Chapter 2

Fundamental Theory

2.1 Field Emission from Metals

Field emission is a quantum-mechanical phenomenon in which electrons tunnel through a potential barrier at the surface of a solid as a result of the application of a large electric field. Field emission is distinct from thermionic emission and photoemission in which electrons acquire sufficient energy via heating or energy exchange with photons, respectively, to overcome the potential barrier. In field emission external electric fields on the order of 10^7 V cm^{-1} are required for appreciable electron currents. The presence of the electric field makes the width of the potential barrier finite, and therefore permeable to the electrons. This can be seen with the Fig. 2.1, which presents a diagram of the electron potential energy at the surface of a metal.

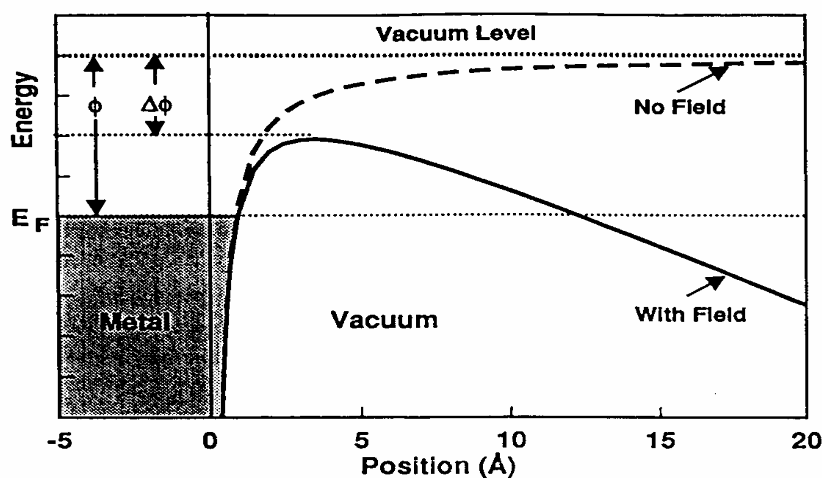


Fig. 2.1 Diagram of potential energy of electrons at the surface of metal.

The dashed line in Fig. 2.1 shows the shape of the barrier in the absence of an external electric field. The height of the barrier is equal to the work function of the metal, ϕ, which is defined as the energy required to remove an electron from the Fermi level E_F of the metal to a rest position just outside the material (the vacuum level). The solid line in Fig. 2.6 corresponds to the shape of the barrier in the presence of the external electric field. As can be seen, in addition to the barrier becoming triangular in shape, the height of the barrier in the presence of the electric field E is smaller, with the lowering given by Eq.(1) [1].

$$\Delta\phi = \left(\frac{eE}{4\pi\varepsilon_o}\right)^{1/2} \qquad \text{Eq. (1)}$$

where e is the elementary charge and ε_o is the permittivity of vacuum.

Knowing the shape of the energy barrier, one can calculate the probability of an electron with a given energy tunneling through the barrier. Integrating the probability function multiplied by an electron supply function in the available range of electron energies leads to an expression for the tunneling current density J as a function of the external electric field E. The tunneling current density can be expressed by Eq. (2) which is often referred to as the Fowler-Nordheitn equation [2]

$$J = \frac{e^3E^2}{8\pi h\phi t^2(y)}\exp\left[\frac{-8\pi(2m)^{1/2}\phi^{3/2}}{3heE}v(y)\right] \qquad \text{Eq. (2)}$$

where $y = \Delta\phi/\phi$ with $\Delta\phi$ given by Eq. (1), h is the Planck's constant, m is the electron

mass, and t(y) and v(y) are the Nordheim elliptic functions; to the first approximation $t^2(y) = 1.1$ and $v(y) = 0.95 - y^2$. Substituting these approximations in Eq. (2), together with Eq. (l) for y and values for the fundamental constants, one obtains Eq. (3) [2].

$$J = 1.42 \times 10^{-6} \frac{E^2}{\phi} \exp\left(\frac{10.4}{\phi^{1/2}}\right) \exp\left(\frac{-6.44 \times 10^7 \phi^{3/2}}{E}\right) \qquad \text{Eq. (3)}$$

where J is in units of A cm^{-2}, E is in units of V cm^{-1} and ϕ in units of eV. Plotting log (J/E^2) vs 1/E results in a straight line with the slope proportional to the work function value, ϕ , to the 3/2 power. Eq. (3) applies strictly to temperature equal to 0°K. However, it can be shown that the error involved in the use of the equation for moderate temperatures (~300°K) is negligible.

