

Capacitance of semiconductor-electrolyte junction and its frequency dependence

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Abstract. The frequency dependent capacitance of semiconductor-electrolyte junction and its relationship to the surface roughness of the semiconductor and the ions in the electrolyte are discussed. Due to very low mobility of the ions, the observed capacitance can be dominated by the Helmholtz double-layer of the electrolyte rather than the space charge layer of the semiconductor. The capacitance will also depend on the frequency. This, often observed power-law frequency dependence of capacitance is ascribed to the contribution of constant phase angle impedance. The power-law exponent can easily be related to the fractal dimension if the semiconductor surface can be described by fractal geometry.

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Capacitance and capacitance-voltage measurements are of great use for characterizing various semiconductor junctions, such as the p - n junction, the semiconductor-metal (Schottky) junction and the semiconductor-electrolyte junction. One application is to extract the doping concentration of the semiconductor from C^{-2} - V plots of these junctions, which are straight lines in the depletion region. Their slopes are inversely proportional to the doping concentration (of the lightly doped semiconductor for the p - n junction) [1, 2]. Semiconductor-electrolyte junctions are more important for this application since C - V measurements can be combined with electrochemical etching to obtain the doping profile of semiconductors [3–5]. Further, the formation of junction is more convenient.

Usually, the measurements of capacitance and capacitance-voltage are carried out at a fixed frequency, since they were thought to be independent of frequency. However, they are often frequency dependent [6–19], confusing the explanation of the experimental results such as the doping concentration [6, 7] and its profile extracted from the C^{-2} - V slope. Some works showed that the capacitance of rough semiconductor-electrolyte junctions is more dependent on the frequency than that of smooth

junctions [7–10], while neither a smooth nor a rough semiconductor-metal (Schottky) junction shows such frequency-dependence [7]. In many cases, the capacitance-frequency relations to semiconductor-solution junctions were found to be the power-law form $C \propto \omega^{-\alpha}$, as will be discussed in Sect. 2.

Since the capacitance is proportional to the dielectric coefficient ϵ and the area S , the frequency dependence of either ϵ or S could be the reason for the frequency dependent capacitance. The frequency dependent dielectric coefficient, $\epsilon(\omega)$, resulting from dielectric relaxation, could explain the frequency dependent capacitance for a semiconductor-electrolyte junction [11], and all other kinds of semiconductor junctions as well. However, dielectric relaxation occurs at frequencies much higher than what are used in most experiments, and it predicts that the capacitance varies with frequency in different way than the observed power law. Thus, it cannot explain the roles of the rough surface and the electrolyte. Little is known about the consequences of these two factors on the frequency dependence of the capacitance of semiconductor-electrolyte junctions.

1 Frequency dispersion of capacitance

C - V characteristics of semiconductor-electrolyte junctions have been extensively studied, due to their potential applications on solar energy. The frequency dependence of the junctions capacitance is often observed, and much has been published concerning the frequency dispersive capacitance, e.g., references [6–19].

Power-law alike frequency dispersion is common in the observed capacitance-frequency relation of semiconductor-electrolyte junctions. Madou et al. [12] found that for GaP electrodes, the capacitance C_s is frequency dispersive, according to

$$C_s = a'f^{1+n} + b', \quad (1)$$

where

$$-2 < n < -1 \quad (2)$$

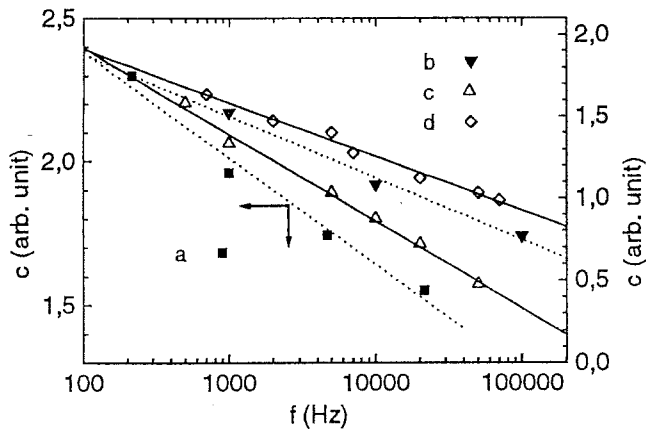


Fig. 1. Frequency dispersion of semiconductor-electrolyte junctions, from published works. **a** *n*-GaAs in 4.5 M NaClO₄ [7], $V/V(\text{SCE}) = 1.0$ V; **b** porous *p*-Si in 35% hydrofluoric acid solution [8], $V = -1.4$ V (against Ag/AgCl); **c** TiO₂, [14] $V = 0.3$ V; **d** CdSiAs₂ in 1 M H₂SO₄ [6], $V = -1.5$ V (SCE)

