Field emission mechanism from nanocrystalline cubic boron nitride films

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Abstract

An electron-emission theoretical model integrating the change in the grain size of nanocrystalline cubic boron nitride (c-BN) thin films was established. To understand better the essence of field emission, an accurate numerical scheme, the transfer matrix method, that can be used to compute the tunneling coefficients of the actual surface barrier, was also adopted. The present results show that the emission current from nanocrystalline grain films is far larger than that from regular grain films or bulk c-BN.

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1. Introduction

In recent years, more and more attention [1–7] has been paid to the use of cubic boron nitride (c-BN) based field emitters as an electron source of a highly reliable performance because c-BN has superior properties such as negative electron affinity (NEA), wide band gap, chemical inertness and mechanical hardness. Moreover, field emission experiments on flat type c-BN [2] have shown that considerable emission currents are attainable. Since the synthesis under low pressure was reported by Sokolowski [8] in 1979, great efforts have been made to grow c-BN thin films. It is worth noticing that almost all c-BN thin films prepared with present techniques are nanocrystalline [6]. On the other hand, a great number of studies concluded that nanocrystalline structures favor the enhancement of field emission. To our knowledge, theoretical investigation on field emission mechanism of nanocrystalline c-BN films has not been reported. As a matter of fact, it is important to establish a theoretical model of electron emission from nanocrystalline c-BN films. Actually, some theoretical models based on Fowler and Nordheim equation [9] of field emission from semiconductor films [10,11] disagree with the experimental results, but these models are valid only for field emission from flat metal or some perfect semiconductors surfaces. In this study, it was tried to establish a field emission theoretical model integrating the change in the grain size of nanocrystalline c-BN thin films.

2. Theoretical mechanism of field emission

Since the theoretical model of field emission was established by Fowler and Nordheim in 1928 [9], the Fowler–Nordheim equation had become a normal analytic formula, which is only valid for metal electron emission. The Fowler–Nordheim theory will be incorrect for electron field emission from semiconductors, and the use of the Fowler–Nordheim law results in an inaccuracy in the extraction of the barrier height that is dependent upon the applied electric field across the oxide, conduction band offset, and temperature [10]. So we used the numerical integration of basic equation to investigate the theoretical mechanisms of field emission from c-BN, the results should be accurate and credible. The general field emission expressions in metals or semiconductors can be obtained:

\[ J = \frac{4\pi q m_r k_B T}{h^3} \int T(E_x) \ln[1 + e^{-E_x - E_F k_B T}] dE_x \]

\[ = \int J(E_x) dE_x \]  

In Eq. (1), \( q \) is basic charge, \( m_r \) is the transverse mass of the electrons in the emitting electrode, \( k_B \) is Boltzmann’s
constant, $T$ is the temperature, $h$ is Planck’s constant, and $E_F$ is the Fermi energy. It is easy to find that the integrand of Eq. (1) is made up of the tunneling coefficient $T(E_i)$ and the density of occupied states decreasing with the longitudinal kinetic energy of effective electron. The extraction of $T(E_i)$ is most important in the whole integrand of Eq. (1). To obtain the emission coefficient $T(E_i)$, the simplest method is to solve directly the Schrödinger equation by adopting a triangular potential barrier, and the more complicated method is to use the Wentzel–Kramers–Brillioun (WKB) approximation for analytical solution in a classical image potential barrier [12]. However, the above methods are not enough valid for realistic barriers in actual emitting surface, so other effective numerical methods that are used to compute the transmission coefficient for arbitrary exact barriers were also developed. This method, called the transfer matrix method [13] is based on the analytical solution of the Schrödinger equation across a linear potential, where the solution can be expressed as a linear combination of the Airy function [13] or the other wave function [14–16]. In this method, the complicated tunneling barrier is divided into as many as possible segments approximated by linear barriers, then the matching of solutions between the Schrödinger equation of adjacent segments yields tunneling coefficient $T(E_i)$ utilizing the transfer matrix procedure. In this paper, we introduce the transfer matrix method to compute $T(E_i)$, with a more complicated and exact image potential, which is [17]

$$V_3(z) = \frac{q^2}{16\pi\varepsilon_0} \sum_{n=0}^{\infty} (\beta\beta')^n \left( \frac{\beta}{ns-z} - \frac{\beta'}{(n+1)s-z} \right)$$

where $s$ is the gap spacing, $q$ is basic charge, $\varepsilon_0$ is dielectric permittivity of the semiconductor, $\varepsilon_0$ is the permittivity of vacuum. $\beta = (\varepsilon_s - \varepsilon_0)/(\varepsilon_s + \varepsilon_0)$, and $\beta' = 1$ for a metal–vacuum–semiconductor junction.

