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DETERMINATION OF WORK-FUNCTION DISTRIBUTION ON METAL SURFACES FROM SURFACE IONIZATION

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DETERMINATION OF WORK-FUNCTION DISTRIBUTION  
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Daniel R. Koenig<sup>□</sup>  $\frac{1}{3}$  L

March 1967

## FROM SURFACE IONIZATION

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Abstract

The fraction of an emitter surface occupied by patches having a given work function can be determined from the ion current-voltage characteristics of vapor diodes. The analysis assumes that emitted ions and atoms are in thermal equilibrium with the emitter surface, transport or space charge effects are negligible, the surface coverage of vapor particles on the emitter is always too small to alter its work function, and the ion emission from each patch is uninfluenced by the neighboring patches. A general expression for the emitter work-function distribution is derived in terms of the first and second derivatives (with respect to the applied voltage) of the observed ion current-voltage curve.

Discussion

The work-function distribution on a patchy emitter surface can be determined from the electron current-voltage characteristic of a diode.<sup>(1)(2)</sup> This method can be extended as follows to include the ion current-voltage characteristics of vapor diodes.

The analysis assumes that transport or space charge effects are negligible, the surface coverage of vapor particles on the emitter is always too small to alter its work function, and the emitted ions and atoms have a Maxwell-Boltzmann energy distribution characterized by the emitter temperature.

The saturation ion-current density  $J_{is}(\phi)$  emitted by an ionizing surface with work function  $\phi$  is

$$J_{is}(\phi) = en_0 \left[ 1 + \frac{1}{\alpha(\phi)} \right]^{-1}, \quad (1)$$

where  $n_0$  is the vapor flux incident on the surface,  $e$  is the electron charge, and  $\alpha(\phi)$  is the degree of ionization (ratio of ions to atoms emitted from the surface) given by the Saha-Langmuir equation,

$$\alpha(\phi) = \frac{g_i}{g_a} \exp\left(\frac{\phi_a - \phi_i}{kT}\right) = \frac{g_i}{g_a} \exp\left(\frac{\phi - V_i}{kT}\right), \quad (2)$$

where  $g_i/g_a$  is the ratio of the statistical weights of the ionic and atomic states of the vapor,  $\phi_a$  and  $\phi_i$  are the atom and ion desorption energies respectively,  $V_i$  is the ionization potential of the vapor,  $T$  is the surface temperature and  $k$  is the Boltzmann constant.

In analogy to the thermionic emission of electron, the application of a retarding potential for ions  $V_D (>0)$  is equivalent to increasing the ion desorption-energy  $\phi_i$  by

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the amount  $eV_D$ . Assuming that the electric field at the emitter surface is too small to affect  $\phi_a$ , the effective degree of ionization is then equal to

$$\alpha(\phi - eV_D) = \frac{g_i}{g_a} \exp\left(\frac{\phi - eV_D - V_i}{kT}\right), \quad (3)$$

and the collected ion-current density is

$$J_i(\phi, V_D) = en_o \left[ 1 + \frac{1}{\alpha(\phi - eV_D)} \right]^{-1}. \quad (4)$$

Consider now the ion emission from a patchy emitter of a vapor diode. The inter-electrode potential  $V_D$  is related to the applied, external emitter-potential  $V_E$  (relative to the collector) by the relation

$$eV_D = \phi - \phi_c - eV_E \quad (5)$$

where  $\phi_c$  is the work function of the collector (assumed uniform). At an operating emitter-potential  $V_E$ , the ion-current density  $j_i(\phi)$  collected from an emitter patch with work function  $\phi$  is, from Eqs. (1) through (5),

$$j_i(\phi) = en_o \left[ 1 + \frac{g_a}{g_i} \exp\left(\frac{V_i - \phi}{kT}\right) \right]^{-1} = j_{is}(\phi), \quad \text{for } eV_E > \phi - \phi_c, \quad (6)$$

$$j_i(\phi) = en_o \left[ 1 + \frac{g_a}{g_i} \exp\left(\frac{V_i - \phi_c - eV_E}{kT}\right) \right]^{-1} = j_{is}(\phi_c + eV_E), \quad \text{for } eV_E < \phi - \phi_c. \quad (7)$$

If it can be assumed that the observed total ion current  $J_i(V_E)$  collected from an emitter of unit area is the sum of the contributions from each patch, then

$$J_i(V_E) = \int_0^{\infty} j_i(\phi) f(\phi) d\phi, \quad (8)$$

where  $f(\phi) d\phi$  is the fraction of the emitter surface having a work function between  $\phi$  and  $(\phi + d\phi)$ . The desired function  $f(\phi)$  can be determined from the observed ion current-voltage characteristics  $J_i(V_E)$  as follows. Equation (8) can be written in terms of Eqs. (6) and (7),

$$J_i = J_i(V_E) = \int_0^{\phi_c + eV_E} j_{is}(\phi) f(\phi) d\phi + \int_{\phi_c + eV_E}^{\infty} j_{is}(\phi_c + eV_E) f(\phi) d\phi. \quad (9)$$

\*\*\* Equation (7) is in contrast to Eq. VII.2 of reference 3 by the author which is unfortunately in error and led to erroneous conclusions.

