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ON THE EFFECTIVE BARE WORK FUNCTION OF bcc THERMIONIC ELECTRODE MATERIALS

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An equation is derived for the effective work function of a polycrystalline metal with a fiber texture. This equation contains two parameters: the temperature and the maximal tilt angle, i.e. the maximal deviation from the fiber axis. A linear relationship is assumed between the work function of a uniform lattice plane and the angle of a low index plane with respect to the uniform lattice plane. The proportionality constant D in the [100] zone is evaluated from experimental data for tungsten: $D = 0.035$ eV/degree. It is expected that D has the same value in other bcc metals. For a given maximal tilt angle, a higher temperature results in a higher effective work function. A reasonable agreement is found for the calculated effective work functions of tungsten with ⟨110⟩ fiber textures of various sharpness and the experimentally determined work functions from the literature. Furthermore, the effective work function of texture-free polycrystalline tungsten is calculated. The agreement with the experimentally determined value reported in the literature is excellent.

1. Introduction

A thermionic energy converter (TEC) is a device which directly converts heat into electricity [1,2]. In order to obtain the optimum output voltage V_0, the barrier index V_b,

$$V_b = \phi_c + V_d, \tag{1}$$

should be minimal. Consequently, the collector work function (ϕ_c) and the plasma drop (V_d) should be as low as possible. The plasma drop is almost linearly proportional to the cesium vapor pressure in the converter. So, in order to reduce V_d we would like to reduce this pressure. However, this would result in a severe current density loss due to the increase of the emitter work function. For, at a lower cesium pressure the desorption rate of the cesium from the emitter is compensated with a lower adsorption rate. A cesiated emitter work function of $\phi_e = 2.5$ eV is preferred at practical emitter temperatures. It is found that the higher the bare work function of the emitter is, the lower the cesium pressure can be in order to obtain this value [1,2]. For this reason, research on thermionic emitter materials is concentrated on the develop-

ment of processes to produce large areas (20 cm^2) of material with a high bare work function. As table 1 shows, the (110) lattice planes of bcc refractory metals have high bare work functions.

Chemical vapor deposition (CVD) is a technique to produce large areas of high bare work function. Films, consisting of many columnar grains, can be deposited with CVD at rightly chosen conditions [3,4]. The axis of a column corresponds to a main axis of the crystal lattice. A macroscopic surface polished parallel to the substrata surface is composed of many lattice planes with the same simple Miller indices. The direction

Table 1

Thermionic work function (ϕ_s in eV) of pure uniform bcc metal planes at 1800 K [1,2,7,13]

Plane	W	Mo	Ta	Nb
110	5.33	5.0	4.7	4.80
112	4.8	4.5	4.3	
100	4.65	4.4	4.15	3.95
111	4.4	4.1	4.0	3.88
116	4.3	4.0	3.9	
105	4.4			
Poly	4.54	4.3	4.12	3.99

perpendicular to these planes (for instance {110} planes) is the direction of the fiber texture (a ⟨110⟩ fiber texture). In a CVD film with a fiber texture there are always grains which crystal lattice axis with simple indices deviates a little from the normal to the substrata surface. As a result, the macroscopic surface of such a column deviates a little from the plane with the simple Miller indices, i.e. it is a vicinal plane. The vicinal plane has an angle of inclination (ρ) with the plane of simple indices. This angle corresponds to the angle between the axis of the crystal lattice and the normal to the substrata, the so-called tilt angle. The maximal tilt angle (ρ_m) in a film can be measured with X-ray diffraction in a cylindrical camera [5,6]. The vicinal plane is supposed to consist of regularly stepped planes. The steps are monoatomic and the terrace is a plane with simple Miller indices. In section 2 the work function of uniform vicinal tungsten crystal lattice planes is outlined. In section 3 a model is presented to describe the effective work function of a film with a texture including the small deviations. In section 4 it is shown how to calculate the effective work function of texture-free polycrystalline material, i.e. a surface consisting of randomly orientated lattice planes.

2. The work function of uniform tungsten lattice planes

Krahl-Urban et al. [7] measured in very careful experiments the bare work function of uniform tungsten planes in a part of the [100] and [110] zone. In their experiments the inclination angle ρ between the various uniform lattice planes and the (110) plane varied from 0° to 10°. We conclude from their values that the dependence of ϕ on ρ (in one zone) can be described with high accuracy by:

$$\phi(\rho) = \phi_s - D\rho, \tag{2}$$

where ϕ_s is the work function of the plane with simple Miller indices, in this case the (110) plane. From the experiments of Krahl-Urban we deduced a D-value of 0.035 eV/degree in the [100] zone (the correlation coefficient $r = 0.9973$). From

