Point Defects in Materials Part II: Applications to Different Materials Problems

David Seidman and Donglu Shi,
Guest Editors

Introduction

This issue of the *MRS Bulletin* follows up on the November issue's five articles on point defect phenomena in a wide range of materials with five more articles on point defects. The present articles emphasize the behavior of different phenomena in various materials—nonstoichiometric metal oxides, intermetallic compounds, type II superconductors and semiconductors—in terms of fundamental properties of point defects. Again, point defects is the unifying theme but the emphasis shifts to material behavior.

This issue begins with Marshall Stoneham's article on the roles theory plays in predicting and understanding material behavior in terms of point defects in the different classes of materials. The following article by Rüdiger Dieckmann discusses the relationships between point defect concentrations in nonstoichiometric metal oxides and diffusion, i.e., mass transport. Next, Georges Martin and Pascal Bellon review their new approach for analyzing the role played by antisite defects in nonequilibrium phase transitions in intermetallic compounds. Then, Donglu Shi focuses on the effect of point, line, and planar defects on three major properties of type II superconductors—the critical transition temperature, the upper critical magnetic field, and the critical current density. Finally, Lionel Kimerling shows how defect engineering is used to achieve a high degree of complexity in product fabrication and greater sophistication in product performance; he illustrates what he means by defect engineering with examples from basic processes used in electronic materials processing.

Marshall Stoneham, director of research for AEA Industrial Technology, Harwell Laboratory, is a well-known solid-state theorist with extremely broad interests in materials science and engineering. He is the author of several books on defects and defect processes in solids, and also the author of many publications. In his article on the theory of solid-state defects—a theoretical paper with no equations—Stoneham demonstrates, with many examples, that studies of materials are often studies of defects since fundamental properties of defects (point, line, and planar) control many important, practical properties of materials. Stoneham's examples cover the main classes of materials—metallic, semiconducting, ionic, and polymeric. He emphasizes the intimate relationship between theory and experiment. And he emphasizes that the role played by theory in establishing experimental priorities is important and that theoretical estimates of significant parameters are extremely useful for showing what needs to be accomplished to improve materials properties. He also points out that theoretical or empirical models provide a framework for unraveling new situations where the critical variables have not yet been ascertained. Stoneham's article is peppered with many practical examples covering a wide range of problems.

Rüdiger Dieckmann, professor of materials science and engineering at Cornell University and a well-known expert on point defects and mass transport in ceramic materials, covers the problem of the relationships between point defect concentrations in nonstoichiometric metal oxides and diffusion. To illustrate the principles involved he cites manganosite, $Mn_{1-\Delta}O$, and spinels of the type $Me_{3-\delta}O_4$ with Fe, Mn, and Co cations. First, Dieckmann discusses the relationship between point defects and nonstoichiometry and shows, subject to the caveat that the point defect concentrations are sufficiently small, that the concentrations of defects have a power law dependence on the oxygen activity. This result allows the investigator to vary point defect concentrations by varying the ambient pressure of oxygen; this strongly contrasts with elemental metals or metallic alloys, where the point defect concentrations or types are not affected, to first order, by the ambient pressure. The experimentally observed dependence of the point defect concentrations on the oxygen activity permits unraveling the point defect structure of metal oxides. The tracer diffusivity of an ion is directly proportional to the concentration of point defects, and the latter is in turn proportional to the oxygen activity to some power. Thus, from measurements of the tracer diffusivity of an ion as a function of the oxygen activity, one may extract the point defect mechanism for diffusion.

Dieckmann demonstrates very carefully and in detail the power of these basic principles in obtaining detailed point defect information for the simple rock salt type oxide $Mn_{1-\Delta}O$. He then talks about the problem of cation diffusion in the spinels ($Me_{3-\delta}O_4$). The point defect structure in the spinels is more complicated than in the simple rock salt type structure oxides because two-thirds of the regular lattice sites are octahedrally coordinated and one-third are tetrahedrally coordinated. In addition, cations occur in different charge states in the same crystal structure. Dieckmann presents detailed information on the β-$Mn_{3-\delta}O_4$ spinel to illustrate the principles involved. He also shows that the presence of grain boundaries in specimens can affect the point defect concentrations and thereby change the bulk diffusivities of the cation; he illustrates this for the tracer diffusivity of Fe in polycrystalline $Fe_{3-\delta}O_4$ compared with single crystal $Fe_{3-\delta}O_4$.

