CHEMICAL VAPOR DEPOSITION EPITAXY ON PATTERNLESS AND PATTERNED SUBSTRATES

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THE ELECTRONIC MATERIALS processing curriculum at Purdue consists primarily of a one-semester course. The objective of this course is to provide chemical engineering students with the basic principles and practical aspects of the most advanced state of electronics processing. The main emphasis of the course is on fundamental processes especially useful for Very Large Scale Integration (VLSI) schemes [1].

About five weeks are devoted to epitaxy, which is a process by which material is deposited onto a crystalline substrate or seed, and the crystalline configuration is maintained. Two and one-half weeks are devoted to Vapor Phase Epitaxy (VPE) on patternless substrates, one week to VPE on patterned substrates typically known as Selective Epitaxial Growth (SEG), one week to doping profiles in epitaxially grown thin films, and one-half week to other kinds of epitaxy (*e.g.*, Molecular Beam Epitaxy (MBE), Plasma Assisted Chemical Vapor Deposition (PACVD)). The purpose of this paper is to focus on Chemical Vapor Deposition (CVD) epitaxy on patternless and patterned substrates in the manner in which it has been developed in our course over the past five years.

Journal articles play a very important role in many educational aspects of the CVD epitaxy on patternless and patterned substrates. A list of such journal articles typically used in class is presented at the end of this paper [7-23]. The rapid developments in the field preclude adequate discussion in a book, and in general there is very little discussion in books, if any, about CVD on patterned substrates.

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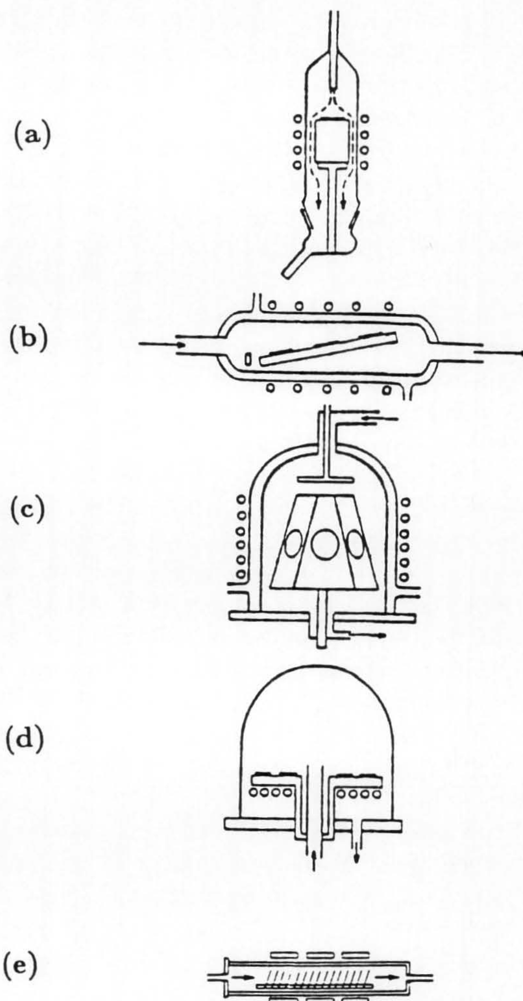

***FIGURE 1.** Schematic representation of (a) vertical, (b) horizonal, (c) barrel, (d) pancake, and (e) low pressure chemical vapor depostition epitaxial reactors.*

classified into types (*e.g.*, VPE, MBE, PACVD, Solid Phase Epitaxy (SPE)) [2, 3, 6], and important features of epitaxy are briefly discussed. At the same time, some potential problems of epitaxy are briefly presented. Such problems with VPE, for example, can be autodoping, pattern shift, and pattern washout [2-4, 6].

CHEMICAL VAPOR DEPOSITION REACTORS

An introduction to different basic types of reactors

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used in the epitaxial thin film growth of electronic materials forms the first stage of our course. For VPE, five types of CVD reactors are discussed [2, 3, 6-11, 22] along with some recent reactor designs such as the Vapor Levitation Epitaxial (VLE) system [24] and the Epsilon One system [25]. They are the vertical (typically used in Metal Organic Chemical Vapor Deposition (MOCVD)), the horizontal, the barrel, the pancake, and the Low Pressure Chemical Vapor Deposition (LPCVD) reactors (see Figure 1). The LPCVD reactor has been increasingly used in reduced pressure epitaxy since problems associated with VPE, such as pattern shift, washout, and autodoping, have been remedied to a significant degree with low pressure epitaxy [11, 13, 14, 19].