the field emission measurements of Todd and Rhodin [8] it can be deduced that the work function in the [100] zone continuously decreases while ρ goes from 0° to 32°. We want to stress that eq. (2) is meant to hold for uniform surfaces. Experimentally, it will be difficult to avoid thermal etching (faceting) at higher inclination angles. In order to avoid thermal etching the oxygen partial pressure in the measuring device should be as low as possible. The (103) lattice plane lies in the [100] zone too ($\rho = 26.6°$). Unfortunately there is no work function deduced from thermionic electron emission measurements available in the literature. However, Hellwig and Block [9] measured the work function of the (103) lattice plane using the field emission technique (temperature $T = 78$ K, $\rho = 26.6°$, $\phi = 4.34$ eV). Using the temperature dependence of the work function of tungsten observed by Krahl-Urban et al. [7] we estimate a work function of $\phi = 4.2$ eV for the uniform (103) lattice plane at 2300 K. This value fits well within the linear dependence given in eq. (2). Since no other reliable experimental data or theoretical values are available for higher inclination angles in the [100] zone we will use eq. (2) as an empirical approximation.

Gardiner et al. [11] have investigated the work function in the entire [110] zone. Maximal work functions were found in the ⟨110⟩, ⟨112⟩ and ⟨100⟩ directions. Minimal work function were found in the ⟨115⟩ and ⟨111⟩ directions. We
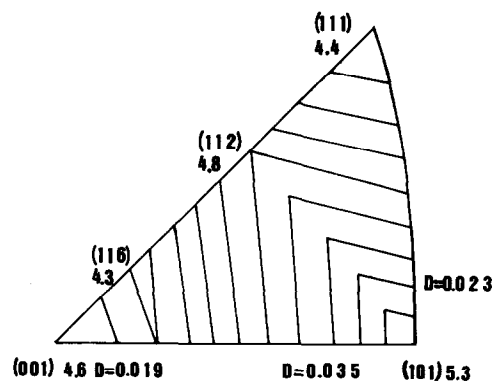

Fig. 1. Contour map of the thermionic work function (in eV) of the uniform lattice planes of a bcc metal. Subsequent contour lines differ by 0.1 eV. The work function values indicated at the main orientations are the values for tungsten (see table 1).

assume a linear dependence of the work function on the inclination angle to exist in the region between the maxima and the minima. For instance, if the work function is supposed to change linearly from ⟨110⟩ to ⟨111⟩ a value of $D = 0.023$ eV/degree is found. With these assumption, a contour map of the work function of the uniform planes of tungsten can be sketched. In the stereographic triangle, reproduced in fig. 1, such a sketch is drawn. In this figure are also indicated the D-values in the various zones.

3. An emitter with a fiber texture

In developing a relation between ϕ and the texture of an emitter it is supposed that the emitter surface consists of columns with a diameter of at least 50 μm. Experimentally, the current density of the electron emission from such a surface can be measured in a diode equipped with guard rings [1]. The inter electrode distance has to be kept as small as possible (10 μm). In the terminology developed by Hatsopoulos and Gyftopoulos [1], the surface is a type I nonuniform surface. The relation between the saturation current density (J in A/cm^2) and the effective work function is described by the modified Richardson equation:

$$\phi_{eff} = kT_e \ln(120 T_e^2/J), \tag{3}$$

where k is the Boltzmann constant and T_e is the emitter temperature in K. The electron current density from the surface is the sum of the current from the vicinal planes of the various columns in a square centimeter:

$$J = \int_0^{\rho_m} F(\rho) \times 120 T_e^2 \exp\left[-\phi(\rho)/kT_e \right] d\rho. \tag{4}$$

$F(\rho)$ is the fraction of the surface consisting of a vicinal plane with angle of inclination ρ, $\phi(\rho)$ is the work function of a vicinal plane with angle of inclination ρ and ρ_m is the maximal angle of inclination. We assume that $\phi(\rho)$ is given by eq. (2). For a ⟨110⟩ fiber texture emitter the plane with the simple Miller indices is the (110) plane with work function $\phi_s = 5.33$ eV. As described in section 2 a coefficient $D = 0.035$ eV/degree for the [100] zone can be deduced from experiments.

For a ⟨110⟩ fiber texture emitter, only the [100] zone is taken into account because in this zone the work function changes most rapidly as the tilt angle is increased, i.e. D has the highest value in the [100] zone, see fig. 1. The deviations from the main direction of the texture will in general follow an error function. However, as a first approximation it is supposed that the deviations are a linear function of the tilt angle. A linear dependence of the area fraction $F(\rho)$ on the angle of inclination is then obtained:

$$F(\rho) = 2/\rho_m - 2\rho/\rho_m^2, \tag{5}$$

where ρ_m is the maximal angle of inclination. As explained in the introduction, the angle of inclination of a vicinal plane is the same as the angle (i.e. the tilt angle) between the main axis of the crystal lattice of the column and the normal to the sample surface. Substitution of eqs. (2), (4) and (5) in eq. (3) and some algebra, results in an equation for the dependence of the effective work function on the maximal tilt angle:

$$\phi_{eff} = \phi_s - kT_e \ln(2b)$$
$$- kT_e \ln\{ b[\exp(1/b) - 1] - 1 \}, \tag{6}$$

