frequency and temperature dependent quantity. Hopping process is found to be dominant at low temperatures and high frequencies while a thermally activated free band process is responsible for conduction at higher temperatures. Capacitance is found to decrease with frequency but increase with temperature. Frequency dependence of loss tangent is observed with a temperature dependent minimum value.

**Keywords:** Free band conduction, activation energy, resistance-capacitance networks, Loss tangent

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## 1. Introduction

Porous silicon (PS) has attracted considerable interest over the last 20 years from both academic and industrial research communities for its luminescence (EL) properties because of the large surface to volume ratio.<sup>1</sup> Investigations have also been carried into this PS material for its potential applications in the field of optoelectronics,<sup>2,3</sup> drug delivery,<sup>4</sup> gas and biosensors<sup>5,6</sup> and biomedical devices.<sup>7</sup> The study of electrical properties of PS layers, therefore becomes important to exploit these developments with further success. Current-voltage  $I(V)$  characteristics of metal/PS/Silicon (Si) structures have been found to be influenced by the type of metal contact. The sputtered platinum film forms an Ohmic contact with the PS while the Schottky barrier exists between copper (Cu) and PS film.<sup>8</sup> No major changes in Fourier transform infrared (FTIR) absorption peaks have been observed for the native PS in the Schottky diode structure formed between 10-40 nm thick radio RF magnetron sputtered Cu film and PS. Values of the barrier height and the ideality factor were found to be 0.678 eV and 2.77, respectively from the  $I(V)$  characteristics.<sup>9</sup> Good rectifying behaviour is observed in the  $I(V)$  characteristics recorded for palladium (Pd)/PS/p-Si structure with the ideality factor increasing from 3.1 to 3.5 at the small forward bias of 0.3 V as PS layer thickness is varied from 30 nm to 90 nm. There exists a 3nm thick interface layer between Pd/PS and voltage redistribution between interface, PS, P-Si occurs with the PS thickness.<sup>10</sup> Tunnelling via migration/diffusion is believed to be responsible for charge transport in an Al/PS/p(+)-Si/Al structure which exhibits an ideality factor very close to unity, a high barrier height in the order of 0.63 eV and small series resistance of 30  $\Omega$ .<sup>11</sup>

Impedance spectroscopy, measuring AC electrical response over a wide frequency range, can predict the conductivity, structural homogeneity and stability considering relative contribution of grain, grain boundary and defect states in thin film materials.<sup>12</sup> This non-destructive AC impedance technique has been successfully employed to examine the surface morphology of macroporous silicon samples, providing the values of 1.52 $\mu\text{m}$  and 54.2% for the sample pore radius and porosity. There exists a good agreement within 2% accuracy between these results and the values obtained from conventional methods such as SEM and gravimetric analysis.<sup>13</sup> AC measurements on gold (Au)/PS/p-Si/Al using the DC bias voltage between  $\pm 2$  V have been made at room temperature only and over the frequency range of 5 Hz to 10

kHz. The structure exhibits the conductor type behaviour for the bias voltage upto 0.5V while the diode type conduction becomes dominant at the medium frequency range<sup>14</sup>

This present article reports results of AC conductivity and capacitance measurements on the Al/PS/p(+)Si/Al structures in the frequency range of 20 Hz to 1 MHz and over the temperature range of 152 K – 292 K. Our steady state current transport measurements on the similar structures at relatively low bias voltages indicate that the rectifying behaviour is similar to one observed for an ideal p-n junction. PS films behave like *n*-type Si due to their depletion of majority hole carriers.<sup>15</sup> An equivalent circuit has been proposed in this investigation, taking the passive components of both bulk and junction regions into account. The data has been analysed in terms of universal power law and 240 K is found to be a critical temperature for charge transport. Hopping mechanism became dominant at temperatures below 240 K while band type conduction was observed above this temperature.

