About the Journal

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Compliant Surface Coatings to Reduce Turbulent Drag and Noise
Through theoretical analyses and computer simulations sponsored by the Office of Naval Research, we are investigating hull coatings that can improve a vessel's performance by reducing the turbulence and associated noise and drag generated by the motion of the vessel through the water.

Detoxification of Environmental Copper in the Common Mussel
Laboratory environmental scientists are investigating the bivalve mollusc Mytilus edulis to understand its ability to metabolize increased quantities of potentially toxic metals found in polluted ecosystems.

Modeling EMP Damage to Semiconductors
Our computer models for predicting EMP damage to semiconductors have generated significant results that should help us design circuits with enhanced survivability.

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About the Cover
The U.S. Baton Rouge under way in a calm sea. The clean hydrodynamic shape of the vessel permits laminar flow over the bow. Distortion of the water surface produces a lens effect that brings numbers painted on the side of the submarine into view. Turbulence, which produces the wake, reduces the efficiency of propulsion. The lead article in this issue (p. 11) discusses the studies of compliant surfaces to reduce turbulence. (Official Navy Photograph. U.S. Naval Institute, Annapolis, MD)

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Compliant Surface Coatings to Reduce Turbulent Drag and Noise

Sponsored by the Office of Naval Research, we are investigating, through theoretical analyses and computer simulations, hull coatings that can improve a vessel's performance by reducing the turbulence and associated noise and drag generated by the movement of the vessel through the water.

It has long been observed that the porpoise swims with remarkable efficiency, keeping pace with fast vessels without overexertion. Many mechanisms have been proposed to account for this enviable efficiency, including dynamic change of the body profile, alteration of surface flow by shifts in the orientation of hair-like fiber bundles, injection of polymeric-like substances into the water layer from below the skin surface, and dynamic compliance and energy absorption by skin. Designers of naval vessels obviously would like to achieve a similar efficiency of motion and lack of skin friction and drag. To this end, we are investigating compliant coatings in the hope of finding ways to reduce the fluid frictional drag on ships, torpedoes, and submarines, both to increase their speed and range and to decrease the turbulence-generated noise they make.

For our purposes, a compliant surface is one that yields and deforms in response to the turbulent flow-induced stresses generated in the thin fluid boundary layer adjacent to the surface. Some compliant surfaces may actually interrupt the formation of turbulence-induced stress, absorbing the energy and reducing the level of turbulence.

Our program emphasizes the development of theoretical and numerical simulations of fluid dynamics and solid mechanics. We use these simulations to analyze and supplement physical experiments currently conducted at the National Bureau of Standards, several.

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Submarines and other submersibles, such as high-speed torpedos, are primary candidates for drag- and noise-reducing coatings to reduce motion-generated turbulence such as that shown in this photograph.

Department of Defense laboratories, and several commercial scientific laboratories. The results of our computations and analyses also are used to help plan and design further experiments and to augment and test some of the more plausible theoretical concepts under study at a number of universities.

We are searching for homogeneous coating materials and internally structured surface coatings that deform in such a way that they reduce the turbulent pressures adjacent to them. The turbulent pressure wave may be reduced by a deforming neighboring surface “trough” just as it may be increased by a deforming neighboring surface “crest” (where “neighboring” is used in the sense of phase). Reducing the intensity of the turbulent pressure field reduces the turbulent shear force and, consequently, the skin friction drag on the vessel. Submersibles and ships whose hulls are coated with such compliant surfaces may operate with substantially lower drag, generate less noise, and require less propulsive power at a given speed than do conventional, uncoated vessels.

To aid in the search for suitable coatings, we are numerically simulating the surface motions of soft, yielding material coatings that deform readily to stresses generated by turbulent flow.\(^1\) The deformations appear as complicated ripple patterns; these patterns may be almost stationary or they may move like waves over the surface. The turbulent pressure forces originate in the energetic but random turbulent fluid motions that are confined to the fluid boundary layer (no more than a few millimetres thick) that clings to the hull of a vessel as it moves through the water.

The cumulative result of these turbulent motions and associated stresses between the water and the surface (see Fig. 1) is known as skin friction drag. At speeds of one to a few metres per second, on a well-designed streamlined hull profile such as that of a modern submarine, skin friction contributes more than half of the total drag. We are typically concerned with drag reduction over a range of speeds from about 3 to more than 30 m/s (6 to 60 knots).

Skin friction drag exacts two penalties in a naval vessel. In the first place, it represents an energy loss that must be overcome by the engines to maintain headway. In addition, the myriad random, turbulent eddy pressure sources in the boundary layer (as well as in the wake, where the turbulent boundary-layer fluid is deposited after it leaves the hull) generate considerable noise. This noise can be detected, with sensitive underwater listening equipment, by other vessels at appreciable distances. The increased propulsive power required to overcome the drag may become, in itself, a major source of unwanted noise on a ship or submersible, a significant concern in naval missions requiring stealth.

At low speeds, turbulence drops dramatically, and the boundary-layer flow becomes smooth and closely parallel to the surface. The fluctuating velocities and pressures in the boundary layer are damped, the flow approaches the laminar-flow limit, and...
the drag is diminished to less than half of its turbulent value (Fig. 2). In this state, the skin friction drag results entirely from molecular surface adhesion, off-surface molecular diffusion, and resulting viscous stresses. Our goal is to find soft material coatings that will absorb most of the turbulent pressure and energy by deforming compliantly, thereby inducing a nearly laminar state of flow.

The potential drag reduction illustrated in Fig. 2 is a direct function of the Reynolds number \( \text{Re} \), which is the ratio of inertial to viscous force in a flowing fluid:

\[
\text{Re} = \frac{U_s l}{\nu}
\]

Here, \( U_s \) is the mean flow speed, \( l \) is the characteristic length (typically the distance from the nose of the vessel to the point where we calculate the turbulence characteristics), and \( \nu \) is the kinematic viscosity coefficient. The Reynolds number is the basic scaling parameter used to compare similar theoretical and experimental flow behavior. It is a property of both the fluid motion and the local thermophysical state of the fluid. The parenthetical numbers in Fig. 2 are the apparent percentages of drag (where the fully turbulent level is given as 100%) that may be realized for a constant Reynolds number of \( 15 \times 10^6 \). Reported experimental results fall within the shaded region.

