PHYSICAL REVIEW B VOLUME 54, NUMBER 14 1 OCTOBER 1996-II

Demonstration of Avrami's kinetics: Connection with rate equations for clustering on surfaces

M. Fanfoni
Dipartimento di Fisica, Università di Roma Tor Vergata and Istituto di Fisica della Materia, Via della Ricerca Scientifica, 00133 Roma, Italy

M. Tomellini
Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica 00133 Roma, Italy

(Received 18 April 1996)

Through an appropriate analogy with the scattering problem a demonstration of Avrami's kinetic theory has been worked out. This approach has been successfully used for obtaining the general solution of the kinetics of the instantaneous growth of multiple phases. It is shown that even in the case of clustering on surfaces, when the nucleation process does not occur at preexisting active sites and Avrami's formula could not hold, the proposed method allows the kinetics of the transformed surface to be computed. The connection between Avrami's theory and the atomistic model for nucleation at solid surfaces has been also discussed in light of the rate equation formalism. [S0163-1829(96)04538-9]

INTRODUCTION

A glance through the literature reveals that the majority of phase transitions kinetics are described on the grounds of the Johnson-Mehl-Avrami-Kolmogoroff (JMAK) phenomenological model.[1–4] A numerical simulation on its validity has been recently performed.[5] According to this model the fraction of transformed phase, as a function of time, is expressed by the following formula:

$$V(t)=1-e^{-V_e(t)}. \tag{1}$$

$V_e(t)$ is called extended transformed phase; below its meaning will be clearer. It is worth remembering that in the JMAK theory grains start growing at preexisting germs and for Eq. (1) to be valid, the germs must be distributed at random throughout the entire space in which the transition takes place. The nucleation rate is assigned phenomenologically and besides being the theory independent of the dimensionality of the space in which the transformation occurs, in Eq. (1) $V(t)$ indicates a volume, a surface, or a line according to the particular system under examination. Indeed, many investigators dealing with nucleation and growth processes have found JMAK's model quite in keeping with their needs.[6–22]

The demonstration of Eq. (1) was given by Avrami.[2,3] He employed arguments somewhat involuted and of no immediate understanding. In this paper we present a demonstration of Eq. (1) and of other results which Avrami reported in the Appendix of his second work on the argument.[3] Moreover, we shall also show how, by means of this approach, it is possible to generalize the Markworth's work,[23] in which the solution of the kinetics regarding the instantaneous growth of multiple phases was given. Finally, the connection to the widely used rate equation approach[24–26] for two-dimensional (2D) clustering on surfaces is reported and a general expression for the kinetics of the covered surface, when preexisting nucleation sites do not exist, is presented and discussed. In order to render the demonstration particularly immediate we shall refer to a 2D phase transformation.

RESULTS AND DISCUSSION

A. Avrami's kinetics as solution of a scattering problem

Let us begin by considering an infinite surface in which N_0 points per unit area are marked at random. The frequency with which k of those points will be found in a small element of surface s is given by the Poisson distribution:

$$P_k(m)=\frac{m^k}{k!}\,e^{-m}, \tag{2}$$

where $m=N_0 s$ denotes the average number of marked points contained in s.

We shall consider a specific shape for s, namely a circle (or disk) of radius r. According to the distribution (2), the probability that no marked points will be found in a circle of radius r is:[27,28]

$$P_0(r)=e^{-\pi N_0 r^2}. \tag{3}$$

For it to occur it is necessary that the center, c, of the circle lays at a distance greater than r from the nearest marked point. On the other hand, tessellating the surface with disks of radius r centered at each of the N_0 marked points, none of them will cross over the center c. As a consequence we can conclude that a point c of the surface will not belong to the tessellated fraction of surface with probability given by relation (3).

