MATHEMATICAL MODEL OF THE ALLOYING PROCESS AT THE EPITAXIAL SEMICONDUCTOR STRUCTURE GROWTH

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REZUMAT. În această lucrare este prezentat modelul matematic al procesului de aliere cu GaAs a straturilor epitaxiale obținute în sistemul Ga-AsCl$_3$-H$_2$ cu transport de reacții. Controlul în sistemul automat se realizează prin reglarea temperaturii dopanților de Zn/Te care alimeantează cu fluxul de vapori camera reactorului. Fluxul de vapori generat în camera sursei este transportat de fluxul de hidrogen şi ajunge în zona de creştere a straturilor epitaxiale cu o reținere. În sistemul automat parametrul de optimizare este timpul de umplere cu vapori a reactorului şi timpul de evacuare.

Cuvinte cheie: GaAs, procesul de aliere straturilor epitaxiale, modelul matematic.

ABSTRACT. In this paper is presented the mathematical model of the alloying process of GaAs epitaxial layers obtained by the transport reactions in the Ga-AsCl$_3$-H$_2$ system. The automatic control system (ACS) works by temperature measurement of alloying substance (Zn/Te). The vapour flux, generated in the chamber of alloying source and transported in the reactor by the hydrogen flow, it is arrived in the growing zone with a delay. In this technological process the optimization parameters are the time of the reactor filling with vapour and the time of evacuation after the vapour flow is interrupted.

Keywords: GaAs, epitaxial technology, alloying automatic control, mathematic model.

1. INTRODUCTION

The technological process is a material base of any production. In this case the securing of the guided technological processes and introduction the automatic control system (ACS) in production represents one from principal means of manufacturing parameters increasing as e.g. output, labour productivity, profitableness, final product quality etc. The mathematical description of the technological process is a virtual base for the structure and ACS algorithm building.

ACS plays the leading part in the epitaxial technology of A^3B^5 semiconductor structures with the reactions transport (HVPE) [1]. The technology utilization for the semiconductor devices industry, for example GaAs, allows to manufacture the competitive devices in the high temperature microelectronics [2].

The problem of ACS introduction in epitaxial technology with reactions transport (HVPE) consists in the deficiency of operative control means of the semiconductor structure parameters on during of the manufacture process. The circumstances of maximum purity in IEC-3/4R installation reactor of epitaxy exclude any direct measure device applied e.g. for concentration of atom impurity in alloying process of the obtained structure.

In this work it is presented the mathematical model of the programmed alloying technological process of GaAs epitaxial structure for indirect automatic control of vapour concentration of zinc (Zn) or tellurium (Te), as well as control quality adjusting of the vapour flow on growing substratum in this conditions.

2. DESCRIPTION OF THE ALLOYING PROCESS THE GAAS EPITAXIAL LAYERS

A. The GaAs epitaxial process in the AsCl$_3$ – Ga - H$_2$ system.

The growing process of the GaAs epitaxial layers in the AsCl$_3$-Ga-H$_2$ gas system takes place in the horizontal reactor of quartz with round form of pipe under the low pressure (p=10-100 Pa). The principle scheme of the gas flows is shown in the Figure 1.

The reactor with GaAs substratum is supplied with three gas flows F_{Zn}, F_{Te}, $F_{Ga,As}$ at the input, which transports the substances of Ga, As, Zn, Te, H$_2$ under the vapour form with specific concentration C_{zn}, C_{Te}, C_{H2} ... etc.

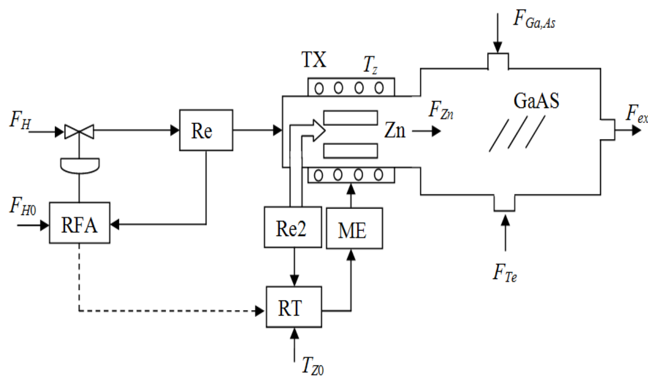

Fig. 1. The principal scheme of gas flows in the epitaxial system $AsCl_3$-Ga-H_2, technology and the automatic control subsystem of zinc vapour flow.

