

## Barrier to oxygen penetration on metal and oxide surfaces

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We investigate how the initial formation of an oxide layer on a metal surface can affect the further incorporation of oxygen into the metal. In particular, we show that the formation of NbO on a Nb surface dramatically increases the potential barrier for oxygen incorporation. On Cu the formation of an oxide layer reduces the barrier. On Cr and on Ni the barriers on the metal and on the oxide are similar. It is shown that the height of the barrier can be significantly reduced by the relaxation of the atoms in the surface oxide. The gain in energy in this process is shown to depend on the magnitude of the elastic constants of the oxide on the surface. We also show that oxides which grow by Cabrera-Mott kinetics have a barrier to oxygen penetration while others do not.

A metal or a metal-compound surface may or may not have a barrier to the incorporation of adsorbates such as O, H, Cl, F, etc. The presence or absence of such a barrier will have a profound effect on catalysis, etching, corrosion, the transition from chemisorption to oxidation, and the kinetics of oxidation itself. Clearly, the knowledge of the magnitude of this barrier and its dependences are of great importance. For example, one of the best known theories of metal oxidation at low temperatures is the theory of Cabrera and Mott.<sup>1</sup> While the validity of this theory depends on the existence of a barrier on the oxide surface to oxygen penetration, the magnitude of this barrier has not been determined by direct experiment, nor was it estimated theoretically before. Because of this, the Cabrera-Mott theory cannot be evaluated,<sup>2</sup> which in turn hinders our progress in understanding low-temperature oxidation. In this communication we restrict ourselves to the estimation of the barrier to oxygen penetration on metal and metal-oxide surfaces, but the same procedure can be used for other systems as well. We will show that through lattice relaxation the magnitude of this barrier depends on the elastic properties of the surface, and that the magnitude of the barrier indeed explains trends in oxidation kinetics.

Cabrera and Mott<sup>1</sup> assumed that an equilibration of the metal Fermi level and the adsorbed oxygen level by electron transfer from metal to oxygen results in the establishment of a negative contact potential  $V_M$  on the surface. Consequently, a large uniform positive electric field  $-V_m/L(t)$  is set up in the oxide, where  $L$  is oxide thickness and  $t$  is time. This electric field is considered to lower the energy barrier  $E_B$  for metal-ion incorporation at the metal-oxide interface, or for oxygen-ion incorporation at the oxide surface.<sup>3</sup> The rate of growth of the oxide film in the strong-field limit is given by

$$\frac{dL}{dt} = N \Omega v \exp(-E_B/k_B T) \exp(-q_i a V_M / L k_B T), \quad (1)$$

where  $\Omega$  is the volume of oxide per metal ion,  $N$  is the number of ions per unit area which are in a position to jump the rate-limiting energy barrier  $E_B$ ,  $v$  is the ionic attempt frequency,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $q_i$  is the charge per particle of the diffusing ionic species, and  $a$  is the distance from the ion's

position to the top of the barrier. Upon integration, Eq. (1) gives an approximately inverse logarithmic rate law.<sup>4</sup> Fehlner<sup>5</sup> introduced kinetic data into the solution<sup>4</sup> of the Cabrera-Mott rate equation, and found reasonable values for both  $N$  and  $V_M$ , and  $E_B$  only in case of Ta, Cr, and Ni. Data for other metals, for example Cu, could not be fitted by Cabrera-Mott kinetics. A plausible explanation would be that oxides which grow by Cabrera-Mott kinetics do have a barrier to oxygen penetration and others do not. We have to emphasize that the field develops *only if* there is a barrier to ion penetration; it is this barrier-induced field upon which the validity of the Cabrera-Mott theory depends. In what follows, we will estimate the barrier height to oxygen incorporation using the effective-medium theory.<sup>6,7</sup>

In effective-medium theory,<sup>6</sup> the embedding energy of an oxygen atom into an inhomogeneous electron host of electron density  $n_0(\mathbf{R})$  can be written

$$\Delta E(\mathbf{R}) = \Delta E_{\text{eff}}^{\text{hgm}}(\bar{n}_0(\mathbf{R})) + \text{higher-order correction terms} . \quad (2)$$

The term  $\Delta E_{\text{eff}}^{\text{hgm}}(n)$  is essentially equal to the embedding energy of an oxygen atom into a homogeneous electron gas of density  $n$ .  $\Delta E_{\text{eff}}^{\text{hgm}}(\bar{n}_0(\mathbf{R}))$  describes the interaction between the oxygen and the valence electrons of the substrate and only depends on the average substrate valence electron density  $\bar{n}_0(\mathbf{R})$  in the vicinity of the oxygen at the position  $\mathbf{R}$ . We will simply assume that the substrate electron density can be obtained by a linear superposition of atomic electron densities.<sup>7,8</sup> With this procedure the substrate electron density will directly depend on the positions  $\{\mathbf{R}_j\}$  of the substrate atoms.

