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ORIGINAL PAPER

Influence of Space Charge During the Oxidation of Metal Surfaces

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Abstract In this work we present a model for the surface oxide film growth considering the influence of space charge. The space charge field E_{sp} is assumed proportional to the charge of moving metal ions and electrons in the oxide layer. The surface charge field E_{ox} decreases as the Cabrera and Motts' oxide thickness X grows to its limit X_1 ($E_{ox} = V_M/X$). E_{ox} remains constant for further growth of the oxide film ($E_{ox} = V_M/X_1$). The obtained equation for the growing rate of the oxide film covers two stages. The first stage is characterized by a negligible space charge and is described by the typical inverse logarithmic law. During transition from thin to thick film, the oxidation growth rate is described by a direct logarithmic law which is confirmed by many experiments. At the end of this stage, the drift of metal ions is replaced by their diffusion that leads to parabolic law.

Keywords Surface oxidation · Cabrera and Mott theory · Oxide film growth · Space charge influence · Metal surfaces

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Introduction

Investigation of regularities and mechanisms of interaction of metals and alloys with an oxidizing atmosphere is one of the most important problems in the physics and chemistry of the surface, and it is directly related to the practical needs of producing oxide coatings with specified properties. There are several theories describing the growth of the oxidation layer on metal surfaces under various oxidation conditions.

The classical Cabrera and Mott theory [1] (CMT) is based on assumption that the electrons can flow freely from the metal to ionize adsorbed oxygen molecules at the oxide/gas interface, so that Fermi levels are equal in the metal and the adsorbed layer. Therefore, there is a uniform field in the film (zero space charge) created by a positive surface charge on the metal and a negative one from excess of oxygen O^{2-} ions on the oxide/gas interface [1, 2]. The CMT assumes that this field drives the ionic transport across the film and causes the oxidation to grow. The electrons continue crossing the oxide–metal interface to maintain zero electrical current. The transport of electrons by tunneling and thermionic emission has been considered in detail by Fromhold et al. [3–5].

In the CMT it is assumed that the adsorbed layer of oxygen ions is in equilibrium with the gas then this same layer provides charges to the surface and a voltage across the film, the Mott potential V_M [1, 2, 6, 7]. Thus, the intensity of this surface charge electric field in oxide film of thickness X is equal to $E_{ox} = V_M/X$ on analogy with a field of parallel-plate capacitor. It is seen that as the oxide film grows the field intensity decreases which should cause a decrease of the electric field influence on the transfer of metal ions into the oxide. From the CMT follows that the logarithm of thin oxide growth rate is inverse proportional to film thickness: $\mathrm{d}X/\mathrm{d}t \propto \exp(1/X)$, or $\log(\mathrm{d}X/\mathrm{d}t) \propto 1/X$. This applies for a film thickness $X < X_1$, where X_1 is the upper limit of thickness for the validity of the CMT about the control of ionic transfer by the electric field in the oxide. This inverse logarithmic law of the thin film growth rate is confirmed by experimental data for oxidation of most metals at low temperatures (less than about 100–200 °C) and in the initial oxidation stages at more high temperatures [7–12].

The transition from thin to thick oxide film occurs in the thickness range from X_1 to X_D [1, 2, 13, 14], where X_D is the critical thickness of the oxide film, above which applies the Wagner's theory, describing the formation of a thick film by parabolic law [15]. This thickness corresponds to the Debye screening length L_D, which value for semiconductors is $L_D \approx 1$ μm [16]. The oxide film growth in this thickness interval is accompanied by the transition from drift-dominated ionic transport for thin film to diffusion-dominated transport for thick film and is described by the direct logarithmic law $\log(\mathrm{d}X/\mathrm{d}t) \propto -X$ that is frequently observed in many experiments at elevated oxidation temperatures [13, 17–25].

We studied the influence of the space charge during the growth of the oxide film in the conditions of drift ionic transport under the electric field inside the oxide based on the following atomistic approach: the moving in oxide the metal ions and electrons screen the electric field in the oxide layer and thereby decreasing the resultant electric field. This influence is amplified as the oxide thickness increases

and results to self-limiting of the film growth. In our previous work we proposed such mechanism of film growth rate limitation [22, 23]. In this work we present the model of the space charge influence on the oxide film growth rate at the transition from thin to thick film.