Now we want to face a more general issue: To find the probability that a point of the surface will not belong to the tessellated surface when the disks centered at the marked points have different radii, or more precisely when a distribution of radii exists. To answer this question it is profitable to tackle a quite equivalent scattering problem. Consider a collection of planes each containing ν_i random-distributed circles of radius r_i per unit surface; overlaps among them are allowed. The planes can be stacked, for instance, in order of

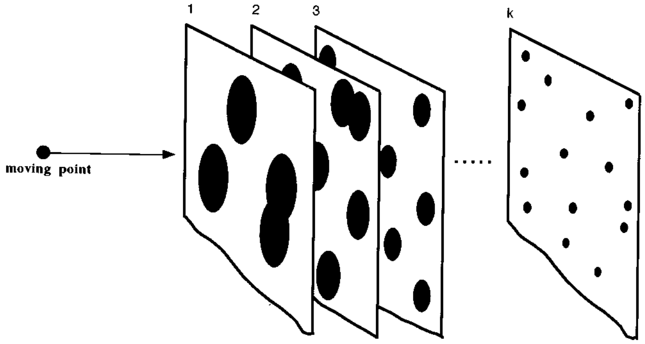

FIG. 1. Pictorial view of the scattering problem whose solution leads to Avrami's kinetics. Clusters that lay on the same plane were born at the same time.

decreasing radius (Fig. 1). What is the probability that a mobile particle (point) will pass through the set of planes without crossing any disk? The answer is immediate and it is

$$Q_0=\prod_i P_{0i}, \tag{4}$$

where P_{0i}, by virtue of (3), reads

$$P_{0i}=e^{-\pi\nu_i r_i^2}. \tag{5}$$

Consequently, the solution of our original issue is

$$Q_0=e^{-\pi\Sigma_i\nu_i r_i^2}. \tag{6}$$

Obviously Q_0 is also equal to the fraction of uncovered surface, 1-S; therefore

$$S=1-e^{-\pi\Sigma_i\nu_i r_i^2}. \tag{7}$$

The last result is the celebrated Avrami's formula, the term at the exponent being nothing but the aforementioned extended transformed phase (disks). Its meaning is clear: it is the total surface of the disks independently of the possible overlaps. There are two points worth noting. One concerns the continuous limit. In fact during a real phase transformation the radius of the disks is a function of time and the extended transformed phase reads

$$S_e(t)=\pi\int_0^t r^2(t,z)\,\frac{dN}{dz}\,dz, \tag{8}$$

where dN/dz is the nucleation rate. The comparison with the exponent in (7) shows that the number of disks in the ith plane, ν_i, is equal to the germs that start growing between time z_i and z_i+dz.

The second remark regards what Avrami called ''phantom germs or nuclei.'' As we have previously described each plane contains a certain number of circles randomly distributed throughout the entire plane, so that there is the possibility that a disk in the ith plane could completely cover another one in the jth plane $(i<j)$. It goes without saying that the covered disks (phantoms) do not contribute to the transformed phase; nevertheless, in order that (7) be correct, its contribution must be taken into account in the calculation of the extended transformed phase. All this because a complete randomness in the entire plane is required in such a way that relation (3) could be applied to each plane. As a consequence, the nucleation rate in the continuous case must include also the phantom germs, whereas the actual nucleation rate turns out to be,[3]

$$dN_a=(1-S)dN. \tag{9}$$

By similar considerations that lead to expression (3), it is possible to show that a point c of a surface tessellated with random-distributed circles of the same size will be overlapped only one time with probability

$$P_1(r)=\pi N_0 r^2 e^{-\pi N_0 r^2} \tag{10}$$

and k times with probability

$$P_k(r)=\frac{(\pi N_0 r^2)^k}{k!}\,e^{-\pi N_0 r^2}. \tag{11}$$

In the case of distribution of radii, by referring to Fig. 1, the probability that the moving point will cross only one disk is

$$Q_1=\sum_q\prod_j P_{\delta(j,q)} \tag{12}$$

and k disks

$$Q_k=\sum_{q_1}\cdots\sum_{q_k}\prod_j P_{[\Sigma_{\nu=1}^k\delta(j,q_\nu)]}, \tag{13}$$

where $\delta(j,q)$ is the Kronecker symbol and multiple sums must be executed with the condition $q_1\leqslant q_2\leqslant\cdots\leqslant q_k$. The expressions (12) and (13) give, respectively,

$$Q_1=S_e e^{-S_e}, \tag{14}$$

$$Q_k=\frac{S_e^k}{k!}\,e^{-S_e}. \tag{15}$$

In Appendix A the demonstration for $k=2$ is reported for the sake of clearness. Again, the proposed method directly leads to the expression of the overlapped surfaces in terms of the extended one (15); this last result was previously reached in[3] through a mathematical treatment based on generalized ascending-descending continued fraction.

