THIN FILMS SCIENCE AND TECHNOLOGY

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Growth of Crystalline Semiconductor Materials on Crystal Surfaces

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PREFACE

The dramatic development of electronics favours continuous progress and improvement of knowledge in the field of materials science applied to thin films used in electronics. The range of materials used is constantly increasing, their quality is improving, new methods emerge for the fabrication of film-type semiconductor structures and for the investigation of their properties, and new types of functional devices employing these structures are produced. Many researchers in solid-state physics and chemistry, crystal and film growth, semiconductor physics and solid-state electronics are working on the problems of thin films materials science and its application in industry. Numerous papers and communications reporting on results and progress in this field are published in many journals (sometimes in special issues) and in proceedings of conferences. There is therefore a need periodically for reviews and monographs on promising scientific and engineering trends in thin films and thin-film materials science.

The present book comprises two parts. The first part discusses the physical characteristics of the processes that occur during the deposition and growth of films, including those on the substrate surface, the principal methods of obtaining semiconductor films and of preparing substrate surfaces on which crystalline films are grown, and the main applications of films. Methods are presented for the theoretical description of film growth on the basis of statistical-probability and kinetic techniques and the simulation procedure.

The second part of the work gives new data on epitaxial interfaces and on ways of reducing transition regions in films and film-type devices, on the processes of crystallization and recrystallization of amorphous films, and on thermodynamic conditions, mechanisms and kinetic parameters of accelerated crystallization. The potentialities of methods of simulation of growth and doping of semiconductor films and the application of multi-layer film structures for light sources are shown.

The book is designed for physicists, chemists, and engineers specializing in crystal and film growth, semiconductor electronics, and various applications of thin films. I shall be grateful to

readers for any comments they may wish to make; these will be carefully considered and taken into account during the preparation of the Russian edition.

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L. ALEKSANDROV

LIST OF SYMBOLS

A	amorphous state
A	integrated property of the crystal
A^*	effective gradient of impurity concentration
AEC	accelerated explosive crystallization
ASC	accelerated shock crystallization
A_R^*	Richardson constant
α	lattice parameter, interatomic distance
α	thermal diffusivity
α_l	thickness of transition region
α_f, α_s	lattice parameters of the film and the substrate
α_i	kinetic coefficients
α_0	interplane distance in the crystal lattice
B	parameter of accelerated crystallization
b	sticking coefficient
$\mathfrak{b}$	Burgers' vector
C	heat capacity
C	concentration
C_0	initial volume concentration
C_s	initial surface concentration
C(x, t)	impurity distribution
C_i	impurity concentration
C_{if}, C_{is}	impurity concentration in the film and substrate
C_{ic}	impurity concentration in a solid phase
C_{i0}	impurity concentration in an initial phase
C_{is}	impurity concentration at the phase interface
$C_{2,t}$	tangential growth rate of grains
c	rate of nucleus growth
D	electrostatic induction
D	diffusion coefficient
D_e	diffusion coefficient in the solution
D_s	surface diffusion coefficient
D_{cr}	critical grain size
D	grain size
D	relative distances between neighbouring grains
$D(C_l)$	diffusion coefficient as a concentration function
d	layer thickness
d^*	maximum radius of the region of accelerated crystallization

d_i	width of crystallized concentric rings
d	critical continuous film thickness
d_m	thickness of transition layer
d_s	distance betwen the evaporator and the substrate
d_2^{ef}	path length of heat diffusion in substrate
d_1, d_2	thickness of the film or substrate
E_A	energy of adsorbed atoms
E_I	energy of the accelerated ions in the beam
E_k	energy of neutral atoms and molecules of the beam
E_T	energy of thermal motion of the substrate atoms
E_{ad}	activation energy of adatom adsorption
E_b	total bond energy of atoms
E_c	latent heat of crystallization
E_d	activation energy of adatom surface diffusion
E_0, E_m	binding energies at the points 0 and m
E^*	heat of crystallization
E_i^*	coupling energy of atoms in a cluster
ΔE_α	activation energy of crystallization
ΔE_f	latent heat of transition
F	distribution function
F_0	beam intensity
F_∞	equilibrium current from source
ΔF	change of free energy of the volume
G	elastic module
G_i	shear module components
ΔG^*	change of an isobaric-isothermic potential
$g^e_{0,\,1}$	energy of plastic deformation
$g^s_{0,\,1}$	elastic phase energy
H	step height
HRC	heat reflecting coating
HTC	heat transmitting coating
H	distance between dislocations
ΔH	latent heat of crystallization
ΔH_{ads}	change in enthalpy with adsorption
ΔH_c	heat of condensation
$\Delta H'$, ΔH_s	heat of sublimation
h	impurity evaporation rate
h	Planck constant
h_{cr}	critical film thickness destroyed coherence interface
I	nucleation rate
IR	infrared region of light emission
I_{im}	incident flow of impurities
I_m	flow of the main substrate