**Compliant Materials and Internally Structured Coatings**

We are examining theoretically a number of soft, pliable surface-coating materials for their spatially and time-varying response. Among those being considered are natural rubbers, artificial rubber-like compounds, and time-cured viscoelastic polymeric gels such as polyvinylchloride (PVC) with very low shear and bulk moduli. We also are examining internally structured coatings fabricated either with open or partially fluid-filled cells and channels or with directionally oriented stiffening ribs.

**Fig. 2**

Dimensionless drag coefficient vs Reynolds number, showing the turbulent and laminar limits and the reported salt-water drag experiments (shaded area). The numbers in parentheses give percentages of drag (referred to the fully developed, turbulent skin friction drag limit as 100%) at a Reynolds number of \( 15 \times 10^6 \).
and adjacent surface deformation, producing a substantial reduction in the fluctuating turbulent pressure and drag.

**Numerical Simulation Procedure**

When we simulate turbulent fluid dynamics, we attempt to reproduce the generation, advection, dispersion, dissipation, and diffusion of the significant turbulent motions and their influences. All of these processes operate over vastly different scales of length. We must resolve scales varying in size by a factor of about ten thousand. We use sophisticated multidimensional finite-element codes to simulate the solid material response, coupled to equally sophisticated simulations of the turbulent flow field. Each numerical simulation of one of these experiments takes several hours of computer time on the Cray 1 and requires the entire available memory of that two-million-word machine.

In an engineering problem, the flow evolution would be modeled approximately using differential or algebraic equations to describe the time-averaged behavior. In our research, however, we are denied the luxury of this simplicity. To detect compliant-surface drag-reduction mechanisms, we must compute explicitly as many of these motion scales as possible. This enables us to calculate directly the evolution in time of the flow and then use the numerical results directly as a flow diagnostic tool. In response to the need for higher resolution to follow these scales of motion, we have used mesh-free phase-space (Fourier-transform) representations of the two- and three-dimensional velocity and pressure fields.

If it were not for the guidance provided by our computational simulations, each of the various combinations of candidate coating materials and internal structures would have to be examined experimentally. Such a trial-and-error program would require many thousands of individual experiments, occupying many scientific lifetimes to complete. Our systematic computational simulations reduce this formidable number of experiments to a much more reasonable goal of 50 or fewer.

The procedure requires simulation of the fully random pressure-velocity field of a turbulent boundary layer at each selected flow condition. Figure 3 displays the Fourier-transformed pressure-frequency spectrum in the turbulent boundary layer at a flow speed of 10 m/s. Our simulations of the turbulent boundary layer incorporate, insofar as possible, all of the physical scales described previously. Properly simulated, this distribution of motion scales will initiate an energetic cascade process that corresponds to the eddy motions interacting with closest neighboring size scales and that progressively distributes the energy to smaller, higher frequency eddy motions. Ultimately, this cascade reaches the limiting small-scale range of molecular dissipation, and the nearby spectral distribution of scales reaches a nearly constant state corresponding to a statistically stationary system, known as a "fully developed" flow with a stationary inertial subscale range. In this way, we simulate the dominant portion of the development of random turbulent motions that combine to produce the overall unsteady viscous fluid motion experienced by the vessel.

Prominent among the simulation techniques that we have adapted are the two- and three-dimensional pseudo-spectral formulations (which combine Fourier-transform and finite-

![Fig. 3](image.png)

The frequency spectrum of turbulent pressure fluctuations generated during the simulation of a 10-m/s boundary-layer flow over a flat surface.
WORK FOR OTHERS
difference methods) originated at
the Massachusetts Institute of
Technology. We have modified these
methods to represent properly the
moving solid boundary of the
compliant surface and to analyze its
influence on the pressure distribution
in the flow near the wall. Our results
provide additional verifications of
the original solution accuracy for
researchers using other computational
and analytic methods.

The Fourier-transformed pressure
spectrum illustrated in Fig. 3 is a
necessary and convenient procedure
for displaying and analyzing random
time and space signals, such as
instantaneous local velocities and
pressures. The transformation helps
reveal, at a glance, features such as
periodicity and stationary (unvarying)
components. Integral relations and
statistical-moment correlations are
obtained as simple products, additions,
and subtractions of the transformed
variables.

In some cases, the Fourier-
transformed spectra enable us to make
closed-form analytical representations
with relative ease. In addition,
it is easy to implement digital
postprocessing (filtration, etc.) with the
transformed variables. This makes it
possible to delete nonphysical random
signal errors (i.e., numerical noise) from
our analysis rapidly, systematically, and
almost automatically, before they lead
to erroneous or misleading
interpretations.

Figure 4 represents the present stage
in the development of our model, a set
of four fixed-time “snapshots” of
the surface deformations along a
streamwise slice of a structured
compliant coating of neoprene
rubber over reinforcing ribs of soft
poly-vinylchloride, at a flow velocity
of 30 m/s (horizontal scale magnified
ten times for ease in visualizing
deformations). Each zone is set initially
to be 5 mm long in the streamwise
direction and 0.5 mm thick. The surface
deformations also may be represented
as time histories at a fixed streamwise
position, as illustrated in Fig. 5. Like
most of our computations, this one is
two dimensional. The coating is
modeled as having finite length and
depth but an infinite span (into the
plane of the figure). Hence, these
results can display only planar strain
and strain-rate behavior.

Even though full three-dimensional
computations are much more expensive
than those done in two dimensions, we
must periodically check the three-
dimensional fluid and solid material
behavior. Three-dimensional
computations are needed to correct for
such features as edge effects, span-wise
gallery changes, transverse surface
curve structure, structural inhomogeneities,
and orientation anisotropies. When
these corrections are applied, we often
find that the sharp, well-defined two-
dimensional behavior is modified and

Fig. 4
Response of a structured coating of
neoprene overlying reinforcing ribs
over a base of polyvinylchloride (PVC).
The finite-element calculation shows
the formation of a random distribution
with time of traveling waves. This ran­
dom distribution shows promise for
destructively interfering with the
random turbulent pressure field that
generates it.
reduced in amplitude and frequency, with occasional phase modulation, as well. The corrections derived from the three-dimensional tests are vital for proper interpretation of our two-dimensional results.

We produced the simulated response shown in Fig. 4 by imposing modeled turbulent pressure-time histories and spatial distributions as boundary conditions for the finite-element computations. We simulated the pressure by an independent and separately applied Monte Carlo method that neglects surface motion and deformation. Hence, the turbulent fluid model is, at present, uncoupled from the compliant surface motions. The wall motions project no influence back into the turbulence calculations.

