
Low Temperature Epitaxial Growth of Semiconductors

Edited by **Takashi Hariu**

World Scientific

TN304.054
H282

9261051

Low Temperature Epitaxial Growth of Semiconductors



E9261051

Edited by **Takashi Hariu**

Tohoku University

Department of Electronic Engineering

Sendai, Japan



World Scientific

Singapore • New Jersey • London • Hong Kong

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 9128

USA office: 687 Hartwell Street, Teaneck, NJ 07666

UK office: 73 Lynton Mead, Totteridge, London N20 8DH

Library of Congress Cataloging-in-Publication data is available.

The editor and publisher are grateful to the authors and publishers for their permission to reproduce the reprinted figures found in this volume. While every effort has been made to contact the publishers of reprinted figures prior to publication, we have not been successful in a few cases. Proper credit will be given to these publishers in future editions of this work after permission is granted.

LOW TEMPERATURE EPITAXIAL GROWTH OF SEMICONDUCTORS

Copyright © 1991 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

ISBN 9971-50-839-7

Printed in Singapore by Utopia Press.

Low Temperature Epitaxial Growth of Semiconductors

PREFACE

Low temperature processes for semiconductors have been recently under intensive development to fabricate controlled device structures with minute dimensions in order to achieve the highest device performance and new device functions as well as high integration density. The lowest temperature of processing in purely thermal process is determined by minimum thermal energy which is sufficient enough to cause, with reasonable speed for technical application, chemical reaction or physical change of materials involved in any particular processing.

It is then necessary to send some additional energy to compensate for the decreased thermal energy if a process should be achieved at a lower temperature. Considering, however, that it is only the surface of substrate that is usually required to be activated for such processes as etching, crystal growth, oxidation and deposition of insulator or metal films in semiconductor device technology, this additional energy can be supplied restrictively to the surface with the rest of the substrate kept at as low temperature as possible, so that the device structures processed before may not be destroyed.

With partly successful industrial application of low temperature processes like plasma etching and deposition of such amorphous films as silicon nitride and hydrogenated silicon, there are vast fields which remain in under-developing state but are desired to be urgently established as low temperature processes. Low temperature epitaxial growth of crystal layers is in fact a technology of this kind.

Two important aspects of crystal growth may be here reminded of. One is the chemical effect to produce molecules which constitute the crystals or to produce on the growing surface a certain chemical adsorption which is energetically more stable than physical adsorption. Photo-chemistry and plasma chemistry to excite valence electrons for chemical reaction at a low temperature, although rather classical, have been attracting renewed attention to apply them for semiconductor device technology.

The other is the physical effect to arrange them into correct positions according to the crystal structure. Classical crystal growth was therefore performed slowly at a considerably high temperature in order to give time long enough for the molecules to migrate and occupy the energetically most stable positions, but not at so high temperature as to introduce high density of crystal defects through entropy effect.

In epitaxial growth, atoms or molecules should migrate over the growing

surface until they arrive at a correct site which is generally the most stable position at the growth temperature. When they find a very large energy difference between the correct site and the other incorrect sites, layer-by-layer growth is possible. It is then important to find out a crystallographic plane, growth conditions and source materials to fulfill this condition. The details will be described in the chapter of Atomic Layer Epitaxy.

With a given crystallographic plane and a given thermal, kinetic energy for migration, we can prevent the formation of molecules, like GaAs on As-plane, which can suppressed to migrate. The technology is now under development as Migration Enhanced Epitaxy. Photons, which have not large momentum enough to increase the kinetic energy of atoms and molecules, can sometimes break chemical bonds which prevent the migration and then can be employed for enhanced migration in addition to the chemical activation. Recent results on this aspect will be reviewed in the chapter of Photo-Activated Epitaxial Growth.

The kinetic energy for migration can be directly enhanced by accelerating ions or ionic clusters by electric field. It is, however, important to restrict the energy so that crystal defects or damages may not be introduced, particularly for structure-sensitive semiconductors. The details will be described in the chapter of Ion Beam Epitaxial Growth in Plasma-Assisted Epitaxy, atomic migration can also be sometimes enhanced by supplying excited atoms through plasma, like excited As atoms instead of As₄ molecules in GaAs growth, in addition to chemical activation and acceleration of ions through ion sheath.