The exposed way to deal with the phase-transition kinetics allows one to generalize the result obtained by Markworth.[23] He faced and solved the problem of describing the phase-transition kinetics involving the *instantaneous* growth of multiple phases. When the nucleation is not instantaneous, i.e., $dN/dt\neq N_0\delta(t)$, the problem can be solved by generalizing the expression (4),

$$Q_0=\prod_\mu\prod_k P_{0k}^{(\mu)} \tag{16}$$

where the superscript refers to the μth phase; Fig. 2 may help in understanding (16). Since $P_{0k}^{(\mu)}=e^{-m_k^{(\mu)}}$ and $m_k^{(\mu)}=\nu_k^{(\mu)}\pi r_k^{(\mu)2}$, (16) becomes

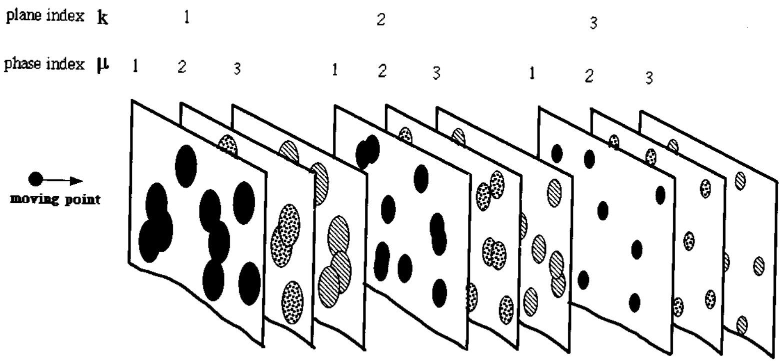

FIG. 2. Pictorial view of the scattering process in the case of growth of multiple phases. In this case two indexes are required, namely, one for the birth time of the nuclei (k) and another for the phase (μ).

$$Q_0=\prod_{\mu}\prod_{k} \exp(-\nu_k^{(\mu)}\pi r_k^{(\mu)2})$$

$$=\prod_{k} \exp(-\pi\Sigma_{\mu}\nu_k^{(\mu)}r_k^{(\mu)2}). \tag{17}$$

The last factor in expression (17) is the solution of Markworth's problem. By defining $S_{ek}=\pi\Sigma_{\mu}\nu_k^{(\mu)}r_k^{(\mu)2}$, one gets

$$Q_0=\prod_{k} e^{-S_{ek}}=e^{-\Sigma_k S_{ek}}=e^{-S_e} \tag{18}$$

but $Q_0=1-S$, then

$$S=1-e^{-S_e}, \tag{19}$$

again Avrami's formula, where the extended transformed phase is now given by

$$S_e=\pi\sum_{k}\sum_{\mu}\nu_k^{(\mu)}r_k^{(\mu)2}. \tag{20}$$

B. Connection with atomistic models for nucleation on solid surfaces

In the 2D case differentiating Eq. (1) one obtains

$$dS=[1-S(t)]dS_e \tag{21}$$

or

$$\int_0^t \partial_t s(t,z)dN_a(z)=[1-S(t)]\int_0^t \partial_t s_e(t,z)dN(z), \tag{22}$$

where the $\partial_t s(\partial_t s_e)$ is the partial derivative of the actual (extended) surface of the single nucleus.

