NASA-TM-88806

NASA Technical Memorandum 88806

Stability of Surface Nucleation

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August 1986

NASA

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      86N30556*#   ISSUE 21   PAGE 3387   CATEGORY 77   RPT#: NASA-TM-88806
      E-3154 NAS 1.15:88806   86/08/00  9 PAGES   UNCLASSIFIED DOCUMENT
UTTL: Stability of surface nucleation
AUTH: A/SALIK, J.
CORP: National Aeronautics and Space Administration.  Lewis Research Center,
      Cleveland, Ohio.
SAP:  Avail: NTIS HC A02/MF A01
CIO:  UNITED STATES
MAJS: /*COATINGS/*NUCLEATION/*STABILITY/*SURFACE PROPERTIES/*THIN FILMS
MINS: / ATOMIC STRUCTURE/ MICROSCOPY/ NUCLEI (NUCLEAR PHYSICS)
ABA:  Author
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E-3154

STABILITY OF SURFACE NUCLEATION

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SUMMARY

The growth and decomposition rates of nuclei on a surface are expressed in microscopic terms. A stability factor is defined and employed for the derivation of a criterion for nucleus stability. Simulation results indicate that the stability factor can be used as a measure of the system stability.

INTRODUCTION

The nucleation of thin films has been the subject of intensive research for a long time (ref. 1). For some reason, however, only a small fraction of this effort was devoted to the problem of nucleus stability, a central topic in classical nucleation theories (refs. 2 and 3). Moreover, some of the few studies which do address this problem (refs. 4 and 5) are based on the classical theories (refs. 2 and 3) and utilize macroscopic quantities such as the free energy and surface tension. As pointed out by Walton (ref. 6), however, the applicability of those theories to nucleation of thin films is questionable, since experimental observations (refs. 7 and 8) have indicated that the critical nucleus in this case is small and consists of but a few atoms. It is thus evident that a different approach, microscopic in nature, is needed in order to treat this problem. Such an approach is presented here.

THEORY

The change in a nucleus size is the outcome of two competing processes, namely growth caused by joining of atoms, and decomposition due to detachment of atoms. We deal first with the growth process. The kinetics of this process depends on the rate of arrival of atoms to the nucleus boundary. When an atom joins the nucleus, a bond (or several bonds) is formed. Thus, this process results in a decrease in energy. Following Metropolis et al. (ref. 9) we assign a value of one to the joining probability. In other words, we assume that every atom which arrives at the nucleus boundary joins the nucleus. When the flux J of atoms arriving at the nucleus boundary is homogeneous, the rate A of arrival of atoms to the nucleus is given in macroscopic terms by

$$A = JL \tag{1}$$

where L is the boundary length.
In microscopic terms the equivalent of L is the number of available growth sites, i.e., the number of accessible lattice sites immediately adjacent to

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the nucleus which we designate by n_g., Thus, the growth rate G is given in microscopic terms by

$$G = Jn_g \tag{2}$$

We now examine the decomposition process. The jump frequency of an adsorbed atom on the substrate surface is given by

$$\nu = \nu_0 \exp\left(\frac{-E}{kT}\right) \tag{3}$$

where ν_0 is a characteristic frequency, E the binding energy, k is Boltzmann's constant, and T the absolute temperature. In the nearest-neighbor model (ref. 10), which we employ here, the binding energy E is assumed to be the sum of single bond energies, i.e.,

$$E = E_a + Z \cdot E_b \tag{4}$$

where E_a is the energy of binding between the atom and the substrate, E_b the energy of a single bond between adsorbed atoms, and Z the number of nearest neighbors. Thus,

$$\nu = \nu_0 \exp\left[\frac{-(E_a + Z \cdot E_b)}{kT}\right] \tag{5}$$

or

$$\nu = \nu_d \exp\left[\frac{-Z \cdot E_b}{kT}\right] \tag{6}$$

where ν_d, given by

$$\nu_d = \nu_0 \exp\left(\frac{-E_a}{kT}\right) \tag{7}$$

is the frequency of jumps of single atoms (i.e., those which are not bound in clusters).
The flux of atoms detaching form the nucleus, i.e., the decomposition rate D, is therefore given by

$$D = \nu_d \sum \exp\left(\frac{-Z_n E_b}{kT}\right) \tag{8}$$

where the sum is over all the nucleus atoms located on the boundary.

The tendency of the nucleus to increase in size can be expressed by means of the ratio between the growth and decomposition rates:

$$\frac{G}{D} = \frac{J \cdot n_g}{\nu_d \sum \exp\left(\frac{-Z_n E_b}{kT}\right)} \tag{9}$$

When this ratio is greater than unity the nucleus has a tendency to increase in size and vice versa.

