Method of Measuring Dielectric Constant By Using Atomic Force Microscopy

Deema Aldaife

Epartment Of Science And Mathematics In Physics Sciences
Wright State University, Dayton, Oh 45435 Usa
Department Of Physics, Faculty Of Science,University College in Qunfudah, Umm Al Qura University
P.O.Box. 715, Makah 21955, Saudi Arabia

Abstract: *In this article, we present a new technique to measure the static dielectric constant which was developed using atomic force microscopy (AFM) system. This technique is polarizability that is produced due to a low-frequency electric field. In addition, it is due to both permanent dipoles in the material and induced dipoles. Our goal was to show some physical, measurable quantity by Atomic Force Microscopy that can be related to the dielectric constant and our method was tested on a material whose dielectric constant is known such as strontium titanate and mica. The advantage of this method is that it does not require using the complex simulations that depend on the geometry of probe tip which is complicated and difficult to characterize.*

I. Introduction

The importance of nanotechnology applications is the precise measure of important physical properties of materials on submicroscopic scales. One of the major goals of nanotechnology is the construction of micro-electromechanical systems which require that the response of these devices to external fields be known very precisely. For this reason, there is much interest in the ability to locally determine the dielectric constant of materials at the micrometer and nanometer levels. Because atomic force microscopy has the ability to detect and record the magnitude of a wide variety of physical forces a surface can produce, it is not surprising that various forms of atomic force microscopy, such as capacitance and electrostatic force microscopy, have been developed to measure the dielectric constant of the nanoscale film [1].

5 years ago, Z types of Atomic Force Microscopy (AFM) were used to measure dielectric constants at the nanoscale using capacitance force microscopy and electrostatic force microscopy. Perhaps, the first attempt to study the dielectric behavior of a material using atomic force microscopy was made by Crider, et al .
Using a non-contact form of scanning probe microscopy that applied a variable, requency biased voltage, [2,3] it was shown that the frequency dependent behavior of a material's dielectric response could be studied. This method was applied successfully to characterize the complex dielectric permittivity of a polymer film, but was unable to provide the actual value of the dielectric constant itself.

Although some probe microscopy has been used to study the frequency dependent part of the dielectric, there are problems with this approach and most research has focused on the static contribution to the dielectric constant [2, 3]. The analysis of the expression that models this interaction does contain some coefficients but the value of these coefficients can be found by using a reference sample. This method gives precise values and it does not depend on the complicated shape of the Electrostatic Force Microscopy (EFM) tip. The method was tested on four materials (mica, polystyrene, silicon dioxide, and polymethyl methacrylate) with silicon dioxide used as the reference material. The results obtained showed good agreement with those reported in the literature [4]. In this article, we apply the "comparative method" of Rivella using two materials, strontium titanate and mica, with mica serving as our reference source[4].   Atomic Force Microscopy (AFM) tip can be used as a probe to detect long-range electrostatic force. This total electrostatic force, F_e , acting between tip and substrate can be represented as a superposition of two interactions: the tip-substrate capacitive interaction and the Coulomb interaction. These forces are due to surface static charges and multiple[5,6].The total force can be written as:

$$F_e = \left(\frac{\partial C}{\partial z}\right)\left(\frac{V^2}{2}\right) + E_s Q_t$$

(1)

Where C is the effective tip-substrate capacitance, z is the effective tip-substrate distance, V denotes the voltage applied to the tip, E_s is the electric field at the tip location that is only created by the charges and/or multiples on the sample surface.

Q_t in (Eq. (1)) describs the charge on the tip as follows (Eq. (2)), [7]

$$Q_t = CV + Q_{im} \tag{2}$$

Where Q_{im} is an image charge induced by the static charge in the substrate.

When the tip is subjected to the voltage and brought closer to the surface of the dielectric film then electric field E_t due to the tip voltage creates the dipoles in the sample.