## 2. Experimental Details

PS layers were prepared by the anodisation of (100) p-type silicon substrates in a 1:1 solution of HF acid (49% in water) and ethanol at current density of 30 mA/cm<sup>2</sup> for 20 min in the dark. Experiments were performed with substrates having different resistivities in the range between 8 Ωcm and 12 Ωcm. Before anodisation, Ohmic contacts were deposited on the back side of the wafers by Al evaporation followed by annealing at 625 K for 30 min. The thickness of the PS layers made under the same fabrication conditions estimated to be in the range of 10–15 μm. Following anodisation, the samples were rinsed in deionised water for 15 min, dried and transferred to a vacuum chamber to deposit thin Au contacts onto the PS surface through a mask. The metal evaporation was performed at a glancing angle between the molecular beam and the wafer in order to prevent the direct contact between the p type silicon substrate and the metal. The active area *A* of the device is 2 mm<sup>2</sup>. AC conductance and capacitance of the samples were measured in the frequency range between 20Hz and 10<sup>6</sup> Hz using HP 4276A LCR meter in a microprocessor controlled system. The amplitude of the alternating signal was 100 mV peak-to-peak with no dc bias. All measurements were taken inside a vacuum system at a pressure of approximately 10<sup>-3</sup> Pa.

### 3. Results and discussions

Experimental results were analysed in order to determine the influence of temperature on charge transport mechanism and dielectric behaviour of Au/PS/p-Si/Al structures. Electrical measurements on these structures at different temperatures are important because of expected variations in pore dimensions.<sup>16</sup> New information has been elucidated from careful comparison of values of physical parameters estimated in this investigation with published data.

#### 3.1 Dependence of conductivity on frequency and temperature

A set of reproducible AC spectra in Figure 1 shows the frequency  $f$  dependence of AC conductivity  $\sigma_{ac}(f, T)$  at six temperatures  $T$  in the range of  $152 \text{ K} \leq T \leq 292 \text{ K}$ . The spectra display three principal features, identified by threshold frequency  $f_{th} = 10 \text{ kHz}$  and transition temperature  $T_i = 200 \text{ K}$ . The first regime is related to the low frequency ( $f \leq 10 \text{ kHz}$ ) but high temperature ( $T \geq 200 \text{ K}$ ). As the temperature is raised, the conductivity becomes progressively less dependent upon frequency for  $f \leq 10 \text{ kHz}$ . The conductivity at room temperature is found to be nearly independent of frequency. Secondly, the conductivity exhibits a significant frequency-dependent behaviour at low temperatures  $T_i \leq 200 \text{ K}$ . This rise  $\sigma_{ac}$  with increasing  $f$  at a given  $T$  can be written in a universal power law form:<sup>17</sup>

$$\sigma_{ac}(f, T) = \sigma_{dc} + Af^s \quad (1)$$

where  $A$  is a complex constant. The exponent  $s$  is dependent upon frequency and temperature.

As shown in Figures 2, the variation of  $s$  in Equation (1) with respect to temperature indicates that there are two mechanisms responsible for the electrical conduction of porous silicon. For relatively high frequencies between 1 kHz and 100 kHz, there is a nearly linear dependence of conductivity on frequency with the exponent  $s$  lying in the range of  $0.6 \leq s \leq 1$ . The values are greater at high frequencies between 1 kHz and 100 kHz than those at relatively low frequencies in the range of 100 Hz to 1 kHz for a specific temperature. However, the value of  $s$  is found to decrease with increasing temperature in both cases. For  $s \leq 1$ , hopping of charge carriers between randomly distributed localized states through PS layer is believed to be responsible for this behaviour.<sup>18</sup> The third regime

refers to the low frequency regime for which is  $s \leq 0.5$ . The dependence of  $\sigma_{ac} \propto f^{0.5}$  for Al/Ps/Si structure has been attributed to activated hopping in a fractal network. The low-frequency regime is governed by the fractal properties of porous Si, whereas the high-frequency dispersion is believed to have arisen from a broad distribution of activation energies.<sup>19</sup> Assuming simple percolation like clusters of Si nanocrystals, the one-dimensional tight binding model has been further proposed for interpretation of power law dependence with  $s < 1$  in high frequency regime.<sup>20</sup>