A special chapter has been prepared to give theoretical background of low temperature epitaxial growth as well as to survey its recent development. This will help us to pursue the refined further development of this particular technology systematically.

It is a great pleasure of the editor to express his thanks to all the authors who accepted his invitation to contribute the respective chapters. All of them have been actively involved in the respective pioneering work for a considerably long period. It is our hope that this volume will make a useful step toward maturing the process of low temperature epitaxy as a whole. The patient effort of Ms. Barbara Aman would be greatly appreciated, without which this volume would not have been possible.

T. Hariu

CONTENTS

Preface	v
Theory of Low Temperature Surface Processes in Epitaxy <i>H. J. Kreuzer</i>	1
Ion Beam Epitaxy <i>I. Yamada</i>	43
Plasma-Assisted Epitaxy <i>T. Hariu</i>	156
Photo-Activated Epitaxial Growth <i>Yoshinobu Aoyagi, Takashi Meguro, and Sohachi Iwai</i>	199
Atomic Layer Epitaxy of GaAs and Related Compounds <i>Salah M. Bedair</i>	291
Low Temperature Growth of GaAs and AlGaAs by Migration-Enhanced Epitaxy <i>Yoshiji Horikoshi, Minoru Kawashima, and Hiroshi Yamaguchi</i>	308

THEORY OF LOW TEMPERATURE SURFACE PROCESSES IN EPITAXY

H.J. Kreuzer

Department of Physics, Dalhousie University

Halifax, N.S. B3H 3J5 Canada

and

Fritz-Haber-Institut der Max-Planck-Gesellschaft

6-8 Faradayweg, D-1000 Berlin 33, Germany

ABSTRACT

After a brief review of the equilibrium aspects of crystal growth, we set up a macroscopic theory of the kinetics of adsorption, desorption and surface diffusion, first in a phenomenological approach and then based on the Onsager theory of non-equilibrium thermodynamics. To understand the microscopic processes involved in epitaxy, we proceed to formulate the kinetic lattice gas model first for a monolayer and then, as the solid-on-solid model, for a growing crystal. In the summary, we highlight the main points about existing theories of epitaxy, and try to formulate some criteria for epitaxy at low temperature.

1. INTRODUCTION

Epitaxy refers to the growth of a single crystal in a unique crystal orientation on a single-crystal substrate either of the same or a foreign material. It can be viewed as a two-step process consisting of the deposition of atoms onto the surface of the growing crystal and migration of these atoms into their proper lattice positions. Thus adsorption, desorption, diffusion and surface reactions are the relevant processes. The rate of adsorption is primarily determined by the incoming particle flux and thus by the pressure, whereas desorption, diffusion and reactions are activated processes, so that their rate constants can be parametrized according to Arrhenius as

$$r = v \exp(-Q/k_B T) \quad (1)$$

Thus temperature plays a crucial role on whether a quasi-equilibrium is maintained during the growth process or not. The term "quasi-equilibrium", used throughout this review, needs some explanation. Obviously crystal growth is a non-equilibrium phenomena whether in the stationary or transient regime. However, growth conditions might be set so that at any stage the distribution of atoms on the surface might be such that if an appropriate vapor pressure were established above the surface, no redistribution of atoms would occur. As an example, consider a situation where the topmost atomic layer exhibits co-existence of a dilute two-dimensional (2-d) gas phase and a dense 2-d solid-like structure. Quasi-equilibrium then maintains if the mass distribution between these two phases is according to equilibrium thermodynamics, in which case the state of the topmost layer of the solid can be characterized by its equilibrium properties, even under growth conditions. Obviously fast surface diffusion is a prerequisite for quasi-equilibrium.