It is well known that polarization P_s are proportional to electric field E_t

and can be expressed as follows (Eq. (3))

$$E_t = a(z)V \tag{3}$$

Where $a(z)$ is a factor related only to the tip – sample distance and tip geometry. Separation between the AFM tip and thin film is so small then we can consider a surface of the sample as an infinite plane. Under this description, electric field nearby the sample surface is generated by polarized dipoles in the sample. The electric field E_s at the tip location can be expressed by (Eq. (4)).

$$E_s = \frac{P}{\varepsilon_0} = \chi_s a(z) \frac{V}{2} \tag{4}$$

The total force $F_v(z)$ on the tip at given voltage V can be expressed as (Eq. (5))

$$F_V(z) = \frac{1}{2}[\frac{\partial C}{\partial z} + a(z)\chi_s C]V^2 + \frac{1}{2}a(z)\chi_s Q_{im}V + F_0(z) \tag{5}$$

Where $F_0(z)$ is the tip-sample interaction at zero voltage associated with van der Waals interaction. (Eq. (5)) is an analytical expression for the force between the biased tip and the thin film (substrate). In order to find this force and the tip-sample separation, the following analysis has to be done (Fig.1):
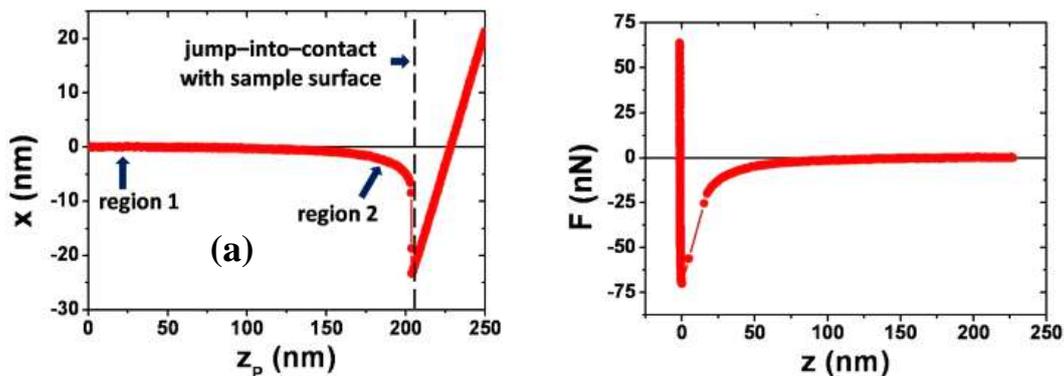

Fig.1. a) Representation of a typical force-curve (cantilever deflection, x,vs. Drive piezo distance,z_p). b) Force vs. nominal separation (z = x −z_p + const) obtained from the force−curve in (a), [4].

− Region 1 in the (Fig.2a) describes the lack of the cantilever deflection (x = 0) because the distance between the tip and the sample surface is large;
− In region 2, the cantilever bends downwards due to Coulomb and van der Waals interactions;
− When the tip suddenly becomes close enough to the surface of the sample, cantilever jumps into-contact with surfaces (at the minimum cantilever deflection) [8-11].

As it is well known, interaction force between tip and sample , F_e can be calculated from restoring force due to cantilever deflection x. The nominal separation, z, is the deflection minus the drive distance, z_p (Eq. (6)), [12]

$$z = x - z_p + const \tag{6}$$

Where the constant represents the choice of zero of separation (Fig.2b).

So, it can be seen in the theoretical basis in the supporting information regarding measuring the force at zero volt and two other different voltages, V_1 and V_2, the coefficient of the quadratic contribution in (Eq. (5)). This can be expressed by (Eq. (11)):

$$F_{V1}(z) = \frac{1}{2} g(z) V_1^2 + \frac{1}{2} a(z) \chi_s Q_{im} V_1 + F_0(z) \tag{7a}$$

$$F_{V2}(z) = \frac{1}{2} g(z) V_2^2 + \frac{1}{2} a(z) \chi_s Q_{im} V_2 + F_0(z) \tag{7b}$$

Subtract $F_0(z)$ from both sides of both(Eqs.(7a)-(7b)):

$$F_{V1}(z) - F_0(z) = \frac{1}{2} g(z) V_1^2 + \frac{1}{2} a(z) \chi_s Q_{im} V_1 \tag{8a}$$

$$F_{V2}(z) - F_0(z) = \frac{1}{2} g(z) V_2^2 + \frac{1}{2} a(z) \chi_s Q_{im} V_2 \tag{8b}$$

