Origin of the High Capacity of Self-Assemble Nano-Composite Thin Film

Cheng Kaijia, Cheng Shuyu, Lin Dongsheng, Xiao Gang
(Northwest Institute of Nuclear Technology, Xi'an 710024, China)

Abstract: TFDC (Thomas-Fermi-Dirac-Cheng) electron theory is applied to analyzing the characteristics of the electrons inside the double layer of the nanometer composite thin films. This paper proposes the new mechanism about the high capacity in both theoretical analysis and experimental measurement.

Key words: TFDC electron theory; double layer; high capacity; thin film
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1 The Charge and Discharge Processes in the Double Layer of the Composite Film

As shown in Fig.1, an nanometer-size ceramic thin film b is coated on a metal base a, and then an interface between the ceramic thin film and the metal does exist. TFDC (Thomas-Fermi-Dirac-Cheng) electron theory proposes two important boundary conditions at the interface that the electron densities and the chemical potentials of two sides must meet the continuous conditions in accordance with the principles of quantum mechanics[1~3]. The satisfaction of these two boundary conditions makes the electron distribution in the boundary significantly changed, which, in turn, affects the properties of both mechanics and electricity of such formed composite thin film. This paper provides an only discussion on the continuity of chemical potentials, since the chemical potentials play more important role in forming high capacity in the double layer than another. Our study is focused on the mechanism of high capacity in the double layer.

Fig.2 shows the energy levels of two materials of the composite thin film. The chemical potential of ceramic, b, is less than the chemical potential of the metal, a. Precisely, since the energy level of the bottom of the vacant band of the ceramic b is lower than the Fermi energy of the metal a (see Fig.2a), the electrons inside metal will transfer into the vacant band of the ceramic(see Fig.2b), so that the total energy of the whole system will be shifted to a new stable state to reach a balance as total energy minimum. Then the new electrons distribution besides of the interface, defined as the "double layer" by the TFDC electron theory, is formed and a new electron phase is just taking place.

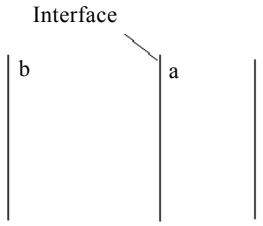

Fig.1 Scheme of the composite thin film

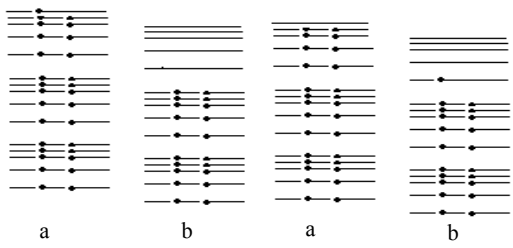

Fig.2 The energy levels of the composite thin film: (a) original energy lever and (b) energy lever after electron

Fig.3 shows the electron distribution inside the composite thin film. In Fig.3a, the electrons, originally located at the higher energy levels of the metal a**,** are moving across through the interface into the side of the ceramic b. Fig.3b denotes the distribution of the electron density $n(x)$ after electrons transfer, related to the coordinate x inside the ceramic thin film.

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Biography: Cheng Kaijia, Academician of Chinese Academy of Science, Northwest Institute of Nuclear Technology, Xi'an 710024 P. R. China

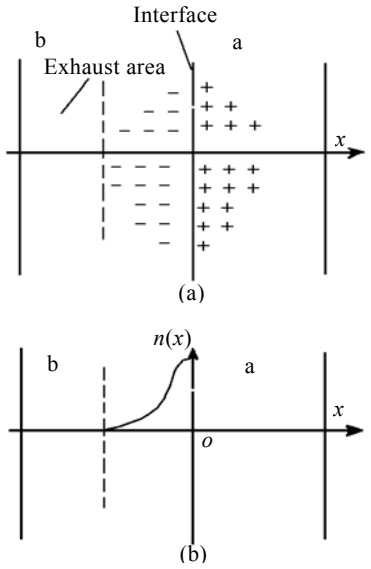

Fig.3　The electron distribution inside the composite thin film

2　The Energy of the Electrons inside the Double Layer of nm Composite Thin Film

2.1　Calculation of the electrons energy

Under the action of Fermi energy, Coulomb energy and exchange energy, the total energy of the electrons inside the film is calculated as follows:

