

Work Function Calculation For Hafnium- Barium System

K.A. Tursunmetov, F.Yu. Turgunboev

Abstract: The adsorption process of barium atoms on hafnium is considered. A structural model of the system is presented and on the basis of calculation of interaction between ions dipole system the dependence of the work function on the coating.

Index Terms: Adsorption barium hafnium structural model dipole work function coating

1 Introduction

The studies of the mechanisms of barium atom adsorption on the metal surface are of theoretical and practical interest [1-4]. They allow not only in-depth understanding of the adsorption process mechanisms but also development of effective emission and anti-emission materials [1, 2, 5, 6]. There are a lot of studies of the emission features of the systems Me-Ba, Me-O-Ba and Me-Cs and Me-O-Cs [1-3]; a number of conclusions on structure and emission features of the systems metal-alkaline earth metal and metal-alkaline metal [4], metal-oxygen-cesium and metal-oxygen-barium [7] were generalized. However, the adsorption of barium atoms on metals with a hexagonal close packed (HCP) structure has been studied insufficiently, especially for the face (1000). The adsorption of the barium atoms on polycrystalline hafnium was studied in [5, 6] where a possibility of using hafnium as an anti-emission material in the Hf-O-Ba system was shown. However, a structure of the Hf-Ba system was not been considered. Therefore, this work tries to theoretically explain on the basis of calculations of ion interaction within a proposed structural model of the system how the hafnium work function changes in the process of the barium atom adsorption.

2 PROCEDURE FOR PAPER SUBMISSION

2.1 Review Stage

The experiments on barium atom adsorption on the hafnium surface were performed according to a technique, technology described in our paper [6]. For example, for the Hf - Ba system the work function dependence (ϕ) on cover degree (θ) at temperature 1000 K is presented in Fig.1. The work function was defined by the methods of total current and contact potential. The work function was calculated by the total current method with the Richardson-Deshman formula

$$\phi = \frac{T}{5040} [\lg A + 2 \lg T + \lg S - \lg I],$$

Where $A = 120.4 \text{ A/cm}^2 \cdot \text{K}^2$ is the Richardson-Deshman constant, T is the sample temperature, S is the hole area of the Faraday cylinder (anode), I is the emission current. The contact potential method of defining the work function is not different from that presented in [1-3]; the work function was defined from the current-voltage diagrams. As seen from the figure, the work function dependence is linear

until the cover degree is $\theta \approx 0.5$ and then monotonical; the minimal work function is $2.26 \pm 0.03 \text{ eV}$ for $\theta \approx 0.67$.

2.2 Final Stage

A decrease in the metal work function in adsorption of electropositive metals can be explained by formation of dipole systems leading to decreasing the surface potential, hence to reducing the surface potential barrier and the metal work function [1-7]. The dipole moment of the Hf - Ba system was defined by the formula $\Delta\phi = 4\pi n p$ within the linear range of $\phi = \phi(\theta)$. Here n is the concentration of the adsorbed atoms, p is the dipole moment of the Hf - Ba system.

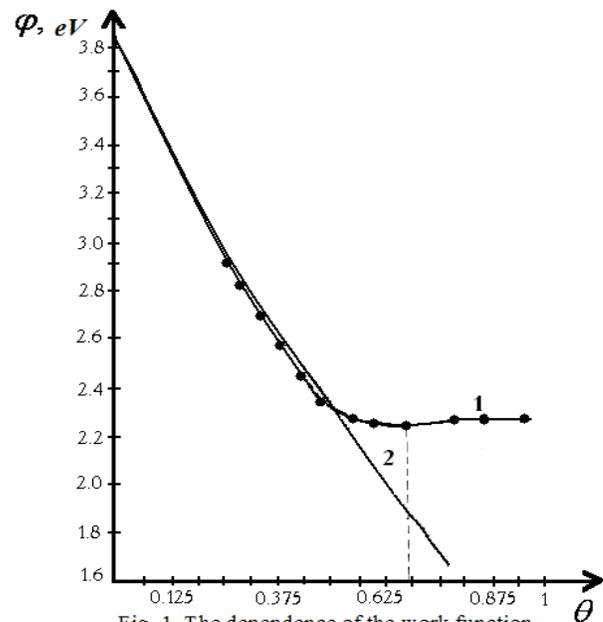


Fig. 1. The dependence of the work function of the Hf-Ba system: 1 – experimental; 2 – theoretical.