Even in their present noninteractive state, however, these calculations are valuable tools for screening and selecting materials. They form the largest body of data we have available for preliminary characterization of material response.

We have successfully simulated qualitatively some recent experimental results obtained at another laboratory. These results indicate that the softer material (polyvinylchloride) forms standing waves at flow speeds of about 1 m/s (2 knots). Such divergence leads to an undesirable quasi-stationary standing wave of large amplitude. This confirms our contention that a development strategy that includes numerical simulation can reduce the time and expense of experiments.

**Current Investigations and Results**

The interactive coupling of the turbulence and materials-response models is one of our most immediate goals. When the models of fluid dynamic motions and pressures are fully and interactively coupled to those of surface deformations, we will be able to see how the fluid and solid media dynamically influence each other. This, in turn, should enable us to isolate the fundamental mechanisms for these dynamic interactions and to identify promising coatings and critical flow conditions for experimental test and further analysis.

One of our most significant investigations is directed toward understanding the interactions between a dynamically responding coating and the adjacent turbulent fluid. Theoretical studies of the dynamics of the interface where the coating surface meets the fluid are being augmented by numerical studies of the way the evolving turbulent fluid flow responds to hypothetical wall motions. Both approaches are necessary in this search for the key dynamical mechanisms.

The development and analytical test of appropriate algorithms for boundary conditions, convergence bounds, and error sensitivity are outgrowths of these theoretical studies. In turn, our computations provide a numerical data base for further test, verification, and guidance in the development of a satisfactory theoretical description of interactive response of the surface to turbulence.

Currently, our most intensive effort involves directly coupling the responses of the coating materials to the motions of the adjacent turbulent field. To do this we are linking the finite-element simulations of dynamic coating response to the simulations of the dynamic evolution of the turbulent fluid.
fluid at incremental time intervals. Our attempts at linking the coating response to the turbulent flow field are augmented by the theoretical descriptions being developed from concurrent studies on the mathematical boundary conditions that govern the interactive coupling.

The resolution of our calculated frequency and amplitude histories for selected coating materials subjected to particular ranges of turbulent flow pressures must, necessarily, be accurate enough to enable us to develop analytical dispersion relations for the interactions between the flow and the material and the propagation of interface disturbances. This information is basic to the understanding and characterization of the dominant response properties of materials and the mechanisms of fluid-solid coupling.

Our investigations, to date, indicate that the softest viscoelastic materials require both an overcoat of stiffer material (e.g., a thin, firm neoprene overlayer possibly one tenth the thickness of the whole coating) and internal stiffeners arranged in the coating. This internal structuring is needed to keep deformation amplitudes within bounds and to increase the frequency of the resulting controlled deformations in the coating. We seek to develop a carefully controlled range of interruptive frequency-amplitude response, where the interruptions are delayed in phase with respect to the forcing frequency.

So far, coatings consisting mostly of the softest, most pliable materials (such as polyvinylchloride gels) in combination with small amounts of firm stiffening materials (such as hard rubbers and plastics) show promise in their deformation response of appropriate frequency, amplitude, and phase over a broad range of flow conditions. In addition, coatings with wide, shallow internal channels look promising for tuning the frequency response of the coating for optimum drag reduction.

Once we have coupled our turbulent fluid model with our material response model, we should be able to simulate

One of our most significant investigations is directed toward understanding the interactions between a dynamically responding coating and the adjacent turbulent fluid.
the entire history of the drag-reduction process from initial acceleration to steady state (constant flow speed). This will require a sequence of studies, conducted at a series of different constant flow speeds and linked by intermediate acceleration intervals. Only those candidate drag-reduction materials that exhibit favorable response over a broad range of flow conditions and immersion depths will be considered for further experiments and analysis.

We are seeking, in our numerical simulations, to confirm the existence of critical thresholds of flow-material properties and responses, such as the onset of standing-wave instability (static divergence), implied by some experimental observations. In particular, we are emphasizing the combination of experimental observations and numerical simulations and analyses, as both types of investigation are essential for a complete understanding of the process of reducing turbulence-generated drag and noise.

Key Words: compliant material; laminar flow; numerical simulation; propulsion efficiency; skin friction; turbulent-boundary-layer noise.

Notes and References
Detoxification of Environmental Copper in the Common Mussel

Although the mussel *Mytilus edulis* is widely known to accumulate copper and other metals from the environment, we do not completely understand either the biochemical mode of detoxification or how the process affects the tolerance of mussels to copper found in polluted ecosystems. Our investigations have focused on two mechanisms for metal detoxification: the binding of copper to metallothionein-like proteins and the incorporation of copper into lysosome-like vesicles.

Many bivalve molluscs contain concentrations of metals that are much higher than those levels found in seawater or shown to be necessary for metabolic purposes. The mussel *Mytilus edulis* has been extensively used as an environmental indicator of the presence of many metals, in part, because of its worldwide distribution. More important, metals can accumulate in the soft tissues of this mussel that reflect the longer-term concentration of metals in the animal's environment. Taking advantage of this process, laboratory scientists are using tissue assays of mussels to identify aquatic environments that may contain elevated quantities of dissolved metals.

Among the metals found in polluted ecosystems, copper is of special interest because it is highly toxic to many aquatic organisms. The adverse effects on mussels of increased copper concentrations are well documented in bioassay studies. High levels of copper elicit a shell-closing response that indicates the animal is attempting to isolate itself from the toxic substance; low levels do not elicit the closing response and may be lethal after long-term exposure. However, the copper concentrations used in most bioassays are higher than those found in polluted habitats. The stress responses resulting from chronic and intermittent exposure to sublethal concentrations of copper—

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the levels actually present in some polluted environments—are not completely understood but may, among other things, reduce the potential for growth, decrease the capacity to reproduce, impair the ability to resist further changes in pollution levels, and hamper the effectiveness in competing with other species in the ecosystem.3

The Laboratory's Environmental Sciences program related to this subject is funded by the U.S. Department of Energy, Office of Health and Environmental Research, Ecological Research Division. Our program includes research on the effects of energy-related residuals on genetic material and detoxification processes in bivalve molluscs, marine worms, and fishes. We have focused our initial detoxification research efforts on populations of mussels exposed to various concentrations of copper. A clearer understanding of metal metabolism not only is beneficial in itself but also would enable us to more precisely establish the levels of various metals that can be tolerated by animals in aquatic ecosystems and determine the extent to which animals are stressed in metal-contaminated environments. (See the box on p. 16 for a brief description of an extension of our work to another species and a practical application of our techniques.)