Dieckmann concludes by noting that though the approach used to date has yielded detailed information, the roles

played by defect interactions, point defect clustering, and the concentration dependences of the point defect mobilities are far from being completely understood, even for the simple transition metal oxides.

Georges Martin and Pascal Bellon of the Section de Recherches de Métallurgie Physique, Saclay, are well-known experts in radiation damage, particularly in the roles played by point defects in understanding the atomic mechanisms for the observed radiation-induced microstructures. Martin and Bellon review a new approach they have developed for treating the role played by antisite defects in nonequilibrium phase transitions in intermetallic compounds, e.g., compounds produced by ion implantation or ion-beam mixing, intermetallics formed during high-energy ball milling, and ordered compounds formed by vapor deposition. They use statistical thermodynamics for a system subjected to a driving force. Their stochastic method involves constructing an effective free-energy function for a "driven system," that is, a system subject to a driving force; e.g., in a specimen being driven by a particle irradiation field, the rate at which atoms exchange places on a lattice involves a temperature-independent jump frequency besides the normal thermally activated jump frequency. The effective free-energy function for a driven system allows one to determine the most stable state for a given driving force. This allows the construction of dynamical equilibrium phase diagrams. These phase diagrams often contain unexpected features that aid in interpreting experimental data as well as predicting completely new physical effects.

As an application of their theory, Martin and Bellon work out the case for an order-disorder transition in the body-centered-cubic lattice (β-brass structure) for compounds such as CuZn or NiTi. For a driven system at particular values of the driving force and temperature, they demonstrate that two locally stable steady states are present—a fully disordered one and a partly ordered one. The partly ordered one turns out to be more stable than the disordered one. At higher temperatures or with a larger driving force, the disordered state is more stable than the partly ordered one. The dynamical phase diagram that is constructed is rich in interesting and new phenomena. Martin's and Bellon's theoretical framework may ultimately help clarify the effects of processing conditions on the end products in complicated alloy preparation techniques or predict the long-term stability of compounds subjected to complex operating conditions.

Donglu Shi of Argonne National Laboratory's Materials Science Division actively researches the relationships between microstructure and properties of A-15 and high-temperature superconductors. Shi's article focuses on the relationship between three major properties of type II superconductors and defects—the critical transition temperature (T_c), the upper critical magnetic field (H_{c2}), and the critical current density (J_c). The crystal structure, chemical stoichiometry, and the microstructure of type II superconductors affect these three properties, and their values vary greatly among different systems. The value of T_c is very sensitive to the degree of long-range crystallographic order, as measured by the long-range order parameter (S). There is strong experimental evidence for the A-15 compounds that T_c is greatest for a given material (e.g., Nb_3Ge) when $S = 1$. For the A-15 structure it is believed that the fundamental mechanism of T_c is connected with the three-dimensional chains of A atom chains in the A_3B structure, and that any disruption of these chains decreases T_c. The value of T_c in the Bardeen-Cooper-Schrieffer theory is proportional to $\exp[1/N(0)V]$, where $N(0)$ is the electron density of states at the Fermi level, and V is the effective matrix element for phonon-mediated electron-electron interactions. The interchange of A and B atoms in the A-15 structure leads to a decrease in $N(0)$ and therefore a decrease in T_c. For the ceramic high-temperature superconductor $YBa_2Cu_3O_x$, it is known that the value of T_c is sensitive to the exact oxygen vacancy concentration along the Cu-O chains in this structure. These oxygen vacancies are very mobile at elevated temperatures and therefore the superconductivity of $YBa_2Cu_3O_x$ is sensitive to the partial pressure of oxygen and temperature. Point defects have also been found to play a role in other ceramic high-T_c superconducting systems, e.g., $Ba_{1-x}K_xBiO_3$ and $La_2CuO_{4-\delta}$. For example, for $Ba_{1-x}K_xBiO_3$ the solid solubility of potassium, which is essential for superconductivity, is controlled by the concentration of oxygen vacancies.

The upper critical field H_{c2} is directly proportional to the normal state resistivity, ρ_n at constant T_c and normal state electronic specific heat; the quantities ρ_n and T_c are, however, coupled and ρ_n cannot be readily changed without affecting T_c. For type II superconductors, plastic deformation and neutron irradiation have been used to increase ρ_n.