The experiments on cesium adsorption on refractory metals were performed first by Taylor and Langmuir [1] and then they were carried out in [1, 3, 8]. In [8] A. Kennedy calculated the energy of cesium ion interaction and how the tungsten surface potential changes in cesium atom adsorption. The work function was defined by the Helmholtz equation $\Delta\phi = 4\pi n p$ and the values of the work function were $\phi = \phi_M - V_s(\theta)$, where ϕ_M is the metal work

function; $V_s(\theta)$ is the contact potential showing a decrease in the surface potential and being a function of cover degree θ only. With this method the work function of the *Hf – Ba* system was calculated in this paper. Consider a model of the barium atoms adsorbed on the surface of polycrystalline hafnium. In structure this surface approximately corresponds to a structure of the (1000) face of (hexagonal close packed) HCP – lattice monocystal. Assume that adsorbed barium in a state of the least energy is on the surface as barium ions experiencing electrostatic attraction by a mirror-reflected charge and additional repulsion as a result of the influence of neighboring adsorbed ions of barium. The potential energy per one charge is defined as a potential and has the form

$$V = k \frac{q}{r}$$

where q is the ion charge and $k = \frac{1}{4\pi\epsilon_0}$ is the electric

constant. According to the estimation of the Auger spectra shift, the charge transfer from the Ba atoms to the W ones is $\approx 1,1e$ for the *W – Ba* system and $\approx 0.96e$ for the *Hf – Ba* system, i.e. the charge of the Ba ions can be approximately equal to $+e$. A method of estimating the charge transfer from adsorbed atoms to target ones was described in detail in [9].

5 EQUATIONS

Let us define the ion potential at a point locating in the distance x from the plane with taking into consideration the effect of the adsorbed layers. At that point the potential influenced by the neighboring ions and their mirror reflection has the form

$$V = (x, r_i) = kq \left[\frac{1}{\sqrt{r_i^2 + (x-R)^2}} - \frac{1}{\sqrt{r_i^2 + (x+R)^2}} \right]$$

Where r_i is the projection, on the plane, of the distance between the ion and neighboring ones and R is the ion radius.

Introduce the dimensionless quantities

$$y = \frac{x}{R} \text{ and } \rho_i = \frac{r_i}{R}$$

Then the equation (2) will have the form

$$V = (x, \rho_i) = \frac{kq}{R} \left[\frac{1}{\sqrt{\rho_i^2 + (y-1)^2}} - \frac{1}{\sqrt{\rho_i^2 + (y+1)^2}} \right]$$

The potential at the point y is equal to a sum of the potentials of neighboring ions, i.e.

$$V(y) = \sum_i V(y, \rho_i)$$

6 HELPFUL HINTS

6.1 Figures and Tables

Now let us define the number of the neighboring ions and calculate ρ_i for them to summarize the potentials according to the equation (5). An assumed structure of the *Hf-Ba* system is given in Fig. 2. The ion (or point) relative to which the potential calculations are performed is shown by white circle (in the center of Fig. 2).

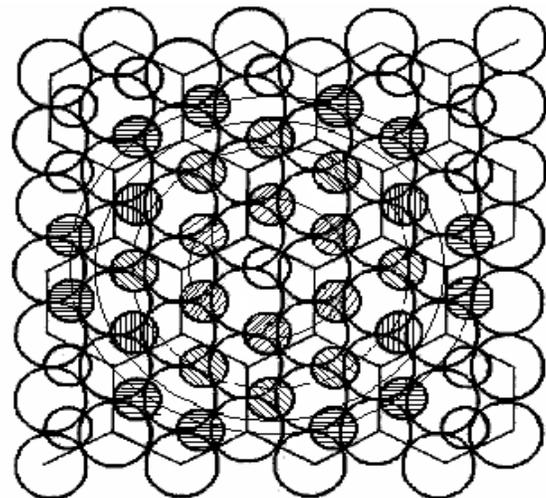


Fig. 2. The proposed structure of the *Hf-Ba* system:

⊘ – first order atoms; ⊙ – second order atoms
⊖ – third order atoms; ⊕ – fourth order atoms

6.5 Theorems and Proofs

The only dense packing for the two-dimensional lattice is a hexagonal lattice. For such an arrangement of the Ba ions on the Ha surface the surface density of atoms is maximal. Therefore, we consider the arrangement of the adsorbed ions as a uniform lattice of hexagons at the centers of which there is one ion. At the distance greater than that of the four neighbors a discrete character of the ion distribution has no significance. Therefore, with the equation (5) it is possible to calculate the sums of the potentials up to four neighbors and then integrate between some distance and infinity. So we defined the distances from the central ion to the neighbors of four order, i.e. the radius of the cell where the central ion and its 30 neighbors are: $r_1 = a$ and

$$\rho_1 = \frac{r_1}{a} = 1; r_2 = \sqrt{3}a \text{ and } \rho_2 = \sqrt{3}; r_3 = \sqrt{5}a \text{ and}$$