2.1.1 Field Emission from Semiconductor

To a large degree, the theory for electron emission from semiconductors can be derived parallel to the theory for metals. However, special effects are associated with semiconductors due to the state of their surface and the fact that an external field applied to a semiconductor may penetrate to a significant distance into the interior. The classic theoretical treatment of electron emission from semiconductors is given in. For the case when the external electric field penetrates into the interior of an n-type semiconductor and the surface states are neglected, $\log(J/E^2)$ is shown to be a linear function of 1/E, as for metals. However, in place of the work function ϕ in the Fowler-Nordheim equation one needs to substitute a quantity $\chi - \delta$, where χ is the

electron affinity defined as the energy required for removing an electron from the bottom of the conduction band of the semiconductor to a rest position in the vacuum, and δ denotes the band bending below the Fermi level. These parameters are illustrated in Fig. 2.2.

The linear dependence of log (J/E^2) on $1/E$ is expected only if the density of the current flowing through the sample is much smaller than the current limiting density $J_{\lim} = en\mu_n E/\varepsilon$, where μ_n is the electron mobility and n is the electron concentration in the bulk of the semiconductor [3-4]. At $J \approx J_{lim}$ the Fowler-Nordheim character of the relationship $J(E)$ passes into the Ohm's law (if the dependence of electron mobility on the electric field is neglected) which results in the appearance of the saturation region in the emission current vs voltage curve. Such saturation regions were observed experimentally for lightly doped n-type semiconductors and for p-type semiconductors [5-6].

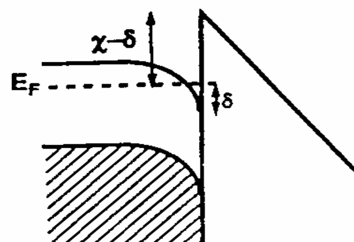


Fig. 2.2 Diagram of potential energy of electrons at the surface of an n-type semiconductor with field penetration into semiconductor interior.

Electron emission from semiconductors has been a subject of more recent theoretical considerations, which takes into account complications due to electron scattering, surface state density, temperature, and tip curvature [7-8].

2.1.2 Fowler-Nordheim Equation for Gated FEA

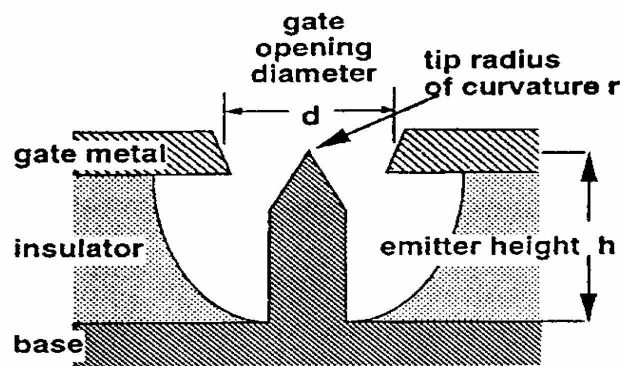


Fig. 2.3 Schematic diagram of a cell of a microfabricated gated FEA.

Fig. 2.3 presents a schematic diagram of a cell in a microfabricated gated FEA. The emitter height is denoted by h, the gate aperture diameter by d, and the tip radius of curvature by r.