Divide through (Eq. (8a)) by V_1 and (Eq. (8b)) by V_2 :

$$\left[\frac{F_{V1}(z) - F_0(z)}{V_1}\right] = \frac{1}{2} g(z) V_1 + \frac{1}{2} a(z) \chi_s Q_{im} \tag{9a}$$

$$\left[\frac{F_{V2}(z) - F_0(z)}{V_2}\right] = \frac{1}{2} g(z) V_2 + \frac{1}{2} a(z) \chi_s Q_{im} \tag{9b}$$

So, subtract (Eq. (9b)) from (Eq. (9a)):

$$\left[\frac{(F_{V_2}(z) - F_0(z))}{V_2} - \frac{(F_{V_2}(z) - F_0(z))}{V_1}\right] = \frac{1}{2} g(z)(V_2 - V_1) \tag{10}$$

Finally, we arrived in quantity of $g(z)$ as follows (Eq. (11)) as shown (Fig.7b)

$$g(z) = \frac{2}{(V_2 - V_1)} \left\{ \left[\frac{F_2(z) - F_O(z)}{V_2}\right] - \left[\frac{F_1(z) - F_O(z)}{V_1}\right] \right\} \tag{11}$$

So, to repeat it, we fixed a voltage V and measured F_v as a function of z, for each voltage. We did three measurements and averaged them.

When the surface is coated with dielectric material, the force produced by the change in the capacitance shows (Eq. (6)), this is the term $[(\frac{1}{2})(\partial C/\partial z) V^2]$. The contribution due to $\partial C/\partial z$ becomes small. So, the predominant term is due to electrostatic interaction between the probe tip and the permanent dipoles in the dielectric sample. Therefore, two different dielectric films of the same thickness were used. Accordingly, the capacitive interaction could be far lower than the electrostatic interaction.

$(\frac{\partial C}{\partial Z} << a(z) C \chi_s)$, and chose that $a(z)$ the same for each of the films. Therefore, (Eq. (12)).

$$g = \frac{\partial C}{\partial Z} + \chi_s a(Z) C \approx \chi_s a(Z) C \tag{12}$$

due to the dielectric constant and the $a(z)C$ is the same for both coatings (Eq. (13))

$$\left[\frac{g(sample\ 2)}{g(sample\ 1)}\right] = \left[\frac{(\frac{\partial C}{\partial z} + a(z)\chi s2\ C)}{(\frac{\partial C}{\partial z} + a(z)\chi s1\ C)}\right] = \left[\frac{(\varepsilon_{r_2} - 1)}{(\varepsilon_{r_1} - 1)}\right] \tag{13}$$

We have chosen one of the dielectric films to be one whose dielectric constant is known and the other is the one we are interested in.

II.   Experimental Data

A commercial Atomic Force Microscope was used and the measurements from strontium titanate were done at $30\,C^{\circ}$. A conductive cantilever was used for the measurements with a coating of $Pt\ /\ In$ Pt/In (on both sides) and a spring constant of $2\,N\ /\ m$. An average force curve for each external voltage ($0V$,$5V$,$10\,V$) was obtained from three force curves; all were taken at the same place on the sample. To make sure the tip did not change during the measurements, the probe radius was measured before and after each test. The average force curve is used to create the force versus tip-to-sample distance curve for each voltage, using the fact that $F = Kx$ and $z = x - z_p + const$ this was done for $0V$,$5V$ and $10\,V$, creating curves $F_0(z)$, $F_1(z)$ and $F_2(z)$, respectively. By inserting these three curves into (Eq. (11)), a $g(z)$ curve is generated for strontium titanate. The $g(z)$ curve for mica was obtained from [4]. The ratio of the strontium titanate $g(z)$ to the mica $g(z)$ is then formed. Using, (Eq. (13)), the dielectric constant for strontium titanate is then found.