Differentiating Eq. (9) with respect to  $eV_E$

$$\frac{dJ_i}{d(eV_E)} = \frac{dj_{is}(\phi_c + eV_E)}{d(eV_E)} \int_{\phi_c + eV_E}^{\infty} f(\phi) d\phi, \quad (10)$$

and

$$\frac{d^2J_i}{d(eV_E)^2} = -f(\phi_c + eV_E) \frac{dj_{is}(\phi_c + eV_E)}{d(eV_E)} + \frac{d^2j_{is}(\phi_c + eV_E)}{d(eV_E)^2} \int_{\phi_c + eV_E}^{\infty} f(\phi) d\phi. \quad (11)$$

The derivatives of  $j_{is}(\phi_c + eV_E)$  are obtained by differentiating Eq. (7),

$$\frac{dj_{is}(\phi_c + eV_E)}{d(eV_E)} = \frac{j_{is}^2(\phi_c + eV_E)}{en_0 kT \alpha(\phi_c + eV_E)}, \quad (12)$$

and

$$\frac{d^2j_{is}(\phi_c + eV_E)}{d(eV_E)^2} = \frac{1}{kT} \left[ \frac{2j_{is}(\phi_c + eV_E)}{en_0 \alpha(\phi_c + eV_E)} - 1 \right] \frac{dj_{is}(\phi_c + eV_E)}{d(eV_E)}, \quad (13)$$

where  $\alpha(\phi_c + eV_E)$  is the degree of ionization evaluated at  $\phi = \phi_c + eV_E$ . Combining Eqs. (10) through (13) yields the desired expression

$$f(\phi) = f(\phi_c + eV_E) = \frac{(1+\alpha)^2}{en_0 \alpha} \left[ \left( \frac{1-\alpha}{1+\alpha} \right) \frac{dJ_i}{d(eV_E)} - kT \frac{d^2J_i}{d(eV_E)^2} \right], \quad (14)$$

where for convenience we have written  $\alpha(\phi_c + eV_E) = \alpha$ .

If the ionization potential  $V_i$  of the vapor is greater than the maximum emitter work function then the degree of ionization is always much smaller than 1 and Eq. (14) reduces to

$$f(\phi) = f(\phi_c + eV_E) = \frac{1}{J_{is}(\phi_c + eV_E)} \left[ \frac{dJ_i}{d(eV_E)} - kT \frac{d^2J_i}{d(eV_E)^2} \right]. \quad (15)$$

Equation (15) is similar to the expression for  $f(\phi)$  obtained from electron emission,<sup>(2)</sup>

$$f(\phi) = f(\phi_c + eV_E) = \frac{1}{J_{es}(\phi_c + eV_E)} \left[ -\frac{dJ_e}{d(eV_E)} - kT \frac{d^2J_e}{d(eV_E)^2} \right], \quad (16)$$

where  $J_e$  is the observed electron-current density at  $V_E$ , and  $J_{es}(\phi_c + eV)$  is the saturation electron-current density evaluated at  $\phi = \phi_c + eV_E$ , i.e.

$$J_{es}(\phi_c + eV_E) = AT^2 \exp\left(-\frac{\phi_c + eV_E}{kT}\right), \quad (17)$$

Where A is the Richardson constant.

### Limitations

The applicability of the ion method described here is essentially limited to vapors whose ionization potential is greater than the average emitter work function. Further, the emitter temperature and the vapor flux are restricted by the requirements that the saturated ion-current density be several orders of magnitude greater than the saturated electron-current density, and also that the fractional surface coverage of vapor particles on the emitter be small (less than 1%). These restrictions may be expressed quantitatively using the following practical considerations:

$$V_i \gtrsim \phi, \quad (18)$$

$$\frac{J_{is}}{J_{es}} \approx \frac{en_0}{AT^2} \exp\left(\frac{2\phi - V_i}{kT}\right) > 10^4, \quad (19)$$

$$\text{surface coverage} \approx en_0 \cdot 10^{-12} \exp\left(\frac{\phi_a}{kT}\right) < 10^{12} \text{ particles/cm}^2. \quad (20)$$

The last two inequalities can be combined to yield the range of vapor flux for which this ion method is applicable,

$$10^5 \exp\left(-\frac{\phi_a}{kT}\right) > en_0 > 10^6 T^2 \exp\left(\frac{V_i - 2\phi}{kT}\right) \quad (21)$$

where  $en_0$  is in units of ampere/cm<sup>2</sup>.

### References

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