American Institute of Chemical Engineers

# Materials Engineering and Sciences Division Newsletter

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New website! *www.che.gatech.edu/MESD*

## AIChE – MESD Short Course
## Flow/Process Induced Crystallization of Polymers

**Sunday, November 3rd, 2002 Indiana Convention Center: 8:00 AM – 4:00 PM**

## TUTORIAL OVERVIEW

Semi-crystalline polymers are an important and significant segment of the plastics that are consumed worldwide. Crystallization of polymers under quiescent or non-flow conditions has been well studied and documented. However, in most commercially significant polymer processing operations (such as injection molding, blown and cast film extrusion, blow molding and fiber spinning), crystallization occurs under the influence of an external flow field (strain). Therefore, the general rules that apply to quiescent crystallization do not completely explain the observations of crystalline morphology attained in products that result from the above-mentioned processes. The lectures in this course are designed to cover a wide range of aspects concerning flow-induced crystallization and will offer educational and discussion opportunities to those attending. The general outline of this daylong tutorial will be as follows:

- Overview of polymer crystallization from quiescent melts.
- Differences between crystallization from quiescent and strained polymer melts.
- Techniques to characterize orientation in polymeric products.
- The early stages of flow-induced crystallization in polymers.
- The role of melt relaxation dynamics on flow-induced crystallization.
- Molecular modeling of polymer crystallization.
- Structure-property relationships in oriented polymeric systems.
- Structure development during fiber spinning and drawing.

## WHO SHOULD ATTEND

Polymer process engineers, industrial product and application development engineers and chemists, industrial R&D engineers, chemists and physicists, technical service engineers, university professors and students.

## REGISTRATION DETAILS

Details can be found on the AIChE website

**www.aiche.org/conferences/annual/shorts/crystalpoly.htm**

In order to register for the course, those interested are required to go to the online registration section for the AIChE 2002 Annual Meeting. Note, you need not be an AIChE member to attend this course. You may register for the annual meeting and the short course simultaneously. However, if you are only interested in attending the short course, you may do so by checking the option "Attending Short Courses, Tutorials or Critical Issues ONLY". As you go through the online registration, please select the short course option: T4 - Flow/Process Induced Crystallization of Polymers. The registration fees are $199/person. ***Lunch will be sponsored by Chevron Phillips Chemical Company, LP.***

## CONTACT FOR QUESTIONS

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Prof. Gregory C. Rutledge, *MIT*
Prof. Jing Wu, *New Jersey Institute of Technology*

### *Election Results*

The election results have been compiled by the national office for the AIChE Division 8 (MESD) Board of Directors. We are pleased to welcome the following new members to the Board:

| | |
|---|---|
| 2nd Vice Chair | **Alon V. McCormick** |
| Directors | **Don Paul** |
| | **Alec Scranton** |

## Chemical Vapor Deposition – Epitaxy on Extended Surfaces to Nanocrystals on Dielectric Surfaces

2001 Stine Award Address

John G. Ekerdt
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*I*t is a great honor to receive the Charles M. A. Stine Award from the Materials Engineering and Sciences Division of AIChE. I am grateful to the DuPont Company, along with AIChE, for sponsoring this award since it serves to recognize the central role of materials in society and the technology enterprise. I am also grateful to my faculty collaborators at The University of Texas, Professors A. H. Cowley and M. C. Downer, and past and present members of my research group K. C. Wong, M. T. McEllistrem, M. S. Jackson, K. Yong, J. Zhu, S. K. Stanley and W. T. Leach whose work this award recognizes. In the paragraphs that follow I will briefly describe two very different challenges in electronic materials growth, designing precursors for the epitaxial growth of compound semiconductors and a manufacturable route silicon nanoparticle arrays on dielectric surfaces.