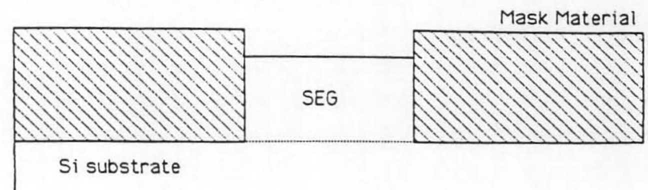
The Epsilon One system is a one-wafer horizontal reactor with very low contact times between gas mixtures and substrates [25]. VLE uses growth vapors and carrier gas not only to provide reactants to a wafer surface but also to lift the wafer and keep it suspended above the growth apparatus during the epitaxial growth process [24]. PACVD reactor systems are also briefly presented. Throughout this section the emphasis is on discussing main features and potential advantages and disadvantages of the various systems used in electronic materials CVD.

CHEMICAL REACTIONS IN EPITAXY

Sources typically used in silicon (Si) or gallium arsenide (GaAs) epitaxy are presented next. Si and GaAs are the base semiconducting materials studied in the Purdue course on microelectronics processing, other materials being conceptually presented as rather simple extensions of these two base ones. Mass spectrometry and other gas phase analytical tools along with *in situ* substrate surface analysis techniques are shown to provide a means of understanding some of the chemical reactions that may occur during epitaxy. On the other hand, important chemical reactions during the pretreatment and preparation of a substrate surface are also discussed in detail. One example from silicon epitaxy is the process of removing all native oxide just before an epitaxial growth step since device quality epitaxial thin film is, perhaps, the main objective of any epitaxial process.

In the context of SEG, only silicon epitaxy on patterned substrates is covered (see Figure 2). There has to be a higher degree of supersaturation for the nucleation of silicon on SiO_2 and Si_3N_4 as compared to that for nucleation on silicon surfaces. Thus, by keeping the supersaturation below a critical value it is possible to selectively deposit silicon on Si substrates masked by either silicon nitride or silicon oxide (*e.g.*, Figure 2). Crystal growth theories as discussed, for example, by Bennema and van Leeuwen [26] explain the initiation of growth by the adsorption of silicon at the growth interface. Adsorbed atoms form little clusters which are thermodynamically unstable until they reach a certain critical size. Thereafter it is energetically more favorable for them to remain in the solid phase than in the vapor phase [27]. The adsorption energy on foreign substrates is generally higher than that for Si. Thus it becomes possible to operate at a point where the nucleus size on the foreign material is held below the critical value, while nuclei of overcritical size can form on the silicon-growth interface. The process is a delicate balance between reasonable growth rates and polynucleation on the masking material, most often SiO_2. The onset of nucleation on the mask is a function of temperature, pressure, mask material, and the Cl/Si ratio in the vapor phase.

Doping profiles in epitaxially grown thin films are presented from two points of view. First, an epitaxial



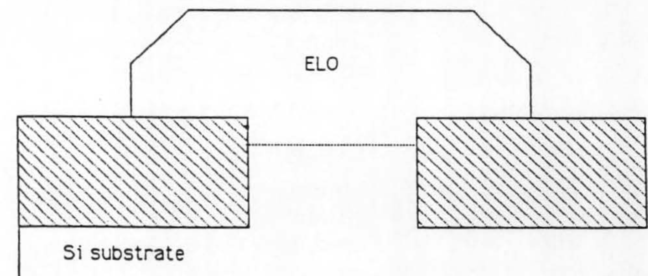


***FIGURE 2.** Selective epitaxial growth and epitaxial lateral overgrowth schematic cross sections.*

layer doped with a desired element can be obtained with a cofeed of a dopant source along with other species of interest. In this case, additional chemical reactions, which include dopant species, have to be accounted for; these additional reactions can significantly affect the quality of growing doped epitaxial layers. Second, intrinsic epitaxial growth of, say, silicon on substrates with buried layers raises questions of doping a growing thin film with impurities coming from these buried layers through autodoping or outdiffusion [2, 3].

CHEMICAL EQUILIBRIUM—THERMODYNAMICS

Thermodynamic calculations of a CVD reaction system are discussed next. Such an analysis may provide important insights into several aspects of the system. Starting with a nonequilibrium inlet state, chemical equilibrium calculations can provide boundary values of operating parameters necessary for successful thin film growth and provide information on the response of the process to changes in operating conditions [7, 28]. Furthermore, the computation of equilibrium compositions with intentionally limited reactants may assist in the assessment of reaction mechanisms. In the course, students are presented with a computer program that allows quick equilibrium calculations of CVD reaction systems.

