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A novel three-jet microreactor for localized metal-organic chemical vapour deposition of gallium arsenide: design and simulation

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Abstract. We present a novel three-jet microreactor design for localized deposition of gallium arsenide (GaAs) by low-pressure Metal-Organic Chemical Vapour Deposition (MOCVD) for semiconductor devices, microelectronics and solar cells. Our approach is advantageous compared to the standard lithography and etching technology, since it preserves the nanostructure of the deposited material, it is less time-consuming and less expensive. We designed two versions of reactor geometry with a 10-micron central microchannel for precursor supply and with two side jets of a dilutant to control the deposition area. To aid future experiments, we performed computational modeling of a simplified-geometry (two-dimensional axisymmetric) microreactor, based on Navier-Stokes equations for a laminar flow of chemically reacting gas mixture of $Ga(CH_3)_3$-AsH_3-H_2. Simulation results show that we can achieve a high-rate deposition (over 0.3 μm/min) on a small area (less than 30 μm diameter). This technology can be used in material production for microelectronics, optoelectronics, photovoltaics, solar cells, etc.

1. Introduction

Gallium arsenide (GaAs), with its high electron mobility and direct bandgap, is traditionally used in RF electronics, photonic devices and solar cells [1]. GaAs monocrystals, layers, thin films and nanowires are produced by the liquid-phase, gas-phase, molecular beam epitaxy, or Metal-Organic Chemical Vapour Deposition (MOCVD) [2,3,4]. Electronic circuit patterns are usually shaped by lithography and etching, which often harm material nanostructure. Moreover, this technology is rather expensive and time-consuming. We are developing a novel approach to material patterning by a microreactor-printing technology for localized deposition of thin films, nanoparticles and nanowires. In our earlier work [5], we described the method and its application to a silicon dioxide CVD single-flow microreactor. In this work we extend the technology and investigate GaAs MOCVD in a three-jet microreactor.

To date there are some works dedicated to GaAs MOCVD simulation. Y. C. Chuang in [6] considers the mathematical model and optimal design of a horizontal MOCVD reactor for GaAs film growth. It 3D model showed a good agreement with experimental data and presented an ability in predicting the GaAs film growth rate and uniformity. Interesting paper by H.Song [7] describes a results of two-dimensional numerical simulation on growth rate nonuniformity of selective area GaAs metallorganic vapor phase epitaxy. Described results and applied method reveal surface kinetics and surface reaction mechanism even in the mass-transport limited growth condition. Disadvantages of the

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selective area growth method is necessity of a mask applying. Our work suggests a solution of the problem. In this paper we firstly describe a microreactor design and then discuss mathematical and computer models which are used in our investigation. Simulations results, discussion and conclusions are presented in the second half of the paper.

2. Microreactor design

To design a microreactor we first choose process parameters. Based on the typical GaAs MOCVD deposition from mixture of $Ga(CH_3)_3$ (a.k.a. TMGa) and AsH_3 diluted by H_2, we set the following process conditions: pressure of 10000 Pa, temperature of 1000 K [8]. The microreactor and substrate wafer are placed in a vacuum chamber with fixed pressure and background gas chemical composition (as shown in Figure 1(a)). The substrate is heated to 1000 K by a heater. Microreactor is situated over the substrate with 10 μm gap. It can be moved by the microreactor X-Y Mobility System in lateral direction to deposit GaAs patterns along the wafer. The vacuum system, heater and X-Y Mobility System are based on standard technical solutions. In the paper we focus only on the microreactor design.

We designed two versions of microreactor geometry:

1. The first simple design (Case 1) is presented in Figure 2(a). It has just one central channel. Inlet gas mixture is injected into the central channel (10 μm diameter) under pressure P_{in}. It then spreads in the gap, reacting with the substrate. Finally, all gases are pumped out from the gap to the vacuum chamber where pressure is P_{ch}.
2. The second microreactor design (Case 2) with three jets is presented in Figure 2(b). It has an additional ring-shaped pumping channel around the central channel, so that the penetration of the inlet mixture is localized in a narrow area of controllable diameter. This microreactor design allows to set three pressure values: P_{in} is the inlet pressure in the central channel, P_{ch} is pressure in the vacuum chamber and P_{out} is outlet pressure in the ring-shaped pumping channel, see Figure 2(b). P_{in} is 10800 Pa, higher than P_{out} and P_{ch}. If the pressure P_{out} is equal or higher than P_{ch}, the gas jets have the same distribution as in the first microreactor design (Case 1). When pressure P_{out} is less than P_{ch}, gas flow in the gap changes direction.

