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Ni/Au 层对碳纳米管薄膜强流脉冲发射稳定性的影响

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摘 要:采用酞菁铁高温裂解法在镀有镍金缓冲层的硅基底上生长了碳纳米管薄膜(Ni/Au-CNT),并采用二极结构在相同的主 Marx 电压下研究了其强流脉冲发射稳定性.结果表明:在脉冲电压峰值为 1.60～1.74 MV(对应的脉冲电场峰值为 11.43～12.43 V/μm)时,Ni/Au-CNT 薄膜首次发射的电流峰值可达 331.2A;Ni/Au 层不仅能提高 CNT 薄膜的强流脉冲发射电流峰值,还能提高其发射稳定性;当冷阴极重复脉冲发射 7 次时,Ni/Au-CNT 的脉冲电流峰值衰减到初值的 72%,而 Ni - CNT 和 Si-CNT 脉冲电流峰值分别衰减到初值的 62%和 32%.

关键词:强流脉冲发射;Ni/Au 层;碳纳米管薄膜;稳定性;归一化电流

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Influence of Ni/Au Buffer Layer on Intense Pulsed Emission Stability of Carbon Nanotubes

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Abstract: Carbon Nanotube (CNT) film was grew on a Ni/Au buffered Si wafer by the pyrolysis of iron phthalocyanine(FePc). The intense pulsed emission stability of as-prepared CNT film was studied by measuring the intense pulsed emission characteristics repeatedly with diode configuration under the same voltage of Marx generator. The results show that, at the peak values of pulsed voltage ranging from 1.60 MV to 1.74 MV (the corresponding electric field intensity range of 11.43～12.43 V/μm), the peak current of the first emission cycle reaches to 331.2 A. The Ni/Au composite buffer layer can not only improve the emission current, but also the emission stability of as-prepared CNT film. When the number of emission cycles is up to 7 times for cold cathodes, the current of the Ni/Au-CNT cathode is 72% for the first current point, and while the Ni-CNT cathode and Si-CNT cathode is 62% and 32%,

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Key words: Intense pulsed emission; Ni/Au composite buffer layer; Carbon nanotube film; Stability; Normalized current

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0 Introduction

Carbon Nanotubes (CNTs) have attracted considerable attentions for their potential use in the field of emission applications due to their characteristics such as nanometer scale, high aspect ratio, superior mechanical strength, good conductance and high chemical stability[1-3], which make CNTs a good candidate as cold cathode in field emission displays, high-resolution electron-beam instruments, lamps, X-ray sources and microwave devices[4-9]. Emission stability is vital to electron emission applications, especially in intense pulsed emission circumstances. The intense pulsed emission characteristics of CNTs cold cathode were studied by Liao qingliang et al, which made CNTs cold cathode a candidate as intense current pulsed electron beam in high power microwave devices. However, the intense pulsed emission stability can be affected by terrible contact between CNTs and substrate[10-11]. In order to improve the intense current pulsed emission ability of CNTs cathodes, buffer layer was considered between CNTs films and silicon substrate[12]. However, the study about influence of buffer layer on intense pulsed emission stability of CNTs is rare in addtion to the literature till now.

In this paper, CNTs were grown on silicon substrate with nickel/gold buffer layer. The emission stability of grown CNT film in intense pulsed emission mode, and the improvement on intense pulsed emission stability by introducing nickel/gold (Ni/Au) composite layer were researched. It can be found that the emission stability of such a CNT film (Ni/Au-CNT) was further improved compared with that of CNT films grown on Si wafer (Si-CNT) and Ni-buffered Si wafer (Ni-CNT).

1 Experimental

1.1 Sample preparation

Ni/Au composite layer coated *N*- type Si wafer (100) with a resisitivity $10^{-2}\sim10^{-3}\,\Omega\cdot$cm was used as substrate. Ni layer was prepared onto the Si substrate by electroless plating. The plating solution was mainly composed of nickel sulfate, NaH_2PO_2, and Trisodium citrate. The PH value was adjusted to 8～10 by ammonia solution. Palladium catalyst was used for Ni plating. Au layer was deposited onto Ni layer by sputtering method with an ion sputter (KYKY SBC-12).

CNT film was synthesized by the pyrolysis of iron Phthalocyanine (FePc)[13]. The CNTs are fabricated by pyrolysis of iron phthalocyanine (FePc) under Ar/H_2 atmosphere at a predetermined temperature on a substrate in a flow reactor comprising of a quartz glass tube and a dual furnace fitted with independent temperature controllers (XD-1200NT). FePc and Silicon substrate with Ni/Au buffer layer are placed in the first and second furnaces, respectively, in the quartz glass reactor. After the second furnace reaches a predetermined temperature of 850℃, the first furnace is heated at 500～750℃ for ca. 10 min. Then, the second furnace is kept at the pyrolysis temperature ca. 10 min to complete the pyrolysis process. After the growth, the furnace is cooled naturally to room temperature under the protection of Ar.