The temperature dependence of the AC conductivity  $\sigma_{ac}$  is also presented in Figure 3(a) at six different frequencies between 20Hz and 1MHz. For the sake of comparison The variation of DC conductivity with temperature is also included for the sake of comparison. The conductivity reaches a frequency dependent saturated value below a transition temperature, the value of which increases with increasing frequency. For example, the conductivity becomes nearly constant at 154 K and 200 K corresponding to 100 KHz and 1 MHz, respectively. The ac conductivity  $\sigma_{ac}$  is believed to increase exponentially with the temperature  $T$  in the Arrhenius Equation form:<sup>21</sup>

$$\sigma_{ac} = \sigma_0 \exp(-E_a/kT) \quad (2)$$

where  $\sigma_0$  is the value of  $\sigma_{ac}$  at  $1/T = 0$  and  $k$  is Boltzmann's constant.

Values of activation energy  $E_a$  were estimated from the slopes in Figure 3(a) for two regimes separated by the temperature of 240K and their dependence on frequency is shown in Figure 3(b). The activation energy is found to be frequency dependent and tends to decrease with the increasing frequency. However, the decrease of  $E_a$  is much sharper for  $T > 240$  K than  $T < 240$  K. Values of 0.35 eV and 0.2 eV were obtained from Equation (2) at 20Hz corresponding to high and low temperature regimes. These results imply a free band conduction process at low frequency resulting from carriers exited from energy levels within the forbidden gap.<sup>22</sup>

### 3.2 Dependence of capacitance on frequency and temperature

The variation in capacitance with frequency (20 Hz - 1 MHz) at various temperatures for the same PS sample is shown in Figure 4. At temperatures  $T_i \leq 182$  K, the capacitance is independent of frequency, whereas the capacitance for  $T_i \geq 182$  K initially decreases

rapidly with increasing frequency . A similar pattern of constant capacitance behaviour for Au/PS/p-Si/Al structures over  $10^2 \text{ Hz}$  and  $10^4 \text{ Hz}$  is explained in terms of an equivalent circuit consisting of an inherent capacitance .<sup>23</sup> The capacitance subsequently approaches the low temperatures value at high frequencies.

The capacitance is plotted in Figure 5(a) as a function of temperature at four different frequencies. It can be seen capacitance becomes independent of frequency that in the low temperature region. However, it begins to diverge as the temperature is raised above  $200\text{K}$  . No Schottky barrier is believed to have existed at the interface between the porous silicon and aluminium electrode. However, Au/PS/p-Si/Al may be treated as a heterojunction and the physical mechanisms at Au/PS and PS/p-Si contacts need to be carefully considered for the interpretation of dielectric relaxation.<sup>24, 25</sup> As shown in Figure 5(b), the behaviour may be explained in terms of an equivalent circuit comprising two parallel resistance-capacitance networks in series combination. The network of capacitance  $C_d$  and conductance  $G_d$  refer to the depletion region while  $C_p$  and  $G_p$  represent the geometrical capacitance and conductance, respectively of the PS layer. The decrease of temperature may cause the transition between  $C_d$  and  $C_p$  at low frequencies, reducing the geometrical conductance of the PS layer<sup>26</sup>.

The admittance  $Y$  is expressed in the form:

$$Y = \frac{(G_d + j\omega C_d)(C_p + j\omega C_p)}{(G_d + G_p) + j\omega(C_d + C_p)} \quad (3)$$

so the net conductance  $G$  and net capacitance  $C$  can be written in the form:

$$G = \text{Re}(Y) = \frac{G_d G_p (G_d + G_p) + \omega^2 (G_d C_p^2 + G_p C_d^2)}{(G_d + G_p)^2 + \omega^2 (C_d + C_p)^2} \quad (4)$$

and

$$C = \omega^{-1} \text{Im}(Y) = \frac{C_d G_p^2 + C_p G_d^2 + \omega^2 C_d C_p (C_d + C_p)}{(G_d + G_p)^2 + \omega^2 (C_d + C_p)^2} \quad (5)$$