$$E=\int\left\{\begin{array}{l}\dfrac{3h^2}{10m'}\left(\dfrac{3}{8\pi}\right)^{\frac{2}{3}}n^{\frac{2}{3}}(x)-\beta e^2\dfrac{3}{4}\left(\dfrac{3}{\pi}\right)^{\frac{1}{3}}n^{\frac{1}{3}}(x)+\\ e\left[V_m(x)/2+V_b(x)\right]-\mu\end{array}\right\}n(x)\mathrm{d}x$$

Where the first term in the big bracket is the kinetic energy of the electrons, the second term is the exchange energy of the electrons, $V_m(x)/2$ is the sum of the potential energy existing between each pair of electrons inside the film, in which factor 1/2 is used for cutting the repeated counts, $V_b(x)$ is the potential energy between each electron in the film and the electron at the interface, μis the chemical potential of the material, h is the Plank constant, e is the electron charge, m' is the effect mass of the electron, n is the electron density.

2.2　The change of electron distribution and the electron energy change inside the double layer

The change of electron distribution inside the composite thin film does not happen until the double layer of the composite thin film is formed.

The electrons energies before and after the formation of the double layer may be described separately as follow:

$$E_0=\int f(n_0)\mathrm{d}x$$

And

$$E=\int f(n)\mathrm{d}x=\int\left[\begin{array}{l}f(n_0)+f'(n_0)(n-n_0)\\+\dfrac{1}{2}f''(n)(n-n_0)^2\end{array}\right]\mathrm{d}x$$

The change of the total energy due to the electrons transfer is as following:

$$\Delta E=E-E_0=\int\left[\frac{1}{2}A\eta^2+\left(B+\frac{1}{2}eV-\mu\right)\eta\right]\mathrm{d}x$$

$$\eta=n-n_0$$

$$\begin{aligned}A&\equiv\frac{h^2}{3m}\left(\frac{3}{8\pi}\right)^{2/3}n_0^{-1/3}-\frac{1}{3}\left(\frac{3}{\pi}\right)^{2/3}e^2n_0^{-2/3}\\B&\equiv\frac{h^2}{2m}\left(\frac{3}{8\pi}\right)^{2/3}n_0^{2/3}-\left(\frac{3}{\pi}\right)^{1/3}e^2n_0^{1/3}\\x>0,&\quad\mu=\mu\\x<0,&\quad\mu=0\end{aligned}\tag{1}$$

Where μ_1 and μ_2 are the chemical potentials of the two materials in the composite thin film, $\mu_1-\mu_2$ is their difference. $\eta(x)$ is the change of the electron density at x, $V(x)$ is the change of the Coulomb potential satisfying the following relation:

$$\Delta V(x)=-4\pi\eta e/\varepsilon\tag{2}$$

Where ε is the dielectric constant of the material. The boundary conditions are as follows:

$$x=0\qquad V(+0)=V(-0)$$

$$\frac{\mathrm{d}V}{\mathrm{d}x}(+0)=\frac{\mathrm{d}V}{\mathrm{d}x}(-0)$$

From eq. (1) and (2), one obtains the following equations about $\eta(x)$

$$\begin{aligned}&A\eta+B+eV-\mu=0\\&\eta=\frac{-1}{A}(B+eV-\mu)\\&\Delta\eta=\frac{4\pi e^2}{A\varepsilon_0}\eta\end{aligned}\tag{3}$$

Then the solutions of $\eta(x)$ are:

$$\begin{aligned}\eta_{\pm}&=\eta_{0\pm}e^{\mp\frac{x}{x_0}}\\x_{0\pm}&=\sqrt{\frac{A_{\pm}\varepsilon}{4\pi e^2}}\\\eta_{+0}&=\frac{1}{\sqrt{A_+}}\frac{B_--B_++\mu}{\sqrt{A_+}+\sqrt{A_-}}\\\eta_{-0}&=\frac{-1}{\sqrt{A_-}}\frac{B_--B_++\mu}{\sqrt{A_+}+\sqrt{A_-}}\end{aligned}\tag{4}$$

Where "+" and "—" represent the two sides of the interface, namely "+" denotes x>0, and "—" denotes x<0.