The tolerance of mussels to increased tissue concentrations of metal may be related to mechanisms that prevent metals from interfering with the functions of essential enzymes. Two processes have been identified in mussels. The first involves the binding of metals to low-molecular-weight proteins that have some properties similar to metallothioneins. Metallothioneins are ubiquitous metal-binding proteins, rich in the sulfur-containing compound cysteine, found in organisms ranging from plants and invertebrates to man. The second process involves the incorporation of metals into membrane-bound vesicles that are similar in appearance to some lysosomes. Lysosomes are cell organelles containing a mixture of digestive enzymes. Our working hypothesis is that metals bound to metallothionein-like proteins and metals contained in lysosome-like vesicles are detoxified in such a way that they are rendered unavailable for competitive binding to the enzymes that are essential for metabolism.4,5

Interrelationships among the processes for accumulating and detoxifying metals in mussel tissues are not well established. Therefore, we examined cells in the digestive gland and other soft tissues of mussels following exposure to the range of copper actually associated with polluted ecosystems. Our first measure was to determine whether there were increased metals in the low-molecular-weight fraction of metal-binding proteins; our second was to evaluate the cytological effects of copper on lysosomes by measuring the unavailability for reaction (i.e., latency) of the lysosomal enzyme hexosaminidase.

Exposure Conditions and Tissue Preparation

Exposure conditions for the mussels used in this study (5 groups of 25 animals each) are shown in Table 1. Whereas the region of South San Francisco Bay from which mussels in group 1 were collected receives both municipal and industrial wastes, the Tomales Bay area is known to be low in environmental pollutants. Mussels from Tomales Bay were randomly assigned to groups 2 through 5 and placed in 20-litre exposure chambers. Seawater containing the indicated copper concentrations was continuously delivered to each chamber. To avoid depletion of reserves in the digestive gland, which occurs during starvation,6 we also delivered a starch solution and a suspension of freeze-dried seaweed (Macrocystis pyrifera).

The digestive glands were quickly dissected on ice, immediately frozen with dry ice in a nitrogen atmosphere, and preserved at —70°C for a maximum of 18 hours before homogenization. The tissue was homogenized in a nitrogen-saturated buffer containing 10% sucrose and 1%
2-mercaptoethanol, a procedure that enhanced extraction and reduced aggregation and degradation of the copper metalloproteins. The remaining soft tissues, consisting of gills, gonad, kidney, foot muscle, labial palps, shell muscles, and mantle, were dissected, pooled, and reserved for analysis.

The procedure for isolating and purifying metallothionein-like proteins is illustrated in Fig. 1. The supernatant fluids of the digestive gland were chromatographed to separate the soluble proteins according to their molecular size. We continuously monitored the eluant for absorbance at 280 nm because proteins containing aromatic amino acids absorb ultraviolet light at that wavelength. Each of the 150 eluted fractions was analyzed for copper, zinc, and cadmium. Zinc and cadmium are of interest in that they may influence one another with respect to binding with metalloproteins.

We verified the copper concentration in the seawater from our exposure chambers by atomic absorption spectroscopy. (This verification was necessary because adsorption of the metal onto the aquarium walls could alter the copper concentration to which the mussels were actually exposed.) Eluants from the chromatograph column were analyzed either directly in the flame or in the graphite furnace of the atomic absorption spectrometer. To validate our analytic procedures, we analyzed samples of a standard reference material (oyster tissue from the National Bureau of Standards) along with our mussel samples.

Three mussels from each group were randomly selected to quantify the cytologic effects of copper on lysosomes. The digestive glands in these subjects were excised and stored on dry ice until they could be sliced into 6-μm sections. The sections were transferred to microscope slides and kept frozen (less than 24 hours) until they could be stained. The stability of lysosomal membranes may change as a function of stress imposed by metal intoxication. Therefore, lysosomal enzymes are more likely to be available to react in the cells of mussels that are exposed to copper. We selected the enzyme hexosaminidase because it is known to be confined primarily in lysosomes and concentrated in tissues that accumulate metals, and it can be quantified in cells by a histochemical reaction. Hexosaminidase was measured by incubating tissue sections in an appropriate substrate and then staining them with an azo dye. Using a scanning dual-beam photometer, we measured the absorbance at 566 nm of the azo-dye-coupled reaction product of hexosaminidase. The value of 566 nm was selected because the reaction product absorbs light at that wavelength.

Sample readings (15 or 16) were obtained from tissue sections after a series of incubation times in the substrate. For control subjects exposed to low levels of copper (low stress), we would anticipate little or no available enzyme at early incubation time and, therefore, a relatively long latency to obtain the reaction product or visible staining. For subjects exposed to high Table 1 Collection information and exposure conditions for the mussels, Mytilus edulis, used in this experiment.

<table>
<thead>
<tr>
<th>Group</th>
<th>Collection site</th>
<th>Collection date</th>
<th>Exposure conditions to copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>South San Francisco Bay(^a)</td>
<td>July 1981</td>
<td>Field exposure to copper from municipal and industrial wastes</td>
</tr>
<tr>
<td>2a</td>
<td>Tomales Bay(^b)</td>
<td>July 1981</td>
<td>Field exposure to low levels of copper in a pristine environment</td>
</tr>
<tr>
<td>2b</td>
<td>Tomales Bay</td>
<td>June 1981</td>
<td>Laboratory controls maintained for 3, 6, 9, and 12 weeks in seawater with no copper added</td>
</tr>
<tr>
<td>3</td>
<td>Tomales Bay</td>
<td>June 1981</td>
<td>25 μg/l copper for 3 weeks</td>
</tr>
<tr>
<td>4</td>
<td>Tomales Bay</td>
<td>June 1981</td>
<td>50 μg/l copper for 3 weeks</td>
</tr>
<tr>
<td>5</td>
<td>Tomales Bay</td>
<td>June 1981</td>
<td>75 μg/l copper for 3 weeks</td>
</tr>
</tbody>
</table>

\(^a\)The California State Water Resources Control Board has reported the level of metal concentration in mussels from this area in their Water Quality Monitoring Report No. 79-22, Sacramento, CA (1980).

\(^b\)The low levels of pollution in this area are documented in the report cited above.