The quantities J and v_d in equation (9) depend on the conditions on the substrate and on the nature of the growing material, respectively. The quantity which depends on the nucleus is the ratio which we will henceforth call the stability factor and designate by s:

$$s = \frac{n_g}{\exp\left(\frac{-X_n E_b}{kT}\right)} \tag{10}$$

Equation (9) can now be written in the following concise form

$$\frac{G}{D} = \frac{J}{v_d} s \tag{11}$$

The flux J is the produce of the concentration and the velocity. Expressing it in terms of the number of atoms crossing a unit of length equal to the lattice parameter in a time unit one obtains

$$J = \theta v_d \tag{12}$$

where θ is the surface concentration.
Substitution to equation (11) yields

$$\frac{G}{D} = \theta s \tag{13}$$

A nucleus is considered stable when its tendency to grow exceeds its tendency to decrease in size. We thus obtain the following criterion for nucleus stability

$$\theta s > 1 \tag{14}$$

We now demonstrate the use of this criterion in two simple examples of nuclei on a two-dimensional square lattice.

Linear Nuclei

For a linear nucleus composed of n monomers and lying along the (1,0) direction the number of available growth sites is 2n + 2, and the stability factor is

$$s = \frac{2n + 2}{(n - 2)\alpha^2 + 2\alpha} \tag{15}$$

where α is the Boltzmann factor

$$\alpha = \exp\left(\frac{-E_b}{kT}\right) \tag{16}$$

Thus, the stability criterion in this case is

$$\theta > \frac{(n - 2)\alpha^2 + 2\alpha}{2n + 2} \tag{17}$$

This form of the criterion is valid, of course, only for the initial configuration. Once an atom joins the nucleus or detaches from it, the nucleus shape changes and a different form of the criterion has to be used.

Square Nuclei

For a square nucleus composed of n^2 monomers and bound by four (1,0) lines the number of available growth sites is 4n, and the stability factor is

$$s = \frac{n}{\alpha^2 + (n - 2)\alpha^3} \tag{18}$$

Thus, the stability criterion in this case is

$$\theta > \frac{\alpha^2 + (n - 2)\alpha^3}{n} \tag{19}$$

Finally, it should be emphasized that throughout this treatment represents the local surface concentration in the immediate vicinity of the nucleus. This is equal to the nominal coverage only before extensive growth has taken place. At later stages depletion zones are formed around the growing nuclei, and this is no longer true.

COMPUTER SIMULATION

The above equations can be easily utilized for computer simulation. By choosing $1/\nu_d$ in equation (6) as the time unit one obtains the following expression for the probability P of each atom (excluding those which are completely surrounded by nearest neighbors) jumping at any time

$$P = \exp\left(\frac{-ZE_b}{kT}\right) \tag{20}$$

Simulation studies using this jump probability were conducted on a square lattice containing 10,000 (100 by 100) sites. Eight simulation runs were performed for each data point and the average as well as the standard deviation were calculated.

Since we are interested now in the stability of the system as a whole, we define a system stability factor S in a manner similar to that used to define the nucleus stability factor, namely

$$S = \frac{n_g}{\sum\limits_{Z<f} \exp\left(\frac{-ZE_b}{kT}\right)} \tag{21}$$

where f is the coordination number of the lattice (in our case $f = 4$) and the sum is over the whole system.

The variation of this factor with time for a surface coverage of 0.1 and several values of E_b/kT is presented in figure 1. A feature which is common to all of these curves is that for all values of E_b/kT the stability factor is a nondecreasing function of time. This is in contrast to other parameters such as the percentage of bound atoms or the cluster density which were found (ref. 11) to decrease with time when $E_b/kT < 0.5$.

Comparison of these curves with the resulting microstructures, presented in figure 2, shows that once S levels off (e.g., for $E_b/kT = 2$ at $t = 100$) no detectable change in microstructure takes place. It may thus be concluded that the factor S can be used as a measure of the system stability.

CONCLUSIONS

The stability of nuclei on a substrate surface has been expressed in microscopic terms, namely the binding energy and the local atomic configuration. A stability factor has been defined and a criterion for nucleus stability has been derived. The results of computer simulation indicate that the stability factor can be used as a measure of the system stability.

