Compositional Modulation and Ordering in Semiconductors

Thomas P. Pearsall and Gerald B. Stringfellow, Guest Editors

The science of materials as a specific discipline is a relatively modern development. Within this rather modern field, the study of semiconductor materials is an even more recent development. Modern textbooks on materials science focus primarily on the properties of metals and second on the properties of ceramics, reflecting the commercial importance of these materials 50 years ago when the transistor was demonstrated using germanium. Today the commercial importance of semiconductor materials is comparable to that of metals and ceramics, and the advances in semiconductor-materials technology are driving rapidly growing business sectors in communications, software, and biotechnology.

Almost all semiconductor devices are based on the control and manipulation of electrons and holes in thin-film structures. These structures are produced commercially in elemental semiconductors like silicon and in semiconductor-alloy structures like Si_xGe_{1-x} or $Ga_xIn_{1-x}As$, for example. Semiconductor alloys have materials properties that can be understood often in terms of similar behavior observed in systems of metal alloys. This is certainly the case with some of the phenomena discussed in this issue, such as solid-phase immiscibility and long-range ordering. However the study of the epitaxial growth of these alloys has also uncovered new materials-growth phenomena that are driven by the highly directional and largely covalent nature of the bonding in semiconductors. There is a large strain energy associated with the stretching and bending of bonds on the atomic scale in semiconductor alloys. This energy is an important factor in determining the reconstruction of the surface during crystal growth. For example we now know that the formation of dimer bonds on the (001) growth surface is directly responsible for atomistic ordering of semiconductor-alloy components. Such ordering phenomena are absent in materials having either metallic or ionic bonding.

The technology of modern semiconductor-device fabrication is predicated on the ability to produce extended planar layers of uniform composition and thickness. Heterostructure devices such as lasers, light-emitting diodes, heterojunction bipolar transistors, or high-electron-mobility field-effect transistors require the presence of epitaxial layers with different compositions and well-controlled thicknesses in the same device. However the growth of any alloy material results in strains in bond length and bond direction because different alloy components have differences in atomic size and bond length. This atomistic strain will lead to spontaneous ordering on the atomic scale and to long-range fluctuations in epitaxial-layer thickness and composition. In addition to effects of the epitaxial layer's long-range structure, ordering on the atomic scale introduces perturbations to the periodic potential of the valence-band electrons. As a result, the bandgap of an ordered alloy is lower than that of the random alloy counterpart with the same overall composition. The materials engineer must be able to control ordering over the entire surface of a wafer. Thus the goal of our research is to replace the phrase *spontaneous ordering* with *controlled ordering*.

The inexorable pressure to reduce the dimensions of semiconductor devices has introduced to materials scientists and engineers the concept of deposition of self-organized structures in the nanometer size regime. These self-organized structures will be technologically useful only to the degree that their size and nucleation density can be controlled. This issue of *MRS Bulletin* focuses on the fundamentals and implementation of the synthesis of self-organized, lateral periodic structures in covalently bonded semiconductor alloys.

Alex Zunger of the National Renewable Energy Laboratory (NREL) reviews the background and theory necessary to understand the phenomena of phase separation and ordering in semiconductor alloys. This work shows the importance of the surface reconstruction in the ordering process, as well as the relationship between ordering and the electronic properties of the ordered alloy.

The macroscopic parameters that a materials engineer uses to control ordering are substrate orientation, substrate temperature, growth composition, and flux. The challenge posed in crystal growth is to use these parameters to create a particular surface reconstruction. At this point, the structure of the ordered phase is determined. The next step is to impose growth conditions so that the forces favoring the formation of the ordered phase dominate the solidification process. The article by G.B. Stringfellow of the University of Utah describes this sequence for the organometallic vapor-phase epitaxial growth of ordered group III-V semiconductor alloys. This work emphasizes the effects of growth parameters such as temperature, vapor-phase stoichiometry, growth rate, and substrate misorientation on atomic-scale ordering. An understanding of these effects will enable control of the ordering process so it can be used as an element in the design of electronic and photonic devices.

Tohru Suzuki from NEC Corporation has approached the topic of ordering in GaInP and AlGaInP in regard to their use for visible laser diodes. He describes the discovery of CuPt ordering in GaInP and the associated reduction in the bandgap energy. His experiments on ordering show how a change in surface reconstruction leads to major changes in the ordered structures observed. These experiments suggest how ordering might be controlled and used in device design and fabrication.

