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A general phenomenological model for work function

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ABSTRACT

A general phenomenological model is presented for obtaining the zero Kelvin work function of any crystal facet of metals and semiconductors, both clean and covered with a monolayer of electropositive atoms. It utilizes the known physical structure of the crystal and the Fermi energy of the two-dimensional electron gas assumed to form on the surface. A key parameter is the number of electrons donated to the surface electron gas per surface lattice site or adsorbed atom, which is taken to be an integer. Initially this is found by trial and later justified by examining the state of the valence electrons of the relevant atoms. In the case of adsorbed monolayers of electropositive atoms a satisfactory justification could not always be found, particularly for cesium, but a trial value always predicted work functions close to the experimental values. The model can also predict the variation of work function with temperature for clean crystal facets. The model is applied to various crystal faces of tungsten, aluminium, silver, and select metal oxides, and most demonstrate good fits compared to available experimental values.

1. Introduction

The work function (WF) is a fundamental property of a metallic surface, important in determining the material's applicability as a contact electrode [1,2] or electron emitter [3]. The work function is defined as the energy given to an electron that enables it to be transported to a field-free region outside the surface. The force on an electron external to the metal surface without applied fields is due to the induced charge by unscreened Coulomb interaction. Classically, this force is calculated by assuming a virtual image charge inside the conductor [4]. Since WF usually has a linear dependence on temperature, the value of WF at zero Kevin is usually given.

Surfaces with low work functions could improve technologies requiring precise control of contact barriers such as organic and printed electronics [2] or devices based on electron emission, ranging from fluorescent light bulbs [5,6] to THz sources [7], thermionic energy converters (TECs) [8], and the photon-enhanced thermionic emission converters (PETEC) [9]. For TEC and PETEC, in particular, discovery of thermally stable materials with work functions of less than 1 eV would allow thermionic conversion of high-temperature (>500 °C) heat or solar radiation directly to electricity with projected efficiencies exceeding 50%.

Halas (2006) in a paper entitled "100 Years of Work Function" [10] traces the progress in our understanding the emission of electrons from material surfaces from an early definition of work function [11] through more recent *ab initio* quantum mechanical [12] and phenomenological models [4,13,14] that can yield quantitative values of WF. Experimental electron sources or cathodes are usually compacts of microcrystals of various sizes, orientation and composition. Hence, their surfaces will consist of randomly oriented crystal facets of different sizes. The work functions of such materials will give some form of weighted average [15–17]. The effect of such patches has been discussed extensively [18].

The phenomenological models cited previously did not distinguish between crystal faces, although they did predict work functions fairly close to the measured values for polycrystalline surfaces. However, they could not be expected to be exact. Other authors have addressed the work function variation between crystal faces, including Smoluchowski (1941) who used a surface dipole model [19], Wojciechowski et al. (1999) who used a model derived from the local polarization of plasma and image force action near a metal surface [20], as well as Pogosov and Kurbatsky (2001) who used density-functional theory of an elastically deformed finite metallic system [21]. The purpose of the present paper is to develop a more general phenomenological model for obtaining the work function of any crystal facet on a metal or semiconductor, both clean and covered with a monolayer of adsorbed atoms based on a previously reported concept of a surface 2-D electron gas [22,23] as opposed to a dipole layer representation [24].

2. The proposed model

A phenomenological approach entails using the measurable parameters of a given system together with simple assumptions consistent

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with fundamental theory to predict various properties of the system. In the proposed model to predict work functions, the following assumptions are made. More detailed analysis and justification for these assumptions are given in Section 6.

2.1. Atoms as spheres

The surface atoms are treated as a regular array of spheres. This assumption is justified by STM images of surfaces [25]. In the case of an elemental metal, each atom is considered to be conducting with a classical radius R. For a compound, the more electronegative atoms are considered to be non-conducting. Note atomic radii are dependent on their bonding state and are in a range of 0.025 nm for H to 0.26 nm for Cs [26].

2.2. Dangling bonds

Atoms in the surface layer contain weakly bonded (or "dangling") unused valence electrons that are required in the bulk for the strong 3-D inter-atomic crystal bonds.

2.3. Surface ions and electrons

These electrons and their corresponding ions reside on the surface. The ions are prevented from dissociating with the surface by their bonds to the sub-surface atoms. The electrons are prevented from leaving by surface fields.

2.4. Surface 2-D plasma

The surface layer of electrons and ions forms a 2-D semiconductor if the surface ions are immobile or a 2-D plasma if they are mobile. For the case of the 2-D semiconductor, periodicity of the surface lattice will give rise to an effective electron mass as in 3-D systems. However, in a plasma, the periodicity is lost by the motion of ions and the electron mass is unchanged. The electron energy is too low to consider relativistic effects. Here we assume the electrons have resting mass and can be considered to form a 2-D Fermi gas without interaction among themselves, due to the presence of mobile surface counter ions. This topic is discussed in greater detail in Section 6.4.

