Vol 10 Suppl., July 2001
1009-1963/2001/10(Suppl.)/S140-04
Chinese Physics
© 2001 Chin. Phys. Soc.
and IOP Publishing Ltd

CLUSTER NUCLEATION LIMITED BY GROWTH PATTERN COVERAGE IN THIN FILM PREPARATION FROM VAPOR*

Shao Qing-yi(邵庆益)[a,b], Zhang Qi-feng(张琦锋)[a], Fang Rong-chuan(方容川)[b], Zhu Kai-gui(朱开贵)[b], Xu Bei-xue(许北雪)[a], Liu Wei-min(刘惟敏)[a], Zhao Xing-yu(赵兴钰)[a], Wu Jin-lei(吴锦雷)[a], and Xue Zeng-quan(薛增泉)[a]†

[a] *Department of Electronics, Peking University, Beijing* 100871, *China*

[b] *Structure Research Laboratory and Department of Physics, University of Science and Technology of China, Hefei* 230026, *China*

(Received 14 March 2001)

In the early stage of thin film preparation from vapor, growth patterns consisting of stable clusters will gradually cover almost the entire substrate surface. During this process, the density of single atoms is zero on growth patterns and the nucleation of clusters will proceed in the substrate parts uncovered by these patterns. The influence of growth pattern coverage on the nucleation of thin films has not been considered wholly in the classical theory of thin films. We will systematically study the influence of growth pattern coverage and give some correction formulas for the widely used classical theory of thin films. It was found that the classical nucleation rate is proportional to the square of the uncovered area. The corrected formulas are of particular importance in the dominant coverage case.

Keywords: thin film growth, nucleation, clusters
PACC: 8115, 6460Q, 6146

I. INTRODUCTION

The growth of thin films is an important subject in science and technology.[1] The application of thin films is rapidly increasing in many fields such as in microelectronics for integrated circuits, in the construction of machines and tools for wear resistance and corrosion protection, and in the manufacture of windows for optical coatings. Thin films are also important within physical science itself for exploring differences between three-dimensional (3D) and (quasi-) two-dimensional (q2D) states of matter. And inprinciple the growth of crystals in the initial stage can be guided by atomic or molecular recognition at interfaces.[2]

The well-known classical theory of thin films was developed nearly thirty years ago.[3,4] At first, the atomic nucleation theory was developed.[5,6] Since the first publications of Zinsmeister, kinetic rate equations had been used to describe nucleation and growth behavior and interpret experiments.[7] Then, the capture numbers, which describe the diffusional flow of single atoms to critical or stable clusters, were much discussed in literature.[8,9] Walton gave the expressions of the nucleation rate for small critical clusters.[10] Researchers have discussed the influences of a coverage of stable clusters on the nucleation rate since the classical theory was drawn up. On the one hand, the correction factor of coverage for the nucleation rate is assumed to be $(1-Z)$,[11] but the influence of the coverage for the expression of density of subcritical clusters was not involved. On the other hand, the correction factor of coverage for the single atom density was used, but the influence of the coverage on the density of free sites was not considered, consequently the correction factor of the nucleation rate was rather uncertain and unsatisfactory.[6] The influence of coverage on the capture rate and rate equations has not yet been studied. In this paper, we systematically consider the coverage influence and give a series of new correction formulas.

II. THEORY SCENARIO

Thin films can be prepared by numerous methods, such as evaporation, sputtering, plasma decomposition, etc. Here, we deal primarily with the growth from vapor.

According to atomic views of nucleation and

*Project supported by the National Advanced Material Committee of China (Grant No. 863-715-002-003) and the National Natural Science Foundation of China (Grant No. 69890221).
†Corresponding author.

growth, the process on the substrate surface in the initial stage of growth can be described as adsorption, desorption, and diffusion of atoms. Initially, single atoms from the vapor source impinge on the substrate at a rate $R_{\rm I}$ (the number of single atoms per second per unit area). On the substrate containing N_0 (per unit area) sites of equal adsorption energy $E_{\rm a}$, adsorption and desorption of the atoms occur with the re-evaporation rate characterized by an average staying time $\tau_{\rm A}$. The atoms of a surface concentration $n_1(t)$ may diffuse over the substrate surface at a diffusivity D and an activation energy $E_{\rm d}$ for diffusion. Surface diffusion leads to the formation and growth of 2D or 3D clusters. Small clusters containing j atoms with the surface concentration $n_j(t)$ may grow or decay. Growth becomes more probable than the decay when the cluster size exceeds a certain critical size i. All clusters larger than the critical cluster can be considered to be stable and may form nuclei even if some atoms leave during subsequent growth.