Modeling

Let us find the condition of an ion transfer by electric field. Following the CMT [1] we consider an ion which can move through the oxide layer by the electric field into the film. The probability ω_1 of the ion to jump in the direction of the field from one equilibrium position to another in the oxide lattice is given by

$$\varpi_1 = v \exp\left(-\frac{U - q_{\rm i}Ea/2}{kT}\right), \tag{1}$$

where v is the oscillation frequency of ions about their equilibrium positions in the oxide; U is the diffusion activation energy; $q_{\rm i}Ea$ is the work done by the electric field of intensity E when an ion with a charge of $q_{\rm i}$ moves to the ionic elementary jump distance a in the oxide; k is Boltzmann constant; and T is the absolute temperature.

The probability ω_2 of an ion to jump in the opposite direction is

$$\varpi_2 = v \exp\left(-\frac{U + q_{\rm i}Ea/2}{kT}\right). \tag{2}$$

The resultant rate u of the ion displacement in the electric field is

$$u = a(\varpi_1 + \varpi_2) = va \exp\left(-\frac{U}{kT}\right) \cdot \left[\exp\left(\frac{q_{\rm i}Ea/2}{kT}\right) + \exp\left(\frac{-q_{\rm i}Ea/2}{kT}\right)\right]. \tag{3}$$

The condition of keeping control of ion transfer by an electric field, i.e., their movements by the field in the same direction, is $q_{\rm i}Ea \gg kT$. Then the expression (3) for an average movement rate of a single ion, controlled by the electric field can be written as:

$$u = va \exp\left(-\frac{U}{kT}\right) \exp\left(\frac{q_{\rm i}E{\rm a}/2}{kT}\right), \tag{4}$$

or

$$u = va \exp\left(-\frac{U - q_{\rm i}Ea/2}{kT}\right). \tag{5}$$

Following the Boltzmann distribution, the metal ions concentration, $n_{\rm i}^{+}$, in the oxide at a distance $x = a$ (about the oxide lattice parameter) from the metal surface is expressed as

$$n_i^+ = n \exp\left(-\frac{W_S}{kT}\right), \tag{6}$$

where n is the concentration of metal ions in the crystal lattice of the metal substrate and W_S is the efficient dissolution energy of a metal ion in the oxide.

The ion flux density J through the cross section of oxide based on Eqs. (5) and (6) is

$$J = n_i^+ u = n \cdot a \cdot v \cdot \exp\left(-\frac{W_S}{kT}\right) \exp\left(-\frac{U - q_i E a/2}{kT}\right). \tag{7}$$

The rate of oxide film formation dX/dt is equal to the product of the ion flux density J by the oxide volume Ω per metal ion

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \Omega \cdot n \cdot a \cdot v \cdot \exp\left(-\frac{W_S}{kT}\right) \exp\left(-\frac{U - q_i E a/2}{kT}\right). \tag{8}$$

Given that the metal ions in the crystal lattice site have three vibration degrees of freedom, we express their energy hv through temperature T, as $hv = 3kT$, where h is the Planck's constant. Then the ion oscillation frequency about the position of equilibrium at temperature T is written as

$$v = \frac{3kT}{h}. \tag{9}$$

The intensity of the uniform surface charge electric field in oxide E_{ox} on the CMT is

$$E_{ox} = \frac{V_M}{X}, \tag{10}$$

where V_M is Mott potential, X is the oxide thickness.

Then Eq. (8), taking into account Eqs. (9) and (10) after some transformations, takes the form

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{3\Omega nakT}{h} \exp\left(-\frac{W_S + U}{kT}\right) \exp\left(\frac{q_i a V_M}{2kTX}\right). \tag{11}$$

or after the logarithm

$$\log\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right) = \log\left(\frac{3\Omega nakT}{h}\right) + 0.434 \cdot \left(-\frac{W_S + U}{kT}\right) + 0.434 \cdot \left(\frac{q_i a V_M}{2kTX}\right). \tag{12}$$

Equations (11) and (12) are the consequence of the CMT for the growth rate of the oxide thin film. It is seen from Eq. (12) that the logarithm of an oxide film growth rate is inversely proportional to the film thickness X, i.e., $\log(\mathrm{d}X/\mathrm{d}t) \propto 1/X$. Inverse logarithmic law of the thin oxide film growth rate is confirmed by experimental data of the metals oxidation at low temperatures for film thicknesses $X < X_1$ as noted above.