is a constant. The observed range was $-1.70 < n \leq -1.09$. Oskam et al. [7] have found that the capacitance-frequency relation of a semiconductor-solution junction is in the form

$$C \propto \omega^{-\alpha} \quad (3)$$

This kind of relation manifests itself in many published C - V plots, though most authors have not explicitly pointed out the form of power law [6, 13–15]. In Fig. 1 we have plotted some of these results [6–8, 14].

An interesting fact is that the frequency dispersion seems to be related to the surface roughness of the semiconductor electrode. In Madou's experiments [12], the general trend was found that when only little surface material was removed, this lead to n -values close to -1 , whereas thorough etching caused n to be more negative. Kiewiet and Fox [16] found that the difference of Mott-Schottky plots of a single crystal TiO₂ – 1M KCl junction, measured at 500 Hz and 5000 Hz, was rather small. After 24 hours aging in H₂SO₄ by using a 200 W Xe lamp, the difference became quite big (about a factor of 4), and the surface of the electrode became rough after aging. Oskam et al. [7] found that the exponent α in equation (3) is rather small for flat *n*-GaAs-electrolyte junctions. After the surface of GAs was roughened by polishing and etching, α increased and was positively correlated to the roughness of the semiconductor surface. Another example is the comparison of Mott-Schottky plots of porous and non-porous silicon/35% hydrofluoric acid solution by Ronga et al. [8]: the former shows considerable frequency dispersion whereas the later does not. There are more such examples [9, 10] and some of these are shown in Fig. 2 [7, 16]. The facts indicate that the frequency-dependence of semiconductor-electrolyte junction capacitance may originate from the roughness of the semiconductor surface.

Surface roughness may be a source of the frequency dispersion, as the experiments mentioned above indicated, but it is not the only one. In Oskam's experiment,

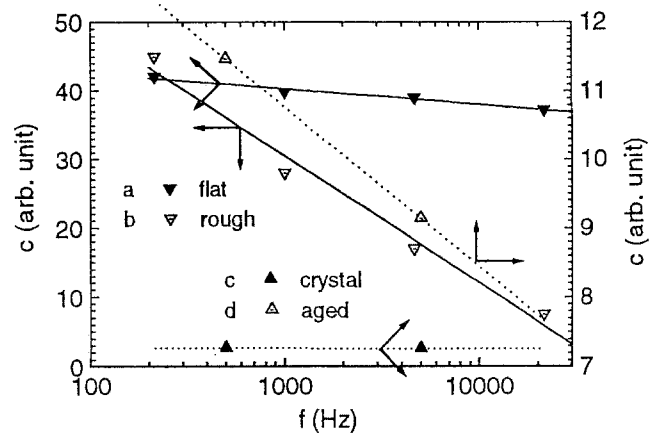


Fig. 2. Frequency dispersion of semiconductor-electrolyte junctions and roughness of semiconductor surface. **a** flat and **b** rough GaAs [7]; **c** crystal and **d** aged TiO₂ [16]

capacitance of Schottky junctions formed with the similar semiconductor wafers were found to be almost frequency independent, both the flat and the rough one. Therefore, the existence of the electrolyte, which is the main difference between Schottky junctions and semiconductor-electrolyte junctions, is another possible source. Both the surface roughness and the ions must be taken into account to understand the source of the frequency dispersion.

2 Junction capacitance, rough surface and Helmholtz double layer capacitance

The semiconductor-electrolyte junction is equivalent to the series of a space charge capacitor C_{sc} and a double-layer capacitor C_{dl} , as illustrated in Fig. 3(a) [2]. Usually the semiconductor is not too heavily doped, and hence C_{sc} is much smaller than C_{dl} . Under this condition, the observed capacitance depends mainly on C_{sc} :

$$C = \left(\frac{1}{C_{sc}} + \frac{1}{C_{dl}} \right)^{-1} \approx C_{sc} \quad (4)$$

This is why it is possible to extract the doping concentration from a C - V measurement on a semiconductor-electrolyte junction. The simplification in equation (4) implies an assumption of classical geometry: The areas of both the semiconductor surface and the semiconductor-electrolyte interface are invariable at different frequencies, and the values are exactly equal. This is true when the surface is ideally smooth.