### 3. Field emission of nanocrystalline c-BN thin films

In order to obtain a high emission current, c-BN as an electron-emission resource material should be deposited as thin films on metal or other semiconductor substrates. Then, due to electron emission originating from nanocrystalline c-BN films, some theoretical emission mechanism based on the bulk semiconductors must be modified to fit for electron emission of the films. As critical dimensions of materials are reduced, some photoelectrical properties of materials will alter distinctly, such as the band gap of semiconductors decreasing. The change in the band gap must lead to the Fermi energy shifting, which will affect the electron emission from thin films as can be seen easily in Eq. (1). According to an analytical approximation [18], the bandgap of nanocrystalline semiconductor depending on the grain size is given by:

$$E_{gl} = E_{g0} + \frac{h^2 \pi^2}{2R^2} \left( -\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{eR}$$

$$+ \frac{e^2}{R} \sum_{n=1}^{\infty} a_n \left( \frac{S}{R} \right)^n$$

(3)

$E_{gl}$ is the band gap of the nanocrystal, $E_{g0}$ is the band gap of the bulk material, $R$ is the grain size, $m_e$ is the electron effective mass, $m_h$ is the hole effective mass, $e$ is the dielectric constant, $S$ is the related position parameter, $a_n$ is the composite dielectric constant and $e$ is the basic electronic charge. If assuming that $\lambda$ is a synthetical parameter with relevant data, and then Eq. (3) will be further simplified

$$E_{gl} = E_{g0} + \lambda E_{g0} \exp(-R/R_0)$$

(4)

The intrinsic electron concentration in the bulk material can be written as:

$$n_i(T) = 2 \left( \frac{2\pi kT}{h^2} \right)^{3/2} \left( m_{ep} m_p \right)^{3/4} e^{-E_i/2kT}$$

(5)

Similarly, the electron concentration of the nanocrystalline material can also be

$$n^*(T) = 2 \left( \frac{2\pi kT}{h^2} \right)^{3/2} \left( m_{ep} m_p \right)^{3/4} e^{-E_i/2kT}$$

(6)

Considering that the nanocrystal and the bulk are the same material, one obtain

$$n^*(T) = n_i(T)e^{(E_F - E_i)/kT}$$

(7)

$E_i$ is the intrinsic energy level that is located at the middle of the bandgap of the bulk material. By combining Eqs. (3)–(6), we can obtain

$$E_F = E_i - \ln \left( \frac{m_{ep} m_p}{m_{e} m_{h}} \right)^{3/4} e^{-E_{g0} \exp(-R/R_0)/2kT}$$

(8)

Then, we can result out field emission from c-BN thin film that is mostly composed of nanocrystalline grains by combining Eqs. (1) and (8).

Fig. 1 shows the bandgap of nanocrystalline c-BN thin films changing with the change in grain size, it can be seen that the change in the bandgap is distinct as the grain size is smaller than 10 nm. When the grain size is larger than 10 nm, the bandgap approaches that of the bulk material. Considering the unsolved equation for actual inhomogeneous semiconductor surfaces [19], we supposed that the c-BN thin film is perfect flat and infinite big. We compare the Fowler–Nordheim (F–N) plots of thin films and bulk c-BN in Fig. 2. The results show that electron emission from nanocrystalline c-BN films far excels from bulk c-BN. Moreover, it is seen as plotted in Fig. 2 that smaller grain size lead to bigger field emission current. To demonstrate clearly the results, the chart of emission current vs. electric field is further exhibited in Fig. 3. Considering
the measurable currents of 0.01 A/m², the threshold voltages of field emission from the nanocrystalline c-BN thin films with grain size of 3 and 12 nm and bulk c-BN, are 604, 829 and 915 V/µm, respectively. If the field enhancement is taken account into electron emission from actual coarse nanocrystalline c-BN thin films, the theoretical result may be consistent with the experimental [5] threshold of 6 V/µm in undoped nanocrystalline c-BN thin films with grain size of 3 nm.

Since the calculated results show that there is an outstanding field emission from nanocrystalline c-BN films of small grain size, it is necessary to find out the physical substance of excellent field emission from small nanocrystalline films. If the $E_F$ is located at fixed position, the conduction band minimum will then shift to higher energy level because of the bandgap widened with the decrease of grain size, which implies the increase in the absolute value of NEA. Generally, the presently accepted field emission mechanism of semiconductors is the Schottky diode with a NEA which its characteristic contributes to more electrons to escape easily from the surface potential [20]. In other hand, we also demonstrated the outstanding field emission of c-BN owes to the wide bandgap [21]. Therefore, it can be concluded that the excellent field emission behaviors of nanocrystalline c-BN may originate from both the NEA enhancing and the bandgap broadening.

4. Conclusions

To investigate the field emission from c-BN thin films, an electron-emission theoretical model including the effect of grain size was established. The F–N plot of field emission from nanocrystalline c-BN thin films showed that the smaller grains would lead to far higher emission current. The computed threshold voltage of grain size of 3 nm may be roughly equal to the experimental result, considering the local geometrical field enhancement. Due to field emission from nanocrystalline c-BN thin films greatly benefiting from small grains, it is indicated that one of the best approaches to find superior semiconductors for field emission is to decrease the grain size of nanocrystalline semiconductor films.

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References