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Novel approach to investigation of semiconductor MOCVD by microreactor technology

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Abstract. Metal-Organic Chemical Vapour Deposition is a very complex technology that requires further investigation and optimization. We propose to apply microreactors to (1) replace multiple expensive time-consuming macroscale experiments by just one microreactor deposition with many points on one substrate; (2) to derive chemical reaction rates from individual deposition profiles using theoretical analytical solution. In this paper we also present the analytical solution of a simplified equation describing the deposition rate dependency on temperature. It allows to solve an inverse problem and to obtain detailed information about chemical reaction mechanism of MOCVD process.

1. Introduction and methodological issues of MOCVD technology

Metal-Organic Chemical Vapour Deposition (MOCVD) is one of the most popular processes for deposition of semiconductor thin films [1,2]. Single-specie (Si, Ge) or compound semiconductors (GaAs, CdTe and others) are deposited as monocrystalline, polycrystalline or amorphous films [3,4]. Materials produced by MOCVD process are widely used in microelectronics and photonics devices [5]. The MOCVD technology has been actively investigated in the past few decades, however there are still open questions and technological issues to be tackled for new materials and reactors [6-8].

MOCVD is a complex process with a large number of technological parameters, which strongly influence film properties. The main process parameters are temperature, pressure, flow rate, chemical composition of gas phase, reactor geometry, residence time and surface properties. This is a big advantage of the MOCVD technology, because we can accurately tune the deposition process to produce a film with the optimal properties for a specific application. At the same time it is a disadvantage, because it is very difficult to find these optimal conditions from the thousands of possible parameter sets. To solve the problem of multi-parameter optimization, researchers and process engineers carry out many laboratory and numerical experiments. To cover all possible sets of process parameters, ideally more than 10⁷ experiments shall be carried out – infeasible in current experimental or computational research. In this paper we propose a new approach to investigation of semiconductor MOCVD by microreactor technology.

Microreactor Chemical Vapor Deposition (μR CVD) is a variation of the CVD method, where the main distinguishing feature is a localized material deposition achieved by a special configuration of gas streams in the microreactor. This gas stream configuration is provided by the microsystem devices located near the substrate, called microreactors.
There are many types of microreactors. The simplest configuration has just one microchannel, as shown in Figure 1. Advanced modifications have additional channels for precise deposition control, investigated in our previous work [9,10].

Typical size of deposition area is around 100 μm. It allows using this approach in two different ways: (1) replacing many time-consuming macroscale experiments with one microreactor deposition with many points on one substrate; (2) deriving chemical reaction rates from individual deposition profiles using theoretical analytical solution. In the following two sections we describe these methods in more detail.

2. Experimental method for deposition of thousands of point-samples by μR CVD process

Equipment for implementation of μR CVD technology can be built from a standard CVD tool, which includes a process chamber, substrate holder with a heater, gas supply and exhaust or vacuum system. We only need to add a microreactor and a system (robot “arm”) for its movement above the substrate.

During the deposition process gases (precursors and carriers) are supplied to the microreactor, which than generates specially configured gas streams. Because the microreactor is located very close to the substrate (at a distance of up to hundreds micrometers), deposition is localized on a small area (less than 100 μm diameter [10]). This way, one point-sample is produced. An array of these point-samples is created by step-by-step movement of the microreactor over the substrate, like in a standard ink printing technology (as shown in Figure 2). For each point we can modify process parameters in an automated programmed regime.

On one 4-inch substrate, we can deposit an array of around 7000 point-samples, so we need only 15 wafers to cover 10^7 experimental points. Then we use standard automatic inspection equipment to investigate the deposition results. They provide chip inspection (optic, electron microscopy, atomic force microscopy, electric testing, spectrum analysis, etc.) on wafers with a rate over 1 wafer per hour. These tools are widely spread on any semiconductor or MEMS factory.

This way, application of μR CVD technology provides abundant experimental information about the CVD process from a single wafer. The number of experimental samples in μR CVD is several orders of magnitude higher than in the traditional CVD experimental technique. Our approach promises a faster progress in CVD research. It is a powerful instrument for development and optimisation of deposition technology.

