On the Mechanism of the Solid Films Roll up into Nanotubes

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

Abstract: An important experiment was reported in Nature by Oliver G. Schmidt and Karl Eberl: nanotubes can be formed from thin solid films of almost any material at almost any position, once these films are released from their substrate. This result can be expounded on the ground of the Thomas-Fermi- Dirac-Cheng (TFDC) electron theory.

Key words: Thomas-Fermi-Dirac (TFD); electron density; internal stress
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1 TFDC Electron Theory

TFDC is the abbreviation of the name of Tomas, Fermi, Dirac and Cheng. TFD equation was proposed by Tomas, Fermi, Dirac and was used to describe the electron distribution $n(r)$ in an atom. As shown in Fig. 1, TFD statistical model describes an atom as a rigid ball, consisting of electrons; $n(r_0)$ is the electron density at the surface[1,2].

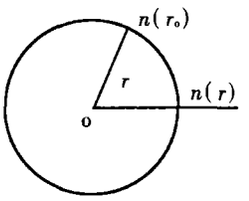

Fig. 1 Electron distribution

The distribution function ϕ of electron density and the electron density $n(r)$ are determined by TFD equation (1) and (2):

$$\frac{d^2\phi}{dy^2} = \phi'' = (1 + \phi^{\frac{1}{2}})^3 \quad (1)$$

$$n^{\frac{1}{3}} = 4m^* e^2 \beta \frac{\left(\frac{\pi}{3}\right)^{\frac{1}{3}}}{h^2}(1 + \phi^{\frac{1}{2}}) \quad (2)$$

Where m^* is the effective mass of electron, h the Plank constant, e the electron charge, β is a constant.

TFD equation is successful in calculating the distribution of electron density inside an atom, so the others. Fig. 2[3] shows an example for the atom form factor of chlorine atom, bar-dot line denotes the calculating results by TFD model, and bar line denotes the measured data. It can be seen that the agreement between them is very well. The results from calculations of the electron density inside atoms by TFD equation are very close to those from the measured atom form factors. TFD model is the application of TFD equation, which is successful in the prediction of equation of state (EOS) of material at high and extremely high pressure, such as the EOS of an explosion. However it is a pity that the TFD model failed in its early prosecution to problems involving boundary conditions of atoms.

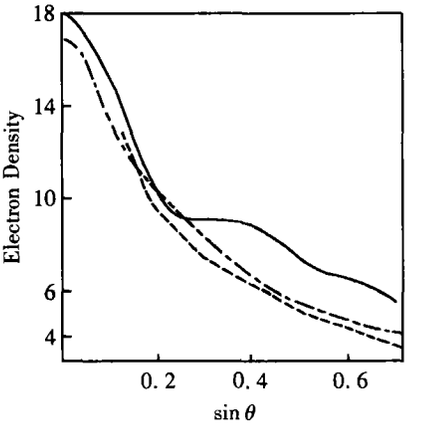

Fig. 2 The atom form factor

TFDC electron theory is proposed on the basis of TFD model, in which electrons distribute under the rule

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Biography: Cheng Kaijia, Male, Academician of Chinese Academy of Science, Northwest Institute of Nuclear Technology, Xi'an 710024, P. R. China, Tel: 0086-29-8222694

of Fermi statistics and the Coulomb interaction from the center to the surface of an atom. The authors have further made an important step to the perfection of the TFD model by proposition of boundary conditions. These boundary conditions[4,5] are: ① the continuity of electron density of each side at the boundary must be made to be equal, i. e. $\Delta n = n_1 - n_2 = 0$, n_1 and n_2 are the electron density of each side at boundary respectively. ② the chemical potential of material of the either side at boundary must be equal, i. e. $\Delta\mu = \mu_1 - \mu_2 = 0$, μ_1 and μ_2 are the chemical potential of two pieces of compound respectively.

The electron boundary conditions are closely related to the various properties of material, such as mechanism, electricity, magnetism, and optical.

In this paper, only will the first condition be considered.

2 Boundary Conditions and Internal Stresses inside Thin Film

As shown in Fig. 3, a thin film a is coated on a substrate b.

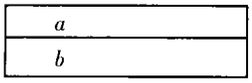

Fig. 3 Scheme of film on a substrate

As we know, many composites of thin films possess novel properties. A huge stress existing inside the film has been known since the beginning of study on casting layer on substrate by researchers. The internal stresses created at interfaces of the composite play dominating roles in changing properties of materials. Conventionally these internal stresses are classified into three types—surface tension, thermal stress and retained internal stress. But the magnitudes of all these three types of stresses are generally below GPas. It is quite inconceivable that experimental observations claim enormous stresses of the order of several GPas existing in coating layers on substrates and inside thin films of composites. The measured values of the internal stresses are in the Table 1 and Table 2[16].