Let us consider the influence of space charge on the oxide film growth rate. First of all, we will discuss the effect of space charge on the surface charge field in the

oxide created by the positively charged metal surface and negatively charged layer of chemisorbed oxygen on the oxide/gas interface surface. The intensity E_{ox} of this uniform electric field can be expressed as for a parallel-plate capacitor as follows

$$E_{ox} = \frac{\sigma_+}{2\varepsilon_0} + \frac{\sigma_-}{2\varepsilon_0}, \tag{13}$$

where σ_+ and σ_- are the surface density of the positive charges on the metal surface and the negative charges of ionize adsorbed oxygen molecules at the oxide/gas interface, respectively.

In general, the oxygen ions $O^{-Z_1 e}$ coming from a gas phase, the metal ions $Me^{+Z_2 e}$ and the electrons coming from a metal surface (z_1 and z_2 are the ionization degrees of the oxygen and metal atoms, respectively) are contained in oxide film. Here we do not consider the electrons and electron holes forming a neutral quasiparticle exciton and cannot transport a net electric charge in the oxide [26]. Charged particles reduce the electric field E_{ox} in the oxide, closing part of its power lines on self. Then, the resultant field E in the oxide of thickness X owing to the screening effect of charged particles is

$$E = \frac{\sigma_+}{2\varepsilon_0} - \frac{\int_0^X \left[e n_e^-(x) + q_i^- n_i^-(x) \right] \mathrm{d}X}{2\varepsilon_0} + \frac{\sigma_-}{2\varepsilon_0} - \frac{\int_0^X \left[q_i^+ n_i^+(x) \right] \mathrm{d}X}{2\varepsilon_0},$$

or

$$E = E_{ox} - \left(\frac{\int_0^X \left[e n_e^-(x) + q_i^- n_i^-(x) \right] \mathrm{d}X}{2\varepsilon_0} + \frac{\int_0^X \left[q_i^+ n_i^+(x) \right] \mathrm{d}X}{2\varepsilon_0} \right), \tag{14}$$

where $\int_0^X \left[e n_e^-(x) + q_i^- n_i^-(x) \right] \mathrm{d}x$ and $\int_0^X \left[q_i^+ n_i^+(x) \right] \mathrm{d}x$ are the space charges of electrons, oxygen ions and metal ions per unit of surface of the oxide film cross section; e, q_i^- and q_i^+ are the charges of electrons, oxygen ions and metal ions, respectively; $n_e^-(x)$, $n_i^-(x)$ and $n_i^+(x)$ are the distribution of electrons, oxygen ions and metal ions along the distance x from metal surface, respectively.

Using the quasi-neutrality condition of oxide plasma $z_2 \cdot n_i^+(x) = z_1 \cdot n_i^-(x) + n_e(x)$ and the law of mass action $z_1 \cdot z_2 \cdot n_i^+(x) \cdot n_i^-(x) \cdot n_e(x) = \mathrm{const}$ Eq. (14) is rewritten in the form

$$E = E_{ox} - \frac{q_i^+ \int_0^X n_i^+(x) \mathrm{d}x}{\varepsilon_0}. \tag{15}$$

We introduce the average concentration of metal ions in the oxide of thickness X, $\bar{n}_i$, and substitute the definite integral in Eq. (15) by the product $\bar{n}_i X$:

$$\int_0^X n_i^+(x) \, \mathrm{d}x = \bar{n}_i X. \tag{16}$$

By substitute Eq. (16) in Eq. (15) we get for resultant field in the oxide

$$E = E_{ox} - \frac{q_i \bar{n}_i X}{\varepsilon_0}, \tag{17}$$

where the space charge field intensity E_{sp} of metal ions and electrons in the oxide film of thickness X is

$$E_{sp} = \frac{q_i \bar{n}_i X}{\varepsilon_0}. \tag{18}$$

We note that the meaning of the right side of this equation is the charge of moving metal ions and electrons in oxide per unit area of the cross section surface of the film divided into ε_0 as for a parallel-plate capacitor.