The emitter has the form of a sharp tip so that advantage can be taken of the well-known enhancement of electric field at surfaces exhibiting high curvature. If voltage V is applied to the gate electrode, the electric field E at the tip is given by Eq. (4).

$$E = \beta \times V_g \qquad \text{Eq. (4)}$$

where the proportionality constant β is called the field enhancement or field

conversion factor. If E is in units of V cm^{-1}, V is in units of V and β is in units of cm^{-1}. If the area of which emission of electrons takes place is denoted as α and Eq. (4) is substituted for E in the Fowler-Nordheim equation Eq. (3), the following expression is obtained [2].

$$I = J \times \alpha = A \times V_g^2 \exp(-B / V_g) \qquad \text{Eq. (5)}$$

where

$$A = 1.42 \times 10^{-6} \times \alpha \times \beta^2 / \phi \times \exp\left(10.4 / \phi^{1/2}\right) \qquad \text{Eq. (6)}$$

and

$$B = 6.44 \times 10^7 \times \phi^{3/2} / \beta \qquad \text{Eq. (7)}$$

In Eq. (5) I is in units of A, α in units of cm^2, β in units of cm^{-1}, ϕ in units of eV and V_g in units of V. Plotting experimental values of electron emission current vs gate voltage in the so-called Fowler-Nordheim coordinates, log(I/V_g^2) vs 1/V, is a common way of analyzing electrical performance for gated field emitter arrays. As can be seen from Eq. (5), such a plot will appear as a straight line over a large portion of the emission region. The constants A and B in Eq. (5) provide a way of comparing performance of FEAs with different geometrical parameters, emitter materials, etc. over a wide range of emission currents. The A and B values can be extracted from the least-squares fit to experimental data with A related to the intercept and B to the slope of the straight line in the Fowler-Nordheim coordinates.

2.2. Bias Enhanced Nucleation of Diamond in Microwave CVD

The nucleation of diamond on defect-free non-diamond polished surfaces, especially on silicon, is difficult in a chemical vapor-deposition (CVD) process. This is due to extremely high surface energy of diamond; large lattice mismatch of diamond and silicon; and relative low sticking probability and low surface mobility of the precursor for the diamond growth.

One pretreatment of the substrate surface, to create active nucleation sites, is thus required in order to obtain high nucleation densities. Both physical and chemical methods have been used to roughen the substrate surface to provide more nucleation sites. Some of the methods used for the substrate pretreatment prior to growth are mechanical damage of the substrate surface either by scratching it with abrasives, usually diamond powder [9-10] or by abrasion in an ultrasonic bath of diamond powder suspension [11], coating od a-C layer in methane-rich hydrogen plasma at low temperature [12-15], coating of carbon clusters and intermediate layers of SiC, c-BN, etc.

Because our substrate has been pre-treated, the former methods will damage our pattern ; other methods must be used in our experiment. From Yugo et al [16-17] have obtained very high density of diamond nuclei by a pretreatment process employing negative dc bias to the substrate in a microwave plasma CVD process, using a

methane-rich hydrogen plasma. An advantage of biasing is that it can be performed in situ, is reproducible, and easy to control. It is no longer necessary to damage the substrate surface by abrading it with diamond powder. The power of bias-enhanced nucleation (BEN) to increase the nucleation density on mirror polished silicon [18] and to provide nuclei for the growth of almost heteroepitaxal layers [19] has made it a widely used tool for the nucleation of CVD diamond on silicon substrates. Although good nucleation results have been obtained all over the world by this process, a lack of knowledge about the mechanisms and phases involved remains.

On the one hand, nucleation enhancement is thought to the negative bias accelerates the ions in the plasma toward the substrate, and the resulting collisions increase the concentration of active species on or above the substrate surface which enhance the reactions responsible for the generation of diamond nuclei. The accelerated ions also enhance the bonding of the carbon atoms to the substrates. Katoh et al [20] have reported that the negative bias accelerates the carbon- containing cations (C^+, CH^+, CH^+_2 , CH_3^+ , etc.) in the plasma to the substrate surface. The bombardment of cations leads to an increased mobility of the carbon species on the substrate. This is considered to be favorable for the generation of diamond nuclei. The formation of a thin a-C layer during biasing pretreatment has been reported in the literature [21]. It is suggested that the a-C layer is formed by the deposition of

positively charged hydrocarbons or carbon cations. This a-C layer and the bombardment of energetic ions cause the creation of diamond nuclei. Some workers have reported the formation of an interfacial carbide layer covered with a very thin non-diamond carbon film [22-24].