As is found by Chakraborty *et al.*,<sup>7</sup> it is crucial to include the oxygen induced substrate relaxation when calculating the potential energy for an oxygen atom close to the surface; to do that we use Eq. (2) and calculate the force the oxygen atom exerts on the lattice atoms at  $\mathbf{R}_i$ ,

$$\mathbf{F}(\mathbf{R}_i) = -\nabla_{\mathbf{R}_i} \Delta E_{\text{eff}}^{\text{hgm}}(\bar{n}_0(\mathbf{R}, \{\dots, \mathbf{R}_i, \dots\})) . \quad (3)$$

The response of the lattice can be described by the lattice Green's function<sup>9</sup>  $G_{\alpha\beta}(\mathbf{R}, \mathbf{R}')$ , which describes the displacement  $u^\alpha(\mathbf{R})$  in direction  $\hat{\alpha}$  of a lattice atom at position  $\mathbf{R}$  when a unit force is applied in direction  $\hat{\beta}$  on a lat-

tice atom at position  $\mathbf{R}'$ . The total displacement of the substrate atoms is thus obtained as

$$u^{\alpha}(\mathbf{R}_i) = \sum_{j,\beta} G_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) F^{\beta}(\mathbf{R}_j + \mathbf{u}(\mathbf{R}_j)) . \quad (4)$$

The energy stored in the lattice upon such a deformation is given by<sup>10</sup>

$$\Delta E_{\text{lat}} = \frac{1}{2} \sum_i \mathbf{F}(\mathbf{R}_i + \mathbf{u}(\mathbf{R}_i)) \mathbf{u}(\mathbf{R}_i) . \quad (5)$$

The lattice Green's function for the substrate is obtained using the continuum approximation for the lattice and can be expressed in terms of the elastic constants  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ .<sup>10</sup> Using Eqs. (2)–(5), the lattice distortions and the potential energy for an oxygen outside the relaxed substrate can be calculated. To illustrate the effects of lattice relaxation we also perform calculations using only Eq. (2) and assume the lattice to be in its unrelaxed configuration. We will focus on the barrier for oxygen moving from a chemisorption position into the nearest interstitial bulk position. In the figures we will plot the potential energy along the path with lowest barrier. The energy zero is assumed to be at the chemisorption position. Although exact geometry and the absolute value of the chemisorption energy depend on the magnitude of the correction terms, the magnitude and shape of the barrier are reasonably given by Eq. (2). As examples we will consider the room-temperature oxidation of niobium (which has very similar oxidation behavior to that of tantalum<sup>11</sup>), chromium, and nickel, which all seem to obey Cabrera-Mott kinetics, and of copper, which does not. The elastic constants used in the calculations are given in Table I.

The oxidation of niobium does not provide an easy example since many niobium oxides exist. From low-energy electron diffraction,<sup>12</sup> valence-band, and core-level photoemission<sup>11,13</sup> it was established that at room temperature, and under ultrahigh vacuum conditions, NbO forms immediately on the surface. Since neither the valence-band

structure nor the work-function change on continuing exposure,<sup>13–15</sup> we conclude that NbO remains on the surface. We believe that NbO is the barrier to oxygen penetration<sup>13</sup> and is responsible for the Cabrera-Mott kinetics, since upon application of a cerium overlayer, which prevents the formation of NbO on the surface, the oxidation kinetics change from Cabrera-Mott to parabolic,<sup>14,16</sup> indicating the absence of a surface barrier. NbO is one of the hardest metallic compounds in nature;<sup>17</sup> therefore, it is a good model for lattice relaxation. In the bulk it contains 25% of both anion and cation vacancies.<sup>17</sup> Using the theoretical procedure discussed above, we have estimated the potential energy barrier for oxygen incorporation into Nb(110) and NbO(110), which forms on the surface of Nb(110).<sup>12</sup> The results of the calculation are shown in Figs. 1(a) and 1(b). The figures contain two curves each, "unrelaxed" and "relaxed." The difference between the unrelaxed and the relaxed potential energy is a measure of the ability of the lattice to deform. As can be seen, the barrier on Nb decreases from 1.2 to 0.7 eV upon lattice relaxation. The lattice relaxation thus facilitates the initial oxidation considerably. On the other hand, the barrier for NbO is very large (7.4 eV in the unrelaxed state). Because of the great hardness of NbO the relaxed barrier remains very high (3.9 eV). The large barrier is the reason why oxidation of Nb proceeds very slowly once NbO is formed on the surface. We also calculated the barrier after introducing arbitrarily an oxygen vacancy in the third layer from the surface. In this case the relaxed barrier becomes 1.2 eV.<sup>18</sup> The barrier on tantalum, estimated from experiments, is 1.6 eV.<sup>4,5</sup>