III.   Result

Cantilever deflections were measured with a varying z_p over the etched area of the $SrTiO_3$ sample. Three force curves were created, for voltages of $0V$,$5V$, and $10\,V$ shown in (Fig.2 -4), respectively. These figures show both the raw deflection data, for one measurement, along with smoothing fits generated with Matlab.
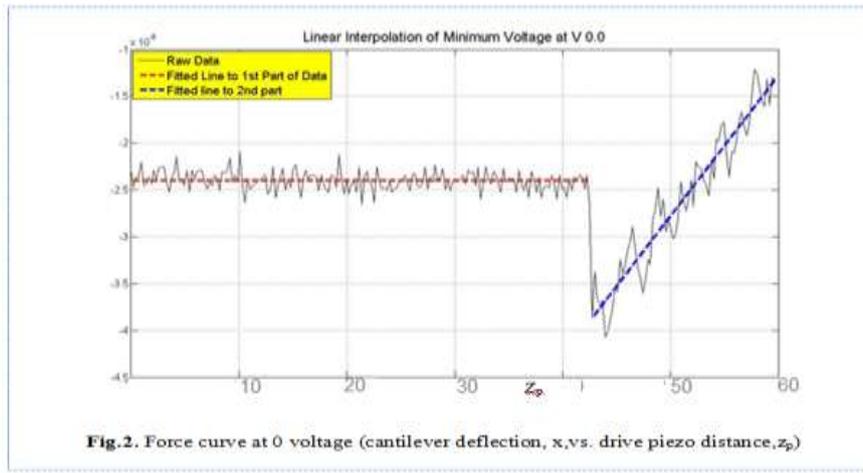

Fig.2. Force curve at 0 voltage (cantilever deflection, x,vs. drive piezo distance,z_p)

force_curve in (Fig.4)

(Eq. (6)), along with Hooke's law *F=kx*, provides the relationship between the tip to sample distance z and the force of attraction F. The spring constant *k* was 2 N/m. The data in (Fig2-3-4) can be modified in order to plot F versus z, and this is shown in (Fig.5-6-7), for all three voltages used. These plots provide $F_0(z)$, $F_1(z)$, and $F_2(z)$ for voltages $0V$,$5V$, and $10\,V$.
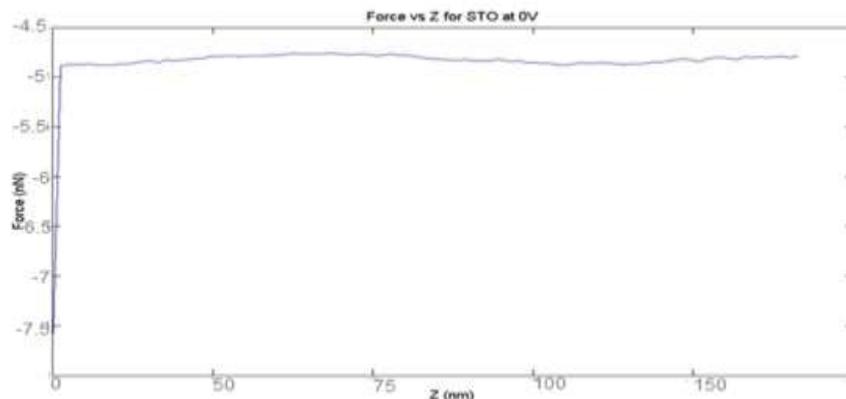

Fig.5. Representation of Force *vs*. Nominal separation

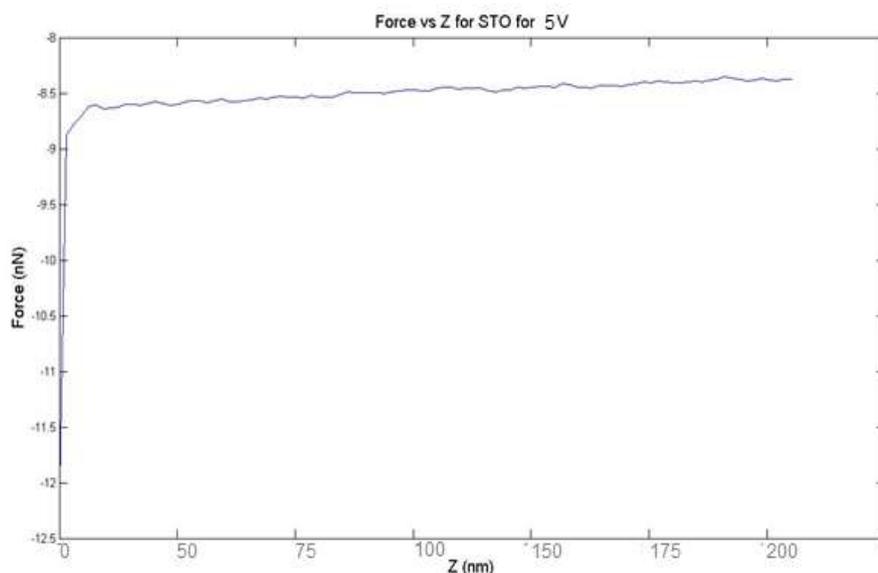(z = x − zp + const) obtained from the force−curve in (Fig.2)