To set a framework for the discussion of epitaxy we want to distinguish four growth regimes: (i) At very low temperature where diffusion is inoperative, impinging atoms from the gas phase get adsorbed randomly producing an amorphous structure or at best a polycrystalline film. This mode will be referred to as random growth. (ii) As temperature is raised, surface migration will set in leading to the nucleation of dense islands which will grow with prolonged exposure to completion of a monolayer. Whether such films are epitaxial depends on the perfection of the substrate, as imperfections and impurities will act as nucleation centers. We will call this the nucleation or condensation growth mode. (iii) The preceding growth mode becomes unlikely on "perfect" crystals and at low impingement rates, as trapped atoms will have sufficient time to migrate to kink sites where their incorporation leads to self-replication of the surface structure in growth by step propagation. Note that growth by condensation or step propagation is not predicated by temperature alone but by substrate perfection and impingement rates. (iv) Above the temperature of the roughening transition, predicted in 1951 by Burton, Cabrera and Frank¹⁾, solid surfaces

do not only exhibit atomic imperfections such as empty sites and atomic steps, but will be rough in that atoms from lower crystal planes are promoted to lattice positions above the zero Kelvin perfect plane, the driving force being the entropy gain in producing long range height fluctuations. For open and vicinal surfaces the roughening transition has been observed at temperatures as low as two-thirds of the melting temperature, whereas for closed-packed surfaces, the roughening transition is expected above melting, i.e. unobservable. The experimental situation of roughening has been reviewed recently by Engel²⁾. Obviously, epitaxy is only of interest below the roughening transition.

Standard high temperature chemical vapor deposition of semiconductors and metals is done several hundred degrees below their melting points whereas low temperature epitaxy, either by chemical vapor deposition or by molecular beams, is usually performed at temperatures as low and lower than half the melting point. Kasper and Jorke³⁾ have listed epitaxial temperatures for silicon above which epitaxial growth with ordered reconstructed surfaces is obtained. Not surprisingly they find that the epitaxial temperature depends on the surface orientation (because surface diffusion is different on different surfaces) and on the supersaturation pressure (because the rate of deposition is different). Thus, when epitaxial growth of a material onto a like substrate is attempted, the epitaxial temperature is determined by the fact that the diffusion rate should be faster than the rate of deposition to avoid freezing in a disordered layer, yet lower than the temperature of the roughening transition.

In the epitaxy of heterostructures further requirements must be met. In particular, temperatures must be so low as to avoid bulk interdiffusion of subsequently deposited materials, yet must be high enough to allow surface diffusion to establish ordered layers. Also the temperature must be low enough to freeze out surface segregation of impurities from the bulk.

This review is structured as follows: In the next section we briefly review relevant aspects of the theory of epitaxy, in particular the Stranski-Kossel theory, Bauer's criteria for the growth modes and the theory of Burton, Cabrera and Frank. In section 3 we will then

outline a macroscopic approach to surface kinetics for adsorption, desorption and diffusion, after which we will be, in section 4, present a microscopic view based on the kinetic lattice gas model. In section 5, we will then summarize some criteria for the low temperature regime of epitaxy.

2. CRYSTAL GROWTH

To understand crystal growth, we start from a clean and inert substrate with a lattice structure and surface orientation that will match those of the crystal to be grown. A gas particle in front of this surface will interact with it via a surface potential $V_S(\mathbf{r})$ that exhibits the translational periodicity of the surface, i.e.

$$V_S(\mathbf{z}, \mathbf{R} + \mathbf{R}_1) = V_S(\mathbf{z}, \mathbf{R}) \quad (2)$$

where we adopt the notation $\mathbf{r} = (\mathbf{z}, \mathbf{R})$ and

$$\mathbf{R}_1 = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 \quad (3)$$

where l_1 and l_2 are integers and \mathbf{a}_1 and \mathbf{a}_2 are lattice vectors in two dimensions spanning a surface unit cell. The minima of this surface potential define a set of localized adsorption sites separated by potential barriers, see Fig.1. We stress that this is the potential seen by a single gas atom. If some atoms are already adsorbed, the lateral interaction between adatoms must be added which might be characterized as nearest neighbor, next nearest neighbor etc. interactions. This leads to the formulation of the lattice gas model defined by a hamiltonian⁴⁾

$$H = E_S \sum_i n_i + \frac{1}{2} V_2 \sum_{\langle ij \rangle} n_i n_j + \frac{1}{2} V_2' \sum_{\langle\langle ij \rangle\rangle} n_i n_j + \dots \quad (4)$$

where we introduced, as microscopic variables, occupation numbers $n_i = 0$ or 1 depending on whether site i is empty or occupied. Arguing that the lattice gas hamiltonian (4) should give the same Helmholtz free