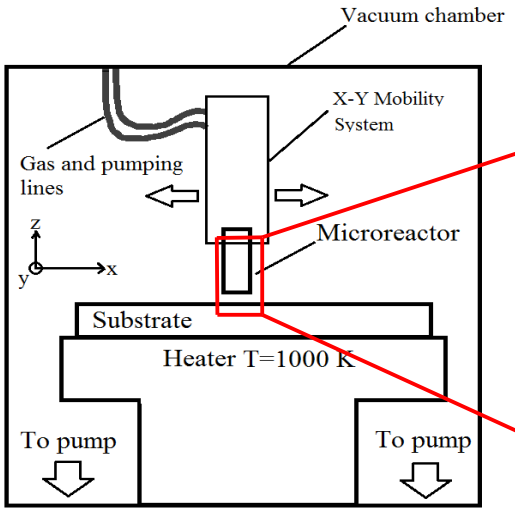

Figure 1(a). Process chamber scheme.

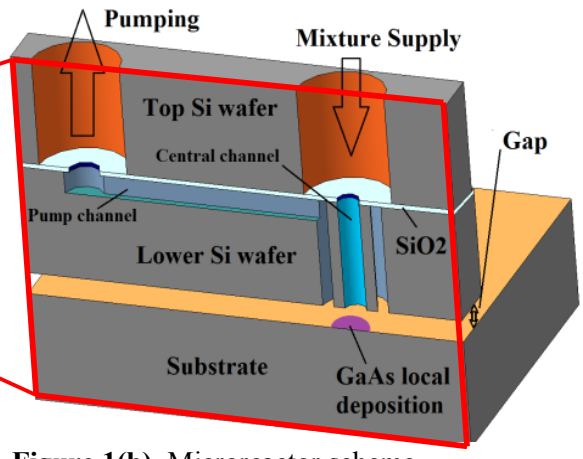

Figure 1(b). Microreactor scheme.

Both microreactor designs can be constructed from silicon chips by microsystem technology [9] . The chip contains two silicon wafers: Top and Lower, see Figure 1(b). Inside the Lower wafer (of 50 μm width) the two channels (Central and pumping) are made by plasma deep silicon etching technology (for instance Bosch-process). Top silicon wafer contains auxiliary microchannels providing interconnections between the channels in the chip and the outer gas supply and pumping

lines. The two wafers are direct-bonded to make a microreactor. Silicon wafers were chosen for microreactor construction material because of its selectivity to GaAs. It allows to use wet chemical cleaning processes during a long-term microreactor operation. Some advanced subsystems (for example cooling) and sensors can be included in the microreactor design, but in this work we did not consider it yet.

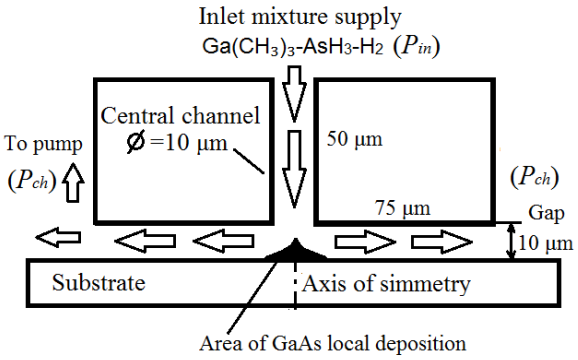

Figure 2(a). The first microreactor design (Case 1).

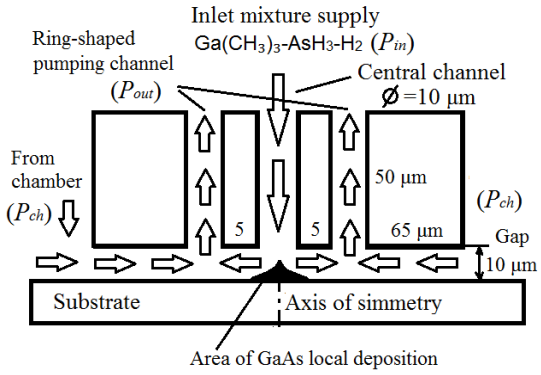

Figure 2(b). The second microreactor design (Case 2).