Substituting Eq. (17) in Eq. (11) and noting Eq. (10), we express the film growth rate considering the space charge as follows

$$\frac{dX}{dt} = \frac{3\Omega nakT}{h} \exp\left(-\frac{W_S + U}{kT}\right) \exp\left[\frac{q_i a}{2kT}\left(\frac{V_M}{X} - \frac{q_i \bar{n}_i X}{\varepsilon_o}\right)\right], \tag{19}$$

or

$$\frac{dX}{dt} = \frac{3\Omega nakT}{h} \exp\left(-\frac{W_S + U}{kT}\right) \exp\left(\frac{q_i a V_M}{2kTX}\right) \exp\left(-\frac{q_i^2 \bar{n}_i a X}{2\varepsilon_0 kT}\right). \tag{20}$$

After logarithm Eq. (20) takes the form

$$\log\left(\frac{dX}{dt}\right) = \log\left(\frac{3\Omega nakT}{h}\right) + 0.434 \cdot \left(-\frac{W_S + U}{kT}\right) + 0.434 \cdot \left(\frac{q_i a V_M}{2kTX}\right) + 0.434 \cdot \left(-\frac{q_i^2 \bar{n}_i a X}{2\varepsilon_0 kT}\right). \tag{21}$$

Let us consider the average concentration of ions $\bar{n}_i$ in the oxide. We assume that the metal ions average concentration $\bar{n}_i$ in the oxide film of the thickness L is equal to

$$\bar{n}_i = \frac{n_i^+(x = a) + n_i^+(x = L)}{2}, \tag{22}$$

where $n_i^+(x = a)$ and $n_i^+(x = L)$ are the metal ions concentration at the distance a from metal surface and at the oxide/gas interface, respectively. The concentration of metal ions at the oxide/gas interface $n_i^+(x = L)$ is assumed to be zero. Then we get

$$\bar{n}_i = \frac{n_i^+(x = a)}{2}, \quad \text{or} \quad \bar{n}_i = \frac{n_i}{2}, \tag{23}$$

where $n_i^+(x = a) \equiv n_i$ is the metal ions concentration described by Eq. (6).

Results and Discussion

Equation (20) describes the oxide film growth rate taking into account the influence of space charge. The first exponential multiplier in Eq. (20) characterizes the retarding influence of the interstitial energy barriers for tearing off ions from the metal surface W_S and their movement into an oxide lattice U, respectively. The second exponential multiplier describes the accelerating influence of the electric field in the oxide E_{ox}. The third exponential multiplier defines the retarding impact of the space charge field E_{sp} on a film growth rate. It is distinguished from Eq. (11) for the thin oxide film growth rate by the presence of the third exponential multiplier, which describes of the space charge influence.

Let us introduce the screening coefficient δ which characterizes the degree of screening of the surface charge field in oxide E_{ox} by the space charge field E_{sp} in the following way

$$\delta = \frac{E_{sp}}{E_{ox}} \tag{24}$$

or, considering Eqs. (10) and (18)

$$\delta = \frac{q_i \cdot \bar{n}_i \cdot X^2}{\varepsilon_0 \cdot V_M}. \tag{25}$$

This coefficient is equal to $\delta = 0$ in the absence of the space charge ($E_{sp} = 0$) when the resultant field $E = E_{ox}$. It equals $\delta = 1$ in the case of complete screening of the surface charge field E_{ox} by space charge at $E_{ox} = E_{sp}$ when the resultant field $E = 0$. Thus, δ coefficient varies from 0 to 1 at the growth of the oxide film from a very thin to thick film.

Let us find the limits of applicability of the proposed model which are determined by the film thickness. For the application of our model we take a nickel surface during oxidation at elevated temperature (β-NiO), investigated by Atkinson [2], following the theories of Cabrera–Motts' and Wagner's. According to the CMT [2], the upper limit of thickness for the oxidation of Ni in air at $T = 500$ °C is $X_1 = 10^{-8}$ m. The value of the screening coefficient for thickness X_1 calculated using Eq. (25) is $\delta_1 = 9.3 \times 10^{-3}$. Since X_1 is the upper limit for validity of CMT, the manifestation of space charge at $T = 500$ °C begins from the screening coefficient $\delta > \delta_1$.