III. SINGLE ATOM DENSITY

According to the classical theory of thin films,[4,8] the density of single atoms $n_1(\boldsymbol{r},t)$ is given by the following rate equation

$$\frac{\partial n_1(\boldsymbol{r},t)}{\partial t} = D\nabla^2 n_1(\boldsymbol{r},t) + R_{\rm I}(1-Z) - n_1(\boldsymbol{r},t)(\tau_a^{-1} + \sigma_x D n_x). \quad (1)$$

The equation states the varying rate of the density of single atoms. The first term on the right hand side is the diffusion contribution. The second term denotes the rate of impingement of single atoms from the gas phase on the uncovered substrate. The third terms are the desorption rate of single atoms and the rates of capture of single atoms by stable clusters respectively. Z is the surface coverage of stable clusters. The capture numbers (σ_x) describe the diffusion flows of single atoms to stable clusters.[8,9] And n_x is the density of the stable clusters, $\boldsymbol{r}$ is the distance from the nucleus at $\boldsymbol{r}$=0. The boundary conditions are

$$n_1(\boldsymbol{r},t) = 0 \quad \boldsymbol{r} = \boldsymbol{r}_k, \quad (2)$$

at the border of an island and

$$\nabla^2 n_1(\boldsymbol{r},t) = 0 \quad \boldsymbol{r} \to \infty. \quad (3)$$

From the density equation of single atoms in the previous theory of thin films,[4] it can be seen that the density of single atoms is defined as the number of single atoms per unit area on the substrate surface. Once stable clusters appear, the single atoms would be captured in the process of jumping that leads to the growth of the stable clusters. Hence, the density of single atoms would be zero on the substrate parts covered by stable clusters. We can see that the density of single atoms used in the previous thin film theory is the average density on the covered and uncovered area of the substrate. In fact, in the area of substrate uncovered by stable clusters, the density of the single atoms m_1 should be different from n_1. With Z denoting the covered fraction of the substrate, m_1 can be expressed as $n_1/(1-Z)$. Then, the density m_1 is just the solution of Eq.(1) divided by $(1-Z)$.

Expressions (1)–(3) can be corrected as

$$\frac{\partial m_1(\boldsymbol{r},t)}{\partial t} = D\nabla^2 m_1(\boldsymbol{r},t) + R_{\rm I} - m_1(\boldsymbol{r},t)(\tau_a^{-1} + \sigma_x D n_x), \quad (4)$$

$$m_1(\boldsymbol{r},t) = 0 \quad \boldsymbol{r} = \boldsymbol{r}_k, \quad (5)$$

$$\nabla^2 m_1(\boldsymbol{r},t) = 0 \quad \boldsymbol{r} \to \infty. \quad (6)$$

If Z is not a spatial function, then Eqs.(1)–(3) will be equivalent to expressions (4)–(6).

IV. CAPTURE RATE OF A SINGLE ISLAND

The capture rate ω_k is defined as the number of atoms captured by an island containing k atoms on the substrate per second, and is given by[4]

$$\omega_k = 2\pi \boldsymbol{r}_k D \left(\frac{\partial n_1(r,t)}{\partial r}\right)_{r_k} = \sigma_k D n_1, \quad (7)$$

$$\sigma_k = \frac{2\pi \boldsymbol{r}_k}{n_1}\left(\frac{\partial n_1}{\partial r}\right)_{r_k}. \quad (8)$$

We consider the density of single atoms as in the above section; expressions (7) and (8) can be corrected as

$$\omega_k = 2\pi r_k D \left(\frac{\partial m_1(r,t)}{\partial r}\right)_{r_k} = \sigma_k D m_1, \quad (9)$$

$$\sigma_k = \frac{2\pi r_k}{m_1}\left(\frac{\partial m_1}{\partial r}\right)_{r_k}. \quad (10)$$

If Z is not a spatial function, then Eqs.(7) and (8) will be equivalent to expressions (9) and (10), respectively.