3. Computer simulation and model parameters

To investigate the properties of microreactors for GaAs MOCVD process we used a computer simulation approach. We modeled a simplified two-dimensional axisymmetric geometry of reactors. The computational model is based on Navier-Stokes equations for a laminar flow (Re=0.02) of chemically reacting gas mixture of $Ga(CH_3)_3$-AsH_3-H_2. A continuum modelling approach is justified at Knudsen numbers $Kn \sim 5 \cdot 10^{-2}$ calculated for our conditions. Equations of the energy conservation and mass balance for each chemical species were include in the model. Ideal gas low was applied as an equation of state for gas media in the microreactor volume. Model of chemical kinetic was taken from [8]. GaAs deposition reaction is modeled on the substrate and all reactor walls.

For the first microreactor design (Case 1) we simulated MOCVD process and investigated a distribution of GaAs deposition rate along the substrate. TMGa mass concentration in the inlet mixture was 0.00001, AsH_3 was 0.06, and H_2 was 0.93999. Inlet mixture supplying was simulated under constant pressure boundary conditions (P_{in} = 10800 Pa), when the pressure in the vacuum chamber P_{ch} was set at 10100 Pa.

For the second microreactor design (Case 2) we carried out two series of numerical experiments to investigate a GaAs MOCVD process in details. At the first series we change the outlet pressure in the ring-shaped pumping channel P_{out} from 7000 Pa to 10100 Pa. The inlet pressure P_{in} was 10800 Pa and pressure in the vacuum chamber P_{ch} was 10100 Pa. TMGa mass concentration in the inlet mixture was 0.02, AsH_3 was 0.06, and H_2 was 0.96. At the second series we changed a TMGa mass concentration from 0.001 to 0.04. AsH_3 concentration was constant and hydrogen was reduced respectively. P_{in} and P_{ch} were set as in the first series and P_{out} was 7000 Pa. Distribution of GaAs deposition rate along the substrate was investigated in all cases.

4. Results and discussions

4.1 The first microreactor design (Case 1).

Simulation results of the first microreactor design showed an insufficient localization of deposition rate of GaAs, see Figure 3(a). Full Width Half Maximum of deposition rate is 84 µm, eight times larger than the diameter of the central channel. In Figure 3(b) the distribution of TMGa (source gas in inlet mixture) is shown. The TMGa concentration is almost uniformly distributed along the substrate in a large area. It causes the distribution of GaAs deposition rate, shown in Figure 3(a). Therefore

Case 1 microreactor design does not allow to obtain localized deposition under the standard conditions considered.

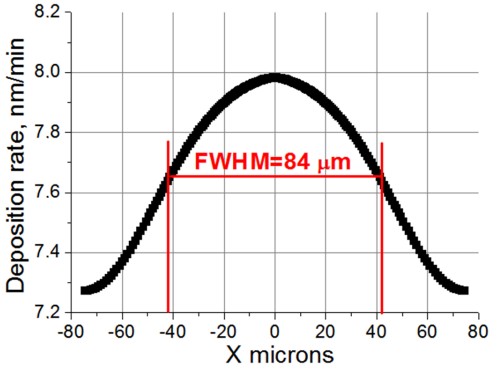

Figure 3(a). Disribution of GaAs deposition rate. The first microreactor design (Case 1).

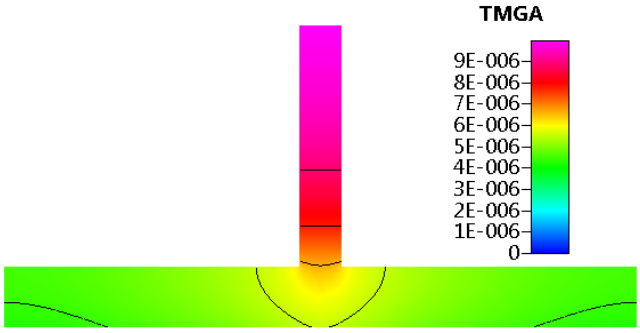

Figure 3(b). Disribution of TMGa. The first microreactor design (Case 1).

4.2 The second three-jet microreactor design (Case 2).

The second microreactor design has an additional ring-shaped pumping channel, which has a strong influence on the flow distribution. In Figure 4(a) stream lines and velocity magnitude distribution in the microreactor are presented.

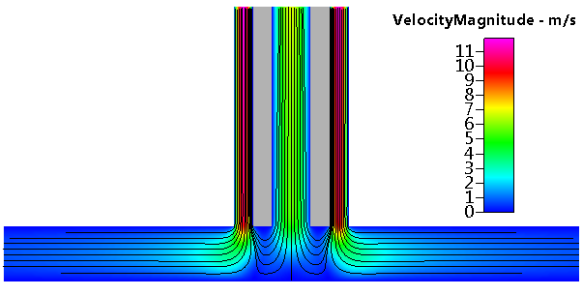

Figure 4(a). Stream lines and velocity magnitude distribution in the microreactor. (Case 2).