Unfortunately, ideal smooth surfaces are almost non-existent in real systems. Real surfaces are always more or less rough. The measurement of area is no longer a trivial problem. Since area is a very important factor for determining the capacitance, this non ideality could influence the effective areas on semiconductor-electrolyte junction capacitance in two aspects.

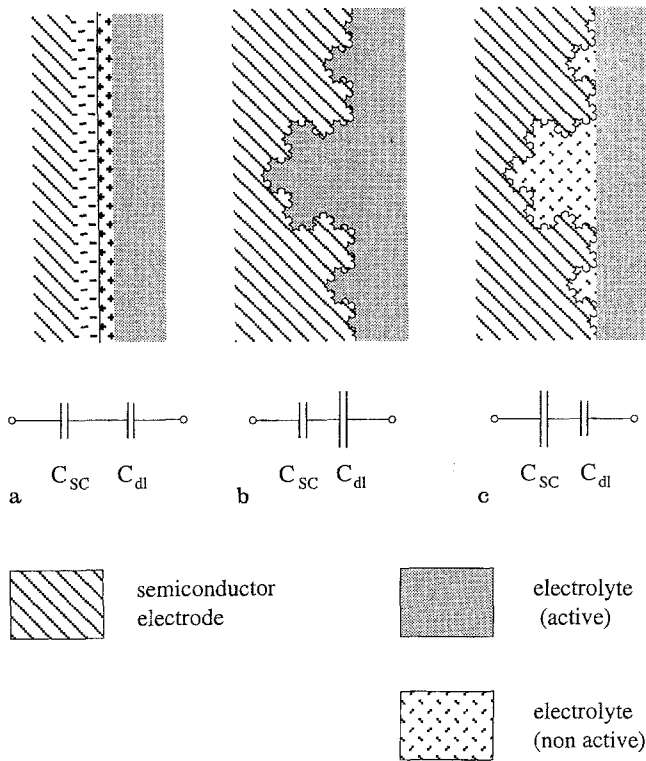


Fig. 3. Semiconductor-electrolyte junction capacitance. **a** smooth surface; **b** fractal surface, at small scale λ_1 ; **c** rough surface, at large scale ($\lambda_1 = 3^5 \lambda_1$)

First, the areas of both sides are no longer constant but a function of scale:

$$S = S(\lambda), \quad (5)$$

A special case will be discussed later in which $S(\lambda)$ is a scaling function of λ . Generally, $S(\lambda)$ is a monotonic decreasing function of λ : the smaller scale always corresponds to the larger area, and vice versa. The question is, what the scale is and how does it vary with the measuring signals.

In capacitance measurement, the “probes” are ions on the solution side and electrons (holes) on the semiconductor side. Their sensitivities in responding to the test signal determined the equivalent scales in relation (5). Since the ions in the electrolyte have relatively lower mobility (2 to 4 orders of magnitude) than the electrons and holes on the semiconductor side, their response to the ac signal is thus much slower than the response of the electrons and holes. In an alternating electric field $E_0 \sin \omega t$, the charge carriers drift periodically in a limited range. The average extent of such a drift is

$$x_m \propto \frac{\mu}{\omega}, \quad (6)$$

where μ is the mobility of the charge carriers. The lower the frequency, the larger the drift extent (x_m), and the finer and deeper recessions of the surface can be reached by the oscillatory drifting carriers, corresponding to a smaller scale and larger area. This is supported by experimentally measured equipotential surfaces at different frequencies

on rough model electrodes by Keddad and Takenouti (Fig. 4 of Ref. 19). That is to say, the scale is a positively correlated function of frequency

$$\lambda = \lambda(\omega), \quad (7)$$

And this, in turn, means that the area is a negative correlated function of frequency

$$S = S(\omega). \quad (8)$$

this is the second aspect: the measuring signal acts as a scale.

