Evaluation of EHS Issues Should be High Priority

To the Editor:

A ranking of desired low-*k* materials characteristics is summarized in the October 1997 *MRS Bulletin*, Table III, p. 22. The very lowest ranking of #15 was given to the "Environmental, health and safety (EHS)" category, which suggests that this area is the industry's lowest priority, potentially to be sacrificed for technological advancement and profit. I hope this ranking results from an inadvertent oversight in deference to a technical emphasis on desired performance features of low-*k* materials.

The expert advice of industrial hygienists, toxicologists, and environmental engineers and scientists is critical to the safe utilization of novel organic polymers and other materials in the semiconductor industry. As research and development engineers and scientists, if we fail to place the highest priority on the competent evaluation of EHS issues, we risk the health of industry workers and the public, as well as create the potential for costly legal vulnerabilities for the industry. While defining the "safety" of an individual chemical is not our area of expertise, we should first defer to trained professionals competent to both assess risks and determine if and how such chemicals may be safely handled and used in a fab environment.

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Shape Changes in Ceramic Particles: A Paradox Explained

A long-standing paradox in the theory of sintering ceramics has been resolved by Alan W. Searcy of the Ernest Orlando Lawrence Berkeley National Laboratory, Jeffrey Bullard of the University of Illinois, and W. Craig Carter of the National Institute of Standards and Technology. In sintering, fine-powder compacts are heated to temperatures only a little lower than their melting points; atoms and molecules are set in rapid motion, and the particles coalesce, reducing porosity and increasing the strength of the finished product.

The "classical" approach to sintering assumes that the initial particles in the compact are spheres and that movements of atoms or molecules are driven by differences in curvature. In order to reduce surface-free energy, atoms supposedly move from particles of smaller radius to particles of larger radius; the concave regions formed by contact between particles are filled by atoms from convex surfaces.

However, the molecules of crystalline particles sometimes move in directions the theory forbids which, according to Searcy, is not surprising, "because the classical theory fails what I think of as the 'single-particle sintering test.' It predicts that an isolated particle of arbitrary shape will evolve into a sphere. On the contrary, most single crystals, if grown slowly enough, are faceted." Unlike an idealized sphere, the surface energies of a crystal depend on the different orientation of the surfaces to the underlying crystal-lattice structure.

"So here's a theory that says you can't get sintering with particles that have planar surfaces and edges," Searcy said, "while in fact many solids, such as magnesium oxide, cobalt oxide, sodium chloride, and lithium fluoride, keep their faceted shapes—or even grow into faceted shapes—while they are being sintered."

Josiah Willard Gibbs, the nineteenth-century founder of chemical thermodynamics, had reported that molecules at the edges between crystalline facets would leave and return to their crystal sites more often than molecules in the facet surfaces because the edge molecules are less strongly bonded. Inspired by what he calls Gibbs's "qualitative description of dynamic equilibrium," Searcy worked with Bullard and Carter to develop equations that explain shape changes during sintering in terms of energy differences among differently oriented surfaces and edges— "rate equations" founded on Searcy's "statistical thermodynamic description of the unstable internal equilibrium" in crystals of any shape.

The new equations are based on two governing principles: First, any change in shape is possible if it reduces total energy—the change need not minimize energy, merely reduce it. Second, among all possible shape changes, the one that actually occurs is the one in which the exchange of atoms or molecules and vacant crystal lattice sites is easiest—the one most favored kinetically.

The new equations show that particles do not grow faster because they are curved; instead the apparent curves are produced by the growth of new crystal layers. "Rounded" edges which appear during sintering are actually small additional facets—kinetically favored to grow because it is easier to move atoms or molecules to those sites. As these small, fast-growing facets multiply, particles begin to appear classically rounded, but become faceted again in the final stages of sintering.

For example, if two cubic crystals of magnesium oxide are in contact with each other, the smaller rapidly transforms into a nearly spherical particle. A rounded neck forms between it and the larger particle, which is still nearly cubic—producing a sort of lopsided dumbbell. Given enough time, a single large cube with slightly rounded edges will form. At every step the changes serve to balance the demands of minimum surface energy; only changes which reduce energy are allowed.

Recently Searcy, Bullard, and Carter used their model to solve a puzzle reported by researchers at Oak Ridge National Laboratory. Observed in a transmission electron microscope (TEM), box-like particles of magnesium oxide slowly grew connecting necks during over two hours of sintering—then in 20 minutes the necks collapsed and disappeared.

Three thermodynamic pathways were suggested by the new equations, one of which matched the observations exactly by taking into account the chemical reaction of the magnesium oxide particles with the supposedly unreactive carbon substrate on which they were mounted. In the vacuum chamber of the TEM, carbon and magnesium oxide react to release carbon monoxide and magnesium vapor, reducing the overall energy of the magnesium-oxygen-carbon system. Searcy and Bullard also report confirmation of a prediction of the new model in the September 1997 issue of the *Journal of the American Ceramic Society*.

Mesostructured Ceramic-Type Materials Form Using Polymer Templates

Scientists at Max-Planck Institute for Polymer Research have reported in the December 5 issue of *Science* the use of polymers as templates to structure ceramic-type