Hence the energy changes of both the ceramic thin film and the metal base ΔE_1 and ΔE_2 are:

$$\Delta E_1 = \int_0^{L_+} \left[\frac{1}{2} A_+ \eta_{0+}^2 e^{\frac{-2x}{x_{0+}}} + (B_+ + eV - \mu)\eta_{0+} e^{\frac{-x}{x_{0+}}} \right] \mathrm{d}x$$

$$\Delta E_2 = \int_{L_-}^{0} \left[\frac{1}{2} A_- \eta_{0-}^2 e^{\frac{-2x}{x_{0-}}} + (B_- + eV)\eta_{0-} e^{\frac{-x}{x_{0-}}} \right] \mathrm{d}x$$

Where L_+ and L_- are the depths of the ceramic thin film and the metal base separately. The total energy change E is obtained:

$$E = \Delta E_1 + \Delta E_2 = -\frac{1}{4}\sqrt{\frac{\varepsilon}{4\pi e^2}} \frac{(B_- - B_+ + \mu)^2}{\sqrt{A_+} + \sqrt{A_-}} \tag{5}$$

2.3 The capacity of the double layer of a composite thin film

The capacity C is defined as follows:

$$E = \frac{1}{2} CV^2$$

Where E is the total energy of electrons inside the double layer of the composite film, namely, the sum of the kinetic energy, the exchange energy and the potential.

Referring to the above capacity definition, one obtains the following relationship of the change of the total energy E:

$$E = \frac{1}{4}\sqrt{\frac{\varepsilon}{4\pi e^2}} \frac{(B_- - B_+ + \mu)^2}{\sqrt{A_+} + \sqrt{A_-}} \tag{6}$$

Where

$$B_+ \equiv \frac{h^2}{2m}\left(\frac{3}{8\pi}\right)^{2/3} n_{+0}^{2/3} - \left(\frac{3}{\pi}\right)^{1/3} e^2 n_{+0}^{1/3}$$

$$B_- \equiv \frac{h^2}{2m}\left(\frac{3}{8\pi}\right)^{2/3} n_{-0}^{2/3} - \left(\frac{3}{\pi}\right)^{1/3} e^2 n_{-0}^{1/3}$$

$$\mu = \mu_1 - \mu_2$$

It can be seen that $B_- - B_+ + \mu$ in eq. (6) is the energy of the electrons, written as

$$B_- - B_+ + \mu = eV$$

So eq.(6) can be rewritten as

$$E = \frac{1}{4}\sqrt{\frac{\varepsilon}{4\pi e^2}} \frac{(eV)^2}{\sqrt{A_+} + \sqrt{A_-}}$$

Comparing it with the definition of the capacity C, one can have the capacity of the double layer:

$$C = \frac{1}{2} e \sqrt{\frac{\varepsilon}{4\pi}} \frac{1}{\sqrt{A_+} + \sqrt{A_-}}$$

$$A_+ \equiv \frac{h^2}{3m}\left(\frac{3}{8\pi}\right)^{2/3} n_{+0}^{-1/3} - \frac{1}{3}\left(\frac{3}{\pi}\right)^{2/3} e^2 n_{+0}^{-2/3}$$

$$A_- \equiv \frac{h^2}{3m}\left(\frac{3}{8\pi}\right)^{2/3} n_{-0}^{-1/3} - \frac{1}{3}\left(\frac{3}{\pi}\right)^{2/3} e^2 n_{-0}^{-2/3}$$

Thus, the capacity of the double layer can be estimated.

2.4 The charge and discharge processes inside the double layers under external potentials

Figure 4 shows a composite thin film under an external potential.

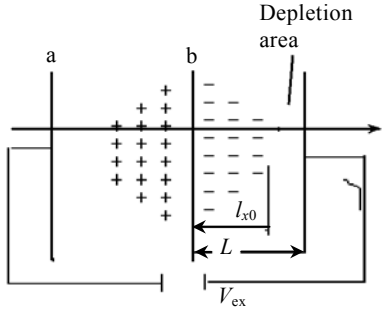

Fig.4　the external power on a composite thin film

It is supposed that, as seen in Fig.4, the depth L of the ceramic film is larger than that of the double layer, l_{x0}, while the external potential V_{ex} is applied on the both sites of the ceramic and its metal base. Some of ideas can be drawn:

(1) There exists a constant electric field between the free surface of ceramic and the edge of the double layer. Thus, the electrical field at the edge of the double layer does not equal to zero, but a limited value, $E(0)$.