1.2 Study on the morphologies of samples

The morphologies of the sample, including Ni layer, Au layer and CNT film were studied using a scanning electron microscope (SEM, JEOL JSM-6700F). Ni/Au-CNT film is analyzed by transmission electron microscope (TEM,FEI Technai G2 T20) and Raman spectroscopy (Renishaw inVia Raman microscope).

1.3 Measurement of intense pulsed emission characteristics

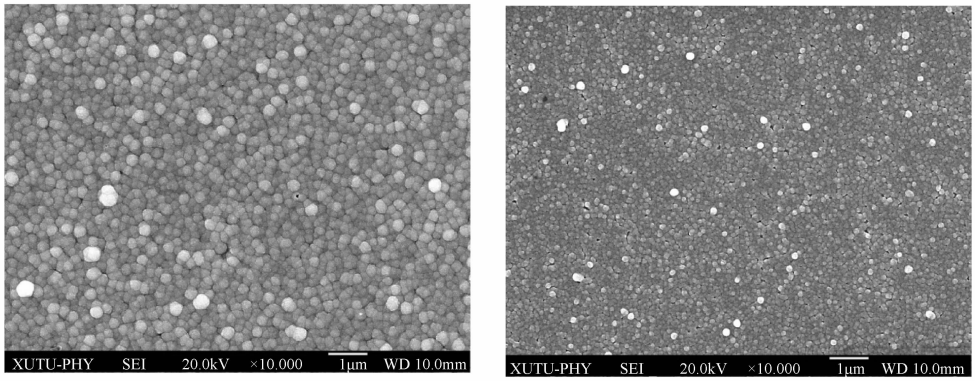
The intense pulsed emission characteristics were measured in diode structure with pulse forming network generator under a vacuum of $\sim5\times10^{-4}$ Pa. The anode-cathode gap is 14 cm. CNT cathodes performed in single pulse mode (i. e. only one voltage pulse was applied for each test procedure) during intense pulsed emission measurement. In order to study the emission stability, we measured the emission currents for Si-CNT, Ni-CNT and Ni/Au-CNT films repeatedly under the same voltage of Marx generator. All the pulsed voltages have the same half-value width of ～100 ns.

2 Results and discussion

2.1 Morphologies of samples

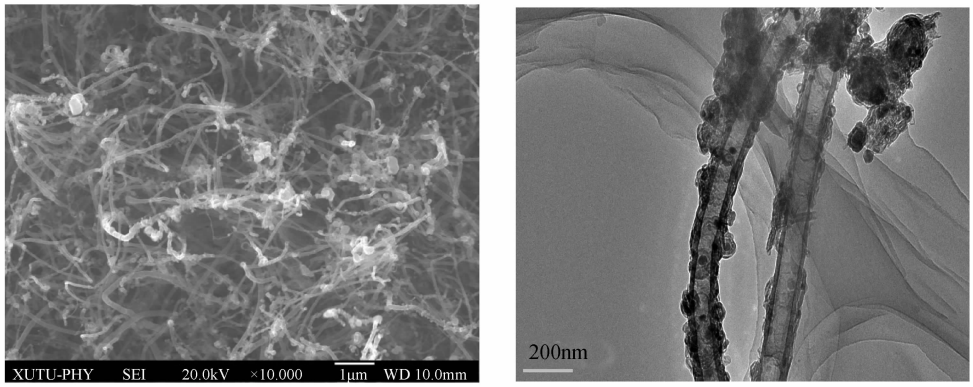
Fig. 1 gives the SEM pictures of Ni/Au multiplex layer, where Fig. 1 (a) and (b) correspond to Ni layer and the Au layer prepared thereon. It can be seen from Fig. 1 (a) that Ni layer looks homogeneous and compact. It is found from high-magnification images (not shown) that the size range of Ni particles is about 150～300 nm, while that of Au particles is about 100 to 150 nm.

The Morphologies of the Ni/Au-CNT film is shown in Fig. 2. From Fig. 2 (a), we can see that the growth density of CNTs is uniform, and that the length is about tens of microns. From Fig. 2 (b), it can be found that CNTs are hollow and their diameters are about 100 nm.



(a) Ni layer (b) Au layer

Fig. 1 SEM images of Ni/Au multiplex layer



(a) SEM image (b) TEM image

Fig. 2 The microscopy images of Ni/Au-CNT film

Fig. 3 is the Raman spectra of the Ni/Au-CNT film and the two patent features are the *D* peak at 1 340 cm^{-1} corresponding to the disorder and the *G* band at 1 582 cm^{-1} manifesting the presence of graphitic carbon. The quality of carbon materials can be characterized by the ratio between the *D* and *G* band. Fig. 3 shows that the intensity of *G* band is less than *D* band, indicating a quantity of structural defects. The results suggest that high density of structural defects in fabricated material are formed in the pyrolysis process.