For calculations, according to Eq. (20) we use the following reference data for β-NiO: $a = 4.18 \times 10^{-10}$ m, $\Omega = 1.31 \times 10^{-29}$ m^3 and $n = 7.64 \times 10^{28}$ m^{-3} [27]. According to Atkinson [2], $U = 2.56$ eV for bulk diffusion. The dissolution activation energy W_S of the metal ions in the oxide is essentially the diffusion activation energy on the phase boundaries U'. The ratio U'/U is in the range 0.35–0.7 [28]. Based on this, we estimate the energy of the *Ni* ions dissolution W_S in the nickel oxide to be 0.44 of the bulk diffusion activation energy U, i.e., $W_S = 1.2$ eV.

The next important assumption in our model considers the intensity of the surface charge field, E_{ox}, caused by the contact potential difference between the surfaces of

metal and of the chemisorbed oxide layer at oxide/gas interface. According to CMT E_{ox} decreases with the film growth ($E_{ox} = V_M/X$). For a parallel-plate capacitor model, this corresponds to the expansion of its plates when they are connected to a current source with the voltage V_M. However, as it is known, the contact potential difference can existent only on the small distance between the contact pair, of an order of electrons mean free path (1–10 nm). In our model we assume that, when the film thickness arrives to the value X_1, the electric contact between metal surface and ionized oxygen layer disappears that corresponds to disconnecting the capacitor plates from the current source. With further film growth the intensity of the surface charge field E_{ox} remains unchanged ($E_{ox} = V_M/X_1$) due to the constant surface charge density which was formed to the moment when $X = X_1$, according to Eq. (13) at $|\sigma_+| = |\sigma_-| = \text{const}|_{x=X1}$ as for a capacitor.

The calculated values of the field intensities E_{ox} and E_{sp} by Eqs. (10), (18) and (23) as a function of the film thickness X for the growth of NiO on Ni at 500 °C are shown in Fig. 1 in logarithmic coordinates. It is seen that, according to our model, the surface charge field intensity in the oxide, E_{ox}, exponentially decreases as the film grows to the thickness X_1 and then it remains constant from X_1. The electric field intensity of the space charge E_{sp} monotonically increases as the film grows. Figure 1 shows two lines for E_{sp} and E_{ox} constructed by our model that intersects at the point $X_D = 10^{-6}$ m, which indicates the complete shielding of the surface charge field by the space charge field at this film thickness.

The thickness X_D can be found by equating Eq. (17) to zero at $X = X_D$

$$\frac{V_M}{X_D} - \frac{q_i \bar{n}_i X}{\varepsilon_0} = 0, \tag{26}$$

from here we get

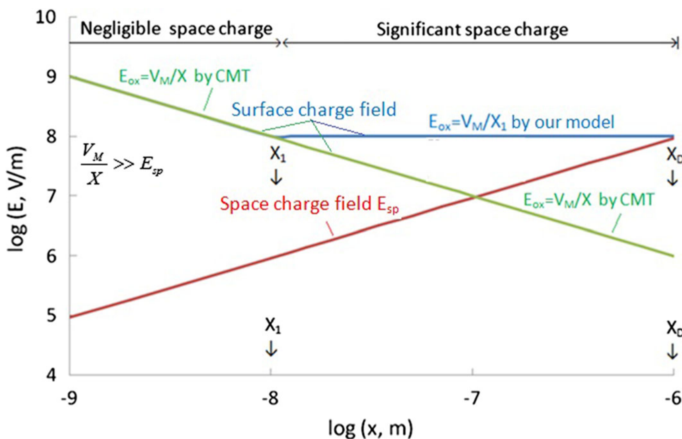

Fig. 1 Electric field intensities E_{ox} and E_{sp} calculated as a function of the film thickness of NiO growing on Ni at 500 °C in logarithmic coordinates

$$X_D = \frac{V_M \varepsilon_0}{X_1 q_i \bar{n}_i}. \tag{27}$$

The calculation value of X_D from Eq. (27) at $V_M = 1$ eV [2, 7, 13] is $X_D = 10^{-6}$ m, which agrees with the experimental and calculated data reported in the literature [1, 13, 22]. According to Atkinson's calculations [2], the value of this limiting thickness is equal to $X_D = 10^{-7}$ m, which corresponds to the intersection point of line E_{sp} with line E_{ox} constructed by the CMT (Fig. 1).