In a way the oxidation of copper is the inverse case of the oxidation of niobium. Here the oxidation rate becomes parabolic once a continuous layer of  $\text{Cu}_2\text{O}$  has formed,<sup>19</sup> which takes place already at 100°C.<sup>20</sup> For exposures where  $\text{Cu}_2\text{O}$  forms, surface potential changes are minimal.<sup>21</sup> From this we infer that  $\text{Cu}_2\text{O}$  is not a barrier to oxygen-ion penetration. In Figs. 1(c) and 1(d), we

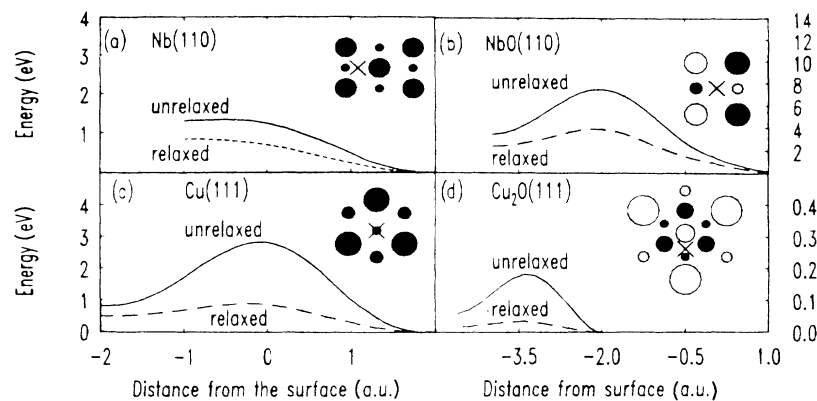


FIG. 1. In (a)–(d), we plot the potential-energy barrier for oxygen outside clean Nb, NbO, Cu, and  $\text{Cu}_2\text{O}$ . In the inset of the figures we illustrate the structure of the relevant surfaces. The closed circles represent metal atoms and the open circles represent oxygen atoms. The sizes of the closed and open circles represent their distance from the top surface layer. The largest symbols are used for the topmost layer. The point where oxygen is expected to pass the first metal layer is indicated with an  $\times$ . The solid line is the result when the lattice configuration is frozen, and the dashed line shows the result obtained when the substrate atoms are allowed to relax. The distance unit is bohrs (a.u.) with zero at the passage of the first surface layer. The energy unit is eV with zero at the calculated chemisorption position. Note the different energy scales in (a)–(d).

TABLE I. Elastic constants, the calculated values of the unrelaxed and the relaxed barrier, and the value of the barrier estimated from experiment. The elastic constants are given in units of  $10^{12}$  dyn/cm<sup>2</sup> and the barrier heights in eV.

|   | $c_{11}$ | $c_{12}$ | $c_{44}$ | $E_B^0$ | $E_B^{cl}$ | $E_B^{exp}$ |
|---|----------|----------|----------|---------|------------|-------------|
| Nb <sup>a</sup>                             | 2.45     | 1.32     | 0.28     | 1.2     | 0.7        |             |
| NbO <sup>b</sup>                            | 4.24     | 1.06     | 1.06     | 7.4     | 3.9        |             |
| Cu <sup>a</sup>                             | 1.69     | 1.22     | 0.75     | 2.8     | 0.9        |             |
| Cu <sub>2</sub> O <sup>c</sup>              | 1.21     | 1.05     | 0.12     | 0.2     | 0.04       |             |
| Cr <sup>a</sup>                             | 3.46     | 0.66     | 1.00     | 2.8     | 1.8        |             |
| Cr <sub>2</sub> O <sub>3</sub> <sup>d</sup> | 3.74     | 1.48     | 1.59     | 4.8     | 1.5        | 1.8         |
| Ni <sup>a</sup>                             | 2.47     | 1.53     | 1.22     | 4.1     | 1.7        |             |
| NiO <sup>a</sup>                            | 2.25     | 0.95     | 1.10     | 5.6     | 1.8        | 1.6         |

<sup>a</sup>Elastic, Piezoelectric, Pyroelectric, Piezooptic, Elektrooptic Constants, and Nonlinear Dielectric Susceptibilities of Crystals, Landolt-Börnstein, New Series, Group 3, Vol. 11, edited by K.-H. Hellwege and A. M. Hellwege (Springer, Berlin, 1979), pp. 9–10, 28.