A variety of methods are used in electronic materials processing to deposit thin films, including chemical vapor deposition (CVD). In CVD the film precursors are gases, such as the gas disilane ($Si_2H_6$), a hydride, or a solid or liquid vapor, such as triethylgallium ($[C_2H_5]_3Ga$), an organometallic molecule. During the CVD process precursors must dissociatively adsorb on vacant sites, the ligands, such as H for disilane and $C_2H_5$ for triethylgallium, must desorb completely, and the adatoms (Si or Ga) must have sufficient mobility to incorporate into the lattice sites. These individual steps are thermally activated and the film grower must find the precursor and growth temperature that produce the purest film and of the highest crystalline order.

### Compound Semiconductor Epitaxy

Group III-V (or 13-15) semiconductors are used in electronic and optoelectronics applications. They generally consist of one or more Group III elements in combination with a Group V element to realize a specific band gap and are grown on a substrate that is as closely lattice-matched as possible with the compound to be formed. One example is $Al_{0.3}Ga_{0.7}As$ grown on GaAs(100) that is used in lasers for compact disk players and in short distance data links. III-V surfaces are dynamic with different surface reconstructions and binding sites present depending on temperature and the overpressure of the Group V precursor to accommodate the relative propensity of the Group V element to desorb at typical growth temperatures. For some alloy systems, such as the antimonides, low temperatures are required (550-875 K) because of the low melting points of the crystal being grown and, at these temperatures, complete precursor ligand removal becomes a controlling issue. For other alloy systems, such at the arsenides, higher temperatures (700-1075 K) can be used and now the incorporation of carbon impurities from ligand decomposition can be a problem. Knowledge of the sites for precursor adsorption/reaction and an understanding of how the precursor ligands react at the surface are needed for the rational design or selection of precursors and in the selection of growth conditions. Motivated by these needs and using the tools of surface science, we examined these reactions and looked to the solution and gas phase reactions of the main group elements to develop a chemical basis for precursor selection and new precursor design.

Recognizing the dynamic nature of the surfaces, one is faced with selecting a model system that captures essential features of growth surfaces. In our case, we selected the Ga-rich GaAs(100)-(4×1), the Sb-rich GaSb(100)-(1×3), and the In-rich InSb(100)-c(8×2) surfaces and explored the reactions of trialkylgallium, triethylindium, triethylantimony on the various surfaces. The surfaces present different reconstructions and surface atoms for bonding [1] and allow the Group III and the Group V contributions to be examined. The studies revealed: 1) the alkyl ligands reacted at a common lattice site, the surface Group III atom; 2) the alkyl groups bonded to the lattice atoms and the alkyl groups bonded to an incompletely dissociated precursor were chemically different and reacted differently; and 3) the alkyl groups were removed in two steps, β-hydride elimination to an olefin and homolysis of the alkyl metal bond to form a radical. Furthermore similar results over GaAs and GaSb surfaces featuring different Ga-Group V bonding illustrate the alkyl reactions are not highly dependent on the local Ga bonding; therefore the results over the three surfaces are expected to apply to other reconstructions as well.

Complete ligand removal is essential to eliminate carbon incorporation from the precursor ligands during film growth. One expects the surface to have adsorbed ethyl groups and hydrogen when growing a film using trialkyl precursors and hydride reactants, such as triethylgallium and arsine. Through a series of studies using selectively deuterated triethylgallium and various trialkylgallium molecules, two of three expected ligand

eliminations pathways were found [2]. β-Hydride elimination was demonstrated and is expected (Figure 1), as this is quite common for alkyl ligands on metals and in organometal complexes. Homolysis was observed at a slightly lower temperature than β-hydride elimination. Interestingly the expected reductive elimination of an alkyl group to the alkane was not observed. The lower energy homolysis reaction suggests the $^{\alpha}$C-Ga or $^{\alpha}$C-In bond is nearly broken in the transition state during the reaction and the alkyl ligand either proceeds to undergo homolysis or eliminates a hydride ligand from a $^{\beta}$C to form the olefin. When comparing the reactivity of ethyl ligands over GaAs and InSb, more homolysis is observed over InSb and this is consistent with gas phase pyrolysis of In-alkyl compounds that show a preference for homolysis over β-hydride elimination [3]. Furthermore, the trends in alkyl ligand reactivity reveal that ligands with more β hydrogens, such as *t*-butyl with nine versus ethyl with two, undergo hydride elimination at the lowest temperatures. The *t*-butyl ligand also forms the most stable radical and it reacts at the lowest temperature. The absence of reductive elimination to the alkane suggests there is limited mobility of alkyl ligands on the surface and the probability of an adsorbed alkyl ligand reacting with adsorbed hydrogen is vanishingly small.