The growth rate of the NiO film in the thickness range from $X_1 = 1$ nm to $X_D = 1$ µm at 500 °C, calculated by Eq. (21) and considering the space charge with the film thickens, is shown in Fig. 2. The film growth rates calculated for two stages separately are shown in Figs. 3 and 4 in the semi logarithmic coordinates.

The plot log (dX/dt) against 1/X (Fig. 3) is a straight line which indicates that the growth rate of the thin film decreases inversely proportional to the film thickness. The plot log (dX/dt) against X (Fig. 4) indicates that the further film growth during the transition from thin to thick film is described by a direct logarithmic dependence on the film thickness. The calculated values of the film growth rate are 1.93×10^{-15} m/s at $X_1 = 10^{-8}$ m and 5.55×10^{-16} m/s at the end of transition region, $X_D = 10^{-6}$ m. These results show satisfactory coincidence with Atkinson's data [2] 2.51×10^{-15} m/s and 6.61×10^{-16} m/s, respectively.

Furthermore, our calculated data are consistent with the experiment results for the oxidation of an Armco polycrystalline iron in artificial air at 450 °C at ambient pressure [29]. It is shown that after 1 h of oxidation the scale kinetics is described by a parabolic law with the growth rate of 3.00×10^{-10} g/cm^2/s or 5.77×10^{-16} m/s and the scale thickness reaches the value of 2.64 µm.

Note that in a theoretical development for the parabolic growth kinetics of thick oxide films, transport of ions and electrons through the oxide layer can be assumed by diffusion in the presence of space charge and surface charge fields with local space charge neutrality. This becomes a good approximation for the interior oxide

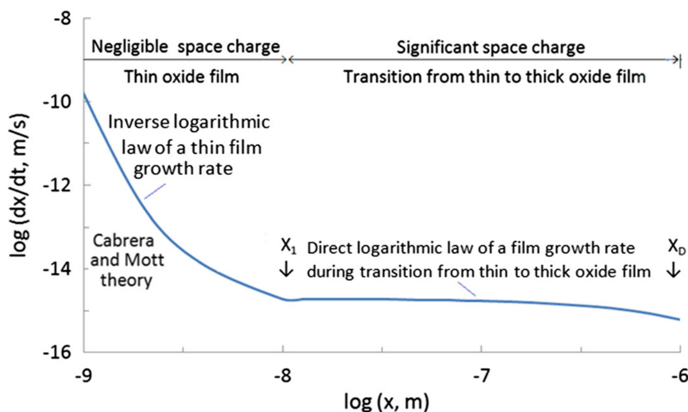

Fig. 2 Dependence of a NiO film growth rate on a Ni surface at 500 °C as film thickness calculated considering the space charge in logarithmic coordinates

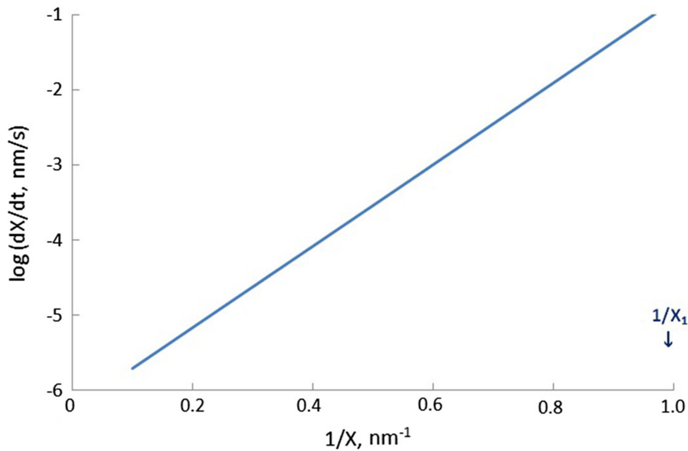

Fig. 3 Inverse logarithmic law of the growth rate for NiO thin oxide film calculated by Eq. (21) in the upper thickness X_1 limit