\(^c\)Some control subjects were maintained in laboratory chambers for these extended intervals so that comparisons could be made with longer term exposure subjects described later in this report.

The California State Water Resources Control Board has reported the level of metal concentration in mussels from this area in their Water Quality Monitoring Report No. 79-22, Sacramento, CA (1980).
Fig. 1
Procedure for isolating, purifying, and analyzing metallothionein-like proteins.

Mussels exposed to copper

Dissected digestive glands pooled

Tissue sample homogenized

Homogenate centrifuged at 5000 × g for 15 min

Supernatant fluid centrifuged at 100,000 × g for 120 min

Pellet containing insoluble copper to atomic absorption spectrometer for metal analysis

Supernatant fluid filtered and passed through chromatograph column; absorbance monitored at 280 nm

Eluted fractions containing metalloproteins collected

Supernatant fluid

Eluted fractions and pellet from centrifuge analyzed for metal content in an atomic absorption spectrometer
levels of copper (high stress), we would anticipate large amounts of enzyme at early incubation time and, therefore, a short latency for staining.

**Metallothionein-Like Proteins**

**Laboratory-Exposed Mussels**

Figure 2 shows copper associated with soluble metalloproteins for the mussels that were exposed in laboratory chambers for 3 weeks. To interpret the data, it is important to understand that metallothionein-like proteins and metalloenzymes are different in size and therefore are eluted in different fractions. Metallothionein-like proteins are known to occur in the low-molecular-weight (LMW) fractions (see peaks on the right in Fig. 2). We may interpret the presence of peaks in LMW fractions as evidence that metals are being bound to metallothionein-like proteins and thereby detoxified. Metalloenzymes, on the other hand, occur in the high-molecular-weight (HMW) and intermediate-molecular-weight (IMW) fractions (see peaks on the left in Fig. 2). Excess copper may displace an appropriate metal cofactor, such as zinc, or may bind nonspecifically to metalloenzymes. The presence of excess metal in the HMW fractions is correlated with toxic effects.

Our outcomes are similar for control subjects and those exposed to copper concentrations of 25 μg/l (see Table 2); however, a substantial increase in concentration is found in subjects exposed to 50 and 75 μg/l. The highest concentration in the HMW fractions appears in the 75-μg/l group, whereas the highest concentration in the LMW fractions appears in the 50-μg/l group. Indeed, most of the copper is recovered in the LMW fractions.

An inspection of HMW data in Table 2 for the 75-μg/l group is instructive. Copper concentrations here are nearly five times greater than for the 25-μg/l group and nearly two times greater than for the 50-μg/l group. The large increases in copper concentration for different copper concentrations for 3 weeks.

<table>
<thead>
<tr>
<th>Copper concentration of bioassay water, μg/l</th>
<th>HMW fractions</th>
<th>LMW fractions</th>
<th>Te</th>
<th>Pellet</th>
<th>Entire digestive glands</th>
</tr>
</thead>
<tbody>
<tr>
<td>~1 (control)</td>
<td>8</td>
<td>330</td>
<td>380</td>
<td>65</td>
<td>460</td>
</tr>
<tr>
<td>25</td>
<td>44</td>
<td>320</td>
<td>420</td>
<td>87</td>
<td>530</td>
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<tr>
<td>50</td>
<td>120</td>
<td>920</td>
<td>1200</td>
<td>250</td>
<td>1500</td>
</tr>
<tr>
<td>75</td>
<td>190</td>
<td>650</td>
<td>1000</td>
<td>210</td>
<td>1300</td>
</tr>
</tbody>
</table>

*High molecular weight (HMW) includes fractions 40 to 50.

*Low molecular weight (LMW) includes fractions 70 to 90.

*Fractions 0 to 150.

Control mussels were maintained in seawater with no added copper and were sacrificed at 3, 6, 9, and 12 weeks. No significant change in copper concentration with exposure time was detected.

![Fig. 2](image)

Elution profiles of copper (tissue copper concentration vs eluant fraction number) in supernatant fluids of digestive gland tissue of *Mytilus edulis* exposed to different copper levels for 3 weeks. The concentrations of copper in the bioassay water are given in micrograms copper per litre. The low- and high-molecular-weight fractions containing, respectively, metallothionein-like proteins and metalloenzymes are shown by the shaded bands.
complexed with HMW proteins for mussels exposed to the highest concentration may indicate that the capacity of the LMW (metallothionein-like) proteins for binding copper was exceeded and that the copper was available to bind to the HMW proteins (metalloenzymes).

We also attempted to quantify the zinc and cadmium present in digestive glands of mussels exposed to copper for 3 weeks. However, in all samples, cadmium concentrations were too low to permit comparisons. Zinc in the HMW fractions was greatest in mussels exposed to copper concentrations of 75 µg/l, the highest concentration studied. However, zinc in the LMW fractions of mussels exposed to copper at either 50 or 75 µg/l was actually less than that of mussels exposed to 25 µg/l. These data indicate that copper may be displacing zinc in the LMW fractions.

A parallel experiment supports our concept that the capacity of LMW proteins to bind with copper may be exceeded. When mussels from Tomales Bay were exposed to copper concentrations of 25 µg/l for 3, 6, 9, or 12 weeks (Fig. 3), the rate of increase of copper bound by proteins in the LMW fractions occurred between 3 and 6 weeks, the shorter exposure times. In keeping with our hypothesis, the greatest rate of increase of copper bound by proteins in the HMW fractions occurred between 9 and 12 weeks, the longest exposure times.

We also observed direct relationships among mussel mortality, copper concentration, and the quantities of copper eluted in the HMW fractions (Fig. 4). Increased mortality with increased copper concentrations in the HMW fractions also was observed in mussels continuously exposed to copper concentrations of 25 µg/l, the lowest exposure concentration, for 12 weeks, the longest exposure time.

Finally, we determined total metal concentrations in the soft tissues of groups 2b through 5 (Table 3). In the gonads and remains, the highest copper concentrations are found in the 75-µg/l group; in the gills, copper is highest in the 25-µg/l group. In other tissues and in the entire soft body, copper is highest in the 50-µg/l group. Little difference is seen in cadmium concentrations; however, large differences in zinc concentrations are observed in the kidneys and gills. Zinc concentrations in the kidneys, for example, are more than 20 times higher than controls in both the 50- and 75-µg/l groups. The lowest zinc concentrations observed in the gills are in the 25-µg/l group. These data indicate that exposure to high levels of copper affects the distribution of zinc, and this may be an important factor in copper toxicity.