where $b = kT_e/D\rho_m$. A plot of the effective work function of an emitter with ⟨110⟩ fiber texture versus the maximal tilt angle is shown in fig. 2. From eq. (6) it can be deduced that for a given
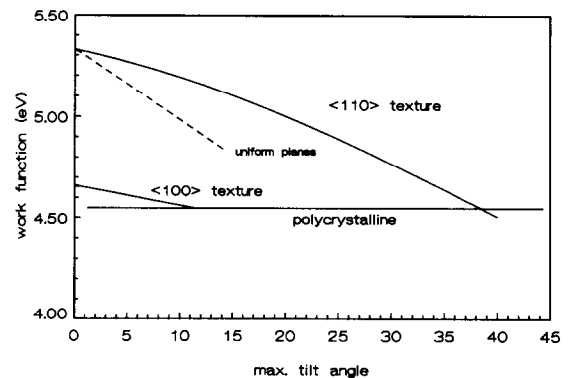

Fig. 2. Effective work function (ϕ_{eff} in eV) of a tungsten emitter with a fiber texture as a function of the maximal tilt angle (ρ_m in degrees). The work function of the uniform lattice planes in the [100] zone are indicated with a dashed line (see eq. (2)). The emitter temperature (T_e) is 1800 K.

Table 2
Calculated and measured effective work functions (eV) of nonuniform tungsten surfaces with ⟨110⟩ fiber texture as a function of the maximal tilt angle (ϕ_s model = 5.11 eV, D = 0.035 eV/degree)

ρ_m (deg)	T (K)	ϕ_{eff} model	ϕ_{eff} exp	Ref.
6	2073	5.03	5.05	[12]
11	2073	4.96	4.93	[12]
18	2073	4.83	4.92	[11]

maximal tilt angle an increase in temperature results in an increase of the effective work function.

The effective work function of an emitter with a ⟨100⟩ fiber texture is calculated in the same way. The plane with the simple Miller indices is the (100) plane with work function ϕ_s = 4.65 eV. A value D = 0.019 eV/degree is found in the neighborhood of the ⟨100⟩ directions, see section 2. Effective work functions of emitter surfaces with ⟨100⟩ fiber textures of various sharpness are shown in fig. 2. Literature values of experimentally determined sets of effective work function and maximal tilt angle are given in table 2.

In order to benefit from the fiber texture the effective work function must be higher than the effective work function of poly crystalline tungsten, i.e. 4.54 eV. It is seen in fig. 2 that the maximal tilt angle should be less than 39° in the ⟨110⟩ fiber texture case, and less than 11° in the ⟨100⟩ fiber texture case. From a manufacturing point of view it is known that in a CVD process, smaller tilt angles are obtained at higher deposition temperature and lower deposition rate.

4. Polycrystalline emitters without texture

Within the scheme developed in section 3 the effective bare work function of a polycrystalline

Table 3
Effective work function of polycrystalline tungsten (T_e = 1800 K)

Zone	ϕ_{eff} (eV)	
100	4.55	Calc.
110	4.55	Calc.
–	4.54	Exp. [2]

surface can be evaluated. It is then assumed that the orientations of the lattice planes at the surface are randomly distributed. Eq. (4) is solved for ρ going from 0° to 360°, where F is taken constant: 1/360. Due to symmetry reasons it is not necessary to take the whole range into account. The integration can be performed over various zones. In zone [100] the same D-values as indicated in fig. 1 were used. In the [110] zone the extra D-values were gathered from the work functions in table 1 and the fact that the work function of the {111} plane is a local minimum, see section 2. Calculated effective work functions are collected in table 3. The agreement with the experimentally determined work function is excellent. An increase of the temperature results in an increase of the effective work function of the polycrystalline emitter.

5. Discussion and conclusions

As is seen in table 1 the hierarchy in the work functions is the same in all bcc metals. The differences in work functions between the various orientations in all these bcc metals are the same. Clearly the value of D – in the various zones – is independent of the constitution of the metal.

A contour map of the work function of the uniform lattice planes of tungsten is sketched in fig. 1. For the other bcc metals the outline of the contour map is the same. However, the work functions of each bcc metal are shifted by the same constant amount (0.3, 0.6 and 0.5 eV for respectively Mo, Ta and Nb). To refine the sketch of fig. 1 more experimentally determined work functions of high index lattice planes are desired.

Many experimentally determined work functions are influenced by contaminations at the surface. Particularly the planes with high work functions are difficult to deal with. An extrapolation of the experimentally determined work functions of Yang and Hudson [12] (see table 2) results in a work function for the ⟨110⟩ plane of ϕ = 5.11 eV, which is lower by 0.15 eV than found in the very careful work of Krahl-Urban et al. [7]. For the comparison of the experimentally determined and the calculated work functions (see table 2) the

value found by Yang is used. Viewed in this light the agreement of the calculated work function of emitters with a fiber texture and the experimentally determined work functions is reasonable.

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