In "hard" superconductors (type II superconductors processed by different metallurgical and ceramic processing techniques) in the mixed state, crystal defects can interact with flux line (or fluxoids, fluxons, or vortices). The critical current density, J_c, of a hard superconductor is defined as the current density at which the Lorentz force is balanced by the depinning force. Thus the values of J_c are directed by the flux pinning strength. The pinning mechanisms are related to the microstructure of the pinning points. The pinning strength reaches a maximum value when the average diameter of the pinning centers is approximately equal to the coherence length of the superconductor. In conventional A-15 superconductors the flux lines are pinned mainly by grain boundaries. In high-T_c superconductors the coherence length is estimated to be $\approx$10 Å, and therefore the dimension of the critical printing centers is reduced to the atomic lattice spacing. In $YBa_2Cu_3O_x$ the value of J_c is believed to be associated with the pinning of flux by oxygen vacancies.

The general picture that emerges from Shi's review is that T_c and H_{c2} are influenced mainly by point defects that affect the density of states at the Fermi level, but J_c is affected by all kinds of defects and the mechanism is related to the pinning of flux lines.

Lionel Kimerling, professor of materials science and engineering at MIT and a well-known expert on electronic properties of point defects in semiconducting materials, considers several popular myths for some generic processes used in the electronics materials processing industry. He first summarizes the limits of the knowledge base for each process, then demonstrates how defect engineering has been used to provide new frontiers in product design, processing, and performance. Kimerling uses the word "product" to emphasize the point that the materials engineer with his knowledge of the data base is in an excellent position to state, "Anything can be done, if it's done correctly." With this viewpoint, the materials engineer can lead in the development of new products and need not be relegated to a supporting role.

For the first often-heard myth, that "defects degrade performance and fabrication yield," Kimerling explains how defects in silicon substrates can be created in a region called the intrinsic gettering zone, and how defects in this region absorb point defects and stray contaminants to leave behind a highly perfect region where the active devices are fabricated. To achieve the gettering effect, he employs the relevant knowledge base for silicon. The second myth Kimerling discusses is the one that states "Preservation of interface coherence is essential for reliability, high process yield, and performance." Epitaxial growth is employed to produce

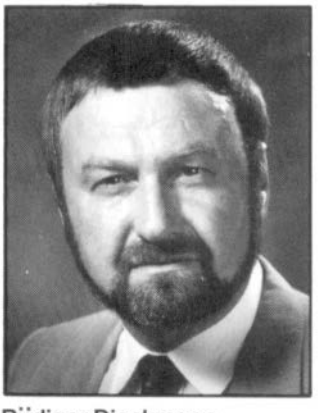
layered device structures, and control of the lattice parameter misfit between the epitaxial layer and the substrate is the key to producing long-lived heterostructure laser devices used in fiber optic telecommunication systems. At present the Si/Ge and Si/GaAs heterostructures are of interest for high electron mobility and optoelectronic integration; both systems exhibit a 4% lattice mismatch that must be accommodated by misfit dislocations. Two approaches are effective for total relaxation of strain with interfacial misfit dislocations while eliminating the deleterious threading dislocations: they are substrate patterning and compositional grading. The relaxation without threading dislocations was achieved by physically patterning the substrate into mesa regions that contain devices or circuit cells; the glide dislocations terminate at edge surfaces and do not penetrate adjacent mesas. Kimerling illustrates the use of this approach to produce a 1 μm thick dislocation free layer of $Ge_{0.30}Si_{0.70}$ on silicon.

Kimerling also shows that defect engineering can be used to dispel several other myths. For example, he demonstrates that the myth, "Perfect, crystalline silicon is required for high efficiency energy conversion," is incorrect. In summary, Kimerling's article is an excellent example of how fundamental concepts involving the properties of atomic scale imperfections can be used to create real products. □


David N. Seidman


Donglu Shi


Pascal Bellon


Rüdiger Dieckmann

David N. Seidman, Co-Guest Editor with Donglu Shi for the November and December issues of the *MRS Bulletin*, is a professor of materials science and engineering at Northwestern University, and was a professor at Cornell University prior to 1985. Seidman's research interests have been in the areas of basic properties of point defects in quenched or irradiated materials, and displacement cascades in irradiated materials. His present research concerns phase transitions and the relationships between the structure and chemistry at internal interfaces in metal/metal, metal/metal oxide, semiconductor/semiconductor, and semiconductor/metal systems using transmission electron microscopy, atom-probe field-ion microscopy and Monte Carlo simulations. Seidman, a member of the Materials Research Society, received his PhD degree from the University of Illinois. His honors include two Guggenheim Fellowships and an Alexander von Humboldt Senior Fellowship at the University of Göttingen.