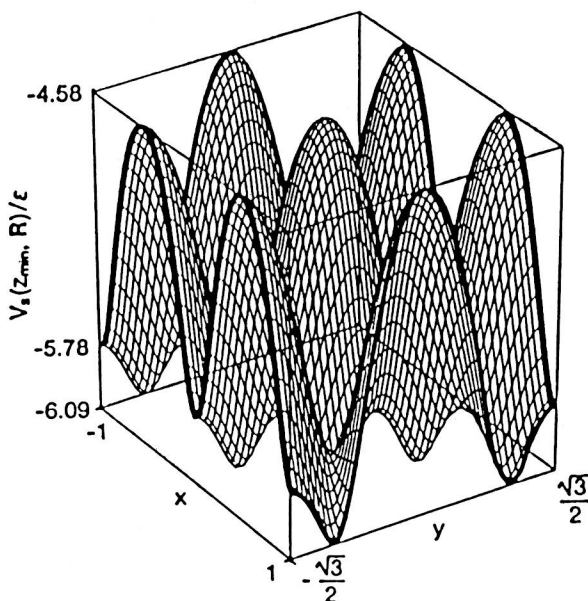


Fig.1: Schematic view of the bottom of the surface potential $V_s(z_{\min}, R)$ over an fcc(111) surface defining on top adsorption sites.

energy as a microscopic hamiltonian (for noninteracting particles), one finds that the single particle energy is given by⁵⁾

$$E_s = -V_0 - k_B T \ln(q_s q_{\text{int}}) - k_B T [\ln(\lambda_{\text{th}}^3 / k_B T) - \ln(Z_{\text{int}})] \quad (5)$$

Here V_0 is the (positive) depth of the surface potential at the adsorption site, and q_s is the single particle partition function of an adsorbed particle, i.e.

$$q_s = q_z q_{xy} \quad (6)$$

where

$$q_z = \exp(h\nu_z/2k_B T) / [\exp(h\nu_z/k_B T) - 1] \quad (7)$$

accounts for the motion perpendicular to the surface with similar expressions for q_{xy} accounting for parallel motion. If the adsorbing species are molecules, their internal partition function for rotations and vibrations might get changed upon adsorption from its free gas phase value Z_{int} to q_{int} , if some of the internal degrees of freedom get frozen out or frustrated. Note that ν_z is the vibrational frequency of the adsorbed particle around the bottom of the adsorption site and is typically of order 10^{12} - 10^{13} s⁻¹. Furthermore in (5),

$$\lambda_{th} = h/(2\pi m k_B T)^{1/2} \quad (8)$$

is the thermal wavelength of a particle of mass m at temperature T . P is the gas pressure above the surface. Returning to (4), we note that the second sum runs over nearest neighbors, denoted by $\langle ij \rangle$, interacting with a strength V_2 , and the third sum accounts for next nearest neighbor interactions of strength V_2' ; further terms can be added, if necessary. It is important to stress that (4) is the effective hamiltonian of a model system in which the motion of the adsorbed atom in its holding potential enters in a global fashion via single particle partition functions. Their temperature dependence being straightforward, see (6-7), it should not be ignored as done frequently in theoretical papers who assign a constant value to (5). Note in particular, that for $T < h\nu_z/k_B = 50$ - 500 K which at least for $\nu = 10^{13}$ s⁻¹ is well within the range of low temperature epitaxy, the temperature dependence is exponential, and thus far from negligible.