The flow of gas F_{ext} at the output of the reactor does not represent the sum of gas flows at the input of the reactor, after chemical reactions of deposition the semiconductor layers.

$$F_{Ga,As} + F_{Zn} + F_{Te} + F_{Ht} \neq F_{ext} \quad (1)$$

where: $F_{Ga,As}$ is equal with mixture of the gallium and arsenic vapours transported in reactor by the hydrogen partial flows, which are fixed (settle) constantly during the whole technological process, [l/s]; F_{Zn} and F_{Te} represent the vapours flows of zinc or tellurium respective, which are transported in reactor by the hydrogen flow F_i through separate channels. The flows are variable from process to process.

$F_{Ht} = F_{H1} + F_{H2} + F_{H3}$ – represent the total hydrogen flow at the input of reactor through respective channels. It is considering equal with hydrogen flow at the exit of reactor.

Holding in account, that the products of chemical reactions are deposited on the GaAs substrates and inside of reactor surfaces, as mono- or poly-crystalline layers, the control of this parameters can't be done during the technological process. Therefore, this parameters can not be utilized in the automation control system.

The reaction of stoechiometric GaAs deposition is determined by partial concentrations [mol/l] of Ga and As substances at the input of the reactor, but this parameters can not be measured directly by the sensors, because those processes take place in the technological conditions with the microelectronic purity at high temperature and the presence of any sensor in the reactor contradicts with it.

Because, the concentrations of zinc and tellurium flows are variable, we will reference to the alternative automation control of the concentrations at the input of reactor and to the experimental adjustment of the final parameter of alloying concentration inside of the epitaxial layers.

B. Determination of the vapour pressure of the solid body.

The chamber for alloying source (Zn or Te) represents a quartz pipe with 7 mm of internal diameter, length 120 mm with the resistive heater winded on the external surface of the pipe (Figure 2).

The alloy material in the cylindrical form with diameter 0.3 cm and length 0.8 cm is installed in the quartz pipe. The hydrogen flow is experimental established equal with 1.0 cm^3/s. The hydrogen delivers the vapors flux F_z from the exit of alloy chamber towards the interior of reactor passing through the pipe transversal section 0.384 cm^2 with 2.6 cm/s of velocity.

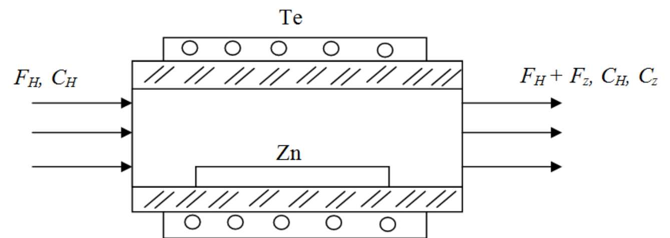

Fig. 2. Physical model of the alloy (Zn/Te) chamber.

In the Figure 2 are presented the following notations: T_0 – heater; F_h, C_h – hydrogen-gas flow and its concentration at the reactor input; Z_n - alloy material (pure Zn/Te); F_z– vapour flow in the heating chamber; C_z – partial concentration of zinc vapour at the exit of the reaction chamber.

Thus, at the exit we have the flow of gas mixture bigger than input flow, which can be controlled:

$$F_{tZ} = F_h + F_{Zn} \quad (2)$$

The flux of vapours F_z can be estimated, if we are analyzing the mono-component gas-liquid system presented in two phases, which have the general condition of the chemical phase equilibrium equal with

$$\mu^l = \mu^g \quad (3)$$

where: μ_i is the chemical potential of i- component.

The chemical potential of all components of one system that is in equilibrium have the same value. The vapour pressure of pure liquid is defined as the vapour pressure what is in the thermodynamic equilibrium with the liquid phase.