Comparison of triethylgallium and triethylantimony reactions on GaAs and GaSb again pointed to the lattice Ga as the site for alkyl ligand removal from the surface and revealed differences in the reactivities of the Group III versus Group V precursors [4]. Triethylantimony is approximately $10^3$ less active than triethylgallium and this difference is suggested to be dependent on the structure and electron density around the central metal atom after the precursor has chemisorbed. The ethyl ligands in triethylgallium are planar and the Ga has an unfilled p orbital. If triethylgallium bonds through this unfilled p orbital to the Group V lattice sites, it will effectively receive some electron density from the surface and the Ga-alkyl bonds will be destabilized much like Group III complexes bonding with electron-donors are destabilized. Triethylantimony has three trigonal-pyramidal bonds between ethyl ligands and Sb, and Sb has a filled lone pair. The lone pair makes Sb an electron donor to the surface and if it bonds at Group III lattice sites, donation of charge may act to increase the Sb-alkyl bond and stabilize the precursor on the surface.

For CVD with organometallic precursors featuring alkyl ligands the studies illustrate ligand removal from the Group III lattice sites will likely be the rate limiting process. This reaction rate depends less on the precursor-alkyl bond energetics and than on the Group III lattice atom-alkyl molecule energetics. Ligands should be selected to facilitate the two loss pathways and secondary and tertiary carbon bonds to the precursor enhance both homolysis and β-hydride elimination. Further if these secondary or tertiary-bonded ligands have β-carbons with hydrogen, β-hydride will also be enhanced.

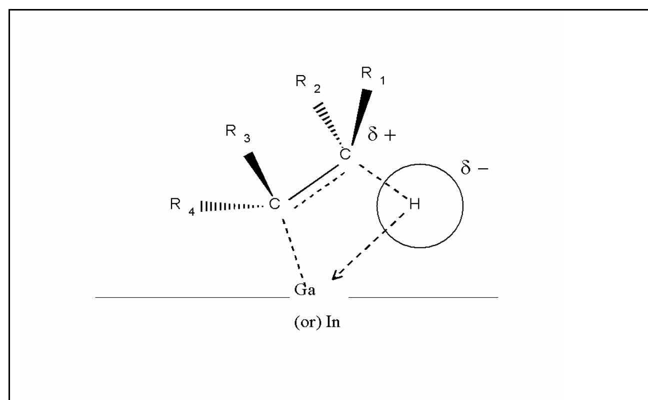


***Figure 1*** *During the β-hydride elimination reaction an olefin forms and the hydrogen located on a β-carbon is transferred to the metal site that was originally bonded to the α-carbon. This hydrogen has hydride character and the site for this reaction is generally thought to be electron deficient, such as the Group III lattice atoms.*

**Silicon Nanoparticle Growth on Dielectric Surfaces**

High-density silicon nanocrystals on dielectrics are required in the production of nanocrystal based floating gate flash memory [5]. Areal densities of $10^{12}$ $cm^{-2}$, corresponding to 5 nm crystals spaced 5 nm apart, are sought to create a substantial threshold shift and ensure an adequate charge retention time. Nanocrystal spacing prevents intercrystal charge transfer and charge leakage, thus allowing thinner tunneling oxides to be used and a consequent reduction in operating voltage.