Thermodynamics calculations are also helpful for the pretreatment and preparation steps of substrates as well as for the growth of thin films doped with a desired impurity. However, in our course on microelectronics processing, the need for chemical equilibrium calculations is emphasized even more in the SEG of silicon on patterned substrates [29]. Nucleation on SiO_2 (or Si_3N_4) during SEG, silicon oxide (or nitride) degradation during SEG, and undesired impurities in SiO_2 (or Si_3N_4) films used for the patterning of a substrate are some of the many additional problems one does not have to worry about in CVD on a patternless substrate. Such issues are addressed in detail for the CVD of epitaxial silicon on patterned wafers.

KINETICS

The chemistry of CVD systems follows their chemical equilibrium calculations. Such chemistry is complex and usually involves surface and gas phase reactions [7]. With respect to gas phase reactions, two approaches are discussed. The first one includes experimental data from studies on individual gas phase reactions. The second approach is theoretical. Starting from basic data of all conceivable species and reactions in a given CVD reaction environment, one can estimate rate constants from kinetic theory. Once this is done, dominating gas phase reactions can be determined at any set of CVD reactor conditions. It is emphasized in class that, typically, a combination of both approaches seems to be best. With such a conceptual understanding of gas phase reactions, particle formation (for example, during Si deposition from silane) can be reasonably well predicted. Thus, because particle formation in the gas phase can be detrimental to the quality of growing epitaxial thin films, the importance of gas phase chemistry and kinetics becomes clear.

On the other hand, it is pointed out that the role of gas phase reactions is becoming less important with decreasing CVD temperatures and partial pressures of the reactants. Therefore, in silicon SEG, which is typically carried out at reduced pressures and temperatures, many gas phase reactions are not expected to play an important role. Yet, both approaches discussed previously are also presented as thorough ways of accounting for gas phase reactions in CVD on patterned substrates.

When it comes to substrate surface reactions in CVD, it is pointed out that little is known even for epitaxial silicon deposition, which is perhaps the reaction system studied the most. Several difficulties in the understanding of CVD surface reactions are discussed. These are the typically unknown extent of gas phase reactions, the typically significant role of transport phenomena in the neighborhood of a substrate in particular (with the only exception perhaps of LPCVD epitaxial reactors), the potentially high levels of undesired impurities in the feed gases or in the reactor itself, the potentially high conversions of key reactants, and the possibility that some reactions may be very near their chemical equilibrium. It is mentioned that in a few studies, spectroscopic techniques have been utilized in CVD so that some surface reactions can be monitored. Although helpful, such studies are shown to provide more questions than answers.

In spite of our incomplete understanding of CVD surface reactions, a few reaction mechanisms for Si and GaAs growth are discussed in detail. Fairly widely acceptable gas phase and surface intermediates are used.

Naturally, the role of surface reactions in CVD on patterned wafers is presented as even more complex. In silicon SEG, there are two kinds of surfaces that any species is in contact with: the silicon seed windows area and the SiO_2 (or Si_3N_4) area. It is indicated to the students that, typically, silicon SEG in the seed windows is assumed to be similar to growth on patternless wafers; that is, the only potential contribution

coming from the oxide (or nitride) surface is assumed to be just surface diffusion close to the SiO_2-Si interface. Yet, recent developments are shown to suggest that the oxide or nitride surface seems to participate to a much greater extent in the overall surface reaction scheme than thought before.

Also, what is usually called "kinetics of epitaxial growth" in several books and some journal articles [2-6] is discussed at the end. The above term includes mass transport in series with a truly kinetic step, the rate expression of which is assumed to be linear. Therefore, the final growth rate expression obtained involves an overall mass transfer coefficient along with a kinetic rate constant. Although such a growth rate expression may help in the understanding of diffusion controlled and surface reaction controlled deposition, it is emphasized that such an analysis is *not* the intrinsic kinetics of epitaxial thin film growth and that it simply provides an elementary, though clear, conceptual understanding of kinetically or mass transfer controlled processes in CVD systems.

CVD REACTOR MODELS—THIN FILM QUALITY

Today more than 70% of all fabricated integrated circuits employ epitaxy in one way or another. The requirements made on the quality of the epitaxially grown layers are stringent: less than ±5% thickness variation over a wafer and from wafer to wafer, less than ±5% doping nonuniformity and high growth rates to suppress dopant redistribution.