I_v	ion or molecular beam intensity
I_2	two-dimensional nucleation rate
i	angle of refraction
i*	number of atoms in a cluster
J	flow of atoms deposited on the substrate
J_F	direct current
J_{0m}	flow of atoms from the 0 point to the mth one
j	ion current density
K	equilibrium constant of reaction
K	heat conductivity
K_1, K_2	heat conductivity of the film or substrate
K_A	optical absorption coefficient
K_i	kinetic coefficients of film growth
K_T	temperature dependence of the lattice parameters
K	factor of proportionality for impurity capture
K	surface height (film thickness) in atomic layers
K'	impurity concentration independent of the rate
k	Boltzmann constant
k_0	absorption coefficient
K_i, K_D	coefficients of capture and desorption by surface reactions
K^*	equilibrium impurity distribution coefficient
K_{eff}	impurity effective volume distribution coefficient
K^s_{eff}	impurity effective surface distribution coefficient
L	number of the nearest neighbours in a lattice
L	total length of steps
L_d	diffusion length for atoms
L_i	radius of crystallized concentric rings
L_p	probability of atoms re-evaporation
L_s	root-mean-square atom displacement by diffusion
L_{sep}	probability of atoms separation
l	length of crystallized region
l, $\bar{l}$	distances between neighbouring grains and average distance
l_i	kinetic parameter of atoms aggregation
l_j	number of neighbours
M	mass value
Δ_M	mass line halfwidth
m	number of liquid samples
m_i	kinetic parameter of atom disaggregation
m_0	total number of samples
N	number of computer cycles

$N(x)$	phosphorus distribution in silicon
$N(R)$	distribution function of growth centres
N_a	acceptor concentration
N_d	donor concentration
N_{imp}	number of impurity atoms
$N_i\downarrow$	atom flow onto the substrate
N_i^{eq}	equilibrium atomic flow
N_L	layer impurity concentration
N_s	two-atomic surface networks impurity concentration
N_{sr}	uniform random surface impurity concentration
N_V	volume impurity concentration
N_0	density of centres on the surface
N_0	initial volume concentration
N_1	number of attached atoms
N_2	number of isolated atoms
n	beam density
n	impurity concentration
n_e	concentration of electrons
n_i	concentration of intrinsic carriers
n_i	density of a gas phase
n_r	reticular density of a singular face
n_s	electron boundary concentration
n_s	adatom concentration
n_0	number of re-evaporated atoms
n_0	reticular density of atoms on the surface
n_1, n_2	electron concentration in heavily and slightly doped sections
P	polycrystalline state
P	period of misfit dislocation
P_A, P_B	partial pressure of the A and B components
P_A', P_B'	partial pressure of the A and B components in a quasi-closed cell
P_d	probability of a diffusion jump per unit time
P_{d_i}	probability of diffusion in different directions
P_I	pressure of monoatomic vapour of iodine
$P_{I_2}^o$	initial iodine pressure
$P_i(t)$	probability of finding the system in the i state
P_m	filled fraction of the mth layer
$P_{m,\,ex}$	extended fraction of the mth layer
p	pressure
p	concentration of holes
Q_a	initial energy of amorphous phase

Q_{ad}	activation energy of adatom adsorption
Q_c	stored energy of crystallized phase
Q_s	acivation energy of adatom surface diffusion
Q_l	thermal effect of crystallization
q	energy released during the crystallization
q	impurity transport coefficient
q	elementary charge
q_D	probability of diffusion transition
q_l	phase transition energy
R	gas constant
R	linear rate of crystallization
R_+, R_{+i}, R_c	density of incident vapour flux
R_0, R_{01}, R_{CO}	rate constants
r	coordinate in the interface plane
r	size of grain
r_a	atom radius
r_D	Debye screening length
r_i	distance from interface to ion
r_0	core radius of dislocation
S	supersaturation (relative)
S	surface roughness as dispersion of film thickness
S	single-crystal state
S(R)	correlation function of growth centres distribution
S_i	entropy of state
S_0	substrate area
ΔS_{ads}	change in entropy with adsorption
T	temperature
ΔT	supercooling
T_a	melting point of amorphous phase
T_c	crystallization temperature
T_{cr}	temperature of the state of the complete shock crystallization
T_{colour}	operating colour temperature of light source
T_e	critical temperature of epitaxy
T_I, T_{ev}	temperature of source, evaporator
T_m	melting point of crystal
T_r^s	temperature of the start of recrystallization
T_s	substrate temperature
$T_{s(cr)}$	critical substrate temperature
T_x	characteristic Debye temperature
T_0	vapour temperature