After substitution of Eq. (9) in Eq. (22) the following expression is obtained:

$$\frac{\partial_t s(t,z)}{\partial_t s_e(t,z)}=\frac{1-S(t)}{1-S(z)}. \tag{23}$$

Equation (23) gives a formula for the ratio between the increments of the transformed and extended surfaces of a single actual grain in terms of the total surface fraction. We observe that any actual grain is not randomly located in the entire surface; its position is, in fact, subject to the restriction that it lay somewhere outside the transformed surface $S(z)$ at the time of its origin, z. This is the physical meaning of the $[1-S(z)]$ term in the denominator of Eq. (23). We may therefore assume Eq. (23) to hold whether the nucleation occurs at preexisting active sites or not, provided the distribution of clusters, in the uncovered portion of the surface, is random. After summing both members of expression (23) on the population of actual nuclei, we get

$$\ln[1-S(t)]=-\int_0^t s_e(t,z)\,\frac{\dot{N}_a(z)}{1-S(z)}\,dz, \tag{24}$$

which is, in general, an integral equation for the $S(t)$ unknown. In Appendix B, Eq. (24) is obtained by following the same method used in the first paragraph.

Rate equations[24–26] are widely used for describing the nucleation stage of thin film growth on surfaces. In the case of homogeneous surface, however, no special nucleation sites exist and Eq. (24) can be appropriately exploited in order to include the description of the island impingements in the rate equation scheme. Clearly, in this case a system of integral differential equations has to be solved. In what follows we exemplify the aforementioned concepts by deriving rate integral-differential equations describing the growth of two-dimensional islands. We assumed the following. (i) Dimers are stable clusters. (ii) The capture coefficients depend on the cluster perimeter.[25] In the framework of the uniform depletion approximation such a condition implies that the diffusion length of monomers is much shorter than the linear island size.[26] (iii) Clusters are supplied only by admonomers.

1. Rate equations

Let N_1 be the density of admonomers per unit of total surface. The equations hold:

$$\frac{dN_1}{dt}=J_0N_0-\frac{N_1}{\tau_a}-2\sigma_1D\,\frac{N_1^2}{1-S}-\rho_c\,\frac{dS}{dt}, \tag{25}$$

$$\frac{dN_a}{dt}=\frac{\sigma_1DN_1^2}{1-S}, \tag{26}$$

where J_0 is the number of gas monomers arriving at the adsorption site per unit time, N_0 is the surface density of sites available for adsorption, and τ_a is the adatom stay time before evaporation. The third term expresses the depletion of monomers due to nucleation with D the surface diffusion coefficient and σ_1 the capture factor for admonomer. The last contribution is related to the incorporation of adatoms into the stable islands due to surface diffusion, ρ_c being the density of atoms in the film. S is the surface fraction that is covered by stable clusters. The reason why the $(1-S)$ term has been introduced in the nucleation rate is easily understood on the basis of the dimensional argument discussed in Ref. 29: the rate constant for nucleation is $\sigma_1 D[N_1/(1-S)]$ since $[(1-S)/N_1]\rho$ is the number of lattice sites available for each adatom. ρ is the surface density of lattice sites at the bare surface.

2. The cluster growth law

The number of adatoms (M) which are supplied, per unit time, to a cluster which started growing at time z is given by

$$\frac{dM}{dt}=\frac{DN_1}{1-S}\frac{p(t,z)}{a}, \tag{27}$$

where $p(t,z)$ is the free perimeter of the island and $a=\sqrt{D\tau}$ being τ the constant lifetime of the admonomers [point (ii)]. Since $dM/dt=\rho_c p(t,z)(dr/dt)$ the following equation is obtained for $r(t,z)$:

$$r(t,z)=\frac{D}{a\rho_c}\int_z^t \frac{N_1(\xi)}{1-S(\xi)}\,d\xi. \tag{28}$$

Equations (24), (25), (26), and (28) are a set of equations for the r, N_1, S, and N_a quantities, with $s_e=\pi r^2$ and, because of the number conservation of surface sites, $N_0=\rho(1-S)-N_1$. Initial conditions are $S(0)=N_1(0)=N_a(0)=0$.