The dependence equation by the temperature of a pure liquid is expressed by the Clapeyron relation, in which the variation of the molar volume at the

vaporization $\Delta Vm.vap$ can be written in function of molar volumes of the study substances in two phases (gas-liquid):

$$\frac{dP}{dT} = \frac{\Delta H_{m.vap.}}{T \cdot \Delta V_{m.vap.}} \qquad (4)$$

where: $\Delta V_{m.vap.}$ and $\Delta H_{m.vap.}$ is referred to the variation of the molar volume of liquid and the molar entropy of the respectively liquid. If $\Delta V_{m.vap.} = V_{m.g.} - V_{m.l.}$, where the volume phase liquids $V_{m.l.}$ can be negligible and at the relatively small pressure it can be applied the ideal gas law. The equation (4) can be written as follows:

$$\frac{dP}{dT} = \frac{P \cdot \Delta H_{m.vap.}}{RT^2} \qquad (5)$$

where: R – gas universal constant equals $R = 8.314(\mathrm{J}\times\mathrm{K}^{-1}\times\mathrm{mol}^{-1})$. Expression (5) can be presented in the follow form

$$d \ln P / dT = \Delta H_{m.vap.} / RT^2 \qquad (6)$$

The formulas (5), (6) are the Clausius-Clapeyron equations specific by the liquid-vapour equilibrium for a mono-component system [3]. The integration of the equation (6) can be simple done if it is admitted that molar latent heat of vaporization $\Delta H_{m.vap.}$ is not dependent of the temperature. This statement is valid for the narrow area of temperature. In this case it can be obtained the following relation:

$$\ln P = -\frac{\Delta H_{m.vap.}}{R}\left(\frac{1}{T}\right) + C \qquad (7)$$

where: C – constant of integration; $\Delta H_{m.vap.}$ - latent molar heat of the vaporization as medium in the given temperature area.

The equation (7) can be expressed in the exponential form as:

$$P = c_0 e^{\left(-\frac{\Delta H_{m.vap.}}{RT}\right)} = c_0 e^{-\frac{A}{T}} \qquad (8)$$

where: $A = \frac{\Delta H_{m.vap.}}{R}$, $c_0 = \exp(C)$ express the fact, that the vapour pressure exponential increases with increasing temperature.

The solid substances have a vapour pressure at temperature less of melting point temperature, but the pressure is dependent of temperature and it can be expressed by the Clausius-Clapeyron equation for liquid-vapour equilibrium, but instead the latent heat of vaporization it is used the molar latent heat of sublimation $\Delta H_{m.sub.}$. In this case equation (7) is presented in the following form:

$$\ln P = -\frac{\Delta H_{m.sub.}}{R}\left(\frac{1}{T}\right) + C = -\frac{A}{T} + C, \qquad (9)$$

where: $A = \frac{\Delta H_{m.sub.}}{R}$, $\Delta H_{m.sub.}$= experimental constant.

If it is known the value of the factor A it is possible to calculate the C constant using a couple $(\ln p - (1/T))$ of values. The knowledge the value of A and C permits in expression (9) to calculate the vapour pressure of solids at some temperatures in the given area.

C. The calculation of the saturated vapour mass in the reaction chamber.

The hydrogen flow at the entrance in the reaction chamber is given as 1.0 cm^3/s. Having molar concentration equals one unit, e.g. mol/l, the hydrogen concentration C_h at the exit of the chamber will be the mixture of zinc/tellurium vapours, which is determined by experimental method [4]. In the Table 1 it is presented the experimental results of the saturated vapour pressure, atomic mass, melting temperature and latent molar heat of vaporization of the alloying materials zinc and tellurium.

Table 1

The saturated vapour pressure of zinc and tellurium as function of vaporization temperature [4]

Material	Molar mass, g	Melting temperature, °C	Pressure, Pa	Vapour temperature, °C	Latent molar heat, kJ/mol
Zinc	65.37	419.5	0.1333	247 (s)	130.5
			1.3332	291(s)	
			13.332	343(s)	
			133.32	487(l)	
Tellurium	127.6	449.8	0.1333	322 (s)	215.6
			1.3332	374(s)	
			13.332	434(s)	
			133.32	525.5(l)	

The methods of determination the saturated vapour pressure [5] are based on the kinetic theory relations of the gas. They are used in the research of small pressure of vapours under the condensed phase about 10 – 10^{-3}

Pa. The m - mass of vaporized substance in vacuum onto unity of surface in one second is calculated by the expression:

$$m = p\alpha\sqrt{M/(2\pi RT)} \qquad (10)$$

where: p – vapour pressure; α - Lengmiur coefficient; M – molecular mass kg; T- thermodynamic temperature at which pressure is measured.