For the equations given below all quantities are given in SI units, except as noted. The zero order, zero temperature formula for the Fermi energy E_F of a simple non-interacting 2-D electron gas is given by [27] as

$$E_F = \frac{h^2}{4\pi m} N = 3.834 \times 10^{-38} N \quad \text{J} \tag{1}$$

where N is the number of electrons/m^2, and h, m, e are the physical constants in SI units. The value of E_F in the commonly used units of electron volts (eV) is obtained by dividing the SI value by e.

If A is the area of a unit surface lattice site, then N_a the number of sites per m^2 is given by

$$N_a = A^{-1} \tag{2}$$

If n is the number of electrons donated to the surface 2-D electron gas from each surface lattice site, then the number of electrons per m^2 can be expressed as

$$N = N_a n = \frac{n}{A} \tag{3}$$

Combining Eqs. (1) and (3) gives

$$E_F = 3.834 \times 10^{-38} \times \frac{n}{A} \quad \text{J} \tag{4}$$

These numbers can be derived for a given crystal facet from measured values of the lattice constant(s) and the available valence electrons from each surface metal atom. For a cubic crystal with lattice constant a, the area A projected per unit surface lattice site in the various directions can be obtained from simple geometric considerations: $A(100) = a^2$, $A(110) = 2^{1/2}a^2$, $A(111) = (¾)^{1/2}a^2$, $A(112) = (3/8)^{1/2}a^2$. Note the 2-D Fermi energy can vary between different facets of a crystal since both A and n can vary between crystal facets. The assumption that the lattice parameters of the surface are the same as for the bulk is not exactly true. This point is discussed more fully in Section 6.9.

2.5. Kinetic energy and uncertainty distance

There is a region bounded by a surface that is a distance d away from the classical metal surface, such that an electron inside the metal can transverse by converting its kinetic energy to potential energy without doing any work (Fig. 1). At zero Kelvin, the 2-D electron gas is assumed to exist within this thin sheet of thickness d. At the inner boundary, the electron has an energy of E_F. At point P_d, its kinetic energy is reduced to zero and the image forces become effective at the outer boundary. Continuous decoherence from quantum to classical states takes place in this region of the 2-D electron gas. The use of such a surface where the image force becomes effective has been theoretically justified by using a first-principles evaluation of the exchange-correlation potential for the electron gas-vacuum interface [28].

2.6. Fermi energy

For an electron with an energy of E_F initially at the tip of a conducting atom, the minimum distance it can appear with zero momentum is given by the uncertainty distance d [29] associated with the change in momentum. Thus

$$\Delta p \cdot d = \sqrt{2mE_F} \cdot d \geq \frac{h}{2\pi} \tag{5}$$

$$\text{or} \qquad d \geq \frac{h}{2\pi\sqrt{2mE_F}} \quad \text{m} \tag{6}$$

2-D Fermi energies typically lie in the range of 2 to 20 eV (3.2×10^{-19} to 3.2×10^{-18} J). This gives rise to d in the range of 0.07 nm to 0.02 nm for lattice constants ranging from 0.6 nm to 0.2 nm in typical cubic crystals.

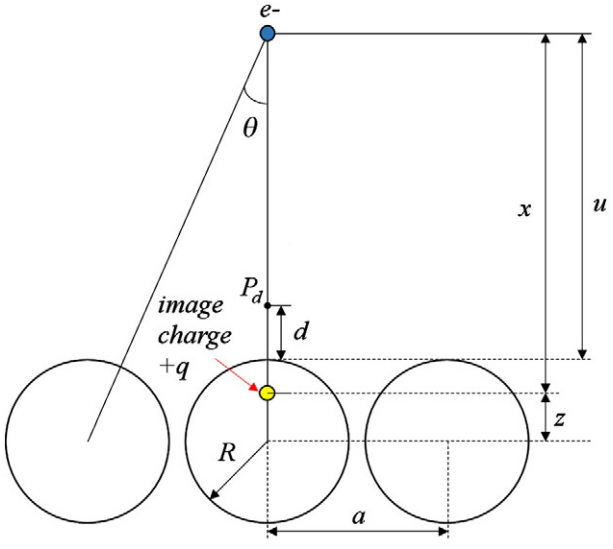

Fig. 1. Schematic showing the topmost layer of atoms and an escaped electron, where d = uncertainty distance.