Fig.6. Representation of Force vs. nominal separation (z = x − zp + const) obtained from
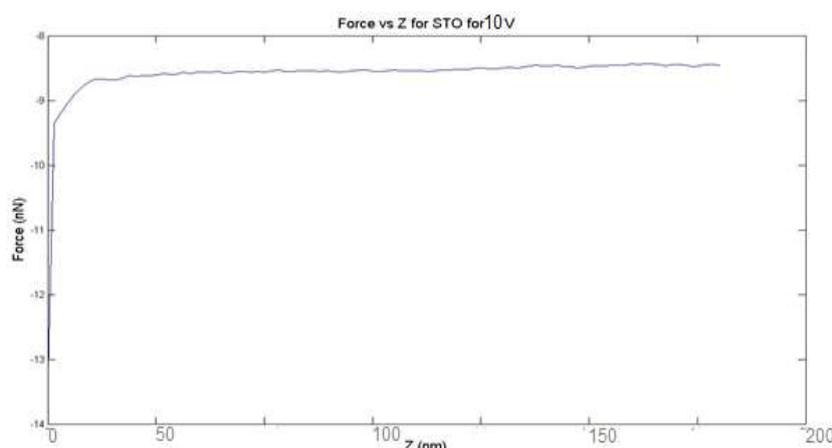the force−curve in (Fig.3)

Fig.7. Representation of force vs. nominal separation ($z = x - z_p + const$) obtained
from the force_curve in (Fig.4)

IV. Dielectric Constant Calculations

We measured the force at the different distance (Fig7a, 8a) and then used this equation and computed it. So, they fixed the a voltage V and measured it as a function of .For each voltage, they did three measurements and averaged them. So, substituting the three force curves into the following formula allows $g(z)$ to be computed for strontium titanate.

$$g(z) = \frac{2}{(V_2 - V_1)} \left\{ \left[\frac{F_2(z) - F_0(z)}{V_2} \right] - \left[\frac{F_1(z) - F_0(z)}{V_1} \right] \right\}$$

The Three forces curves are illustrated in (Fig.7), and the resulting $g(z)$ is shown in
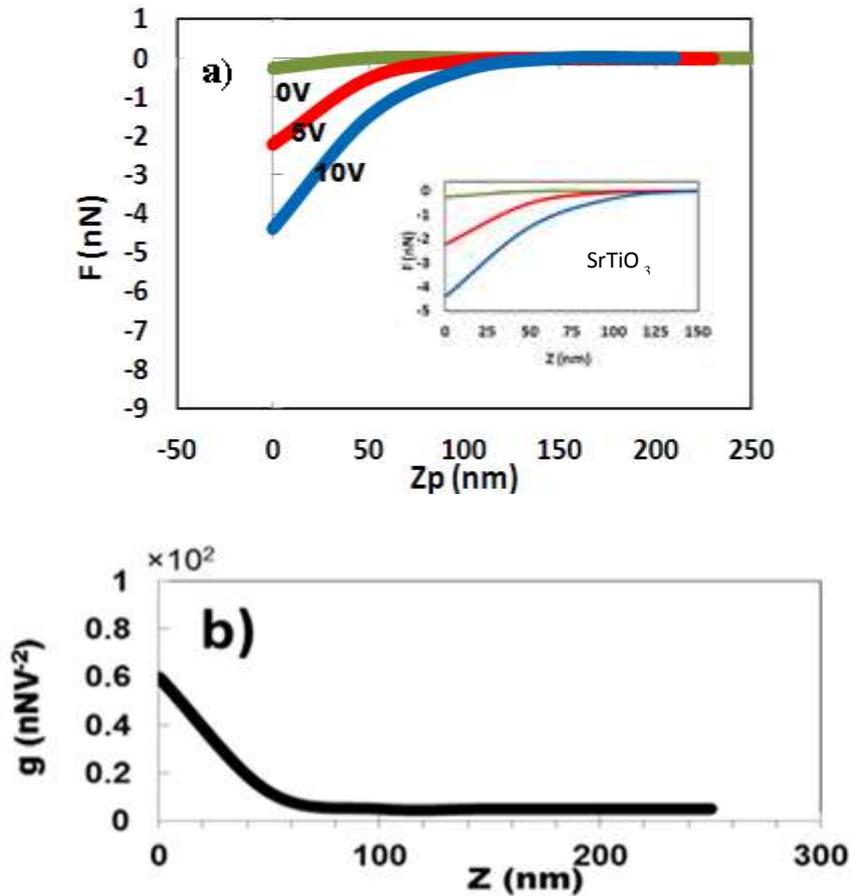
Fig.8. a) Force-curve obtained on a SrTiO3 substrate at tip bias of 10, 5 and 0 volts.b) Value of g(z) versus tip-sample distance, obtained from the force-curve on a surface represented in Figure 2a and using eq 11.