$\rho_3 = \sqrt{5}; r_4 = \sqrt{7}a \text{ and } \rho_4 = \sqrt{7}$. According to the above stated, the equation (5) can be rewritten as follows

$$V(y) = k \frac{q}{R} \left[\sum_{i=1}^4 g_i \left(\frac{1}{\sqrt{\rho_i^2 + (y-1)^2}} - \frac{1}{\sqrt{\rho_i^2 + (y+1)^2}} \right) + 2\pi n r^2 \int_{\rho_a}^{\infty} \rho d\rho \left(\frac{1}{\sqrt{\rho^2 + (y-1)^2}} - \frac{1}{\sqrt{\rho^2 + (y+1)^2}} \right) \right] \quad (6)$$

where g_i is the number of the neighbors. If the second term of this equation is integrated then the equation (6) has the form

$$V(y) = k \frac{q}{R} \left[\sum_{i=1}^4 g_i \left(\frac{1}{\sqrt{\rho_i^2 + (y-1)^2}} - \frac{1}{\sqrt{\rho_i^2 + (y+1)^2}} \right) + 2\pi n r^2 \left(\sqrt{(y+1)^2 + \rho^2} - \sqrt{(y-1)^2 + \rho^2} \right) \right] \quad (7)$$

For $y=0$ the surface potential is equal to zero; for infinity, i.e.

$y \rightarrow \infty$, the potential has a final value. For $y = \frac{x}{R} \rightarrow \infty$

the first term of the equation (7) is equal to zero and the second one tends to 2. Then

$$V_C = V(\infty) = 4k\pi n q R$$

i.e. we obtain the Helmholtz expression showing a decrease in the surface potential, hence a decrease in the electron work function. If $y = 1$, i.e. $x = R$ where R is the ion radius, then the equation (7) has the form

$$V_S = kq \left(\frac{\sqrt{3}n}{2} \right)^{\frac{3}{2}} 2R^2 S \left(\frac{1}{r^3} \right)$$

$$\text{Here } S \left(\frac{1}{r^3} \right) = \sum_{i=1}^4 q_i \left(\frac{a}{r_i} \right)^3 + \frac{4\pi}{\sqrt{3}} \frac{a}{r_a}$$

For our case the calculations show that $S \left(\frac{1}{r^3} \right) \approx 11,14$.

Then

$$V_S = 0,75V_C \theta^{\frac{1}{2}}$$

For our system $V_C \approx 3.25eV$ and for $\theta = 0.50$ a change in the potential barrier is $V_S \approx 2,00eV$. That means that in barium adsorption on hafnium the Ba-Hf system work function decreases up to $\varphi = \varphi_M - V_S = 3.85 - 2.00 \approx 1.85 eV$.

4 CITATIONS

However, that does not correspond to the experimental data according to which the work function of the Ba-Hf system is $\approx 2.30 eV$. The dependence of the work function of hafnium in a flow of atoms on a cover degree

$\varphi = \varphi_M - 0,75V_C \theta^{\frac{1}{2}}$ is given in Fig.1. From this figure it is seen that for the degree of covering the hafnium surface by the barium atoms up to $\theta \leq 0.5$ this dependence is in satisfactory agreement with the experimental data. However, for more dense covering ($\theta \geq 0.5$) the interaction of the dipole systems becomes more significant [4,8], which leads to dipole depolarization, hence, to a decrease in the surface potential and to a change in the minimum of the electron work function of the Ba-Hf system [1, 2, 4]. The potential energy of dipole interaction is defined by the

formula $W_o = k \frac{2p^2}{r^3}$. According to the experimental data

(Fig. 2), for the cover degree $\theta \geq 0.5$ there is a discrepancy between the experimental dependence of the work function and the theoretical one. Within the range of the cover degree of barium adatoms $\theta = 0.5 - 0.67$ a barium adatom film becomes more compact [4] and the distances between the barium atoms decrease from $r_0 = a$ to

$r = \frac{a}{\sqrt{3}}$, where $a = 3.18A^\circ$. If one assumes that within

that range of distances between the ions the significant dipole depolarization takes place then it is possible to estimate the energy of dipole interaction with the formula

$W_o = k \frac{2p^2}{r^3}$ and energy changes

$$\Delta W_o = k \left(\frac{2p^2}{r_2^3} - \frac{2p^2}{r_1^3} \right). \quad \text{The calculations of this}$$

assumption show that the changes in the potential energy of interaction, and hence in the surface potential or potential

energy, is $\approx 0.29 eV$ for $k = 9 \cdot 10^9 \frac{N \cdot m^2}{C^2}$, $r_1 = a$ and

$r_2 = \frac{a}{\sqrt{3}}$, $p = 4.45 \cdot 10^{-30} C \cdot m$. In this case the work

function should be

$$\varphi = \varphi_M - \varphi + \Delta\varphi_q \approx (3.85 - 2.00 + 0.29)eV = 2.14eV$$