**Field-Exposed Mussels**

Figure 5 shows metal profiles for the supernatant fluids of digestive glands from mussels collected in the two sites (groups 1 and 2a). Our first result of interest is that both the HMW peaks, fractions 10 through 20, and the LMW peaks, fractions 25 through 37, are much smaller for all metals, especially copper and cadmium, in the mussels from Tomales Bay (Fig. 5a) than in those from South San Francisco Bay.
Cadmium concentrations in the Tomales Bay mussels are below our detection limits. These data confirm that mussels from San Francisco Bay contain high contents of copper, cadmium, and zinc, that a large proportion of metal is bound to metallothionein-like proteins in what is considered to be a nontoxic form, and that excess metal is associated with metalloenzymes.

Table 4 shows metal concentrations in both homogenates and entire digestive glands. Once again, the quantities of metal are much higher in the mussels from South San Francisco Bay. The largest differences are those associated with the LMW fractions; therefore, we have evidence that metallothionein-like proteins may account for most of the differences in the total quantities of metals eluted. For the Tomales Bay mussels, intact digestive glands contain zinc in greater concentration than copper in greater concentration than cadmium; for the South San Francisco Bay mussels, the order is copper greater than zinc greater than cadmium.

Lysosomal Latency

Laboratory-Exposed Mussels

The latency (i.e., unavailability for reaction) of lysosomal hexosaminidase was determined for mussels exposed for 30 days to copper in the laboratory and then examined for metallothionein-like proteins. A dose-dependent reduction in latency is induced in the mussels exposed to copper concentrations of 25, 50, and 75 µg/l (Fig. 6). The absorbance increases rapidly between 1 and 20 min and then asymptotically approaches a maximum after 70 min. Because mussels exposed to 50 and 75 µg/l had considerably higher tissue concentrations of copper than did control mussels or those exposed to 25 µg/l, and because accumulations were histochemically demonstrated to have the same distribution as the hexosaminidase reaction product, we have strong evidence that copper is present in the lysosomes and, indeed, causes stress at

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Metal concentration (µg/g dry wt) in pooled tissues from 25 <em>Mytilus edulis</em> exposed to different soluble copper concentrations for 3 weeks.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of copper in bioassay water</td>
<td>Digestive gland</td>
</tr>
<tr>
<td>µg/l</td>
<td>Kidney</td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>~1</td>
<td>12</td>
</tr>
<tr>
<td>25</td>
<td>14</td>
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<tr>
<td>50</td>
<td>45</td>
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<tr>
<td>75</td>
<td>40</td>
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</table>

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Metal concentration (10⁻¹ µmol/g wet wt) in components of digestive gland tissue from <em>Mytilus edulis</em>.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collection site</td>
<td>HMW fractions</td>
</tr>
<tr>
<td>Tomales Bay</td>
<td>8</td>
</tr>
<tr>
<td>South San Francisco Bay</td>
<td>480</td>
</tr>
<tr>
<td>Tomales Bay</td>
<td>ND</td>
</tr>
<tr>
<td>South San Francisco Bay</td>
<td>140</td>
</tr>
<tr>
<td>Tomales Bay</td>
<td>330</td>
</tr>
<tr>
<td>South San Francisco Bay</td>
<td>450</td>
</tr>
</tbody>
</table>

*High molecular weight (HMW) includes fractions 10 to 20.

*Low molecular weight (LMW) includes fractions 25 to 37.

*Fractions 0 to 50.

*Not detected.
Metal-Binding Proteins in Bluegill Fish

As an extension of our work to another species and a practical application of our techniques, we studied the bluegill population in the cooling lake of the H. B. Robinson Nuclear Power Station near Florence, South Carolina. In the late 1970s, the research staff of the Carolina Power and Light Company observed decreases in reproductive capacity and increases in structural deformities in bluegills native to the area. Their efforts to determine the basis for such changes were unsuccessful.

In 1979 and 1980, Laboratory scientists analyzed the copper concentration and speciation in the intake and discharge waters. We determined that copper was present in chemical forms and amounts that could potentially have adverse effects on some fish populations. Next, we investigated the kinds and quantities of metals associated with the metalloproteins in livers of bluegills that were collected from three sites: from the cooling lake near the effluent discharge, near the water intake to the cooling system (4 miles south, downstream, of the discharge site), and from a control pond (5 miles north, upstream, of the site). Livers were removed and processed in the same manner as tissues from mussels collected from South San Francisco Bay.

Elution profiles of the supernatant fluids from the livers showed large differences in quantities of metals associated with metalloproteins. Copper concentrations in the low-molecular-weight metalloprotein fractions (sites of detoxification) were highest in bluegills from the discharge site and lowest in those from the control pond (see figure below). Evidence of overloading of the metallothionein-like proteins was found in bluegills living in the discharge site. Additional data showed that copper was displacing zinc from metalloenzymes (sites of toxic action) in the intermediate- and high-molecular-weight protein pool.

Soluble copper released from the cooling system of the power station was therefore implicated in the increased deformities and reduced reproductive capacities of bluegills in the adjacent cooling lake. Our conclusion that copper was a causal factor was based on two findings. First, copper was present in the metalloenzyme pool at concentrations that could potentially interfere with normal metabolic activity. Second, copper concentrations in the livers of bluegills from the discharge site were similar to those of fish that were demonstrated in laboratory studies to have reduced fertility.

Further research is required to define the duration of exposure that adult and developing bluegills can tolerate without adverse effects. In addition, the turnover of copper in metallothionein-like proteins should be evaluated for all life-history stages. Such information could then be used to set emission standards that permit continued operation of power generating stations while protecting our natural resources.
the subcellular level by changing the latency of lysosomal enzymes.

Field-Exposed Mussels

In the mussels exposed to copper in the field, the absorbance of the dye-coupled reaction product of hexosaminidase in the sections of digestive gland increased rapidly with incubation time (Table 5). Comparison of mean absorbances of the sections showed that the staining intensity at each incubation time was consistently greater in the mussels from South San Francisco Bay than in those from Tomales Bay.

Discussion

To understand the causes of metal toxicity, we must first elucidate the cellular and biochemical processes involved in the metabolism of metals. Our results, together with other recently published data, indicate that the complexing of metals with metallothionein-like proteins and the incorporation of metals into lysosome-like vesicles are important processes related to metal detoxification in Mytilus edulis.