2.3 Reference

1. S.M Sze, Physics of Semiconductor Devices, Wiley, New York, 1981.

2. I. Brodie, P.R Schwoebel, Proceedings of the LEEE 82. p1006 (1994).

3. N.A. Cade, R. Johnston, Proc. 3rd Int. Vacuum Microelectronics Conf., Monterey, CA, 1990.

4. R. Greene, H.E Gray, Proc. Ist Int. Vacuum Microelectronics Conf., Williamsburg, VA, 1988.

5. L.M. Baskin, O.I. Lvov, G.N. Fursey, Phys. Stat. Sol. 47, 49 (1971).

6. S.Kanemaru, T. Hirano, H. Tanoue, J. Itoh, J. Vac. Sci. Technol. B14, 1885 (1996).

7. K.L. Jensen, J. Vac. Sci. Technol. B 13, 516 (1995).

8. K. L. Jensen, A. K. Ganguly, J. Vac. Sci. Technol. B 11, 371 (1993).

9. M.Ihara, H. Komiyama, and T. Okubo, Apply. Phys. Lett 65 (9),192 (1994).

10. H.C. Barsilia, B. R. Mehta, and V.D. Vankar, J. Mater. Res. 11,1019 (1996).

11. Y.S.Park, S.H.Kim, and J.W.Lee, Jpn. J. Appl.Phys.33 (11), 6320 (1994).

12. Z.Feng, K. Komvopoulos, I.G.Brown,and D.B.Bogy, J.Mater. Res. 9,2148 (1994).

13. J.J.Dubray, C.G. Pantano, M.Meloncelli,and E.Bertran, J.Vac.Sci. Technol. A 9 (6), 3012 (1991).

14. P.N.Barnes and R. L. C.Wu, Appl.Phys.Lett 62 (1), 37 (1993).

15. L.Chow, A.Horner,H.Sakouri,B.Roughani,and S.Sundaram, J.Mater. Res. 7, 1606

(1992).

16. S.Yugo, T. Kanai, T. Kimura, and T.Muto, Appl.Phys.Lett. 58 (10),1036 (1991).

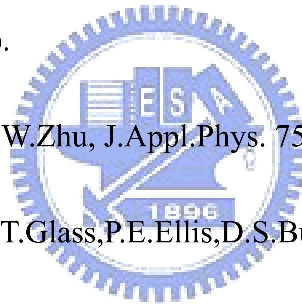
17. S.Yugo, T. Kanai, T. Kimura, Diamond Relat .Mater. 1.388 (1992).

18. B.R.Stoner,G.H.Ma,S.D.Wolter and J.T.Glass,Phys.Rev.B,45,11067 (1992)..

19. X.Jiang,C.P.Klages,R.Zacgai,M.Hartweg and H.J.Fusser,Appl.Phys.Lett ,62,3438 (1993).

20. M. Katoh, M.Aoki, and H.Kawarada, Jpn .J. Appl.Phys. 33, (2A).L194 (1994).

21. B.W.Sheldon, R.Csencsits, J.Rankin, R.E.Boekenhauer, and Y.Shigesato, J. Appl. Phys.75, (10), 5001 (1994).



22. F.Arezzo,N.Zacchetti, and W.Zhu, J.Appl.Phys. 75 (10), 5375 (1994).

23. S.D. Wolter, B.R.Stoner, J.T.Glass,P.E.Ellis,D.S.Buhaenko, C.E.Jenkins, and P. Southworth, Appl. Phys.Lett, 62 (11), 1215 (1993).

24. B. R. Stoner and J.T, Glass, Appl. Phys.Lett. 60 (6) 698 (1992).