However, this value of the work function differs from the experimental one ($\varphi_{\min} \approx 2.26 \pm 0.03eV$) by approximately

by 0.10 eV. If an indirect mechanism of adatom (ion) interaction is taken into account, i.e. a Friedel component of the electrostatic interaction [4, 10], which is significant for the cover degree $\theta \geq 0.5$ and the interaction energy for alkaline-earth adatoms is about 0.1 eV [4] then it is possible to non-contradictory explain the work function dependence on a cover degree. Thus, one can conclude that the work function of the metal-barium system is defined by electrostatic interactions of ions of the surface layers and adatoms and by interactions of dipoles and a Friedel component of the electrostatic interaction.

REFERENCE

- [1] Dobretcov L.N., Gomoyunova M.V. Emission Electronics, Moscow, Nauka 1966.
- [2] Kudintceva A.B. et all. Thermionic Cathodes. Moscow, Energiya, 1966, 366p.
- [3] Kiselev A.B. Metal-Oxide Cathodes of Electronic Devices. Moscow, MFTI, 2002, 239p.
- [4] Braun O.M., Medvedev V.K. Interactions between Particles Adorbed on Metal Surface. UFN 1989 **157**(4) 631-666.
- [5] Tursunmetov K.A., Khamidjonov I.Kh., Turgunbaev F.Yu. Thermoemission features of W-Hf-Ba system. Uzbek Physical Journal 2010 **1-2** 71-75.
- [6] Tursunmetov K.A., Gurkov Yu.V. Studies of emission features of pure and oxidized titanium, zirconium and hafnium in barium atom flow. Uzbek Physical Journal 1993 **5** 49-55.
- [7] Tursunmetov K.A., Imamov E.Z. On model structure of emission systems Me-O-Cs and Me-O-Ba. Inorganic materials. 1999 **9** 1-4.
- [8] Kennedy A. Caesium adsorption on refractory metals. In: Thermoemission transformation of energy. Moscow, Atomizdat, 1964 164-175.
- [9] Sarade P.R., Ramasesha S., Madhusudan W.H., Rao C.N. Relation between effective atomic charge and chemical shifts in x-ray absorption spectra of transition-metal compounds. Z. Phys. C.: Solid State Phys., 1979 **12**(12) 2439-2445.
- [10] Electron and ion spectroscopy of solids. Ed.: L. Firmans et all, Moscow, Mir, 1981 466p.

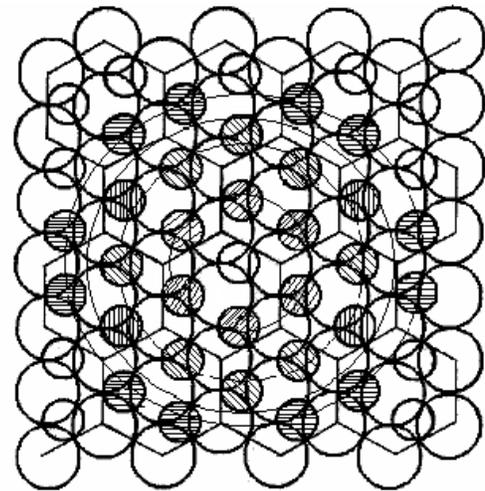


Fig. 2. The proposed structure of the Hf-Ba system:

- – first order atoms; ◐ – second order atoms
- ◑ – third order atoms; ◒ – fourth order atoms

Figure captions

Fig. 1. The dependence of the work function of the Hf-Ba system: 1 – experimental;

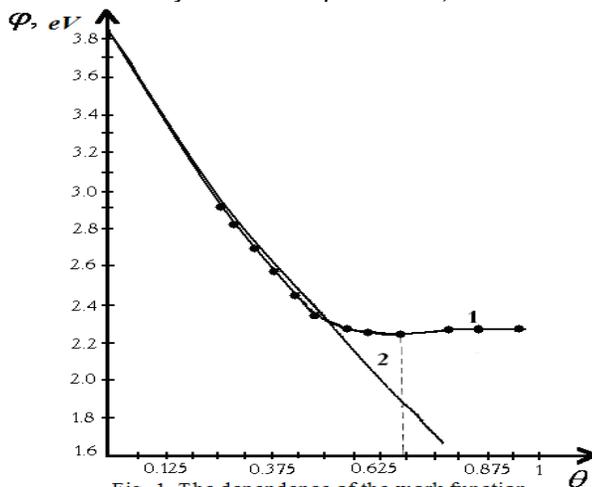


Fig. 1. The dependence of the work function of the Hf-Ba system: 1 – experimental; 2 – theoretical.