Selective epitaxy is even more sensitive to the variation of parameters than is epitaxy on patternless wafers; one has only a limited operating range in which nucleation on SiO_2 (or Si_3N_4) does not occur. Also, local depletion effects can significantly alter growth rates.

The basic continuity, momentum, energy, and mass equations of a comprehensive model of a CVD reactor are covered through the detailed modeling of a pancake reactor. Such equations in their general form apply to any type of reactor, the main variations being related to entrance effects and to whether natural convection plays an important role in a given CVD reactor system. Also, the special geometry and inlet and exhaust configurations of the reactor used have to be accounted for in a CVD reactor model. Gas phase chemistry is shown to be included in these modeling equations, whereas surface chemistry is accounted for through appropriate boundary conditions for a chosen CVD system. Important differences between cold-wall and hot-wall reactors are discussed in detail.

Results from the detailed model of a pancake reactor are presented in detail for patternless and patterned substrates [30]. It is readily seen that one result of the solution of a detailed reactor model is an understanding of velocity, temperature, and species mass fraction profiles throughout the reactor of interest. Another result is predictions of the growth rate profiles on substrates.

Because of our incomplete understanding of CVD kinetics, it is emphasized that any CVD gas phase and surface chemistry should be tested in at least two different types of reactors. Furthemore, even within each reactor, wide regimes of operating parameters such as substrate temperature and reactor pressure are suggested for testing. However, even if such a model is able to predict all trends of thin film growth rate profiles quantitatively, it may not be able to predict other features such as defect density, surface resistivity, and quality of Si/SiO_2 interfaces that can characterize the quality of a grown thin film. The quality of a thin film grown in an epitaxial CVD system is also shown to be a fairly strong function of the quality of the substrate used, the purity of gases or other materials used, the impurities of the reactor itself, and the predeposition treatment. Film characterization after an epitaxial processing step is presented as an essential integrated part of any CVD on patternless or patterned substrates [2, 3, 6].

SELECTIVE EPITAXY

Specific focus on VPE on patterned substrates follows. SEG of silicon is presented as being most often carried out by employing an SiH_2Cl_2-HCl system at reduced pressure and temperatures of about 800-1000°C [31-35]. SEG leads to structures exhibiting distinct faceting which depends on substrate orientation and seed window alignment relative to crystal planes. It is pointed out that (100) substrates and pattern alignment along [100] directions seem to give the best results for application purposes [36]. At reactor pressures greater than about 20 torr, SEG rates appear to depend rather strongly on the amount of exposed silicon area. However, a reduction of pressure below 20 torr or an increase of the reactor inlet ratio Cl/Si is shown to decrease such a loading effect. In a fabrication line it is indicated that both these remedies may be undesirable because they result in smaller growth rates.

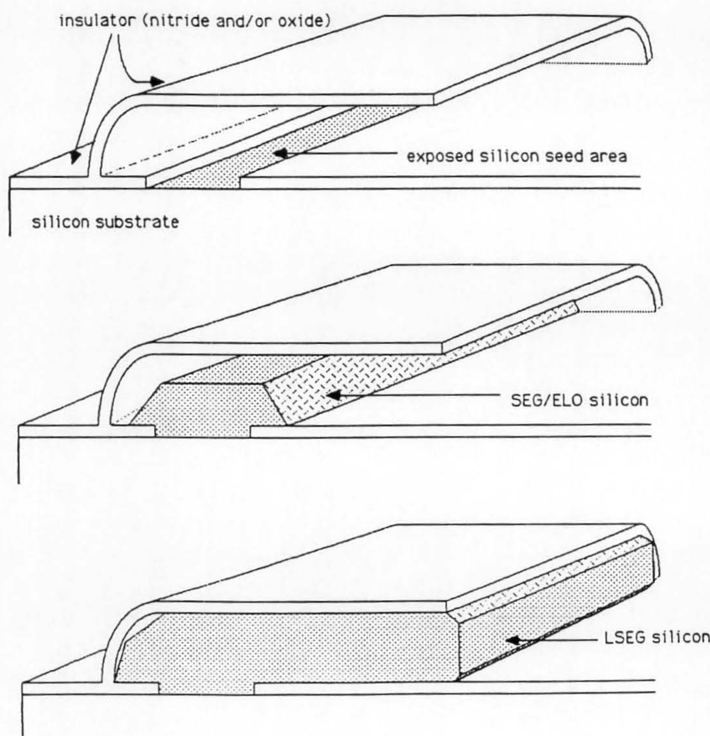
If the film is grown longer than necessary to fill the void created by the etching of the SiO_2 mask, it will not only grow vertically but horizontally as well (Epitaxial Lateral Overgrowth (ELO), Figure 2). This leads to a Silicon-on-Insulator (SOI) type structure which is very desirable from a device application point of view. Typical ratios of horizontal growth rates over

vertical ones, *i.e.*, aspect ratios, are pointed out to be about 1:1.