In the same way, the sensitivity of carriers to the detailed interface structure is positively correlated to the mobility, since they can move further for a period at a certain frequency, corresponding to a smaller scale. Thus the functions $\lambda(\omega)$ and $S(\lambda)$ may be different on each side

$$\lambda_{sc} = \lambda_{sc}(\omega), \quad S_{sc} = S_{sc}(\omega), \quad (9)$$

and

$$\lambda_{dl} = \lambda_{dl}(\omega), \quad S_{dl} = S_{dl}(\omega). \quad (10)$$

The (effective) mass of electrons or holes on the semiconductor side is very small and the mobility is large compared to ions, whereas the ions on the solution side are much heavier and slower. This results in a relatively smaller effective area on the solution side (S_{dl}) than on the semiconductor side (S_{sc}). The difference increases with the frequency. This means that there is a crossover frequency f_0 at which C_{dl} begins to overpass C_{sc} , and becomes dominant in the junction capacitance:

$$C = \left(\frac{1}{C_{sc}} + \frac{1}{C_{dl}} \right)^{-1} \approx C_{dl} \quad (11)$$

In some cases not far from the crossover frequency, both C_{dl} and C_{sc} must be taken into account if they are comparable [18]. f_0 is not easily determined without further knowledge about the relations $\lambda_{sc} = \lambda_{sc}(\omega)$, $S_{sc} = S_{sc}(\omega)$, $\lambda_{dl} = \lambda_{dl}(\omega)$, and $S_{dl} = S_{dl}(\omega)$. But we can show the general trend. The crossover frequency f_0 depends not only on the dopant concentration of semiconductor and the solution concentration of electrolyte, but also on the difference between S_{sc} and S_{dl} . The former is a constant which determines the ratio of C_{dl} and C_{sc} in the ideal case. The latter depends on the surface roughness, increasing with the frequency and it is therefore more important than the former. The rougher surface corresponds to the greater difference between S_{sc} and S_{dl} , and this in turn corresponds to the lower crossover frequency f_0 . Thus we understand why the frequency dispersion occurs only on semiconductor-electrolyte junctions in some experiments [7]. The area of a semiconductor-semiconductor junction, even with a very rough interface, can only be a weak function of frequency. The difference between areas of both sides should be very small, due to small difference in mobilities.

We notice that equations (1)–(3) are similar to the CPA impedance, see discussions below. According to (11), the junction capacitance is dominated by the Helmholtz double layer capacitance C_{dl} . Then we can further explain the experiment fact (2) and (3). The impedance of a

Helmholtz double layer is often found to be of the form [19, 21–24]

$$Z(\omega) = Z_0(i\omega)^{-\eta} = Z_0\omega^{-\eta}(\cos \theta - i \sin \theta), \quad (12)$$

where $i = \sqrt{-1}$, Z_0 and η are constant, ω the angular frequency of the electrical signal. The impedance of (12) is called “constant phase angle” (CPA) impedance because its phase angle $\theta = (\pi/2)\eta$ is a constant. η is between 0 and 1, negatively correlated to the roughness of the electrode surface.

The interface impedance on the electrolyte side can be equivalent to series of a capacitance C_{dl} and a resistance R_{dl} , then

$$Z(\omega) = R_{dl} + \frac{1}{i\omega C_{dl}}. \quad (13)$$

Note that R_{dl} is not the bulk resistance, which is a constant and small compared to the capacitance impedance at low frequency, while R_{dl} is proportional to the capacitance impedance. It is the resistance of the electrolyte in the vicinity of the interface.

By comparison of real and imaginary parts in (12) and (13) we have

$$R_{dl} = R_0\omega^{-\eta} \quad (14)$$

$$C_{dl} = C_0\omega^{-(1-\eta)} \quad (15)$$

where $R_0 = Z_0 \cos \theta$ and $C_0 = (Z_0 \sin \theta)^{-1}$. Equation (15) is similar to (1) and (3) except for a constant (b') in (1). Comparison between (1) and (15) gives $n = \eta - 2$, and $0 < \eta < 1$ which corresponds to $-2 < n < -1$, in agreement with (2). Thus, the experimental results in Fig. 1 can be explained by the dominant of CPA impedance. However, we still do not know the relation between the frequency dispersion and the surface roughness.

3 The frequency dispersion of fractal models

Many rough surfaces can be well described by fractal geometry introduced by Mandelbrot [25–28]. The area S of a fractal surface is related to the scale λ by the scaling law:

$$S(\lambda) = S_0\lambda^{-(D-2)}, \quad (16)$$

D is called the fractal dimension of the surface. A smooth surface has a dimension of 2 and hence a constant area. Fig. 4 shows a model of such a rough surface; its profile is generated by repetitions of Koch curves. The fractal dimensions of the surface and its profile are 2.26 and 1.26 respectively. Of course, this is again an idealized model. For a realistic rough surface, fractal geometry is valid in certain range of scales between the lower limit A_{min} and the upper limit A_{max} . We can define three different surfaces as follows:

- $\lambda < A_{min}$: the inner surface, $D = 2$ (non fractal)
- $A_{min} < \lambda < A_{max}$: the fractal surface, $2 < D < 3$
- $\lambda > A_{max}$: the outer surface, $D = 2$ (non fractal).