<sup>b</sup>The elastic constants were extracted from the long-wavelength region of the phonon dispersion curves measured in P. Röddhammer, W. Reichardt, and J. Hufnagl, Progress Report, Kernforschungszentrum Karlsruhe, No. KfK 3051, 1980 (unpublished), pp. 5–8.

<sup>c</sup>Elastic, Piezoelectric, Pyroelectric, Piezooptic, Electrooptic Constants, and Nonlinear Dielectric Susceptibilities of Crystals, Landolt-Börnstein, New Series, Group 3, Vol. 18, edited by K.-H. Hellwege and A. M. Hellwege (Springer, Berlin, 1984), p. 14. <sup>d</sup>From H. L. Alberts and J. C. A. Boeyens, J. Magn. Magn. Mater. 2, 327 (1976).

show the results of the calculation of the potential energy of an oxygen atom outside Cu and Cu<sub>2</sub>O. We chose to study the (111) facet since this is the most close packed. Figure 1(c) shows how the barrier for clean Cu is reduced from 2.8 to 1.2 eV by surface atom relaxation. Figure 1(d) shows that the barrier for Cu<sub>2</sub>O is very small, only about 0.2 eV, which reduces to about 0.04 eV upon lattice relaxation. This is due to both a very open lattice, as reflected by the unrelaxed potential energy, and a very soft lattice, reflected by the relatively large relaxation energy which amounts to 80% of the initial barrier. These results explain why Cu oxidizes easily under a continuous layer of Cu<sub>2</sub>O.

Both chromium and nickel form single oxides upon oxidation, Cr<sub>2</sub>O<sub>3</sub> and NiO, respectively.<sup>2</sup> Table I shows the unrelaxed and relaxed barriers calculated on Cr, Cr<sub>2</sub>O<sub>3</sub>, Ni, and NiO. Note that the relaxed barriers are similar

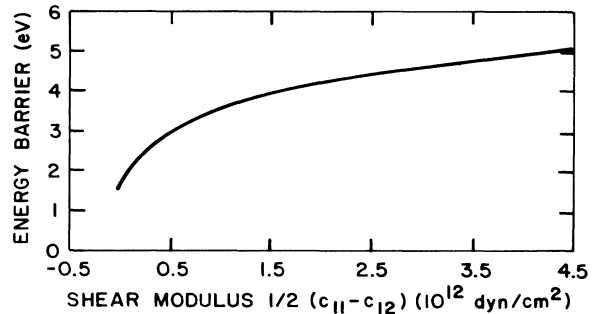


FIG. 2. Dependence of the barrier height for oxygen incorporation in NbO on the second shear modulus  $\frac{1}{2}(c_{11} - c_{12})$ .

for the metal and oxide for both cases. The table also shows the barriers estimated from kinetics experiments.<sup>5</sup> While we used a simple approximate scheme, the agreement is very good.

As is illustrated in Fig. 1, lattice relaxation plays an important role in decreasing the barrier for oxygen penetration into a surface. While the relationship between lattice relaxation and elastic constants is a complex one, we found the greatest dependence on the second shear modulus  $\frac{1}{2}(c_{11} - c_{12})$ . This dependence is shown in Fig. 2. It was found that the force constant of a nickel surface is 1.2 times the bulk force constant, while an oxygen overlayer reduces the first- and second-nickel-layer force constants to 70% of the bulk value.<sup>22</sup> Although we expect these effects to be smaller in oxides, Fig. 2 shows that even a reduction of the substrate force constants by 50% would leave a substantial barrier for NbO, and the general validity of our conclusions remains unchanged.

In conclusion, we have illustrated that whether or not an oxide film grows by Cabrera-Mott kinetics depends on the magnitude of the barrier for oxygen incorporation. The magnitude of this barrier depends, through lattice relaxation, on the shear modulus of the oxide formed. Since a large value of the shear modulus means great hardness, this result also has the practical consequence that protective oxide films should be *mechanically hard*. Details about the calculation of the barrier to oxygen penetration will be given in a follow-up report,<sup>18</sup> which will also include a discussion of the effect of structure as illustrated by the oxides of the first series of transition metals.

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