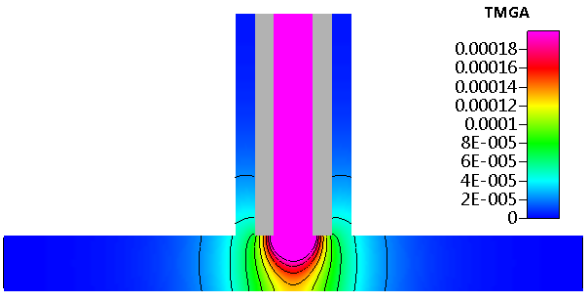

Figure 4(b). Disribution of TMGa. The second microreactor design (Case 2).

The distribution of the TMGa is presented in Figure 4(b). Comparing it to Case 1 distribution (Figure 3(b)), we can note that distribution TMGa is localized in a small volume between the central channel and the ring-shaped pumping channel. The localization of precursor concentration leads to localization of the GaAs deposition rate.

To study the influence of different outlet pressures P_{out} and mass concentration of $Ga(CH_3)_3$ in the inlet mixture, we conducted two series of numerical experiments described in Section 3. In Figure 5 the distribution of normalized (to its maximum) deposition rate for different outlet pressure is presented. In all cases the deposition rate has a maximum in the center. At high outlet pressures P_{out}=10000 Pa and 10100 Pa (close or equal to P_{ch}=10100 Pa), the deposition rate at the edges (x=+/- 75 μm) is very high, meaning poor localization. The gas flow distribution in these two cases is similar to the first microreactor design (Case 1). When the outlet pressure in the ring-shaped microchannel P_{out} is less than 9000 Pa, the distribution of the deposition rate is highly localized. In these cases Full Width Half Maximum is 27 μm. Remarkably, reducing the outlet pressure from 9000 Pa to 7000 Pa does not change the normalized deposition rate distribution. The absolute value of

deposition rate in the center slightly changes from 0.1667 μm/ min at 9000 Pa to 0.1655 μm/ min at 7000 Pa.

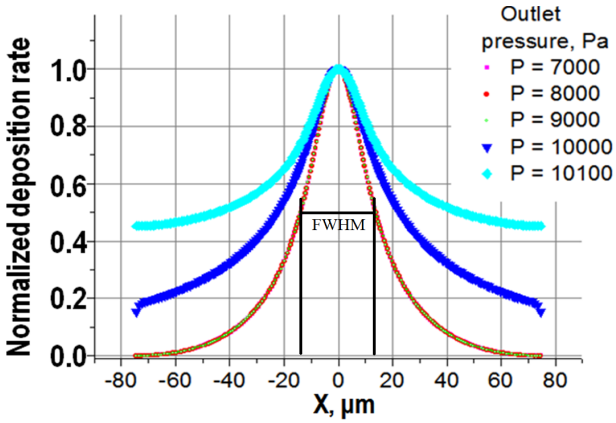

Figure 5. Distribution of normalized deposition rate for different outlet pressure values (P_{out}). P_{in} =10800 Pa, P_{ch}=10100 Pa, mass concentration of $Ga(CH_3)_3$ is 0.02.

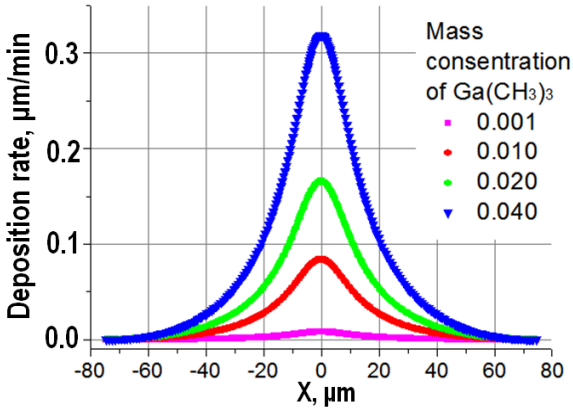

Figure 6. Distribution of deposition rate for different mass concentration of $Ga(CH_3)_3$. P_{in}=10800 Pa, P_{ch}=10100 Pa, P_{out}=7000 Pa.