3. Mathematical model of chemical kinetics mechanism in μR CVD process

The second application of μR CVD for investigation of CVD technology is deriving chemical reaction rates from individual deposition profiles using theoretical analytical solution. We developed a mathematical model of one-jet axisymmetric microreactor to show a dependency between the profile and kinetic parameters of chemical processes during the deposition. In the model we make several assumptions: constant gas density, one-dimensional “ideal plug flow” reactor, the microchannel is replaced by a point gas source of zero width (see Figure 3).
We consider two ring cross-sections (L) and (N) as shown in Figure 3. In cross-section (L) at a distance \( r \) [m] from the point gas source, volume concentration of gas precursor “A” is \( C_A(r) \) [mol/m\(^3\)] and velocity is \( V(r) \) [m/s]. In cross-section (N) at the distance \( \delta r \) [m] from cross-section (L), concentration and velocity are \( C_A(r+\delta r) \) and \( V(r+\delta r) \) respectively. Point gas source provides gas flow \( G \) [kg/s] (for gas with constant density \( \rho \) [kg/m\(^3\)], volumetric flow rate is \( Q \) [m\(^3\)/s]). Gas precursor “A” is chemically reacting and leading to material deposition on the substrate. This deposition flux on the surface has rate \( \chi \) [mol/(s·m\(^2\))], from which we can calculate deposition rate \( \chi \) [μm/s] of CVD process using density of material \( \rho_m \) [kg/m\(^3\)].

![Point gas source](image)

**Figure 3.** Explanatory scheme for a mathematical model of one-jet axisymmetric microreactor.

As the first approximation, we neglect mass transfer by diffusion along the radius, which is justified a small radius and high gas velocities. In this case the mass balance equation for volume between the cross-sections (L) and (N) can be written as

\[
-\frac{G}{\rho} C_A(r) + \frac{G}{\rho} C_A(r+\delta r) + \pi(-\chi)((r+\delta r)^2 - r^2) = 0,
\]

where the first term is molar flux of precursor “A” through cross-section (L), the second term is molar flux of precursor “A” through cross-section (N) and the third term stands for consumption of precursor “A” due to the surface chemical reaction. Using a Taylor series and omitting the terms of \( O(\delta r^2) \), we transform (1) in (2):

\[
-\frac{G}{\rho} C_A(r) + \frac{G}{\rho} C_A(r+\delta r) + \pi(-\chi)((r+\delta r)^2 - r^2) = 0,
\]

\[
Q \frac{dC_A(r)\delta r}{dr} + 2\pi(-\chi)r\delta r = 0,
\]

\[
-\frac{dC_A(r)}{(-\chi)} = \frac{2\pi}{Q} r dr,
\]

\[
-\int_{C_{A0}}^{C_A} \frac{dC_A(r)}{(-\chi)} = \frac{2\pi}{Q} \int_0^r r dr,
\]

\[
\frac{\int_{C_{A0}}^{C_A} \frac{dC_A(r)}{(-\chi)}}{(-\chi)} = \frac{\pi}{Q} r^2
\]

Equation 2 is the basic equation for calculation of precursor concentration in a one-jet axisymmetric microreactor. We consider two cases. The first case is a zero-order surface chemical reaction, meaning

\[ (-\chi) = k_0, \]
where \( k_0 \, [\text{mol/s} \cdot \text{m}^2] \) is a reaction rate coefficient. In this case equation (2) can be re-written as

\[
\int_{C_{A0}}^{C_A} \frac{dC_A(r)}{k_0} = \frac{\pi}{Q} r^2
\]  

(3)

After integration we obtain

\[
C_A(r) = C_{A0} - \frac{\pi k_0}{Q} r^2,
\]

(4)

where \( C_{A0} \) is the concentration of precursor “A” at the point source. The zero-order reaction is independent from the concentration of precursor “A”, thus the deposition profile is uniform \((-\chi) = k_0)\) from the center till \( r_{crit} \), which is calculated from conditions

\[
C_A(r_{crit}) = 0,
\]

\[
r_{crit} = \left( \frac{QC_{A0}}{\pi k_0} \right)^{1/2}
\]

(5)

During experimental investigation we set \( C_{A0} \) and \( Q \) and measure the deposition profiles. In this way we obtain value of \( r_{crit} \) and from (5) we calculate \( k_0 \) for the surface reaction. Carrying out two experiments for different \( Q \) we find \( C_{A0} \) if its value is not known with sufficient accuracy. In addition, based on equation (5) we find gas flow \( Q \) and precursor concentration \( C_{A0} \) to obtain a deposition area of a specified size.