V. NUCLEATION RATE

A. Liquid drop model

In the classical theory,[12] the nucleation rate J is defined as the nucleation number per second per unit area on arbitrary parts of the substrate. In fact,

growth only occurs in the parts covered by the stable clusters (nuclei), while nucleation occurs in uncovered parts. Hence, we define the nucleation density rate $V_{\rm u}$ as the nucleation number per second per unit area on uncovered parts. The nucleation density rate $V_{\rm u}$ is the growth rate of critical clusters at the uncovered sites. Similar to the treatment of the nucleation rate J,[4] we have

$$V_{\rm u} = Z^* \omega_i m_i, \tag{11}$$

where Z^* is the Zeldowich factor, ω_i is the number of atoms which flow per second to a critical cluster, and in analogy to m_1 we take m_i as the equilibrium density of critical clusters in the uncovered parts.

In equilibrium the following relation is valid

$$m_j = m_1 \exp\left(-\frac{\Delta G_{\rm K}(j)}{k_{\rm B}T_{\rm s}}\right) \quad (j \le i), \tag{12}$$

where m_j is the density of clusters of the size j in uncovered parts, $k_{\rm B}$ is the Boltzmann constant, $T_{\rm s}$ is the substrate temperature, and $\Delta G_{\rm K}(j)$ is the Gibbs free energy of formation of a cluster j.

The nucleation density rate $V_{\rm u}$ is given by

$$V_{\rm u} = Z^* \sigma_i D m_1^2 \exp\left(-\frac{\Delta G_{\rm K}(i)}{k_{\rm B}T_{\rm s}}\right). \tag{13}$$

In the calculation of classical theories the coverage of nuclei is usually neglected. The nucleation rate J becomes the nucleation density rate $V_{\rm u}$. In general, according to the classical theory,[4] we have

$$J = Z^* \sigma_i D n_1^2 \exp\left(-\frac{\Delta G_{\rm K}(i)}{k_{\rm B}T_{\rm s}}\right). \tag{14}$$

Therefore, we obtain

$$J = (1-Z)^2 V_{\rm u}. \tag{15}$$

According to Eqs.(13) and (15) and because $V_{\rm u}$ is a time constant, J is a function of the growth time and rapidly decreases to zero with the coverage Z increasing to 1 in the growth process of thin films. We can see that it is a very rough approximation that J is a time constant as a result of the classical theories.

B. Walton's expressions

For small clusters (several atoms), the use of macroscopic surface energy for computing the free energy of formation is not only somewhat dangerous, but the concept of surface energy itself is subject to certain doubts.[13] Walton gave the related expressions for small clusters.[10]

On a substrate devoid of stable clusters, the density of clusters n_j can be calculated by the equilibrium relation[10]

$$\left(\frac{n_j}{N_0}\right) = \sigma_j c_j \left(\frac{n_1}{N_0}\right)^j \exp\left(\frac{E_j}{kT}\right), \tag{16}$$

where c_j is a statistical weighting factor. The values of c_j were overestimated by Frank and Venables.[14] To account for the departure from equilibrium in rate equations, the Zeldowich factor should be incorporated in the nucleation rate.

$$U_i = \sigma_i C_i N_0^{(1-i)} D n_1^{i+1} \exp\left(\frac{E_i}{kT}\right). \tag{17}$$

In fact, stable clusters appear on the surface of the substrate. It should be noted that in these expressions, as in the other equations, the density $n_1(\boldsymbol{r}, t)$ is the average number of atoms per unit area on the covered and uncovered parts of the substrate. As it is commonly assumed that the coverage fraction Z is so small that the necessary condition of Walton' theory is approximately satisfactory, and Walton's relation can be used. Similar to the above section, it is more reasonable to use the density $m_j = n_j/(1-Z)$ on the uncovered field and the free site density $M_0 = N_0/(1-Z)$ in the description of the presence of stable clusters. The nucleation density rate on the uncovered parts of the substrate is

$$V_{\rm u} = \sigma_i C_i M_0^{1-i} D m_1^{i+1} \exp\left(\frac{E_j}{kT}\right), \tag{18}$$

$$= \frac{1}{(1-Z)^2} U_i. \tag{19}$$

$$U_i = (1-Z)^2 V_{\rm u}. \tag{20}$$

This equation is similar to expression (15).