To obtain the equilibrium structure of N atoms adsorbed on N_s adsorption sites, one minimizes the Helmholtz free energy obtained from (4), usually employing Monte Carlo methods, thus generating the phase diagram of the adsorbate. If crystal growth were to always proceed layer by layer under equilibrium conditions with the completed layers acting as inert substrates, the task of a theorist would be complete at this stage. However, there are aspects of crystal growth that do not fit this simple picture: (i) A second layer may get started before the

first layer is completed; (ii) the completed layers are usually not inert but in thermal motion allowing for interdiffusion, particularly annoying if heterostructures are being fabricated; and, most importantly (iii) kinetic restrictions may prevent equilibrium structures to be formed in the first place.

An adsorbed atom diffusing across the surface may impinge on and join a cluster of adatoms and thus bring about growth. If such growth leads to the successive addition of two-dimensional monolayers, it proceeds in the Frank-van der Merwe growth mode. If growth is initiated by the formation of three-dimensional islands or hillocks, we are dealing with Volmer-Weber growth. And, lastly, if Frank-van der Merwe growth is followed by Volmer-Weber growth, we are faced with Stranski-Krastanov growth. Bauer⁶⁾ suggested simple criteria for these growth modes based on free energy considerations. We denote by σ_o , σ_s and σ_i the surface free energies of the overlayer, the substrate and the substrate-overlayer interface, respectively. Bauer's criteria can then be summarized as follows

$$\begin{array}{ll} \Delta\sigma = \sigma_o + \sigma_i - \sigma_s \leq 0 & \text{Frank-van der Merwe} \\ > 0 & \text{Volmer-Weber} \end{array} \quad (9)$$

suggesting, in particular, that the growth of a substance on itself is classified as Frank-van der Merwe. These criteria have been improved upon by including effects due to intermixing, mismatch, anisotropy, supersaturation and line tension around islands, as discussed in detail by van der Merwe⁷⁾.

As it is the ultimate aim of crystal growth to produce an equilibrium structure, it is worth our while to consider in more detail the novel features arising from the finite size of a growing crystal. We recall that the theory of large perfect crystals (at zero temperature) is rendered so simple by the fact that all atoms are considered to sit in identical bulk positions with the number of atoms on faces, corners and edges negligible. This allows one to introduce the concept of a repeatable unit cell for an infinite crystal, generated mathematically by periodic boundary conditions. Needless to say that this simple pic-

ture of a crystal breaks down at nonzero temperature when dislocations start to play a role. Kossel⁸⁾ tried to salvage the simplicity of infinite perfect crystals by constructing the surface of a finite crystal in such a way that a repeatable step will self-replicate the crystal. Stranski⁹⁾ identified this element as the half-crystal position or

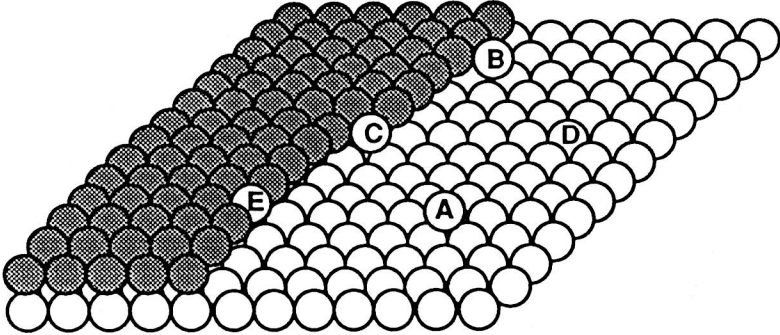


Fig.2: The surface of a solid with imperfections and the half-crystal position (C).

"Halbkristallage", indicated in Fig.2 for a square lattice. As atoms are added to this position during crystal growth, the shape and thus the specific thermodynamic properties of the finite crystal do not change. We can quantify these arguments by considering the chemical potential (per particle). For an infinite crystal we get in the harmonic approximation

$$\mu_C = -\phi_0 - k_B T \ln(q_3) \quad (10)$$

as the sum of a potential energy and an entropy contribution. Obviously for a finite but large crystal the chemical potential must be the same in all equilibrium crystal positions as well. Yet, for the lattice positions indicated in Fig.2, the potential energies, calculated in the simplest picture as the sum of nearest, and perhaps, next nearest neighbor bonds, are clearly not the same; neither are their vibrational entropies. However, for a particle in the half-crystal position we can