(2) As the system reached a balance state, the potential V'_{ex} on the depletion area is an integration along the track of electric field:

$$V'_{ex} = -E(0)(L - l_{x0})$$

Since the chemical potential keeps constant anywhere in the electrical layer, the electron transfer from one side to another of the composite thin film is made possible by electric field inside the nonconductive layer.

The experiment shows that $E(0)\neq 0$ exists only in the case that the depth of the ceramic is large, which may be explained as the quantum tunnel effect (if this effect is ignored, $E(0)$ is taken as zero). The cold negative pole effect is similar to it. They are all deduced from the potential barrier of the electrons under the effect of the quantum bag. When electric field is large, the electrons transfer in the Schottky cold form, so that the effect of the external electric field is eliminated. Under the weak electric field, the tunnel electric current is small. It is the reason why it causes the different electrical characteristics for the nm thin film and the normal film. The dimension effects are related to the difference between the electric fields of the two kinds of film under the external electric field. Once the electric field inside the nm film is too large, the depletion area inside the

film layer may be broken up.

During the broken up process of the depletion area inside the thin nm ceramic film under the external electric field, the electrons there repel the electrons in the double layer. As the external electric field increases continuously and the double layer may still maintain in normal, new balance states of the minimum energy keep coming up, and the charging processes in the double layer have not been successfully carried out until the broken up of the depletion area. If once the two poles of the composite thin film connect to an outside electrical load, the stored energy inside the double layer would be lost quickly, as a discharge process. Because the electrons inside the double layer, which are now moving in the direction just opposite to the moving direction of that in charge process, are forced by strong electrical fields, the moving speeds are very high. Thus the discharge processes are certainly carried out so extremely fast that the energy release processes can be seen as instantaneously, which is necessary to generate the electrical pulses of very short widths.

2.5 The calculation of the ceramic-metal composite film capacity

Let us take the ceramic TiO_2 film based on a stainless steel as an example. Calculate the capacity by using eq.(7):

$$C = \frac{1}{2} e \sqrt{\frac{\varepsilon}{4\pi}} \frac{1}{\sqrt{A_+} + \sqrt{A_-}}$$

$$A_+ \equiv \frac{h^2}{3m}\left(\frac{3}{8\pi}\right)^{2/3} n_{+0}^{-1/3} - \frac{1}{3}\left(\frac{3}{\pi}\right)^{2/3} e^2 n_{+0}^{-2/3}$$

$$A_- \equiv \frac{h^2}{3m}\left(\frac{3}{8\pi}\right)^{2/3} n_{-0}^{-1/3} - \frac{1}{3}\left(\frac{3}{\pi}\right)^{2/3} e^2 n_{-0}^{-2/3} \quad (7)$$

Where '+' denotes the ceramic, '—' denotes the steel.

The reference data (in CGSE) for the capacity calculation for the both materials of the composite film are as follows:

$e = -4.8\times10^{-10}$, $m = 91\times10^{-27}$, $h = 6.62\times10^{-27}$, $\varepsilon = 100$, $n_{+0} = 2.42\times10^{24}$, $n_{-0} = 2.77\times10^{23}$。

Thus one obtains the capacity C:

C=65.5 μF

It is identified that the capacity formed in composite thin films are much larger than those in normal manufacture.

3 Experimental Study on High Capacity of Composite Thin Film

The capacitor samples were synthesized by using a Plasma-enhanced Vacuum Arc Deposition Setup. Glass and 1Cr18Ni9Ti stainless steel were chosen as the bases of the samples. The nanostructure TiO_2 films and the Ti electrodes were deposited on the samples bases. Then, a series of capacitor samples were obtained, their areas and capacity are listed in Table 1.