A different technique for growing epitaxial silicon over SiO_2 is also discussed [37]. Jastrzebski, *et al.* [37] report almost nucleation-free growth by growing without any HCl for a short time and then etching with HCl for about the same amount of time. These steps are repeated until the desired film thickness is achieved. The aspect ratio is about 1:1.

Large aspect ratios (much greater than 1:1) are shown to be of great interest for advanced dielectric isolation and the design of new three dimensional integrated circuits. One promising avenue for such a high aspect ratio is pointed out to be Lateral SEG (LSEG), which is depicted in Figure 3 [38]. The top structure is a cavity with prepared wing layers of different etched-rate materials and with a seed hole deep inside. In the center structure, selective growth extends up into the cavity and is technically ELO at this stage. As the top of the ELO meets the cavity ceiling, growth is now constrained to proceed only laterally, as shown in the bottom structure. This lateral growth is referred to as LSEG.

The importance of selective epitaxial growth in VLSI is stressed because it allows for novel device isolation techniques with higher densities as well as new device structures such as silicon on insulator arrangements [13, 14, 31-34, 38].



Lateral selective epitaxial growth of silicon [38).

TABLE 1
Titles of Final Projects in CVD Epitaxy on Patternless and Patterned Substrates

- Silicon on Insulators: A Focus on Epitaxial Lateral Overgrowth
- Solid Phase Epitaxy of Silicon
- GaAs Contacts: Theory and Practice
- Kinetics in the Vapor Phase Epitaxy of GaAs
- Recent Studies on the Kinetics of Epitaxial Silicon Growth
- Metalorganic Chemical Vapor Deposition of III-V Compounds
- Chemical Vapor Deposition of II-VI Materials
- Recent SOI Technologies
- Increasing the Throughput of High Electron Mobility Transistors Grown by III-V Molecular Beam and Chemical Beam Epitaxy
- Plasma Enhanced Chemical Vapor Deposition
- Silicon Epitaxial Growth Research at Purdue University: An Overview
- Silicon on Insulator Technologies

DOPING PROFILES IN EPITAXIAL LAYERS

Two potential problems associated with the doping profiles in such epitaxial thin films are addressed as being very important: autodoping (etchback) and solid state diffusion. Typically, a lightly doped epitaxial layer may have to be deposited on a heavily doped substrate with the same kind of dopant, or vice versa (*e.g.*, n^- or n on n^+, p^- or p on p^+). Also, for the formation of a pn junction, a p-doped epitaxial layer has to be deposited on an n-doped substrate or vice versa.

Autodoping is discussed first in detail. Etchback is shown to result in sharper transitions from the dopant concentration level in a substrate to the dopant level in the growing epitaxial layer, as substrate temperature or reactor pressure decreases. Simple semi-empirical models are developed for autodoping. These models are shown to be able to predict trends like the ones just mentioned as well as a shift in the position of the pn junction delineated by the two layers [2]. Comprehensive models of autodoping are briefly presented. Furthermore, although increased etchback is pointed out to be technologically undesirable, it is demonstrated that autodoping may be a very useful tool in determining velocity profiles just above a susceptor in some CVD reactors (*e.g.*, a pancake reactor).

Solid state diffusion is presented next. Although redistribution of the dopants because of diffusion during epitaxial growth of a (doped) thin film may not be very important compared with the redistribution that takes place during subsequent processing, a simple

model for solid state diffusion is discussed. This model is shown to result in a graded junction between substrate and epitaxial layer and in a shift of the pn junction delineated by the two layers. This shift, though, seems to compensate for the junction lag due to the autodoping effect. The intensity of solid state diffusion effects is shown to depend on the substrate temperature during epitaxy, the duration of this step, and the magnitude of solid state diffusivities at standard conditions. Also, a brief discussion of redistribution of dopants due to diffusion during subsequent processing is presented.

FINAL PROJECTS

After a brief coverage of other kinds of CVD epitaxy, such as PACVD, the last stage is a final term paper. Each student works on his/her own project after choosing a topic. Within such projects, students are expected to critically review any existing literature and to present their own "innovative ideas" in improving or developing various CVD epitaxial processes.

Topics in the chemical vapor deposition epitaxy on patternless and patterned substrates covered in the past four years are listed in Table 1.

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