say that its potential energy and entropy contributions add up to μ_c , although they might individually be quite different from the values in (10). Indeed, the potential energy of a particle in the half-crystal position plays a decisive role in determining the shape of crystals and the thermal roughness of its faces. Only particles with an adsorption energy (the negative of the potential energy) equal or greater than that of the half-crystal position can be considered as condensed. Particles in other sites are more properly designated as a dilute, self-adsorbed layer. Referring to Fig.2, we note that particles in sites A and B have lower adsorption energies than those in D and E (and also in C) due to the smaller number of nearest neighbors, also, their vibrational entropies are lower, creating an overall chemical potential difference. Thus moving atoms initially adsorbed at sites A and B to sites D and E, respectively, will remove the chemical potential gradient and smoothen the surface except at higher temperatures where thermal excitations as depicted in Fig.2, become likely. Whether smoothing actually takes place, of course depends on the rate of surface diffusion to which we return below. Considerations of the chemical potential for the equilibrium shape of crystals have been reviewed very lucidly by Mutaftschiev¹⁰⁾ stressing in particular the role of dislocations in crystal growth. More recent advances have been described by Wortis¹¹⁾.

Within the Kossel-Stranski model of a perfect solid surface, Burton, Cabrera and Frank¹⁾ have developed a kinetic theory for crystal growth in the step propagation mode. Starting from a stepped surface as depicted in Fig.3, growth proceeds via particles impinging with a flux G and migrating toward and attaching themselves at the step etches which act as a particle sink thus generating a gradient in the 2-d density, $n(x,t)$. The relevant diffusion equation can then be written as

$$dn(x,t)/dt = Dd^2n(x,t)/dx^2 + v(t)dn(x,t)/dx + G/a \quad (11)$$

to be solved subject to the boundary conditions, $n(x=0,t)=0$, where $x=0$ is the position of the step advancing with a velocity $v(t)$. In the original work by Burton et al. $v(t)=0$. Note the assumptions in this model:

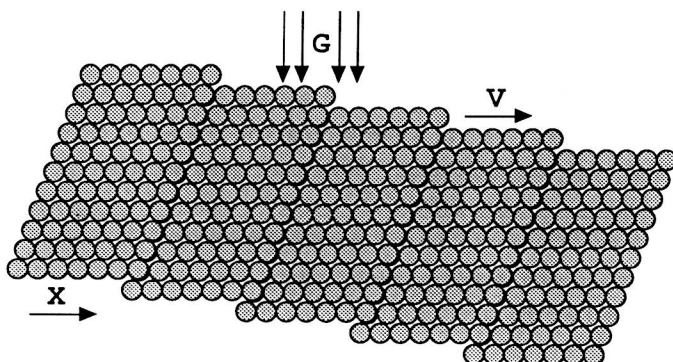


Fig.3: A staircase of parallel steps, perpendicular to the x-direction, separating terraces of equal width.

(i) Surface diffusion is so fast compared to adsorption that the number of particles on the terraces remains small. This implies (ii) that the diffusion coefficient remains independent of density and (iii) that interactions between particles on the terraces are negligible. Note that under equilibrium conditions, i.e. with the solid in equilibrium with its 3-d vapor, the density of particles adsorbed on the terraces is so small that a 2-d ideal gas model obtains

$$\Pi A = N k_B T \quad (12)$$

where Π is the 2-d spreading pressure, i.e. force per unit line, A is the area of a terrace and N is the number of particles adsorbed on it. The Burton-Cabrera-Frank model then applies under conditions of small supersaturation, i.e. when the average spreading pressure (average, because there is a density gradient on the terrace) is not much larger than the equilibrium pressure at that temperature along the co-existence line of solid and 3-d vapor.

Growth conditions for metal and semiconductor epitaxy are usually such that large supersaturation is encountered. This implies that particles adsorbing onto the terraces will encounter other adsorbed particles and form dimers, trimers and larger clusters due to their mutual attraction, before they can attach themselves at the steps. Starting