

Theoretical Analysis of the Growth Mode for Thin Metallic Films on Oxide Substrates

David Fuks*

*Materials Engineering Department, Ben Gurion University of the Negev, Beer-Sheva 84105, Israel
and Fachbereich Physik, Osnabrück Universität, Osnabrück, 49069, Germany*

Simon Dorfman

Department of Physics, Technion-Israel Institute of Technology, Haifa, 32000 Israel

Eugene A. Kotomin

*Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, Riga LV-1063, Latvia
and Max Planck Institut für Festkörperforschung, Heisenbergstrasse 1, Stuttgart 70569, Germany*

Yuri F. Zhukovskii[†] and A. Marshall Stoneham

*Center for Materials Science, Department of Physics and Astronomy, University College London, Gower Street,
London WC1E 6BT, United Kingdom*

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We show how the growth mode of a thin metallic film on an insulating substrate can be predicted theoretically by combining thermodynamic considerations with *ab initio* calculations for ordered metal/insulator interfaces at low coverage. Our approach is illustrated by calculations for Ag film deposited on an MgO substrate. *Ab initio* calculations predict high mobility of adsorbed Ag atoms on MgO, even at low temperatures, which greatly aids their aggregation.

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Metal-oxide interfaces play important roles in many technological applications, including catalysis, metal-matrix composites, and microelectronics [1–3]. The variety of need and behavior means such interfaces remain the focus of intensive theoretical studies, many at the *ab initio* level (e.g., [4–7]). Applications are more concerned with the resulting metal film, and this can grow on an oxide substrate either as 3D metal clusters, or by a monolayer-by-monolayer mode [2]. In particular, there has been much debate on the growth mode for Ag on MgO: some experimental studies [8–10] support a 3D island (cluster) mode, whereas others [11,12] find the metastable growth of monolayer films. It has been shown [8,9,11] that 2D silver films grown at low temperature are unstable, and evolve rapidly towards an island structure when the temperature is raised to just above room temperature. Clearly, kinetic factors are involved [13]. Although experimental systems will always contain such uncontrolled factors as defects, impurities, and surface reconstruction it is crucial to understand *theoretically* the conditions for the first stages of the growth of high quality metal films. Our paper combines for the first time a thermodynamic approach and *ab initio* electronic structure calculations to put some light on this problem.

In the *ab initio* calculations we use the Hartree-Fock (HF) formalism as implemented in the CRYSTAL-95 code (CC) [14], with the Perdew-Wang generalized gradient approximation and *a posteriori* electron correlation corrections to the total energy [15]. The 8-51G basis set (BS) for oxygen used there was optimized earlier for the calculations on MgO crystalline solids [16] and contains po-

larization and diffuse *3sp* function. In [7] we checked reliability of this BS and analyzed various electronic properties including multipole moments, densities of states, and electron charge distribution for different interface configurations. CRYSTAL-98 code provides a possibility to perform calculations according to both HF and Kohn-Sham (KS) computational schemes using localized BS. However, BS optimized for the HF approach is often not valid for the KS approach, including the Ag/MgO(100) interface. We did not reoptimize it specially for this purpose, but in [7] just HF-CC was used to describe Me/MeO interfaces adequately. We studied the effects of BS superposition error (BSSE) and found that for different coverages the BSSE changes from 0.005 to 0.02 eV, and they are taken into account with the corresponding results presented in the paper. Our calculations showed that Ag atoms are more stable above surface O, rather than Mg atoms, the binding energy above O being about 10% greater. The equilibrium Ag substrate distance changes by less than 3% (2.58 to 2.55 Å) upon increasing the Ag coverage from 1:4 to 1:1.

In this paper we have made further calculations for 2×2 extended surface unit cells, so as to model three kinds of Ag *superstructures* on MgO. These structures correspond to two possible 1:2 Ag coverages (Figs. 1a and 1b) and a 1:4 coverage (Fig. 1c). The binding energies per Ag are 0.23 eV (case 1a), 0.09 eV (case 1b; this case is less stable), and 0.23 eV (case 1c, 1:4 coverage). The lateral interactions of adjacent Ag atoms are quite small for both 1:2 and 1:4 coverages; this is why their stable configurations (cases 1a and 1c) have the same binding energy. For monolayer Ag coverage, the binding energy is somewhat

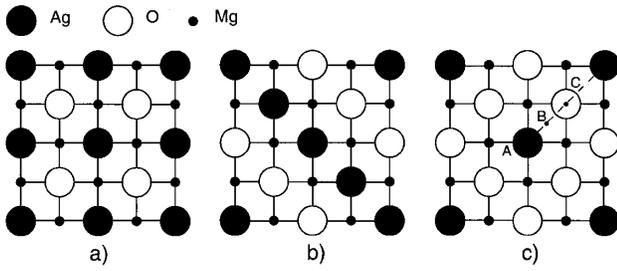


FIG. 1. Top view of the MgO(100) surface with different superstructures of Ag atoms placed atop it. (a), (b), and (c) correspond to Ag coverages of 1:2 (square distribution), 1:2 (striped distribution), and 1:4, respectively.