It is worth noting that the particular case discussed by Eq. (28) deals with island growth rate that is only a function of the running time: $\dot{r}=\dot{r}(t)$. However, growth rates expressed in the more general form $\dot{r}=\dot{r}(t,r)$ can also be employed in the kinetic model, with some restrictions for the case $\partial\dot{r}(t,r)/\partial r<0$.[5]

3. Quasiequilibrium approximation

It goes without saying that if the nucleation rate can be expressed in the form

$$\dot{N}_a=f(z)[1-S(z)], \tag{29}$$

$f(z)$ being an appropriate function of z, Eq. (24) will reduce to Avrami's solution [Eqs. (1) and (8)]. It is interesting to show that also for the atomistic model of nucleation, where special surface sites for nucleation are not present, particular conditions may be realized for which Eq. (29) is satisfied. This is the case of quasiequilibrium approximation[26] in the high temperature regime where desorption of adatoms represents the main process for admonomer depletion on the surface. The steady state of the adatom surface density reads [Eq. (25)]

$$N_1=J_0N_0\tau_a. \tag{30}$$

Moreover, the quasiequilibrium approximation allows one to use the law of mass action to express the surface concentration of critical islands in terms of the adatoms density:[24,30,31]

$$\left(\frac{N_n}{N_0}\right)=\left(\frac{N_1}{N_0}\right)^n e^{-\Delta G_n^0/kT}, \tag{31}$$

where n is the size of the critical cluster and ΔG_n^0 is the standard free energy change for critical cluster formation. For a low value of the surface coverages of subcritical islands the number conservation of the surface sites reads

$$N_0+N_1\approx\rho(1-S). \tag{32}$$

The surface density of adatoms is computed using Eqs. (30) and (32):

$$N_1=\frac{\rho(1-S)J_0\tau_a}{(J_0\tau_a+1)} \tag{33}$$

and the nucleation rate is

$$\dot{N}_a=\frac{\sigma_n DN_1N_n}{(1-S)}, \tag{34}$$

where D is the surface diffusion coefficient of adatoms and σ_n is the capture factor of adatoms at the critical cluster edge.[25] Combining Eqs. (30)–(34) the nucleation rate is eventually computed as follows:

$$\dot{N}_a=\frac{D\sigma_n}{(1+J_0\tau_a)^2}(J_0\tau_a)^{n+1}e^{-\Delta G_n^0/kT}\rho^2(1-S)=\gamma(1-S), \tag{35}$$

where, according to Eq. (34), the contribution to cluster growth due to the direct impingement of gas monomers at critical clusters has been neglected.

Finally, it happens that in several physical cases the measured nucleation is so fast compared to the time required to attain $S=1$ that its rate does not deviate substantially from a Dirac δ function.[32,33] The nucleation rate reads $\dot{N}(t)=N_s\delta(t)$ where N_s is the density of cluster when nucleation is over. A typical expression for the saturation value in the cases of stable dimers and complete condensation of admonomers $(\tau_a\rightarrow\infty)$ is[34]

$$N_s\approx\rho\left(\frac{J_0}{\nu_d}\right)^{1/2}e^{E_d/2kT}, \tag{36}$$

where E_d and ν_d are the activation energy and the frequency for the surface diffusion, respectively. Accordingly, the $S(t)$ kinetics reduces to the well known stretched exponential form $S(t)=1-e^{-N_s\pi r^2(t)}$, widely used in the literature.[21]

CONCLUSIONS

By solving an appropriate "scattering" problem a demonstration of Avrami's kinetics has been derived. The proposed method exhibits its potentiality in treating the kinetics of growth of multiphase systems, for which a general solution to the Markworth's problem is obtained.

In general, once the requirement of preexisting nucleation sites is relaxed, Avrami's formula does not hold anymore and a different definition of the extended transformed phase is required. Such an expression has been obtained which could be used in connection with rate equations for clustering on surfaces.