Research on mammals has documented that LMW proteins rich in sulfhydryl groups are involved in the intracellular binding of metals. Our results on the metal-binding proteins isolated from digestive glands of mussels reveal that metallothionein-like proteins perform a similar function in natural populations of mussels. The quantities of metals associated with these proteins are greater in mussels from a metal-rich habitat or laboratory environment than in mussels from a pristine environment.

Intracellular binding of metals to LMW proteins has been documented in another natural population of mussels. Metalloproteins that bind cadmium, copper, and zinc in the gills and viscera were identified in Mytilus edulis collected from the cadmium-polluted areas of Corio Bay, Australia. However, the relative concentration of metals in both the HMW and LMW fractions in Corio Bay mussels differed greatly from those we established in our samples from San Francisco Bay. In Corio Bay mussels, the concentration of cadmium in the two peaks was much greater than the quantities of copper and zinc in San Francisco Bay mussels, we found the opposite relationship, i.e., copper and zinc concentrations were lower.

Table 5

<table>
<thead>
<tr>
<th>Incubation time, min</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Mean</th>
<th>Standard deviation</th>
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<tr>
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<td>14 000</td>
<td>3000</td>
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</tr>
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<td>20 000</td>
<td>4800</td>
</tr>
<tr>
<td>17.5</td>
<td>18 000</td>
<td>3800</td>
<td>25 000</td>
<td>7700</td>
</tr>
</tbody>
</table>

Fig. 5

Elution profiles of copper, zinc, and cadmium in supernatant fluids of digestive gland tissue from Mytilus edulis collected from (a) the pristine environment of Tomales Bay and (b) an area of South San Francisco Bay known to receive industrial and municipal wastes.
much greater than cadmium. In fæ Corio Bay mussels have some of the highest concentrations of cadmium in the world. If, as the data indicate, the metals associated with metallothionein-like proteins are affected by the concentrations of metals in the environment, then the analysis of intracellular metal-binding proteins could provide a fingerprint of the bioavailability to mussels of the metals in the ecosystem.

Although mussels can detoxify elevated concentrations of soluble copper, our results on laboratory exposure to increased copper indicate that saturation of metallothionein-like proteins occurs at 3 weeks in the 75-μg/l group and at 6 weeks in the 25-μg/l group. Thus, the ability to tolerate copper is certainly related to both the concentration and duration of exposure. The formation of metallothionein-like proteins may serve as an important adaptive mechanism for tolerating intermittent exposures to copper, complementing the shell-closing response that is triggered at higher concentrations.

Our observed decreases in the latency of the lysosomal enzyme hexosaminidase are related to increases in copper concentrations in the digestive gland. Copper in the cells of the digestive gland appears to be localized in the lysosomes; we found that the histochemical distribution of copper is the same as that of the hexosaminidase reaction product.

Other researchers have reported that short-term exposures to sublethal copper concentrations can affect the latency of lysosomal enzymes. In a recent study, investigators observed changes in copper concentration and lysosomal latency in another species of mussel, Mytilus galloprovincialis. These mussels were exposed to copper concentrations of 50 μg/l for 3 days and then detoxified in copper-free seawater for 3, 6, and 12 days. Copper exposure for 3 days resulted in a significant reduction in lysosomal latency that persisted during the detoxification period. During detoxification, the levels of copper decreased in the mitochondrial, soluble, and microsomal (light) fractions; however, copper levels increased in the lysosomal (heavy) fraction and in the residual bodies.

More data on lysosomal latency are needed before we can elucidate the causal relationships among other metal detoxification mechanisms in mussels.

**Conclusions**

Changes in the kinds and quantities of copper-binding proteins and in the latency of lysosomal enzymes occur in the digestive gland cells of Mytilus edulis exposed to metals. Chronic exposure of mussels to copper results in copper concentrations in low-molecular-weight metallothionein-like proteins that are dependent on the exposure concentration and time. The copper concentration associated with high-molecular-weight proteins is directly related to the mortality of mussels. Copper exposure also results in a dose-dependent reduction in the latency of lysosomal hexosaminidase activity. Overall, we can conclude that, our study supports the hypothesis that exposure to sublethal concentrations of copper produces cytotoxic responses that appear to induce stress syndromes such as reduced body weight, low reproduction, and increased incidence of disease.

**Key Words:** copper; hexosaminidase; lysosome; metal-binding protein; metal detoxification; metalloenzyme; metallothionein; mussel—Mytilus edulis, Mytilus galloprovincialis.
Notes and References


Modeling EMP Damage to Semiconductors

We are assessing the mechanisms that can cause damage to p-n junction devices in an EMP environment and the existing models for these mechanisms, with the objective of developing models that can accurately predict the input power threshold for device failure.

Many components of both military and civil electronic devices are vulnerable to the sudden intense bursts of electric and magnetic fields known as EMPs (electromagnetic pulses) that accompany nuclear explosions, lightning flashes, and the passage of a radar beam.

It is extremely difficult to effectively shield electronic subsystems from EMP-induced currents, as electromagnetic radiation can leak through very tight and tortuous paths to reach sensitive components. Systems that contain connections to the outside world such as an antenna or power line are especially vulnerable. Any scheme for hardening electronic systems against EMPs, therefore, must include assessments of the hardness of the components themselves to the expected threat. We are conducting studies to investigate the operation of semiconductor p-n junction devices (see the box on p. 22) during an EMP so that we may eventually be able to harden those devices to EMP-induced failure. We chose semiconductor devices because they are the electronic components most vulnerable to EMP-induced failure.

Our approach is to assess both the known mechanisms that can cause damage to p-n junction devices in an EMP environment and the existing models for these mechanisms. The objective is to extend or modify existing models so that they can accurately predict the input-power threshold for device failure. Two of the Laboratory's models have been in operation for a year or so and have generated significant results, and a third model is now beginning to give results. With our models, we have been able to demonstrate the existence of two kinds of second breakdown, something we had suspected from experimental data but had been unable to show theoretically.

P-N Junction Breakdown Mechanisms

When a strong current pulse enters a semiconductor device, the immediate effect, called first breakdown, is an
avalanche of electrons and holes, producing an abnormally high current through the device. This is followed by a second breakdown that increases the currents even more. Second breakdown is the mechanism that generally causes degradation or damage to a device. First and second breakdown are discussed in detail below.