larger, 0.26 eV. We used a one-side adsorption model of the Ag/MgO(100) interface with different Ag coverages of a three-layer substrate slab and the model of two-side Ag adsorption over both sides of a five-layer MgO(100) slab. We analyzed different structural and electronic properties of both models and did not find essential differences between them; the influence of the artificial dipole layer on interface properties is rather negligible. We use our results as the basis for a thermodynamic scenario of the initiation of a growth of Ag film. We concentrate on an oxide surface partially covered by Ag atoms, and describe the specific disposition of Ag atoms in terms of a two-dimensional (2D) lattice whose sites are located above the O atoms of the underlying (100)MgO surface. In this 2D lattice, the Ag atoms and the vacant (“empty” or “E”) sites may be considered as a 2D *solid solution* (SS). For such SS, the thermodynamics may be formulated in terms of the *effective mixing potential* [17]:

$$\tilde{V}(\vec{r}, \vec{r}') = V_{AgAg}(\vec{r}, \vec{r}') + V_{EE}(\vec{r}, \vec{r}') - 2V_{Ag-E}(\vec{r}, \vec{r}'), \quad (1)$$

where “E” indicates an “empty-site” quasiparticle. $V_{AgAg}(\vec{r}, \vec{r}')$, $V_{EE}(\vec{r}, \vec{r}')$, and $V_{Ag-E}(\vec{r}, \vec{r}')$ are effective potentials between Ag atoms, between quasiparticles, and between Ag atoms and quasiparticles, respectively; \vec{r} and \vec{r}' are the positions of the sites in 2D lattice. The problem of thermodynamic stability of this 2D-SS transforms into the study of the ordering and/or decomposition tendencies in such a binary system. This can be done in terms of the phase diagram (PD). This approach has been applied to many different systems, including single crystal surfaces, magnetic systems, systems with long-range repulsive interactions, or purely attractive interactions (see, e.g., [18,19], and references therein). We use a concentration wave (CW) approach [20].

In this theory, the distribution of atoms A in a binary alloy is described by a single occupation probability function $n(\vec{r})$, namely, the probability to find the Ag atom at site \vec{r} of the crystal lattice. It may be shown that the 2D superstructures displayed in Fig. 1 are described by CWs with the following wave vectors: $\vec{k}_1 = \frac{2\pi}{a}(1, 0)$

(Fig. 1a); $\vec{k}_{2_1} = \frac{2\pi}{a}(\frac{1}{2}, \frac{1}{2})$ (Fig. 1b); and $\vec{k}_1 = \frac{2\pi}{a}(1, 0)$, $\vec{k}_{2_1} = \frac{2\pi}{a}(\frac{1}{2}, \frac{1}{2})$, and $\vec{k}_{2_2} = \frac{2\pi}{a}(\frac{1}{2}, \frac{1}{2})$ (Fig. 1c). Here a is the 2D lattice parameter. The internal energies of formation for these phases read

Case 1a:

$$U_1 = \frac{1}{2} \tilde{V}(0)c^2 + \frac{1}{8} \tilde{V}(\vec{k}_1)\eta^2, \quad (2)$$

Case 1b:

$$U_2 = \frac{1}{2} \tilde{V}(0)c^2 + \frac{1}{8} \tilde{V}(\vec{k}_2)\eta^2, \quad (3)$$

Case 1c:

$$U_3 = \frac{1}{2} \tilde{V}(0)c^2 + \frac{1}{32} \tilde{V}(\vec{k}_1)\eta_1^2 + \frac{1}{16} \tilde{V}(\vec{k}_2)\eta_2^2. \quad (4)$$

Here c is the atomic fraction of Ag, $\tilde{V}(\vec{k}_j)$ is the Fourier transform of the mixing potential, and $\tilde{V}(0)$ is the corresponding value for vector $\vec{k}_j = 0$. The long-range order parameters η_s are defined in such a way that they are all equal to unity in a completely ordered state in which $n(\vec{r})$ are either equal to unity or to zero for all lattice sites $\{\vec{r}_j\}$.