In Figure 5 distribution of deposition rate for different mass concentration of TMGa is presented. Increasing TMGa concentration leads to the growth of deposition rate. FWHM of the peaks slightly increase from 26.7 μm at 0.001 TMGa concentration to 27.9 μm at 0.04 TMGa concentration. Maximum value of GaAs deposition rate is 0.3188 μm/min for the highest TMGa concentration (0.04). Such deposition rate can provide an efficient "printing" of topological patterns. It is possible to consider a practical application of the microreactor MOCVD process to produce a novel GaAs devices.

5. Discussion and recommendations

To explain the presented results we consider some theoretical topics about microreactor CVD technology. In general the deposition rate is a function of temperature, pressure and precursor concentration. Therefore, to obtain a localized deposition rate we should localize one of the factors limiting the reaction rate. In our process conditions, pressure and temperature are constant, hence we can change only a precursor concentration in the microreactor.

For reactor which is working in ideal displacement regime the precursor concentration reducing along stream lines due to its consumption in chemical reactions, what leads to concentration gradient in the reactor volume. We apply the phenomena in the first microreactor design (Case 1) and observed a reducing TMGa concentration along stream lines in the reactor. The ration between the surface reaction rate and convective mass transport in gas flow and diffusion in the Case is low. TMGa spreads in the gap along large area and provide an almost uniformly deposition.

To provide a high gradient of precursor concentration and localized deposition the ratio between the surface reaction rate and mass transport should be high. To increase the ratio it is possible to rise a temperature (and surface reaction rate) or decrease an initial concentration of precursor in the inlet mixture. It is an universal solution for the first type of CVD microreactor (Case 1). For considered process parameters (fixed temperature) and chemical system, which determines a surface reaction rate, GaAs MOCVD in the first design of microreactor do not provide a localized deposition. To solve the problem we change a scheme of gas flows and design the second version of the microreactor (Case 2). This approach shows perfect results and the localized deposition with 27 μm FWHM was obtained.

Further analyzes of the process and deposited profiles leads to the important suggestion. To narrow down the area where GaAs have been deposited, we suggest to perform an additional etching step after deposition in microreactor. The main idea is uniform etching of GaAs thin film on the whole wafer. In Figure 7 the film profiles of deposited patterns before and after such etching process are shown. Etching process also reduces a FWHM of the peaks. This approach has the most efficiency in case of high selectivity of the etchant to substrate material.

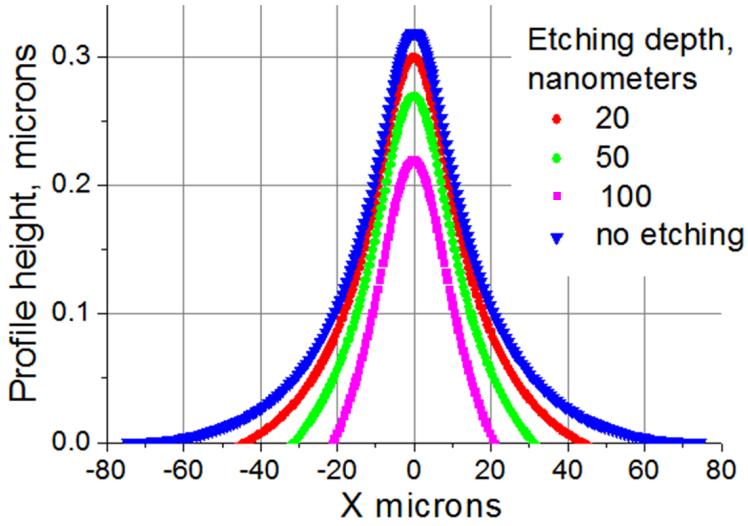

Figure 7. Profiles of deposited film profiles before and after etching process. P_{in}=10800 Pa, P_{ch}=10100 Pa, P_{out}=7000 Pa, mass concentration of TMGa is 0.02. Time of deposition is 1 min.

6. Conclusions and future work

In this work we present a novel three-jet microreactor design for localized deposition of GaAs by low-pressure MOCVD. Two microreactor designs were simulated. Results of simulations shows a possibility to localized deposition of GaAs with 27 μm of FWHM by using the three-jet microreactor design.

We obtain that increasing a pressure (P_{in}) in the ring-shaped pumping channel up to pressure in the chamber (P_{ch}) leads to poor localization of GaAs deposition rate, similar to the first microreactor design. Increasing a TMGa mass concentration in the inlet mixture from 0.001 to 0.04 leads to growth of maximum deposition rate up to 0.3188 μm/min and do not change a deposition distribution. The differences between simulation results in Case 1 and Case 2 were discussed and explained. We suggested addition treatment step to improve a profile after deposition. The next step of this research is the hardware construction of these microreactors and experimental investigations.

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