Table 1 Main parameters of TiO_2 thin film capacities

Sample number	Area of surface /cm^2	Capacity /mF
1	0.5	0.1
2	0.6	0.95
3	0.7	4.12
4	1.2	15.0

All samples in the table were made with TiO_2 thin films, their thicknesses are ranged from 1 μm to 100 μm. The dielectric constant of bulk agglomeration of TiO_2 is usually assumed to be 80~150, their magnitudes of capacities are among mF scales. In comparison to the conventional samples, each of them has surface area 1.2 cm^2, thickness 100 nm, dielectric constant 150, however, the maximum capacity among them is estimated to be only 1.6 μF. It is obviously concluded that the capacities of the nanostructure TiO_2 films are much larger than those of conventional samples. To deal with such capacitors of large capacities and determine their electronic performances several approaches have been adopted: equivalent connections both in series and in parallel, measurements of impedance plural angle, joining the charging and discharging processes, etc.

3.1 The equivalent connections in both series and parallel

The aptitude testing apparatus ZL5 was used to test the samples through measurements of the equivalent impedances. If we were taking the equivalent method either in series or in parallel connections to test the samples, the resistance may be as equivalent as the capacity; if we adopt both methods to make testing, the samples can be affirmed to be as the resistance or the capacity.

Table 2 compares the equivalent method in series with the method of parallel connection of the samples of TiO_2 film. From the table, we validate all the samples are the capacities, not the resistances.

3.2 The determination of impedance plural angles

In the ideal conditions, the plural impedance angles of the resistors and capacitors are exactly 90º and 0º separately, but actual measurements show that these values are bigger than 80º and less than 20º separately. The experimental results investigated through aptitude testing apparatus of ZL5, both impedances amplitudes and their angles, are shown in table 3. Thus we can conclude that the samples are made as qualified

capacitors, but an amount of leak currents certainly exists.

Table 2 The capacity of TiO_2 thin film determined by different equivalent methods

Value/μF (in series)	Value/μF (in parallel)
914.1	956.7
959.6	1051.2
921.5	1004.8

Table 3 The impedances and loss angles of composite thin films

Sample 1	Impedance	15	16.8	18.9	20	17
	Impedance angle/(°)	70	67	82.9	84	80
Sample 2	Impedance	1.62	1.8	1.7	2.0	1.9
	Impedance angle/(°)	68	73	73	69	67

3.3 The method of charging and discharging processes

The square wave was produced by the signal generator and applied to testing the standard capacities, the standard resistances and the experimental samples. It is clearly found that the waves from the samples were as same as those from standard capacitors.

4 Summary

The mechanism about the charge and the discharge processes of the composite thin film and then formed capacity are theoretically proposed and discussed, and the experimental setup and conductions are provided in detail. The researches show the analysis and the calculation of the capacity. The experiments of the composite thin film (nm TiO_2 film based on a glass and 1Cr18Ni9Ti) have been designed and completed with manufacturing the composite thin films and measuring the charge and discharge processes. The final results of very large capacity which have been derived from the model of TFDC electron theory are in agreement with the experimental measurements. The research and result have opened a new approach to generate the electrical pulses with very short widths.

References

[1] Cheng Kaijia(程开甲). *Progress in Nature Science*(自然科学进展)[J], 1996, 6(1): 12

[2] Cheng Kaijia(程开甲)，Cheng Shuyu(程漱玉). *Rare Metal Materials and Engineering*(稀有金属材料与工程)[J], 1998, 27(4): 189

[3] Cheng Kaijia(程开甲)，Cheng Shuyu(程漱玉)，*Progress in Nature Science*(自然科学进展)[J], 1996，6(6): 693

纳米复合薄膜特异电容机制探讨

程开甲，程漱玉，林东升，肖 刚

(西北核技术研究所，陕西 西安 710024)

摘 要：TFDC(Thomas-Fermi-Dirac-Cheng) electron theory 用于分析讨论了纳米复合薄膜二极层中电子的特性。根据 TFDC 电子理论研究和实验测试提出了纳米复合薄膜二极层特异电容产生的机制。

关键词：TFDC 电子理论；二极层；大电容；薄膜

作者简介：程开甲，男，中国科学院院士，教授，西北核技术研究所，陕西 西安 710024