Equations (2)–(4) determine the internal energy of the phases with respect to the reference state that was chosen in a conventional way (see, e.g., [21]) as the weighted with atomic fractions sum of total energies per lattice site for the empty 2D lattice and the 2D lattice filled with Ag atoms. For the ordered state we obtain from our *ab initio* calculations the values: $U_1 = 0.020304$ a.u., $U_2 = 0.03709$ a.u., and $U_3 = 0.030439$ a.u. These energies are positive. All three superstructures have higher energy than the reference state. Thus only disordered SS may appear as the temperature increases. We performed similar calculations with different models of correlation corrections and found that the deviation of these results does not exceed 25%. Solving the system of Eqs. (2)–(4) for the parameters $\tilde{V}(0)$, $\tilde{V}(\vec{k}_1)$, and $\tilde{V}(\vec{k}_2)$, the key energy parameter describing SS is $\tilde{V}(0) = -0.1026$ a.u. We have assumed here that the energy parameters do not depend on concentration (this assumption is based mainly on results of x-ray diffuse scattering data for alloys [22] and for complex oxides [23]; in [24] we discuss the concentration dependence of these energy parameters and different ways to extract them from *ab initio* calculations). The influence of the model of correlation corrections on $\tilde{V}(0)$ is less than 10%, and the effects of BSSE do not exceed 1% of $\tilde{V}(0)$. The excess free energy for the disordered SS is

$$F(c) = -\frac{1}{2} \tilde{V}(0)c(1-c) + kT[c \ln c + (1-c) \ln(1-c)], \quad (5)$$

where the chemical potential term is included. PD calculated using our *ab initio* results and Eq. (5) is given in Fig. 2. Its sensitivity to $\tilde{V}(0)$ obtained with different correlation corrections is within 10%. PD has the miscibility

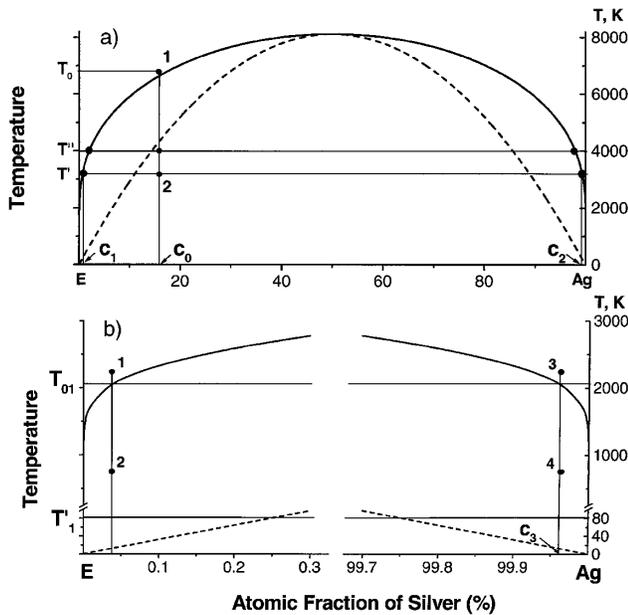


FIG. 2. (a) The calculated PD of 2D Ag-E SS. The bold line is a solvus and the dashed line is a spinodal. The existence of SS is assumed in the given temperature range. A line at T'' illustrates conditions leading to the increase of Ag contents in a phase with low Ag concentration and a decrease of Ag contents in an Ag-enriched phase. At T'' a fraction of the Ag-enriched phase decreases in comparison with T' . (b) A part of PD enlarged in the vicinity of the corners. The system is metastable with respect to nucleation and growth of metal clusters between the solvus and spinodal lines. See description of marks in the text.

gap, and the decomposition reaction takes place because of the obtained value $\tilde{V}(0) < 0$.

The solubility curve is determined by the minimum condition $dF(c)/dc = 0$, and the spinodal curve by the equation $d^2F(c)/dc^2 = 0$. Figure 2a shows that the solvus has a maximum at such high temperatures that real MgO would evaporate. The solubility regions at moderate temperatures are very narrow. To analyze the decomposition in the SS let us start from point 1 in Fig. 2a, representing the high-temperature state of SS with an equilibrium concentration of Ag atoms c_0 at temperature T_0 . This is a *single-phase* state in which Ag atoms *randomly* occupy the sites of the 2D lattice atop the (100)MgO surface. When cooling the system down to the temperature T' , we come to the state 2 (below the spinodal). This is a *two-phase* state of SS. The mechanism of the formation of this state is a *decomposition* of a single-phase state 1 into a mixture of two random SSs in the Ag-E system. The relative fraction of phase 2 (rich in Ag) in a two-phase mixture is defined by the *lever rule* and equals $(c_0 - c_1)/(c_2 - c_1)$, while the fraction of phase 1 (low in Ag) is much larger and equals $(c_2 - c_0)/(c_2 - c_1)$.