APPENDIX A

At $k=2$ Eq. (15) reads

$$Q_2=\frac{S_e^2}{2}\,e^{-S_e}. \tag{A1}$$

This expression can be obtained starting from Eq. (13) which, for $k=2$, becomes

$$\begin{aligned} Q_2={}&P_2P_0\cdots P_0+P_0P_2P_0\cdots P_0+\cdots+P_0P_0\cdots P_2\\ &+P_1P_1P_0\cdots P_0+P_1P_0P_1P_0\cdots P_0+\cdots+P_1P_0\cdots P_1\\ &+P_0P_1P_1P_0\cdots P_0+P_0P_1P_0P_1P_0\cdots P_0+\cdots\\ &+P_0P_1P_0\cdots P_1+\cdots+P_0\cdots P_1P_1; \end{aligned} \tag{A2}$$

here the ordering of each n-tuple is important; the position index has been omitted for rendering the notation less cumbersome. Substituting Poissons' expression with the appropriate mean value one gets

$$\begin{aligned} Q_2={}&e^{-\Sigma_i m_i}\left(\frac{m_1^2}{2}+\frac{m_2^2}{2}+\cdots+\frac{m_N^2}{2}+m_1m_2+m_1m_3+\cdots\right.\\ &+m_1m_N+m_2m_3+m_2m_4+\cdots\\ &\left.+m_2m_N+\cdots+m_{N-1}m_N\right)\\ ={}&\frac{(\Sigma_i m_i)^2}{2}\,e^{-\Sigma_i m_i}=\frac{S_e^2}{2}\,e^{-S_e}. \end{aligned}$$

APPENDIX B

In this appendix we wish to evaluate, by the same arguments employed in the work, the equation describing the evolution of surface coverage when the nucleation takes place at random in the part of the surface not covered by the already grown phase. In this case no ''phantoms'' can be formed.

Germs born on the ith plane have a density per unit area of uncovered surface given by $\nu_i/(1-S_{i-1}^{i})\equiv\nu_i/(1-S_i^{i})$, where ν_i is the number of germs in that plane and

$$S_q^Q=\sigma_{Q-1}^{(\nu_1)}\cup\sigma_{Q-2}^{(\nu_2)}\cup\cdots\cup\sigma_{Q-q}^{(\nu_i)}=\bigcup_{k=1}^{q}\sigma_{Q-k}^{(\nu_k)}, \tag{B1}$$

S_q^Q being the transformed phase up to the qth plane when the total number of planes is Q, $\sigma_{Q-k}^{(\nu_k)}$ is the surface coverage of the kth plane where ν_k germs were born and $\sigma_0=0$. According to Eq. (7) one has

$$\sum_{k=1}^{Q}\frac{\pi r_{Q-k}^2\nu_k}{1-S_{k-1}^k}=\ln\left(\frac{1}{1-S_{Q-1}^Q}\right). \tag{B2}$$

The finite difference is

$$\begin{aligned} \ln\left(\frac{1-S_{Q-1}^Q}{1-S_Q^{Q+1}}\right)&=\sum_{k=1}^{Q+1}\frac{\pi r_{(Q+1)-k}^2\nu_k}{1-S_{k-1}^k}-\sum_{k=1}^{Q}\frac{\pi r_{Q-k}^2\nu_k}{1-S_{k-1}^k}\\ &=\sum_{k=1}^{Q}\frac{\pi(r_{(Q+1)-k}^2-r_{Q-k}^2)\nu_k}{1-S_{k-1}^k}+\frac{\pi r_0^2\nu_{Q+1}}{1-S_Q^{Q+1}}. \end{aligned} \tag{B3}$$

By expanding the logarithmic function up to the first order, since the last term of (B3) is null ($r_0=0$), we obtain

$$S_Q^{Q+1}-S_{Q-1}^Q=(1-S_Q^{Q+1})\sum_{k=1}^{Q}\frac{\pi(r_{(Q+1)-k}^2-r_{Q-k}^2)\nu_k}{1-S_{k-1}^k}, \tag{B4}$$

whose continuous limit is the differential form (in dt) of Eq. (24).

Remark. At variance with Eq. (7), in Eq. (B2) the subscript index of r does not coincide with that of ν. As a matter of fact, to demonstrate Avrami's formula it is enough to consider a given situation at a given time, so that the subscript index simply is used for identifying different planes. Conversely, since in this case [Eq. (B2)] we need to evaluate the difference between two successive sets of planes, it is necessary to assign to r an index which carries kinetic information.