The formula (10) can be utilized for determination the vapour flow in the epitaxial process at the same pressure interval with linear velocity of hydrogen flow of 2.6 – 3.0 cm/s. The performed calculation results are presented in the Table 2, where the concentration of zinc and tellurium vapour it was calculated from the experimental data (Table 1) and the vaporized source surface at the constant hydrogen flow $F_h = 0.446\cdot10^{-4}$ mol/s.

Table 2

The concentration of Zinc and tellurium vapours.

Material	Surface, m^2	Pressure, Pa	Temperature , K	Vapour mass, $mol/m^2\cdot s$	Vapour flow, $mol/s\cdot10^{-4}$	Exit concentration, molar part
Zinc	0.38 10^{-4}	1.333	564	0.03	0.0114	0.0249
		13.332	616	0.29	0.11	0.2466
Tellurium	0.42 10^{-4}	1.333	647	0.02	0.0084	0.0185
		13.332	707	0.19	0.0798	0.152

3. THE MATHEMATICAL MODEL FOR THE PROCESS OF MIXTURE

In the volume V of the chamber from Figure 2 is taking place the mixture process between hydrogen flow F_h and the vapour flow of zinc/tellurium F_{zn}. It is necessary to obtain the gas mixture with datum concentration of the alloying material. For the stationary regime of the process can be written the following relation:

$$\rho F_h C_h + \rho F_{zn} C_{zn} - \rho F_{e_0} C_{e_0} = 0 \qquad (11)$$

where: ρ – vapour density, F_h – hydrogen debit, F_{zn} – vapour debit, C_h – hydrogen concentration, F_{e0} – debit of chamber evacuation, C_{e0} – vapour concentration of mixture.

The dynamic regime of the process is described by the relation:

$$\rho F_h C_h + \rho F_{zn}(t) C_{zn} - \rho F_e(t) C_e(t) = \rho V C_e(t)/dt \qquad (12)$$

where: $C_e(t) = C_{e_0} + \Delta C_e(t),\ F_{zn}(t) = F_{z_0} + \Delta F_{zn}(t)$.

After replacing and omission the terms of high order it was obtained the following relation:

$$(V/F_{e_0})[dy(t)/dt] + y(t) = \left[(C_h - C_{e_0})/C_{e_0}\right]\left(F_{zn_0}/F_{e_0}\right)m(t)$$

where: controlled magnitude is $y(t) = \Delta C_e(t)/C_{e_0}$; execution magnitude is $m(t) = \Delta F_{zn}(t)/F_{zn_0}$.

The transfer function of the dynamical model is inferred by the operational calculus:

$$H_p(s) = \frac{k_p}{(\tau_p s + 1)} \qquad (14)$$

where: $k_p = \left[(C_h - C_{e_0})/C_{e_0}\right]\left(F_{zn_0}/F_{e_0}\right)$ and $\tau_p = (V/F_{e_0})$.

It follows, the gas mixture process behaves as a first order element with inertia.

6. CONCLUSIONS

The elaborated mathematical model of the alloying process of GaAs epitaxial layers, obtained by the technology with reactions transport in the Ga-AsCl-H_2 gas system permits adjustment the automat control quality of vapour concentration (Zn/Te) in growing zone of the reactor while the automat controller is operating with the substances temperature as a dimension of control. The flow of vapour generated in the alloying source chamber and transported to the reactor by the hydrogen, it is arrived in growing zone with a delay because the reactor volume is bigger than the alloying chamber. In this technological process the optimization parameters are the time of the reactor filling with vapour and the time of evacuation after the vapour flow is interrupted. They are in the direct relation with the productivity of the vapour source and we must to minimize it by introducing the override-control of the temperature.

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