Let us consider now the case when, after the cooling from temperature T_{01} (points 1 or 3 in Fig. 2b) to temperature T'_1 , the system comes to the region of PD *between* the solvus and the spinodal (points 2 or 4). In all points c' inside this interval, the curve $F(c')$ is concave, so that

the homogeneous SS is stable with respect to infinitesimal heterogeneity, yet remains unstable with respect to the formation of two-phase mixture with phase composition c_α and c_β (which are substantially different from the SS composition). The decomposition reaction in this case involves the formation of finite composition heterogeneity and follows the *nucleation-and-growth* mechanism. Well-separated particles of the Ag-rich phase should be formed in this region of PD. They may be considered as isolated Ag clusters. This is typical for decomposition of binary disordered SS with limited solubility [25,26].

Figure 3 can be used to understand our predictions for the Ag film growth on MgO. As we cover the MgO surface by Ag atoms at a fixed rate at $T = T_1$ (Fig. 3) we start at very low coverages with the random Ag distribution over the surface (point 1). At metal concentrations above fractions of percent we move into region 2 of a metastable SS where very small metal clusters are formed. Further increase of a metal coverage brings us to point 3, representing the dominant range of Ag concentrations (from 2% up to 98%; we are assuming that formation of a second layer of Ag atoms can be ignored) where the system is in the equilibrium two-phase state. If the system passes through this region in a single-state mode, with randomly distributed Ag atoms at increasing concentrations, there is a small chance that the system could remain in this state for $c = 1$, which would result in a layer-by-layer growth mode. However, the most probable *scenario* is that the system will decompose into two phases with fast Ag cluster nucleation in the region of point 4. If so, further increase of Ag concentration would lead only to the growth of Ag (probably, 3D) clusters serving as nuclei for further aggregation.

The kinetics of the single-phase decomposition is controlled mainly by long-range single Ag atom diffusion. We have used the *ab initio* method to calculate the energy barrier at 1:4 coverage for the Ag atom diffusion along the (110) direction from a position above an O atom, over a gap position, to the next O atom, as shown by points A, B, and C in Fig. 1c. This barrier turns out to be very small,

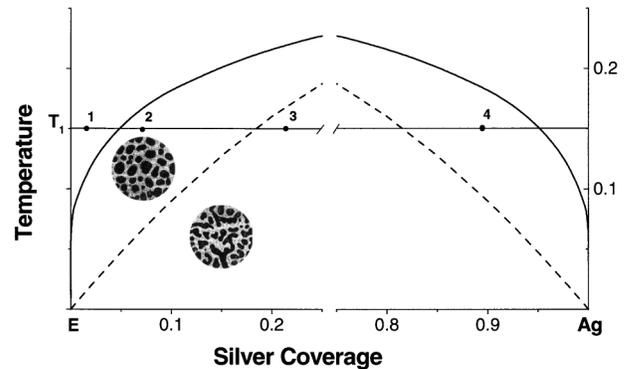


FIG. 3. Modes of the Ag film growth on MgO at moderate temperatures on PD. Black areas are Ag, grey MgO. Temperature in units of $k/\tilde{V}(0)$.

about 0.05 eV. Thus, surface Ag atoms should be highly mobile even at low temperatures. For alternative diffusion pathway between nearest O and Mg atoms the diffusion barrier is almost 3 times higher (0.13 eV). Using our calculated activation energy, the characteristic time for Ag atom diffusion approach on a lattice covered by 1% of Ag at 100 K may be estimated as short as 10^{-6} s: efficient Ag aggregation should be a very fast process.

At the low Ag side of PD, we can describe available experimental data [11] in terms of decomposition. The analogous decomposition pattern was observed in the Ag-rich side of the diagram [8]. Electron micrographs in Fig. 6a [11] and Fig. 1 in [8] indeed visualize a spinodal decomposition predicted by our theory. This means that, in these experiments, substrates were kept at temperatures below the spinodal. These microstructures are typical for spinodal decomposition morphology (see, e.g., Figs. 2, 3, and 6 in Ref. [25] and Fig. 4-38a in Ref. [26]). Lastly, Fig. 6b of Ref. [11] shows a metal *cluster* formation region. In this case the system is in the region of PD located *between* the solvus and the spinodal. Our approach is also supported by the data of Ref. [9], which confirm that thin 2D Ag films grown at room temperature evolve rapidly toward an island structure when the temperature is increased to just above room temperature. In terms of PD in Fig. 3, this means that the system transfers from the region below the spinodal to the region between the spinodal and the solvus.

Summing up, we suggest a thermodynamic formalism based on *ab initio* supercell calculations of metal/oxide interfaces for metal superstructures with low surface coverages. A novel approach applied to these systems permits the prediction of the conditions for metal atoms to aggregate into clusters, and to estimate the metal density in such clusters. The relevant analysis for the Ag/MgO shows that monolayer metal film could grow via the spinodal decomposition mode. However, the high mobility of Ag atoms on the MgO surface makes 3D metal island formation almost unavoidable.

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*Corresponding author.

Email address: fuks@bgumail.bgu.ac.il

†Visitor.

Permanent address: Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, Riga LV-1063, Latvia.

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