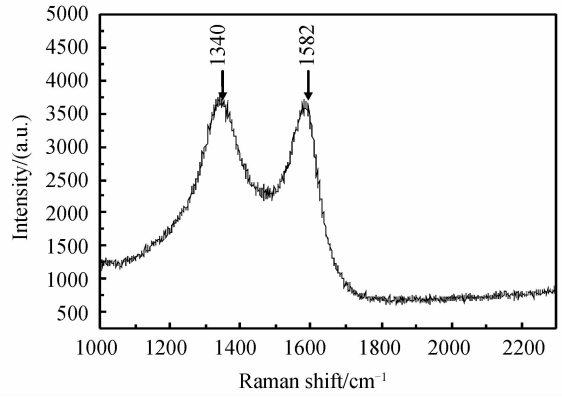


Fig. 3 The Raman spectra of the Ni/Au-CNT film

2.2 The stability characteristics of intense pulsed emission current

Fig. 4 give the typical wave forms of the diode voltages and the emission current from one pulse emission. Channel 1 is anode current pulse curve collection of Faraday tube with 7.32A/div; channel 2 is

the cathode voltage curve with 1MV/div, peak values of pulsed voltage is 1.68MV, corresponding field is 11.43 V/μm, and channel 3 is the emission current curve with 293A/div, peak current is 331.2A. This article does not discuss anode current pulse signal, mainly discuss the relationship between peak values of the emission current and emission cycle number.

As shown in Fig. 5, the peak current values of the first emission cycle for Ni/Au-CNT cathodes is 331.2 A which is larger than 109.4 A for Si-CNT and 180.5 A for Ni-CNT (Ref. [12]). The peak values of the emission current decayed generally with increasing measurement number (emission cycle number), though there was fluctuation of peak emission current in the measurement results.

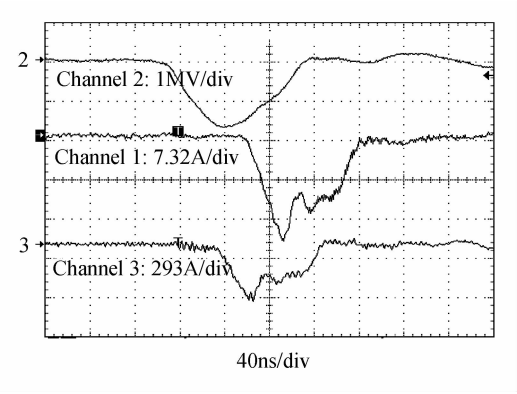


Fig. 4 The typical wave forms of the diode voltages and the emission current from one pulse emission

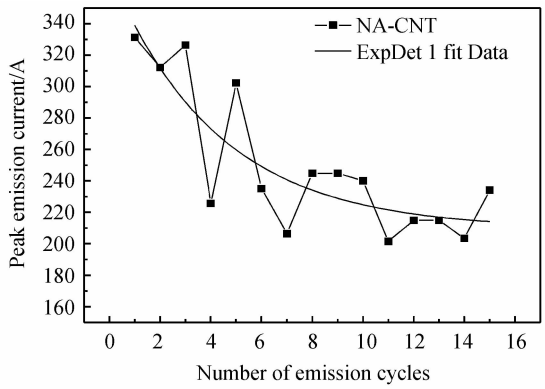


Fig. 5 The stability of Ni/Au-CNT cathodes in intense pulsed emission mode

The fluctuation in the emission current can be attributed to the applied pulsed voltages and the error from manual numerical reading. Although all the measurements on emission current were performed under the same voltage of Marx generator, the output pulsed voltages between anode and cathode were different for each time. The range of peak values of pulsed voltage and electric field intensity for all the emission stability measurements of Ni/Au-CNT are 1.60～1.74MV and 11.43～12.43 V/μm, respectively. Table 1 gives the values of pulsed voltage, electric field intensity and emission current for each measurement. This affected the current measurement results, but it did not change the current attenuation trend.