So, they used two different dielectric films ($SrTiO_3$ and mica) of the same thickness. The film can be chosen such as $a(z)C$ which is about same for each. Therefore

$$g = \frac{\partial C}{\partial z} + \chi_s a(z)C \approx \chi_s a(z)C$$

Due to the dielectric coating and since a(z)C is about the same both coating

$$\frac{g(SrTiO_3)}{g(mica)} \approx \frac{\chi_{s-Sto}}{\chi_{s-mica}} = \frac{\varepsilon_{r\_Sto} - 1}{\varepsilon_{r\_mica} - 1}$$

For the mica sample, data from, [4] was used, shown in (Fig.8). Figure 8a illustrates the average force curves for $0V$, $5V$, and $10V$, and (Fig.8b) illustrates the $g(z)$ plot forward
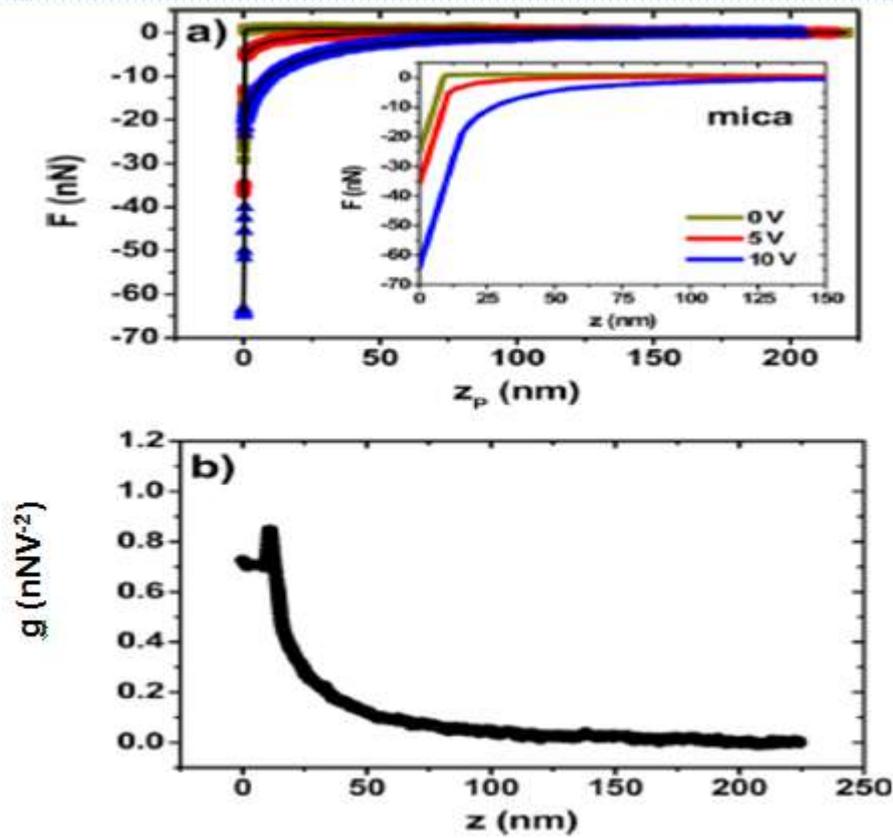
Fig.9. a) Force-curve obtained on a mica substrate at tip bias of 10 ,5 and 0 volts.

 b) Value of $g(z)$ versus tip-sample distance, obtained from the force-curve on a mica surface represented in Figure 2a and using eq11.