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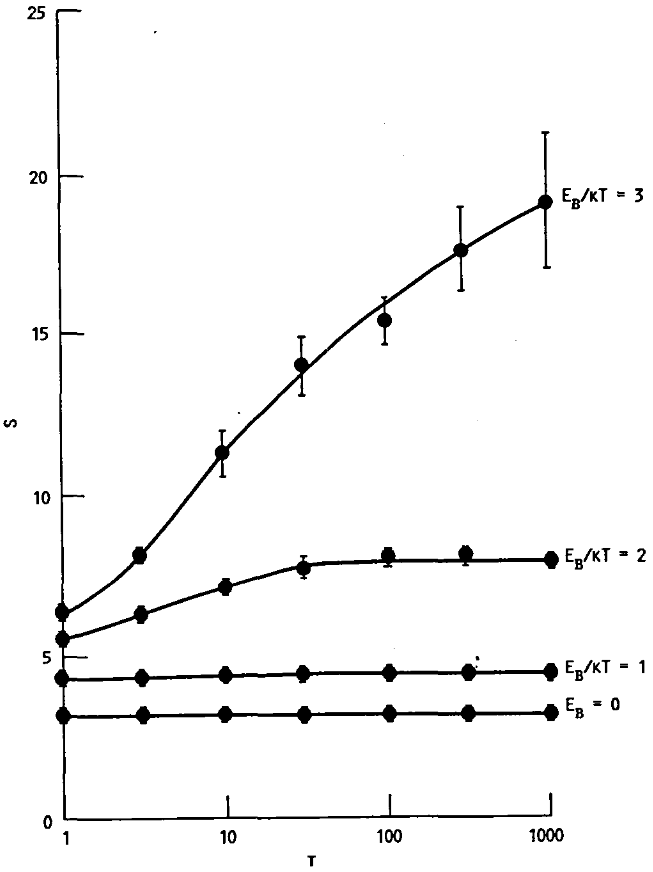

FIGURE 1.- VARIATION OF THE SYSTEM STABILITY FACTOR S WITH TIME FOR SEVERAL VALUES OF $E_B/\kappa T$.

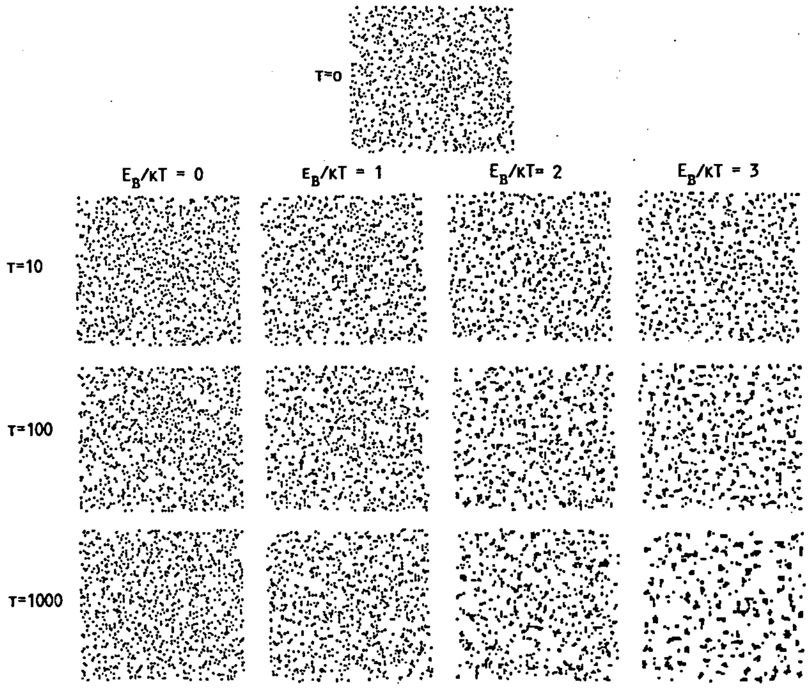

FIGURE 2.- EVOLUTION OF MICROSTRUCTURE WITH TIME FOR SEVERAL VALUES OF $E_B/\kappa T$.

1. Report No. NASA TM-88806	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

Stability of Surface Nucleation

5. Report Date

August 1986

6. Performing Organization Code

505-90-01

7. Author(s)

Joshua Salik

8. Performing Organization Report No.

E-3154

10. Work Unit No.

9. Performing Organization Name and Address

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

11. Contract or Grant No.

13. Type of Report and Period Covered

Technical Memorandum

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

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16. Abstract

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17. Key Words (Suggested by Author(s))

Surface nucleation
Coatings
Nucleation

18. Distribution Statement

Unclassified - unlimited
STAR Category 77

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages	22. Price*

*For sale by the National Technical Information Service, Springfield, Virginia 22161

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Space Administration

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