Although many facts have revealed these novel situations, yet pity is that so far nothing has been done by a century for a deeper scrutiny. Up to now, no one can explain thus the huge internal stress. According to TFDC electron theory, this inconceivable fact would be sure. In order to explain clearly, take two atoms as example (Fig. 4) first, the same is to two pieces of specimen.

Table 1 The internal stresses inside thin films of composites

Substrate	Film	Film thickness /μm	Stresses /GPa
W18Cr4V	TiN	2	-6 ~ -8*
		6	-3 ~ -6*
Al	TiN	2	-4.3

Table 2 The internal stresses of Zn-Al alloy at 700℃

Phase	Atom ratio Al:Zn	Internal stress /MPa	Breaking stress extension/MPa
α	38:62	74	86
β	1:99	76	40 ~ 90

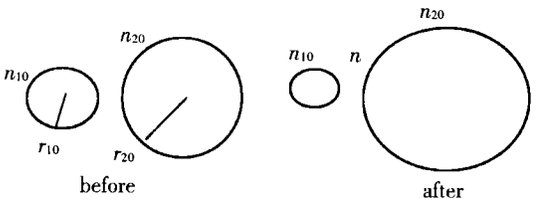

Fig. 4 The volume change of two atoms before and after contacting

From above figure, it can be seen that the surface electron density n_{10}, n_{20} of two atoms are different from each other before contacting, $n_{10}<n_{20}$, the radii of atoms in specimens are r_{10} and r_{20} respectively. As mentioned above, the equality of electron densities at the interface of two specimens in contact must satisfy, so electron density of two atoms must be equal at interfaces once they contact each other. In order to adjust the surface electron densities of them to a common value, the strain of each atom will occur, the volume of the atom with n_{10} decreases, and the volume of the atom with n_{20} increases, hence the new type of huge stresses are generally induced.

Same to films in Fig. 5, a specimen of thickness d_2 with electron density n_{20} is coated on other specimen of thickness d_1 with n_{10}. In general, the electron densities of two specimens are different before contacting. Continuity of electron density must be sustained while being brought to contact. Then the specimen with smaller electron density will be compressed and the other extended. Thus, strain and huge internal stress would result in inside two specimens, the material with smaller electron density is pressed, and the other with larger electron density will be extended. The analysis and computation about the stress in the thin film coated on the substrate have been given based on TFDC electron theory together with the conventional elastic theory of the bulk material.

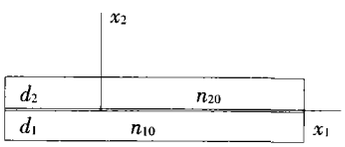

Fig. 5 Scheme of two specimens

The equation of conventional elastic mechanics and the special TFDC boundary condition are as follows:

$$\Theta = \frac{\partial \xi_1}{\partial x_1} + \frac{\partial \xi_2}{\partial x_2} \tag{3}$$

$$X_{ij} = \mu\left(\frac{\partial \xi_i}{\partial x_j} + \frac{\partial \xi_j}{\partial x_i}\right) + \lambda\Theta\delta_{ij} \tag{4}$$

$$\mu\Delta\xi_i + (\lambda + \mu)\frac{\partial \Theta}{\partial x_i} = 0 \tag{5}$$

$$n^{(1)} = n^{(2)} \quad x_2 = 0, \quad x_1 = 0 \sim \pm 1$$

$$p(n) = (\frac{2}{3}\mu + \lambda)\Theta$$

Solving this set of elastic equation under usual boundary condition and the TFDC boundary condition, one has the shear stress P at the interface as follows:

$$P^1 = \left(\frac{dp}{dn}\right)_1 (n_{20} - n_{10}) \tag{6}$$

Where X is the stress, $\xi_1(x_1, x_2)$ *and* $\xi_2(x_1, x_2)$ represent the elastic displacement of the medium along x_1 *and* x_2 axis at the coordinates (x_1, x_2), Θ is the volume strain, μ, λ are the elastic coefficients. Upper note "1" corresponds to the specimen 1.

3　Experiments and Results

The internal stresses at the interface of two specimens have been analyzed and calculated based of TFDC electron theory. Some experiments have also been done and some valuable results have been gotten, based on which the expounded mentioned above have been demonstrated.

1. As shown in Table 1, the measured stresses data in film TiN coating on substrate stainless steel are -6 to -8 GPas, the calculation in TFDC electron theory gives -5 GPa stress in TiN on Fe substrate in perfect harmony with observed data.

2. When Si_2Co film is coated on the substrate Si, film cracks take place easily from substrate.

By use of TFDC theory, the calculation of stress in Si_2Co coated on the films Si_xC_y is as follows and the result is given in Table 3:

$$-p_{Si_2Co} = (n_{Si_xC_y} - n_0)\zeta_{Si_2Co} \tag{7}$$

$$n_0 = n_{Si_2Co}$$

$$\left(\frac{\partial p}{\partial n}\right)_{Si_2Co} \equiv \zeta \quad \left(\frac{\partial p}{\partial n}\right)_{Si_xC_y} \equiv \xi$$

Where $p_{Si_xC_y}$ is experiment data, p_{Si_2Co} is the result of calculation.