Table 1 The values of pulsed voltage, electric field intensity and emission current for each measurement

SN	Voltage/MV	Electric filed/(V·μm^{-1})	Emission current/A
1	1.68	12.00	331.2
2	1.70	12.14	312.0
3	1.60	11.43	326.4
4	1.62	11.57	225.6
5	1.74	12.43	302.4
6	1.70	12.14	235.2
7	1.68	12.00	206.4
8	1.71	12.21	244.8
9	1.70	12.14	244.8
10	1.70	12.14	244.0
11	1.74	12.43	201.6
12	1.72	12.29	215.0
13	1.70	12.14	215.0
14	1.68	12.00	203.5
15	1.62	11.57	234.2

According to the discussion in Ref. [12], the degradation behaviour was described with exponential decay model. Suppose the emission current decreased with the first order exponential decay model, the decay model can be described as

$$y=y_0+A\exp(-x/t) \tag{1}$$

The decay formula and the fitting curve of the experimental data can derived from the Eq. (1), the decay formula of emission current of Ni/Au-CNT cathode can be written as

$$I = I_0 + A\exp(-x/t) = 209.35376 + 164.04848\exp(-x/4.2328)(A) \quad (2)$$

where $I$is the peak current of Ni/Au-CNT cathode, x is the emission cycle number.

The smooth curve labelled as "ExpDec 1 fit Data" in Fig. 5 is the fitting curve of Ni/Au-CNT cathode fitted with exponential decay model in the first order.

The normalized emission current was utilized to characterize the stability of intense pulsed emission current for the cathode. The normalized emission current is defined as the ratio of the peak current values of each point in fit curve to that of the first point. The normalized current is actually a dimensionless relative current, given by

$$I_n = \frac{I}{I_{Max}} \quad (3)$$

where I_n is the normalized current; I is the fitted current; and I_{Max} is the initial value (Maximum value) for the fitted current.

The normalized emission current curve of Ni/Au-CNT cathode was shown in Fig. 6. To compare the decay trends directly, the normalized current curves of Ni -CNT and Si-CNT cathodes (Ref. [12], The intense pulsed emission characteristics of Ni/Au-CNT, Ni-CNT and Si-CNT were measured under the same conditions with same pulse forming network generator.) were given as curves in Fig. 6.

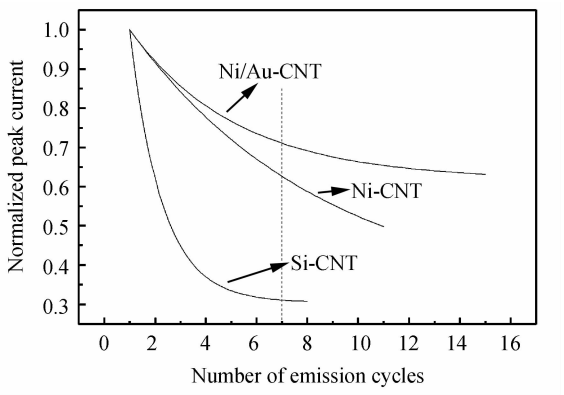


Fig. 6 Comparison of the emission current decay trends

It is convenient to use normalized emission currents for comparing the emission stability on different cathodes . The emission cycle numbers corresponding to the same normalized current can be used as a criterion for the evaluation of the decay speed. For example, When the number of emission cycles is up to 7 for cold cathodes, the current of the Ni/Au-CNTs cathode is 72% for the first current point, and while the Ni-CNT cathode and Si-CNT is 62% and 32%, respectively. We can find that Ni/Au-CNT cathode has better emission stability than both Ni-CNT and Si-CNT cathodes.

2.3 Discussion

The field emission stability is influenced by the factors, such as surface reactions between CNTs and gas molecules[14], the CNT-substrate interface[15] and damage to the nanotubes[16-17]. Generally, such damage can be caused by resistive heating from high-current field emission.

In intense pulsed emission modes, the CNT cathode emits a very high current. The damage caused by resistive heating may be the primary factor in the decay of the emission current. Introducing a Ni/Au composite layer has positive effect resulting in improvement to the emission stability, i. e. the resistance of the Ni/Au layer is lower than those of the Si and Ni substrates. Since the Ni/Au layer can further decrease the resistance of CNT-substrate interface compared with Si and Ni substrate. The Ni/Au buffer layer can further decrease the Joule heating during electron emission. On the other hand, according to our experimental results, the bonding of CNTs to the Ni/Au and Ni layer is better than that to the Si substrate. This can decrease the resistance of CNT-substrate interface. These two effects decrease the damage caused by resistive heating from the high-current field emission and thus improve the emission stability.

3 Conclusion

CNT film was synthesized on a Ni/Au buffered Si wafer by the pyrolysis of FePc. Ni layer was grown onto the Si substrate by electroless plating. Au layer was deposited onto Ni layer by sputtering method with an ion sputter. The emission current decreased with the first order exponential decay model. By comparing the normalized emission current, It is found that emission current of different CNT cathodes have different decay trends. When the number of emission cycles is up to 7 for cold cathodes, the current

of the Ni/Au-CNT cathode is 72% for the first current point, and while the Ni-CNT cathode and Si-CNT cathode is 62% and 32%, respectively. It indicated that metal buffer layer can improve the emission stability of as-grown CNT film. Ni/Au composite buffer layer can improve the emission stability of CNT film more than Ni buffer layer.

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