To compute the dielectric constant for strontium titanate (ε_{r_sto}), the following equation is solved for ε_{r_sto}:

$$[\frac{g(Sto)}{g(mica)}] = [\frac{\varepsilon_{r\_Sto} - 1}{\varepsilon_{r\_mica} - 1}] \tag{14}$$

For both the strontium and the mica, the $g(z)$ values are used when $z = 0$. For mica, $g(z = 0)$ is $0.7 \, nN \ /V^{2}$, and for strontium titanate, $g(z = 0) = 60 \, nN \ /V^{2}$. The dielectric constant for mica is taken to be 7.4 . Solving this for the strontium dielectric constant gives a value of $\varepsilon_{r-sto} = 400$. The accepted dielectric constant value for strontium titanate is 300 [4, 5]. Therefore, the measured value is an approximation, and the reason for the difference will be discussed in the next chapter.

V.   Discussion

In this section, we discuss the electrostatic properties of the *SrTiO*$_{3}$ and mica samples, and the computation of the dielectric constant. The Atomic force microscopy measurements enable us to record the interaction between the probe and the sample surface in term of cantilever deflection. The theoretical model allows us to connect the sample dependent cantilever deflection with the dielectric constant of the material under study (Eq. (13)).

We used a method of comparison to measure the dielectric constant of strontium titanate, which is relatively thick (about 500 *nm* or thicker), using the technique outlined in [4]. This technique allows for a comparison of the dielectric properties of materials with relatively low and similar values, and it works at the nanometer scale. A nice feature of the technique is that it avoids complex simulations involving the irregular shape of an AFM tip. This method can also significantly reduce the measurement time as well as the requirement on the amount of experimental data needed. Among the advantages of the method can also be

mentioned that it is independent of tip geometry and the contact area and does not need the computation of cantilever stiffness.

The method relies on force curves such as those shown in (Fig3-5), where the voltage between the tip and sample is $0V$, $5V$, and $10V$. It can be noticed that as the voltage is increased, the electrostatic force causes greater deflection of the tip as it approaches the surface of the sample. This most useful electrostatic deflection data occurs at a tip to sample distances of $10 - 40\ nm$. At distances below $10\ nm$, the tip is nearly jumping to the surface, which creates instability in the data. At distances greater than 40nm, the electrostatic force is too small to reliably measure.

The measured value for the strontium titanate dielectric constant was 400, but the accepted value is 300. This difference could be due to several reasons. First, the $g(z)$ values were used for $z = 0$, but at this low value of tip to sample separation where the tip is nearly jumping to the sample, the data can be unstable. To correct this, it may be better to use $g(z)$ values for larger z, in the range of $20 - 25\ nm$. The second reason for the difference is the fact that different types with different spring constants are used to measure the strontium titanate and the mica. The mica data, taken from, [4], were generated with a tip that had a spring constant of $3\ N/m$. The tip used for the measurement of strontium titanate had a spring constant of $2\ N/m$. Also, it is not known if the geometry of the two tips is the same. This means that $a(z)$, which depends on tip geometry, may be different for the two different tips. In (Eq. (13)), it is assumed that the $a(z)$ is cancelled out, but this may not actually be true. To correct this problem, it would be better to use the same tip to generate $g(z)$ for both samples. A third way to improve the dielectric calculation would be to generate the $g(z)$ ratio for a range of z values, and then perform an average. This would reduce the effects of noise on the calculation. Another possible explanation for errors in this technique is that it assumes that the capacitance gradient ($\partial C/\partial z$) is zero, which is not entirely true and which would affect the result.

Refferances

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