T_0	substrate temperature
T_1	initial film-substrate temperature
T_1^s, T_2^s	temperature of the start of recrystallization
t'	dimensionless time
t^*	maximum time of accelerated crystallization pulse
t_m	growth time of continuous layer
t_1, t_2	time of the start of recrystallization
U	accelerated voltage
U	voltage
U	activation energy of grain growth
U_{eff}^r	effective activation energy of recrystallization
U_b	binding energy in the lattice
U_f	forward bias
u	silicon evaporation rate
u	deformation
V_c	film growth rate
V_{eff}	effective rate of film growth
$\mathcal{V}_{eff}^n$	effective growth rate by nucleation
$\mathcal{V}_{eff}^s$	effective growth rate by step movement
$\mathcal{V}_{imp}$	rate of arrival of impurity
V_{laser}	laser scan velocity
V_n	normal growth rate of grains
V_p	growth rate of grains by recrystallization
$\mathcal{V}_r$	critical film growth rate
V_t	tangential growth rate of grains
VR	visible region of light radiation
W	initial capacity of the layer source
W	dimensionless rate of film growth and evaporation
W_{ads}	adsorption energy on the surface
W_c	activation energy of crystallization
W_{eff}	effective activtion energy of growth
W_L	activation energy of melting
W_{NC}	activation energy of crystallization by furnace heating
W_S	activation energy of atom incorporation into the lattice
W_3	energy of three-dimensional nucleus formation
W^*	activation energy of crystallization
x	coordinate along the axis
X	relative composition of solid solution
X_0	distance between the dislocation and interface substrate-transition region

y	direction of movement
y_0	distance between step
α	degree of the beam ionization
α	absorption coefficient
β	kinetic coefficient for rate growth
β, β'	geometrical factors
β_0	coefficient of heat losses
β_i	relative excess of incident flux for an excess component
β_p	coefficient of volume packing of atoms in the lattice
γ	coefficient of surface packing of atoms
γ_i	relative excess of the component
γ_0	energy of residual stresses in an amorphous phase
γ_1	energy of residual stresses in a crystalline phase
γ_{12}	interface fraction occupied by misfit dislocations
δ	diffusive layer of growth
ϵ	mismatch of the lattice parameters
ϵ_0	permitivity of the environmental phase
ϵ_1	permitivity of the nucleus
η	constant of thermal background
η	fraction of the bulk crystallized
θ	degree of the surface covered with an adsorbent
θ	angle of deviation from singular surface
θ	angle of disorientation at the interface and between grains
θ_{max}	angle of disorientation with maximum surface energy
Λ	characteristic length of property change
Λ_0	length of property change by e times
λ	wavelength of light
λ_c	free path length of charge carriers
λ_i	transition probability from state E_i to E_{i+1}
λ_m	free path length of molecules in vacuum
$\lambda_{s, im}$	average diffusion length of impurity atoms
$\Delta\lambda$	displacement of spectral transmission dependence
μ, $\Delta\mu$	chemical potential of state and its change
$\mu(x)$	carrier mobility distribution in the film
μ_e	mobility of conduction electrons
μ_c	carrier mobility in the layer
μ_i	transition probability from state E_i to E_{i-1}
ν_α	frequency of atom attachment
ν	adatom vibration frequency
ν_i	atomic flow of components of a gaseous phase
ν_0	oscillation frequency of an atom

ν' Poisson's ratio

ν_i^{eq} equilibrium atomic flow of components

ξ kinematic viscosity of solution

ρ specific resistivity

ρ density

σ', σ surface tension of a two- and three-dimensional nucleus

$\sigma(x)$ film conductivity at a distance x from an interface

σ_i layer conductivity

σ_e dispersion of distribution for distances between grains

$\sigma_{\ell', im}$ image stress components

σ_{mn} thickness of transition region (arbitrary units)