The second case is the first order of surface chemical reaction. It means

\((-\chi) = k_1 C_A(r), \)

where \( k_1 \, [\text{m/s}] \) is a reaction rate coefficient. In this case equation (2) can be written as

\[
\int_{C_{A0}}^{C_A} \frac{dC_A(r)}{k_1 C_A(r)} = \frac{\pi}{Q} r^2
\]  

(6)

After integration we obtain

\[
C_A(r) = C_{A0} \exp \left( -\frac{\pi k_1}{Q} r^2 \right)
\]

(7)

Expression for a deposition rate distribution \( X \, [\text{m/s}] \) is

\[
X(r) = \frac{M k_1 C_A(r)}{\rho_m},
\]

(8)

where \( \rho_m \, [\text{kg/m}^3] \) is density of deposited material, \( M \) is molar mass of deposited material. Expressing \( C_A(r) \) from (8) and substituting it in (7), we derive an expression for the deposition rate distribution:

\[
X(r) = X_0 \exp \left( -\frac{\pi k_1}{Q} r^2 \right)
\]

(9)

From (9) we derive an equation for the reaction rate coefficient (10). With a known flow rate \( Q \) we measure the deposition rate in two points \( X(0) \) and \( X(r) \) to find this coefficient:

\[
k_1 = \frac{Q}{\pi r^2} \ln \frac{X(0)}{X(r)}
\]

(10)

Reaction rate coefficients usually depend on temperature, as described by equation (11)

\[
k(T) = A_p \exp \left( \frac{-E_a}{RT} \right),
\]

(11)

where \( A_p \) is pre-exponent factor and \( E_a/R \) is activation temperature. It is easy to obtain a temperature dependence of surface reaction rate coefficient providing process of \( \mu \text{R CVD} \) at different temperature. It is possible to calculate pre-exponent factor and activation temperature from the experimental data.
4. Results of mathematical modelling of chemical kinetics mechanism in μR CVD process

To illustrate a microreactor deposition process described in our model, we consider an example of the microreactor with the following parameters: source concentration $C_{AO}$ is 0.01 mol/m$^3$, density $\rho_m$ and molar mass $M$ of deposited material are 2000 kg/m$^3$ and 0.046 kg/mol respectively. For these conditions, we consider the zero-order and first-order surface reaction. We then investigate the distribution of precursor “A” and deposition profiles in the microreactor at different temperatures. The results are presented in Figures 4 and 5.

![Figure 4](image4.png)

Figure 4. Distribution of precursor concentration (a) and deposition rate (b) in microreactor for the zero-order reaction and flow rate $Q=5 \cdot 10^{-11}$ m$^3$/s. Surface chemical reaction has pre-exponent factor $A_p=0.0025$ and activation temperature $E_a/R=1000$ K.

![Figure 5](image5.png)

Figure 5. Distribution of precursor concentration (a) and deposition rate (b) in microreactor for the first-order reaction and flow rate $Q=10^{-10}$ m$^3$/s. Surface chemical reaction has pre-exponent factor $A_p=0.25$ and activation temperature $E_a/R=1000$ K.

Figures 4 and 5 illustrate the property of microreactors to provide localized deposition at different temperatures. It is possible to design reactors for μR CVD process taking into account these graphs and equations (4)-(11). In addition these equations give a way to analyze the deposition profiles and to calculate rate coefficient for surface chemical reaction.

5. Conclusions and future work

We propose microreactors for replacing time-consuming macroscale experiments with one microreactor deposition and for extracting chemical reaction rates from individual deposition profiles. This way, a very large number of experiments (around 7000) can be carried out on one wafer. This abundant amount of experimental results is a great value in itself. The second way to use microreactor deposition is deriving chemical reaction rates from individual deposition profiles. In this paper we
developed a simplified mathematical model of a one-jet microreactor and provided an analytical solution to calculate chemical kinetics parameters. Therefore we propose to apply the method of μRCVD for detailed investigation of chemical processes during MOCVD.

Our model makes some assumptions. We plan to develop more detailed analytical models with multistep reactions and diffusion to study the influence of these assumptions. A complete mathematical model cannot be solved analytically, thus we will use numerical approaches and computer simulations based on our previous research [9,10]. In addition the next step of our research will include experimental application of microreactors in investigation of semiconductor MOCVD.

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