These nanocrystals can be produced in a variety of methods and we sought to establish the factors that are critical to controlling particle density and size distribution during chemical vapor deposition [6]. The likely surface processes are represented in Figure 2. In this schematic the silicon precursor is disilane and it dissociatively adsorbs on dielectric surfaces, such as $SiO_2$ or $Si_3N_4$, to generate adsorbed silicon atoms that begin to accumulate on the surface. Eventually enough silicon adatoms have accumulated on the surface that dimers, trimers, etc. form and decompose in an equilibrated process. Above a critical size the cluster is stable, and it is shown as six silicon atoms in the figure; however, recent modeling studies suggest it could be as small as a dimer on $Si_3N_4$. Once the critical nucleus forms, it no longer decomposes, rather it grows by more adatoms diffusing to the

perimeter and attaching to it or by direct disilane epitaxy from the vapor.

Our studies have revealed it is possible to realize densities greater than $10^{12}$; however this cannot be realized by CVD alone. We find: 1) High densities require high Si adatom concentrations and these high concentrations must occur in the shortest possible time. Si adatoms can be physically deposited on the dielectric surface by cracking disilane over a hot tungsten filament (1500-1800 K) and these adatoms serve two purposes. First they are more reactive toward disilane than the dielectric surfaces and enhance the deposition of more Si adatoms. Second they contribute to the total adatom population on the surface. In effect the seeding “uncouples” the nucleation and nanoparticle growth steps by producing a significantly higher concentration of adatoms than could be realized in thermal CVD alone. 2) High densities require the Si adatom deposition rate to be greater than the Si adatom desorption rate. Silicon adatom desorption could not be measured from $Si_3N_4$ and was a strong function of temperature over $SiO_2$. Higher densities are always observed over $Si_3N_4$ for this reason. The growth temperature over $SiO_2$ must factor in Si desorption as SiO and the hydride pressure partial pressure must be selected to ensure the adatom deposition rate overwhelms any desorption process. 3) There is an upper limit to particle density since eventually the nanoparticles begin to coalesce. Seeding to get the highest possible density of critical nuclei at the start and then limiting the size of the nanoparticles can control this. Indeed, densities of $2.1\times10^{12}$ $cm^{-2}$ with an average center-center distance of 7 nm and a size of 4-6 nm as measured by scanning tunneling microscopy are observed.

There are numerous unanswered questions and challenges. The exact nature of the active site on dielectric surfaces remains unknown. It is tempting to speculate that the Si-OH groups that terminate lattice defects are the active sites on $SiO_2$ and experiments are underway to test this idea. Further, the size of the critical nucleation cluster is unknown on any dielectric surface; knowing this will better enable one to separate nucleation from growth and control the size distribution. The answer to critical cluster size will likely come from first principles modeling. Finally, at present the best CVD can do is form random arrays of nanoparticles and methods are needed to grow nanoparticles of selected sizes in precise locations on the dielectric surface.

**Acknowledgement**
The author is grateful for financial support from the National Science Foundation, The Robert A. Welch Foundation, and Motorola, Inc.

**References**

1. See for example, G. E. Franklin, et al., Phys Rev B 41 (1990) 12619; M. T. Seiger et al., Phys Rev B 52 (1995) 8256; P. John et al., Phys Rev B 39 (1989) 1730; Biegelsen et al., Phys Rev B 41 (1990) 5701.

2. K. C. Wong et al., Surface Science 396 (1998) 260; K. C. Wong et al., Surface Science 416 (1998) 480.

3. K. Yong and J. G. Ekerdt, Surface Science 490 (2001) 13.

4. K. Yong and J. G. Ekerdt, Surface Science 448 (2000) 108.

5. S. Tiwari et al., Appl. Phys. Lett. 68 (1996) 1377.

6. W. T. Leach et al., J. Crystal Growth, 240 (2002) 415; W. T. Leach et al., J. Crystal Growth 243 (2002) 30; J. Zhu et al., J. Applied Physics 92 (2002).