Donglu Shi, Co-Guest Editor with David Seidman for the November and December issues of the *MRS Bulletin*, is a research scientist at the Materials Science Division, Argonne National Laboratory. He has worked on the characterization and processing of superconducting materials for the past nine years, and has concentrated on critical currents, flux pinning, vortex behavior, and microstructure analysis of conventional A-15 superconductors and high T_c oxides. Shi has also been involved in research on phase transformations, rapid solidification, crystallization, interfaces, defects analysis, alloy and ceramic processing, amorphous materials, and other aspects of the relationship between properties and structure of the metallic compounds. He holds a PhD from the University of Massachusetts and is a member of MRS.

Pascal Bellon is a research scientist at the Section de Recherches de Metallurgie Physique, Centre d'Etudes de Saclay. He graduated from Ecole Superieure d'Electricite in 1984 and received his doctorate from Universite de Paris 6 in 1989. His research work involves experimental and theoretical studies of driven systems such as alloys under irradiation or epitaxial semiconducting layers.

Rüdiger Dieckmann, professor in the Department of Materials Science and Engineering at Cornell University, received his PhD in engineering from the Technical University of Clausthal in 1975, and completed his habilitation in physical chemistry at the University of Hannover in 1983. He worked at Hannover's Institute for Physical Chemistry and Electrochemistry until 1987 as a Heisenberg Fellow, and was awarded the Nernst Prize in 1984 by the German Bunsen Society for Physical Chemistry. Dieckmann's research has spanned point defect structure of inorganic, nonmetallic compounds, the transport of matter and charge in ceramic solids, the kinetics of solid-state reactions, the thermodynamic stability of phases, and recently the growth of ceramic single crystals. He is a member of the editorial board of the journal *Reactivity of Solids*, and a member of the American Ceramic Society, The Minerals, Metals & Materials Society, and several professional associations abroad.

Lionel C. Kimerling is the Thomas Lord Professor of Materials Science and Engineering at the Massachusetts Institute of Technology (MIT), where he earned his BS in metallurgical engineering and his PhD in materials science. He also chairs MIT's Electronic Materials Degree

Program. Prior to joining the Institute, he headed materials physics research at AT&T Bell Laboratories, and before that, served as Captain at the Solid State Sciences Laboratory of the Air Force Cambridge Research Laboratories. Kimerling is chairman of the editorial board of *Journal of Electronic Materials*, a Fellow of the American Physical Society, director of the Electronic, Magnetic and Photonic Materials Division of TMS-AIME, and a member of the Materials Research Society and numerous other professional associations. He conducts an active research program in the structure, properties, and processing of semiconductor materials, and he has authored over 150 technical articles.

Lionel C. Kimerling

A. Marshall Stoneham

Georges Martin

Georges Martin graduated from Ecole des Mines de Paris in 1963 and earned his Doctorat d'Etat in Physics from Universite d'Orsay. He worked as a research scientist in Centre d'Etudes Nucleaires de Saclay (1964-84), mainly on solid-state kinetics. In 1984 he became director of the Centre d'Etudes de Chimie Metallurgique (CNRS-Vitry), and since 1989 has headed the Section de Recherches de Metallurgie Physique at Saclay. He received the 1985 Humbolt award for Franco-German scientific cooperation.

A. Marshall Stoneham is director of research for AEA Industrial Technology. After receiving his doctorate from the University of Bristol, he moved to Harwell, becoming in turn leader of the Solid State and Quantum Physics Group and then head of Materials Physics and Metallurgy Division. In 1989 he was elected a Fellow of the Royal Society and later a Fellow of Wolfson College, Oxford. His wide accomplishments in materials science include books on defects in solids and on the reliability of nondestructive inspection, as well as nearly 300 papers. As a theorist, he particularly enjoys the stimulus of applied science and working alongside good experimenters. □