The depletion capacitance  $C_d$  can be written in the form:

$$C_d = A \sqrt{\frac{qP_0 \epsilon_0 \epsilon_r}{2V_0}} \quad (6)$$

$C_p$  is taken to be independent of temperature and frequency since the PS layer is highly depleted in the first instance. It can also be assumed that  $G_d \gg G_p$ . With these approximations, Equations (4) and (5) can be written in the form:

$$G = \frac{G_d^2 G_p + \omega^2 G_d C_p^2}{G_d^2 + \omega^2 (C_d + C_p)^2} \quad (7)$$

and

$$C = \frac{C_d G_p^2 + C_p G_d^2 + \omega^2 C_d C_p (C_d + C_p)}{G_d^2 + \omega^2 (C_d + C_p)^2} \quad (8)$$

There are two limiting cases: for  $\omega \rightarrow 0$ ,  $G = G_p$  and  $C = \frac{G_p^2}{G_d^2} C_d + C_p$ .  $G = \frac{C_p^2}{(C_d + C_p)^2} G_d$

and  $C = \frac{C_d C_p}{(C_d + C_p)}$  for  $\omega \rightarrow \infty$ .

Using values of permittivity of free space  $\epsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}$ , dielectric constant  $\epsilon_r = 11.9$  for silicon and the hole concentration  $p_0 = 10^{21} \text{ m}^{-3}$  corresponding to the resistivity of  $10 \text{ } \Omega \text{ cm}$  for the p(+)Si substrate,  $C_d$  is found to be  $22 \text{ nF}$ . The porous silicon is completely depleted of holes so the value of  $C_p$  is estimated to be  $15 \text{ nF}$  by replacing  $V_0 = E_g = 1.5 \text{ eV}$  in Equation (8).  $C_d$  and  $C_p$  are found to be of the same order of magnitude.

Figure 6 shows the typical variation of the loss tangent ( $\tan \delta$ ) with frequency at temperatures  $152 \text{ K} \leq T \leq 292 \text{ K}$  for the same device, where the angle  $\delta$  is the phase angle of the impedance. It is clearly observed that  $\tan \delta$  decreases with frequency and attains a minimum value ( $\tan \delta_{\min}$ ) then slowly increases. The value is, however, smaller than one obtained for porous silicon oxynitride ceramics by a factor of four, indicating that suitability of its use as a low loss substrate.<sup>27</sup> The position of ( $\tan \delta_{\min}$ ) is shifted to a higher frequency with increasing temperature. Residual electrolyte in the pores of a PS sample is reported to have influenced dielectric spectrum.<sup>28</sup> However, PS samples left for more than three months to dry exhibited the same conductivity behaviour as the freshly made PS samples, implying that the residual electrolyte has no effect on ac conductivity of PS samples.

#### 4. Conclusions

An investigation of the frequency and temperature dependence of the AC conductivity in PS suggests that the electrical conduction at low temperatures is essentially dominated by hopping of charge carriers through the PS layer. Free band conduction with activation energy of 0.35 eV was observed for high temperatures and low frequencies. Capacitance was found to decrease with increasing frequency at high temperatures and frequency independent at low temperatures. Loss tangent initially decreases with increasing frequency to reach a temperature dependent minimum value and then start to increase slowly with frequency.

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## Figure Captions

- Figure 1. Frequency dependence of AC conductivity  $\sigma_{ac}$  at six temperatures  $T$  in the range of  $152\text{ K} - 292\text{ K}$  for the Al/PS/p(+)Si/Al structure.
- Figure 2. Dependence of the exponent  $s$  of the universal power law on temperature at two frequency ranges: (i)  $10^2\text{ Hz} \leq f \leq 1\text{ kHz}$  and (ii)  $1\text{ kHz} \leq f \leq 100\text{ kHz}$  for the same structure as in Figure 1
- Figure 3. (a) Arrhenius plot of AC conductivity for six frequencies and (b) Dependence of activation energy on frequency for  $T < 240\text{ K}$  and  $T > 240\text{ K}$
- Figure 4. Dependence of capacitance on frequency at different temperatures for the same structure as in Figure 1.
- Figure 5. (a) Temperature dependence of capacitance at different frequencies and (b) Equivalent circuit consisting bulk and junction passive circuit parameters.
- Figure 6. Dependence of loss Tangent on frequency at different temperatures.