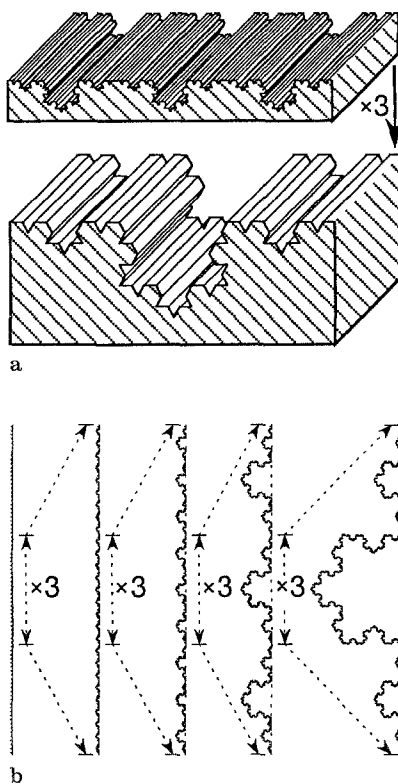


Fig. 4. a A model electrode with the Koch curve alike rough surface. b Its profiles at different magnification

Both the inner and the outer surfaces are non fractal. We call the area of the fractal surface the “effective” area. Its relation to the scale is as equation (16).

The power law behavior of frequency dependent capacitance of rough semiconductor-electrolyte junctions implies the possible links to fractal geometry, since the capacitance is directly proportional to the area. Now there are two different surfaces. One is the semiconductor surface; its area keeps invariable. The other is the effective surface of the Helmholtz double layer; its area varies with scale. The Helmholtz double layer capacitance, which is proportional to the area of the Helmholtz double layer, is a function of scale, and so is the observed junction capacitance:

$$C \approx C_{dl}(\lambda) \propto S(\lambda) = S_0\lambda^{-(D-2)}. \quad (17)$$

In order to link the capacitance to frequency, we must find the relationship between the scale and the frequency. Fortunately, this can be done with the help of theories developed to interpret the constant phase angle impedance.

As mentioned before, the impedance of a Helmholtz double layer is often found to be “constant phase angle” (CPA) impedance. η is between 0 and 1, negatively correlated to the roughness of the electrode surface. η is close to 1 for a very smooth electrode such as mercury and crystal, corresponding to pure capacitive impedance:

$$Z(\omega) \rightarrow \frac{Z_0}{i\omega}. \quad (18)$$

While for a very rough electrode, η is close to zero, therefore

$$Z(\omega) \rightarrow \text{const.} \quad (19)$$

The origin of the CPA had not been understood for decades. After the fractal concept was introduced by Mandelbrot in the mid 1970s, there have been attempts to relate the CPA to the fractal geometry of a rough electrode surface. In Liu's Cantor bar model [21], the CPA exponent η is simply related to the fractal dimension D of the electrode surface

$$\eta = 3 - D. \quad (20)$$

This is consistent with the trends of (18) and (19) at both smooth ($D \rightarrow 2$) and very rough ($D \rightarrow 3$) limits.¹ Sapoval et al. [22], Y.T. Chu [23], R.M. Hill and R.A. Dissado [24] reached the same relation as Liu through different models. To substitute (20) with (14) and (15) gives

$$R_{dl} = R_0 \omega^{-(3-D)}, \quad (21)$$

and

$$C_{dl} = C_0 \omega^{2-D}, \quad (22)$$

where C_0 is a constant. This is in accordance with experiments in the power form. The exponent indicates the deviation of the surface from an ideal plane. The frequency dispersion is direct linked to the surface dimension. Therefore, it is a measure of the surface roughness. Furthermore, comparison of (22) and (17) gives the important relation between frequency and scale

$$\lambda = \lambda_0 \omega \quad (23)$$

Equations (20)–(23) can also be obtained in another approach [29]. It is obvious that the capacitance C_{dl} varies with scale according to (17), which is related to frequency by equation (23). Now we discuss the real part. In the smooth case, R_{dl} is a constant and negligible compared to the bulk resistance of the solution, since it involves only a very thin layer of solution. While in the rough case, the resistance of those solutions between outer and effective interfaces will vary with frequency, contributing to the total impedance as its real part and not negligible, as illustrated in Fig. 5. The interface resistance, i.e., the resistance of the solution layer between the outer and effective interface, is difficult to analyze exactly. However, it should be proportional to the average depth the ions can reach in a period, which is proportional to x_m , and inversely proportional to the area:

$$R_{dl} \propto \rho \frac{x_m}{S} \propto \rho \frac{\mu}{\omega S_0 \lambda^{-(D_s-2)}} \propto \frac{\lambda^{D_s-2}}{\omega}. \quad (24)$$