As shown in Table 3, our experiment shows that the stress in the Si_2Co film decreases from 1.29 GPa to 0.71 GPa while doping carbon $2.8 \times 10^{16}C/cm^2$ into Si substrate and existing transition layer Si_xC_y, as the electron density of substrate doped by C approaches to the electron density of Si_2Co film. Here, x and y are the concentration of Si and C in transition layer Si_xC_y respectively.

Table 3　The stress in Si_2Co

x	n_{SiC} $\times 10^{-22}$	n_0 $\times 10^{-22}$	$p_{Si_xC_y}$ /GPa	p_{Si_2Co} /GPa
1.00	8.45	8.78	-1.29	-1.15
0.98	8.48		-0.968	
0.96	8.52		-0.907	
0.94	8.55		-0.792	
0.92	8.59		-0.714	

3. Two kinds of films with different electron density, say Al and Mo in the experiments, the electron density of Al is 1.05×10^{23} and Mo is 1.80×10^{23}. When they touch together, the volume of Al decreases and the volume of Mo increases, there exists internal stress at the interface between them according to the TFDC electron theory. When Al film is coated on substrate Si then Mo on Al and in reverse order, the results show that the film Al-Mo on the substrate Si is concave, and the film Mo-Al on the substrate Si is convex.

4. An important experiment was reported in Nature by Oliver G. Schmidt and Karl Eberl: nanotubes can be formed from thin solid films of almost any material at almost any position, once these films are released from their substrate[7]. This fact is certainly in the TFDC electron theory.

When the thin film Ge (material 1 in Fig. 6) is coated on the substrate and the thin film Si (material 2 in Fig. 6) on thin film Ge, the stress between Ge and Si exists. The computed values of electron density of Ge and Si are 1.056×10^{23} and 0.845×10^{23} respectively;

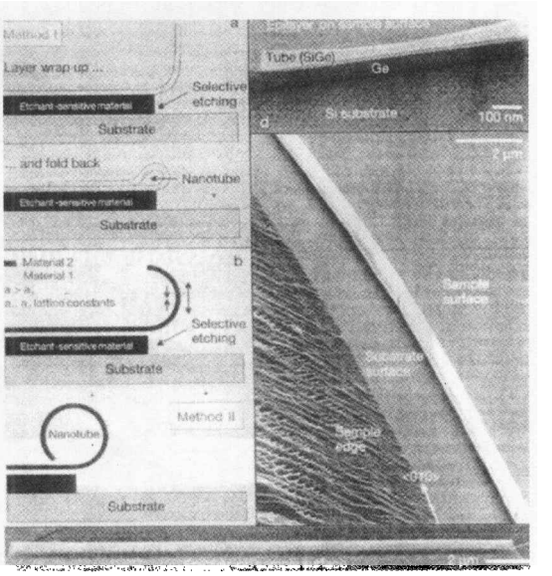

Fig. 6　Si-Ge nanotube

the radii of Ge and Si are 1.74×10^{-8} and 1.66×10^{-8} respectively. So in the Ge-Si films, Ge film should be extended, Si film compressed. Hence an internal moment of force is present which courses Ge-Si thin film to roll up inwards to the free surface of Si thin film once Ge-Si thin films are released from the substrate, and the Ge-Si nanotube is formed.

On the other hand, the effect of the thickness of thin film on the diameter of nanotube has been studied applying TFDC theory. The computation for the bending moment and curvature of Ge-Si thin film shows that ratio of diameter to thickness is 12, which agrees well with the observed values 14.4 (diameter 230 nm/thickness16 nm) and 8.37 (50 nm/ 6 nm).

4 Conclusion

Our research shows that the bending moment due to the internal stress at the interface of two thin films contributes to the solid films roll up into nanotubes. It is perfectly possible that TFDC electron theory is applicable to design nanotubes with various kinds of materials and diameter of tube.

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论固体膜形成纳米管的机理

程开甲,程漱玉
(西北核技术研究所,陕西 西安 710024)

摘 要:Oliver G. Schmidt 和 Karl Eberl 在自然杂志上发表了 1 个重要的发现:几乎对于任何材料的固体薄膜,一旦薄膜从基体上剥离开,几乎在任意部位都可以形成纳米管,这个试验结果可以用 TFDC(托马斯 - 费米尔 - 迪拉克 - 程氏)电子理论来解释。

关键词:TFD(托马斯 - 费米尔 - 迪拉克);电子密度;内应力

作者简介:程开甲,中国科学院院士,西北核技术研究所,陕西西安 710024, 电话:029-8222694