The changes in surface reconstruction brought on by strain at the atomic level also affect macroscopic surface properties, notably the surface-diffusion co-

efficients. These changes reflect the symmetry of the surface reconstruction so that anisotropy is introduced into surface diffusion. A direct result of this anisotropy is a long-range periodic modulation of the composition oriented along specific crystallographic directions. The article by J. Mirecki-Millunchick along with workers at Sandia National Laboratories and NREL describes the long-range lateral ordering that results from this strain-induced surface reconstruction during crystal growth by molecular-beam epitaxy. The period of long-range ordering is determined by a complex interaction between surface features such as step density, reconstruction, and kinetics with energetic considerations such as strain, entropy, and chemical potential.

These considerations are further developed by S.D. Hersee and his group at the University of New Mexico, who are studying ordering effects in the growth of group-III nitride semiconductors by metalorganic vapor-phase epitaxy.

This series of articles shows that the tendency for semiconductor alloys to form spontaneously ordered structures during growth is based on interactions at the growth surface that can be understood from fundamentals of strain and surface reconstruction. Materials engineers who learn how to control these interactions through the measurement of macroscopic characteristics such as substrate temperature and growth composition will have added an instrument of tremendous power in their arsenal of crystal-growth techniques. The ability to choose deposition of an ordered phase or a random phase for a semiconductor alloy will prove an essential capability for the synthesis of self-organized nanostructured materials. □

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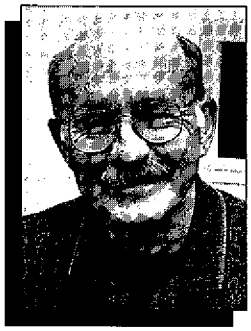

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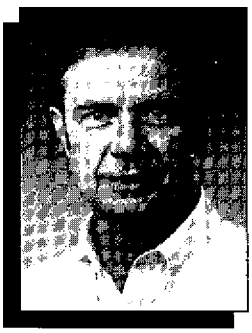

D.M. Follstaedt

Thomas P. Pearsall is a professor and Boeing-Johnson Chair at the University of Washington where he holds positions in the Department of Electrical Engineering, the Department of Materials Science and Engineering, and the Department of Physics. He is a Fellow of the American Physical Society and the Institute of Electrical and Electronics Engineers. He was recently named Fulbright Senior Scholar and is studying electronic transport in high magnetic fields at the Centre National de la Recherche Scientifique in Grenoble, France. Pearsall can be reached at the Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195, USA; fax 206-543-3100.

Gerald B. Stringfellow's research interests center on the fundamental aspects of semiconductor alloys: phase diagrams, solid-phase immiscibility, ordering, and doping. He is also a pioneer in the use of organometallic vapor-phase epitaxy (OMVPE) for the epitaxial growth of III-V semiconductor materials. This work emphasizes the materials science of OMVPE growth, including the thermodynamic and kinetic aspects of the process and the development of new source materials. Recent work has focused on ordering in III-V alloys, including GaInP, particularly the ordering mechanism. He has published over 300 papers in these research areas and has delivered 20 invited papers at national and international conferences during the last five years. Stringfellow can be reached at the Department of Materials Science and Engineering, University of Utah, 304 EMRO, Salt Lake City, UT 84112, USA; phone 801-581-8387; fax 801-581-4816; e-mail stringfellow@ee.utah.edu.

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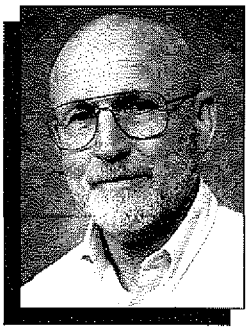
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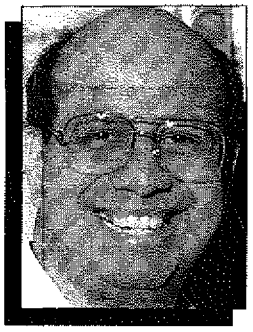
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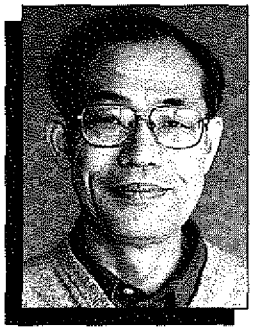

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