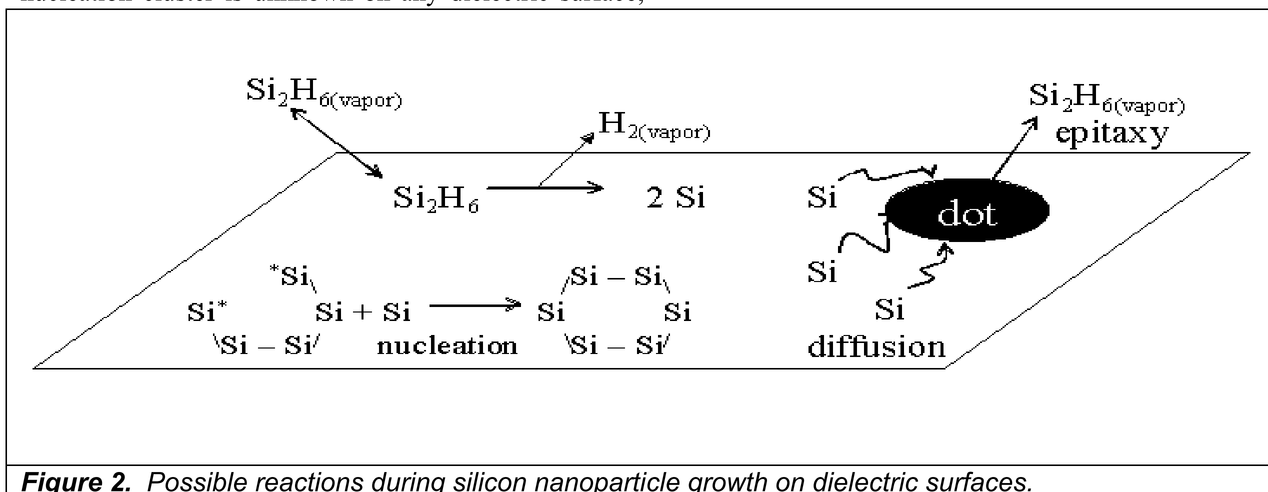


*Figure 2. Possible reactions during silicon nanoparticle growth on dielectric surfaces.*