σ_{ss} solid-solid surface boundary energy

σ_{vs} vapour-solid surface boundary energy

σ_{ls} liquid-solid surface boundary energy

$\sigma_{\Delta\alpha}$ heteroepitaxial stresses

τ optical transmission coefficient

τ stress of dislocation origination

τ normalized time

τ_d adatom diffusion jump time

τ_i time of incorporation

τ_m monolayer formation time

τ_n period of nonstationarity

τ_s adatom lifetime on the growth surface

τ_o atom vibration time

$\tau_{\Delta\alpha}$ shearing stresses

τ' dimensionless time

$\Delta\tau$ time interval for one elementary event

$\Phi(D)$ distribution function for relative distances

$\Phi(X)$ distribution function of the statistical law

Φ_B potential barrier height of a boundary

Φ_M metal work function

Φ_S chemical potential for electrons

$\Phi(X)$ electrostatic potential

$\Phi(X)\ \Phi_s^*\ \Phi_B-\Phi_s^*$ barrier height parameter at the interface, in the heavily and slightly doped sections

φ wetting angle

φ energy of the bond between neighbour atoms

φ potential

φ_{oi} bond energy of the ith atom with one neighbour

χ electron affinity of a semiconductor

ω_i concentration dependence of the lattice parameters

ω_i frequencies of atom separations

Chapter 1

PRODUCTION OF SEMICONDUCTOR FILMS

Over the two last decades thin film physics has become an independent subject in science. The number of publications in this field now exceeds 20000 (ref. 1). The area of research is rapidly extending owing to both a wide use of thin films in technology and fundamental studies in physics, chemistry and electronics, and to the development of new effective chemical (gas-transport reactions) and physical (plasma-ion sputtering, molecular beams in vacuum) methods of thin film production.

Much attention is paid to studies of films of solids: metals, semiconductors, dielectrics, in which properties connected with a zone structure are combined with film peculiarities. Use of the term "film" usually means a three-dimensional structure with one geometrical parameter (thickness) that is much less than the other two. Films in the thickness interval 0.01-1 μm are generally called "thin" and those from 1 to 100 μm "thick" (ref. 2). However, a physical measure of film "thinness" is the length of operation of various characteristic parameters, e.g. a Debye screening length r_D, dislocation spacings, free path length of charge carriers λ_S. The thinner the film, the more its properties are determined by its surface. Therefore, with a variation of thickness within the limits comparable with typical parameters, the film properties change and the observation of size effects indicates the influence of thickness on the properties. The most important requirements of the growth processes for obtaining semiconductor films are that they provide a film of uniform thickness in a wide interval of doping, and stability with time.

1.1 Growth and Structure of Epitaxial Semiconductor Films

Among a wide range of crystal growth problems, epitaxial growth of crystals and films deserves special attention to enable one to obtain single-crystalline films of semiconductors, ferroelectrics, and other materials at oriented crystallization on single-crystal-substrates. The properties of crystals and films necessary for microelectronics, opto- and acoustoelectronics are obtained more optimally on single-crystalline structures, except for some special cases. On the other hand, the homoepitaxial film growth is real-

ized many times in all processes of crystal growth, which are a totality of layers grown in succession.

The general concept of the processes of epitaxial (oriented) film crystallization has recently been advanced considerably because much experimental information has been obtained. However, a quantitative description of the kinetics of epitaxy and film structure formation and of the effects of epitaxial conditions on the film parameters is not always possible even for simple cases such as condensation of single materials in high vacuum. Of great importance is the initial stage of epitaxy, at which both film and transition layers are formed. The problem of reducing the transition region is part of a more general problem, i.e., the need to obtain homogeneous films in depth. The solution of this problem requires a complete elucidation of the mechanisms of epitaxial film growth. Some progress in obtaining semiconductor films, including superlattices with a periodic structure of several monoatomic layers of the GaAl-GaAs type, has been achieved by computer-controlled molecular beam epitaxy in vacuum. In this system, continuous control of the film properties and the corresponding necessary changes to the film growth and deposition conditions are made by a computer (ref. 3). However, formation of vacancies, stacking faults, inclusions, and dislocations are difficult to control. The conventional methods of epitaxial film deposition differ from each other in their formation processes, which depend on a non-equilibrium vapour, liquid, or solid phase whose transition into an equilibrium state on the oriented single crystal surface leads to film formation.

There are three principal methods to describe thin film growth. The first is the thermodynamic method, which evaluates the system deviation from the equilibrium state and considers nucleation and growth as quasiequilibrium processes. The atomistic method uses the molecular-kinetic concept of the interaction between atoms adsorbed on the substrate and between the adatoms and the substrate. The kinetic method considers the lifetime conditions of atoms on the substrate and describes successive states of adatom clusters of different sizes with a set of linear differential coupling equations.

Thermodynamic and kinetic parameters of epitaxial growth

The thermodynamic description of film growth is the most well established and consistent description. The main thermodynamic parameters of deposition are temperature and pressures (concentra-