¹Although Liu et al. later found that equation (20) may not hold in the "general" case, which means that the profiles of the surface along different directions have different fractal dimensions. Still equation (20) holds in the more common *homogeneous* case. We can apply the relation (20) at least in these cases.

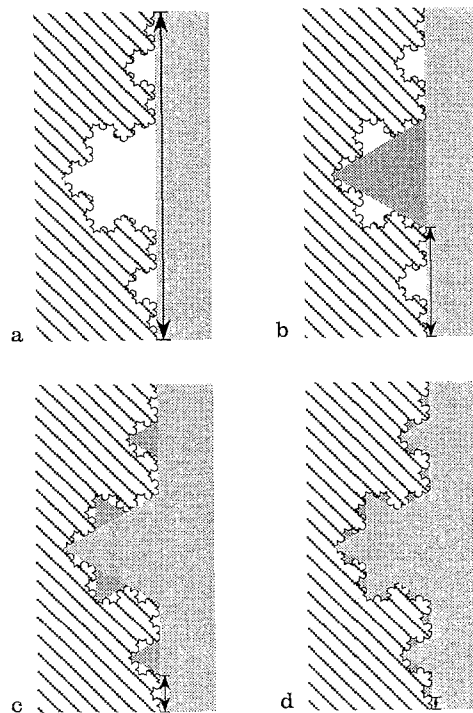


Fig. 5a–d. Illustration of effective area and interface resistance vs. scale (frequency). Arrows indicate the different scales. The darker gray shows more electrolyte contributions to resistance. **a** $\lambda = \lambda_0$; **b** $\lambda = \lambda_0/3$; **c** $\lambda = \lambda_0/3^2$; **d** $\lambda = \lambda_0/3^3$

Substitution of C_{dl} in (13) with (17) and R_{dl} from (24) gives

$$Z(\omega) = R_0 \frac{\lambda^{D_s-2}}{\omega} - iC_0 \frac{\lambda^{D_s-2}}{\omega} = \frac{\lambda^{D_s-2}}{\omega} (R_0 - iC_0) \quad (25)$$

R_0 and C_0 are constants. Thus, we find that the phase angle $\theta = -\text{arctg}(C_0/R_0)$ is a constant. In order to satisfy the experiment fact that λ must be proportional to ω (see (19)), we obtain the frequency-scale relation

$$\lambda = \lambda_0 \omega \quad (23)$$

Applying (23) to (24), we obtain

$$Z(\omega) = \lambda_0 \omega^{D-3} (R_0 - iC_0). \quad (26)$$

Comparison (23) with (12) yields the relation between η and D , namely

$$\eta = 3 - D. \quad (20)$$

Relation (26) is consistent with the trends of (18) and (19) at both smooth ($D \rightarrow 2$) and very rough ($D \rightarrow 3$) limits. Equations (23), (26) and (20) are general relations, independent of any specific model.

4 Conclusions

In the summary, we have discussed the frequency dispersion of the semiconductor-electrolyte junction capacitance

and its relations to the semiconductor surface roughness and the properties of the ions. If the semiconductor has a rough surface, the effective area on the solution side will depend on the frequency, which corresponds to the scale, and so will the capacitance of Helmholtz double layer. Due to much lower mobility of ions compared to that of electrons (holes) in the semiconductor, the observed capacitance can be dominated by the Helmholtz double layer capacitance. The capacitance-frequency relation is then expected to be a power law, similar to that of the imaginary part of the commonly observed constant phase angle (CPA) impedance. The exponent is related to the surface roughness and can easily be related to the fractal dimension according to the fractal models of CPA impedance. Without ions with very low mobility, the physical connection between frequency and geometry, other semiconductor junctions behave in different ways: their capacitance is not dependent on the frequency as are the semiconductor-electrolyte junctions. Subsequently the frequency dispersion and its dependence on surface roughness of the semiconductor-electrolyte junction capacitance can be explained.

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