---

[1] W. A. Johnson and R. F. Mehl, Trans. Am. Inst. Min. Eng. **135**, 416 (1939).

[2] M. Avrami, J. Chem. Phys. **7**, 1103 (1939).

[3] M. Avrami, J. Chem. Phys. **8**, 212 (1940).

[4] A. N. Kolmogoroff, Bull. Acad. Sci. USSR (Cl. Sci. Math. Nat.) **3**, 355 (1937).

[5] V. Sessa, M. Fanfoni, and M. Tomellini, Phys. Rev. B **54**, 836 (1996); P. Vebele and H. Hermann, Modelling Simul. Mater. Sci. Eng. **4**, 203 (1996).

[6] E. M. Griswold, L. Weaver, M. Sayer, and I. D. Calder, J. Mater. Res. **10**, 3149 (1995).

[7] P. Gondi, R. Montanari, and A. Sili, Mater. Sci. Forum **94-96**, 591 (1992).

[8] R. A. Vandermeer and D. J. Jensen, Met. Mater. Trans. **26A**, 2227 (1995).

[9] R. J. Behm, G. Ertl, and J. Wintterlin, Ber. Bunsenges. Phys. Chem. **90**, 294 (1986).

[10] P. Kruger and E. Woldt, Acta Metall. Mater. **11**, 2933 (1992).

[11] M. C. Weinberg, J. Non-Cryst. Solids **134**, 116 (1991); **142**, 126 (1992); E. Zanotto and M. C. Weinberg, *ibid.* **105**, 53 (1988).

[12] G. Shi and J. H. Seinfeld, J. Mater. Res. **6**, 2097 (1991).

[13] A. Kolb-Telieps and Tan Shu-Song, J. Non-Cryst. Solids **107**, 122 (1988).

[14] M. A. Gibson and G. W. Delamore, J. Mater. Sci. **22**, 4550 (1987).

[15] J. Gonzales-Hernandez and R. Tsu, Appl. Phys. Lett. **42**, 90 (1983).

[16] N. Asahi and A. Miyashita, Jpn. J. Appl. Phys. **27**, 875 (1988).

[17] D. Kashchiev, J. Cryst. Growth **40**, 29 (1977).

[18] M. Tomellini and M. Fanfoni, Surf. Sci. **349**, L191 (1996).

[19] M. Tomellini, J. Appl. Phys. **72**, 1589 (1992).

[20] P. H. Holloway and J. B. Hudson, Surf. Sci. **43**, 123 (1974).

[21] F. Arciprete, S. Colonna, M. Fanfoni, F. Patella, and A. Balzarotti, Phys. Rev. B **53**, 12 948 (1996).

[22] M. Fanfoni and M. Tomellini, J. Electron Spectrosc. Relat. Phenom. **76**, 283 (1995).

[23] A. J. Markworth, J. Chem. Phys. **94**, 3282 (1991).

[24] M. Zinke-Allmang, L. C. Feldman, and M. H. Grabow, Surf. Sci. Rep. **16**, 377 (1992).

[25] G. Zinsmeister, Thin Solid Films **4**, 363 (1969); **7**, 51 (1971).

[26] J. A. Venables, Philos. Mag. **27**, 697 (1973); Phys. Rev. B **36**, 4153 (1987).

[27] U. R. Evans, Trans. Faraday Soc. **41**, 365 (1945).

[28] J. L. Meijering, Philips Res. Rep. **8**, 270 (1953).

[29] Y. W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **66**, 1998 (1991); Surf. Sci. **268**, 275 (1992).

[30] D. Walton, J. Chem. Phys. **37**, 2182 (1962).

[31] M. Tomellini, Appl. Surf. Sci. **99**, 67 (1996).

[32] B. M. Trafas, Y. N. Yang, R. L. Siefert, and J. H. Weaver, Phys. Rev. **43**, 14 107 (1991).

[33] H. Brune, H. Röder, C. Boragno, and K. Kern, Phys. Rev. Lett. **73**, 1955 (1994).

[34] R. M. Logan, Thin Solid Films **3**, 59 (1969).