## 2002 Annual Meeting MESD Events

| | MONDAY | TUESDAY | WEDNESDAY | THURSDAY | FRIDAY |
|---|---|---|---|---|---|
| **8:30 AM** | [41] Thermodynamics of Polymers I, *Room 208 - ICC* | [189] Biomaterials I *Wabash Ballroom 2 - ICC* | **[198] Plenary Session: Stine Award,** *500 Ballroom - ICC* | [341] Advances in Tissue Engineering, *Indiana Ballroom G - Marriott* | [204] Plasma Processing I, *Wabash Ballroom 3 - ICC* |
| | [184] Cure & Degradation Kinetics, *Wabash Ballroom 3 - ICC* | [190] Polymer Processing & Rheology I, *Wabash Ballroom 3 - ICC* | [377] Novel Catalytic Materials I, *Room 208 - ICC* | [206] Chemical Vapor Deposition II, *Wabash Ballroom 2 - ICC* | [150] Nanostructured Materials & Particles II, *Room 124 - ICC* |
| | [136] Nanostructured Materials & Particles I, *Room 121 - ICC* | [192] Diffusion in Polymers & Membranes I, *Room 209 - ICC* | [200] Nanostructured Biomaterials I, *Room 124 - ICC* | [217] Biomolecules at Interfaces, *Wabash Ballroom 3 - ICC* | [216] Composites Processing I, *Wabash Ballroom 1 - ICC* |
| | [181] Structure & Prop. of Polymers I, *Wabash Ballrm 1 - ICC* | [191] Polymer Thin Films & Interfaces II, *Lincoln-Marriott* | [199] Nanostructured Adsorbent Materials *Room 123 - ICC* | [381] Reactor Design & Analysis for Electronic Materials, *Rm 203 - ICC* | [214] Synth. & Process. of Nanocomposites, *Room 122 - ICC* |
| | [182] Polymerization, Kinetics, Catalysis & Reaction Engineering 1, *Reception Room - ICC* | [193] Structure and Properties of Polymers III, *Wabash Ballroom 1 - ICC* | [298] Novel Carriers for Drug and Cell Delivery II, *Indiana Ballroom C/D - Marriott* | [207] Liquid Phase Synthesis of Nanomaterials & Particles *Room 124 - ICC* | [261] Batch Process Operation & Control for Microelectronic Manuf., *Room 205 - ICC* |
| | [183] Multiscale Characterization & Modeling of Polymers *Wabash Ballroom 2 - ICC* | | [352] Composites & Laminates Based on Forest and Biobased Prodcts I, *Rm 124 - ICC* | [205] High Temperature Synthesis & Process. of Ceramics *Wabash Ballrm 1 - ICC* | [215] Transport Phenomena in Electronic Matrls Process., *Wabash Ballrm 2-ICC* |
| | | | [354] Composites & Laminates Based on Forest & Biobased Prodcts III, *Wabash Ballrm 2 - ICC* | [344] Biomimetic Approaches to Material Design, *Indiana Ballroom D - Marriott* | [407] Molecular Modeling of Nanostructured, Nanocrystalline & Amorphous Materials, *Room 123 - ICC* |
| | | | [201] Nanoparticle Coatings & Molecular Simulation of Materials Process., *Room 122 - ICC* | [208] Nanoscale Structure in Polymers: Self Organization in Plmrs I, *Room 123 - ICC* | |
| **2:00 PM** | [187] Thermodynamics of Polymers II, *Room 208-ICC* | [194] Biomaterials II *Wabash Ballroom 2 - ICC*<br>[195] Diffusion in Polymers & Membranes II, *Room 209 - ICC* | [117] Advances in Ceramic & Nano-Composite Membranes, *Ballroom 6 - Marriott* | [213] Biomemetics *Room 122 - ICC*<br>[211] Semiconductor Surface Chemistry, *Wabash Ballroom 2 -ICC* | [209] Plasma Processing II, *Wabash Ballroom 3 - ICC* |
| | [42] Polymer Thin Films & Interfaces I, *Lincoln-Marriott* | [197] Polymer Processing & Rheology II, *Wabash Ballroom 3 - ICC* | [203] Nanostructured Biomaterials II, *Room 124 - ICC* | [212] Nanoscale Structure in Polymers: Polymer Nanocomposites I, *Room 123 - ICC* | [219] Nanoscale Structure in Polymers: Polymer Nanocomposites II, *Room 123 - ICC* |
| | [185] Polymerization, Kinetics, Catalysis & Reaction Engineering II, *Reception Room - ICC* | [196] Modeling & Simulation of Materials Processing, *Wabash Ballroom 1 - ICC* | [64] Chemical Vapor Deposition I, *Wabash Ballroom 2 - ICC* | | |
| | | [295] Novel Carriers for Drug & Cell Delivery I, *Indiana Ballroom C/D - Marriott* | [319] Polymers & Matrls f. Renewable Resources I, *Indiana Ballrm F - Marriott* | [210] Reaction Kinetics in Electronic Mat. Process., *Wabash Ballrm 1 - ICC* | [218] Self-Assembled Biomaterials, *Room 121 - ICC* |
| | [186] Structure & Properties of Polymers II, *Wabash Ballroom 1 - ICC* | [315] Bio-Inspired & Bioimimetic Polymeric Materials, *Indiana Ballroom G - Marriott*<br>[353] Composites & Laminates Based on Forest & Biobased Products II, *Room 124 - ICC* | [202] Polymers for Photonics & Microelectronic Applications, *Wabash Ballroom 1 - ICC* | [127] Nanostructured Adsorbent Materials II *Indiana Ballroom A - Marriott* | |
| **4:30 PM** | [188] MESD Poster Sessn,*Exhibit Hall - ICC* | | | | |

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