VI. KINETIC GROWTH THEORY

The rate equations can be written as[3,4]

$$\frac{{\rm d}n_1}{{\rm d}t} = R - \frac{n_1}{\tau_{\rm A}} - \frac{{\rm d}(n_x W_x)}{{\rm d}t}, \tag{21}$$

$$\frac{{\rm d}n_j}{{\rm d}t} = 0 \qquad (2 \le j < i), \tag{22}$$

$$\frac{{\rm d}n_x}{{\rm d}t} = U_i - U_{\rm c} - U_{\rm m}, \tag{23}$$

$$\frac{{\rm d}(n_x W_x)}{{\rm d}t} = (i+1)U_i + n_x \sigma_x D n_1 + RZ, \tag{24}$$

where W_x is the average number of atoms per cluster, n_x is the density of stable clusters, $n_x W_x$ is the number of atoms in stable clusters. U_i denotes the nucleation rate J. $U_c = 2n_x({\rm d}Z/{\rm d}t)$ is the loss rate

due to the growing together of clusters. RZ is the direct impingement rate of vapor atoms on stable clusters. U_m is the loss rate by the coalescence of mobile clusters. We now consider the coverage Z and local density $m_j (j < i)$ of subcritical clusters on the uncovered parts of the substrate. Taking $m_j = n_j/(1-Z)$ instead of $n_j (j < i)$, Eqs.(21)–(24) can be corrected as

$$\frac{\mathrm{d}m^1}{\mathrm{d}t} = R - \frac{m_1}{\tau_\mathrm{A}} - \frac{\mathrm{d}(n_x W_x)}{\mathrm{d}t}\frac{1}{1-Z}, \tag{25}$$

$$\frac{\mathrm{d}m_j}{\mathrm{d}t} = 0 \qquad (2 \le j < i), \tag{26}$$

$$\frac{\mathrm{d}n_x}{\mathrm{d}t} = (1-Z)V_\mathrm{u} - U_\mathrm{c} - U_\mathrm{m} = \frac{U_i}{(1-Z)} - U_\mathrm{c} - U_\mathrm{m}, \tag{27}$$

$$\frac{\mathrm{d}(n_x W_x)}{\mathrm{d}t} = \frac{(i+1)U_i}{(1-Z)} + n_x \sigma_x D m_1 + RZ. \tag{28}$$

VII. CONCLUSION

Based on the detailed consideration, we use the density of subcritical clusters m_j on the uncovered parts of the substrate instead of the average density n_j and obtain a series of correction rate equations. It has been found that the classical nucleation rate is equal to the square of the uncovered area multiplied by the nucleation density rate. The classical nucleation rate will vary from a certain value to zero when the coverage changes from zero to one. The corrected formulas are especially important in the dominant coverage case of thin film preparation from vapor.

References

[1] Zhang Z Y and Lagally M G 1997 *Science* **276** 377

[2] Aizenberg J, Black A J and Whitesides G M 1998 *Nature* **394** 868

[3] Venables J A, Spiller G D T and Hanbucken M 1984 *Rep. Prog. Phys* **47** 399

[4] Reichelt K 1988 *Vacuum* **38** 1083

[5] Venables J A and Price G L 1975 *Epitaxial Growth*, Part B (New York: Academic)

[6] Lewis B and Anderson J C 1978 *Nucleation and Growth of Thin Films* (New York: Academic)

[7] Zinsmeister G 1966 *Vacuum* **16** 529
Zinsmeister G 1968 *Thin Solid Films* **2** 497
Zinsmeister G 1969 *Thin Solid Films* **4** 363
Zinsmeister G 1970 *Kristall. Tech.* **5** 207
Zinsmeister G 1971 *Thin Solid Films* **7** 51

[8] Venables J A 1973 *Phil. Mag.* **27** 697

[9] Lewis B and Ree G J 1974 *Phil. Mag.* **29** 1253

[10] Walton D 1962 *J.Chem. Phys.* **37** 2182

[11] Stowell M J 1972 *Phil. Mag.* **26** 361

[12] Pound G M and Karge H 1966 *Basic Problems in Thin Film Physics* (Gottingen: Vandenhoek and Ruprecht)

[13] Reiss H 1952 *J. Chem. Phys.* **20** 1216

[14] Frankl D R and Venables J A 1970 *Adv. Phys.* **19** 409