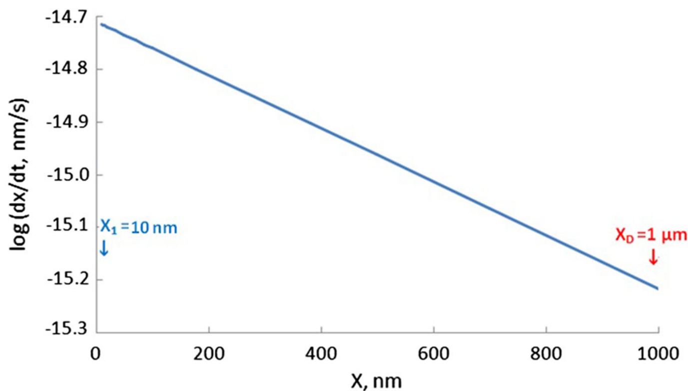

Fig. 4 Direct logarithmic law of the growth rate of the NiO oxide film calculated by Eq. (21) in the transition stage thickness limits from X_1 to X_D

away from the interfaces. The corresponding built-in voltage across the oxide is predicted to have a thickness-independent value [30].

Therefore, the obtained Eqs. (20–21), considering the effect of space charge, describe two stages of growth of an oxide film on the surface of metals. In the first stage, the electric field of the space charge E_{sp} is negligibly small compared to the surface charge field E_{ox} (Fig. 1). Kinetics of the thin oxide film growth on this stage, calculated from Eq. (20), is described by inverse logarithmic law (Fig. 3) following the CMT. The electric field of the space charge is manifested from film thickness bigger than X_1 and corresponding to the screening coefficient δ_1 (Fig. 1). The resultant electric field in the oxide ($E = E_{ox} - E_{sp}$) decreases with the film growth and becomes zero at $X = X_D$ (Fig. 1), during transition from thin to thick film. The drift of metal ions in the oxide field is replaced by their diffusion starting this

thickness when the oxide field is fully screened by space charge ($\delta = 1$) that leads to a parabolic law of the film growth according to the Wagner's theory [15].

Summary and Conclusions

The influence of the space charge during transition from thin to thick oxide film on metals surface is analyzed by a modeling of a single-phase oxide film growth in the conditions of drift-dominated ionic transport in an electric field inside oxide on the base of the CMT. The intensity of the space charge field E_{sp} is assumed equal to the charge of the moving metal ions and electrons in oxide per unit area of the cross section of the film divided into ε_0. The value of E_{sp} is proportional to the film thickness. The intensity of surface charge field E_{ox} (caused by the contact potential difference V_M) decreases as the film growth ($E_{ox} = V_M/X$) to the thickness X_1 corresponding to the upper limit of the CMT applicability. When the film thickness arrives to the value X_1, electric contact between metal surface and ionized oxygen layer disappears. With further film growth the intensity of the surface charge field E_{ox} remains unchanged ($E_{ox} = V_M/X_1$) due to the constant surface charge density what was formed to the moment when $X = X_1$.

To illustrate our model, we used NiO as model oxide which kinetic calculations were carried out by Atkinson for *Ni* oxidation at $T = 500$ °C. According to his data, the value of upper limit of thickness for validity of the basic assumptions of the CMT is $X_1 = 10^{-8}$ m. Following our model, the influence of space charge starts to manifest from thickness X_1 which corresponds to the value of screening coefficient $\delta_1 = 9.3 \times 10^{-3}$ ($\delta = E_{sp}/E_{ox}$).

The obtained equation of oxide film growth rate covers two oxidation stages. The first stage is characterized by a negligible space charge and is described by the inverse logarithmic law within the film thickness X_1 according to the CMT. The influence of space charge on the ion transport becomes significant starting from X_1. During transition from a thin to thick film in the range from X_1 to X_D the growth rate of the film is described by a direct logarithmic law which is confirmed by many experiments. At the end of this state, the surface charge field is fully screened by the space charge, and the drift of metal ions in the oxide is replaced by their diffusion that leads to a parabolic law of the film growth according to the Wagner's theory.

Thus, the present model, taking into account the screening influence of space charge on ion transport in the oxide, connects between themselves two classical theories, namely the Cabrera–Mott theory and the Wagner theory and contributes to the understanding about the mechanisms of oxide films growth at the various stages of metal oxidation.

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