In order for a junction to break down, charge carriers must be introduced into the depletion region. These may be injected from the outside or generated in place. Although electrons exist in large numbers throughout the depletion region, these are not conduction electrons but valence electrons, which are bound to the atoms that make up the semiconductor. If the bond between an electron and an atom is broken, a free conduction electron and a hole are produced. Since an electric field exists in this region and since the electron and hole are of opposite charge, they are quickly separated and moved to opposite ends of the depletion region. This motion of the charge carriers produces the breakdown current. If the electron and hole were not quickly separated, they would recombine and no longer be available for conduction.

Three major mechanisms are associated with junction breakdown: tunneling, impact ionization, and thermal generation. The particular mechanisms that play a part in any breakdown are dependent on the circumstances. The parameters that have the most influence on the breakdown mechanisms are the applied voltage and its rate of application, the doping profiles in the device, and the device temperature. (The doping profile is the density distribution of the material used to dope the semiconductor; the dopant determines whether the material is n or p type.)

According to quantum mechanics, electrons can tunnel through energy barriers that according to classical theory would stop them. Since both the bond that ties an electron to an atom and the electric field in the depletion region are energy barriers for an electron, tunneling (as described in Fig. 1) is a method by which current can flow through a junction. Tunneling increases with increasing temperature, an effect that is used to distinguish tunneling from impact ionization, as discussed below.

Impact ionization is another breakdown mechanism that usually precedes tunneling. When an electron that has been accelerated to a high velocity strikes an atom, the collision can knock one or more electrons off the atom. The original electron plus the knocked-off electrons can then be accelerated by the electric field and can collide with more atoms to release more electrons. Thus, each collision geometrically increases the number of charge carriers (electrons and holes) available for conduction. This increase can quickly produce a large number of charge carriers and result in a large current flowing through the junction.

This rapid multiplication of charge...
carriers is known as avalanche multiplication, which is most strongly affected by the driving electric field and by the temperature. In contrast to tunneling, avalanche multiplication decreases with increasing temperature.

At absolute zero, all of the electrons in a semiconductor (or any material, for that matter) are bound to atoms. As the temperature of the semiconductor is increased, thermal excitation causes a small number of electrons to be torn from their atoms and released as charge carriers. At low temperatures, these constitute a negligible number of charge carriers; however, when the temperature reaches a critical value (600 to 800 K), the number of thermally generated charge carriers becomes significant and increases dramatically.

First Breakdown
The different types of breakdown in an electronic device are characterized

P-N JUNCTIONS

When a piece of p-type semiconductor material (e.g., boron-doped silicon) is joined to a piece of n-type semiconductor (e.g., arsenic-doped silicon) a p-n junction is formed. P-type material is filled with free, positively charged holes (a hole is an empty place in a crystal lattice where an electron could be but is not; thus, it behaves like a positively charged electron), moving in a background of fixed, negatively charged ions. N-type material is filled with free, negatively charged electrons moving in a fixed background of positively charged ions (a). When a p-n junction is formed, the negative electrons and the positive holes are attracted to each other and begin to move toward each other and recombine near the junction. This recombination removes electrons and holes from the conduction process and uncovers the fixed ions near the junction (b).

The original materials are in a condition of space-charge neutrality. Thus, in the n-type material, the number of free electrons equals the number of fixed positive ions, and in the p-type material, the number of free holes equals the number of fixed negative ions. When the electrons and holes begin to recombine near the junction, the materials in that region are no longer in a condition of space-charge neutrality. As more and more charges recombine, the n-type material near the junction becomes positively charged and the p-type material near the junction becomes negatively charged. This separation of charge creates an internal electric field that, when it is large enough, keeps the electrons and holes away from the junction and stops the recombination process (b). This region near the junction, which has now been emptied of electrons and holes, is known as the depletion region. Since electrons and holes can no longer pass across the junction (because of the internal electric field), the depletion region serves as a barrier to the flow of electricity.

When a negative potential is applied across the junction (positive to n-type, negative to p-type), the junction is said to be reverse-biased. This potential creates an external electric field that adds to the field in the depletion region. Increasing the field in the depletion region causes it to get wider. Since the depletion region is a barrier to the flow of electrons and holes, no current will flow in a reverse-biased p-n junction (c).

If a positive potential is applied across the junction, it is said to be forward-biased, and the external electric field subtracts from the field in the depletion region. When the field in the depletion region gets smaller, the width of the depletion region also gets smaller. When the applied field just cancels the internal field, the depletion width goes to zero, and a current begins to flow (d). Thus, a p-n junction is essentially a one-way valve for electricity.
by the phenomena associated with the breakdown mechanism. First breakdown (avalanche and tunneling) is apparent in moderately overbiased p-n junctions. Avalanche occurs when the applied voltage exceeds the breakdown voltage required for impact ionization and results in a higher current through a junction (Fig. 2). Tunneling also can result in increased currents in some special devices. Avalanche and tunneling are not necessarily damaging to an electronic device, as long as the currents are kept to reasonable levels. In fact, some devices (e.g., Zener diodes) are designed to operate in these modes.

**Second Breakdown**

There are two modes of second breakdown—thermal and current. Which of these takes place is a function of the energy of the EMP-induced pulse. The two modes can be illustrated as follows:

1. **Thermal Breakdown**
   - Electric field
     - Electric field
     - Electric field
     - Electric field
   - p-n junction
   - Depletion region increases
   - Charge density
     - Internal + external
   - Position
     - Positive fixed ions
     - Negative fixed ions
     - Holes
     - Electrons

2. **Current Breakdown**
   - Electric field
     - Electric field
     - Electric field
     - Electric field
   - p-n junction
   - Depletion region decreases
A p-n junction is said to be reverse-biased when a negative potential is applied across it and forward-biased when the applied potential is positive. When the applied voltage is in excess of the breakdown voltage, the junction goes into first breakdown. If the breakdown is excessive, the device will begin to heat up. At some critical temperature (600 to 800 K), thermal generation of charge carriers becomes significant, and the device goes into thermal-mode second breakdown. Current-mode second breakdown develops much faster, in nanoseconds, compared with microseconds for thermal-mode second breakdown.

In thermal-mode second breakdown, which is thought to predominate below a certain energy level, the current from first (or avalanche) breakdown reaches a quasi-equilibrium that is maintained long enough to cause significant heating of the semiconductor. As the temperature rises, thermal generation of charge carriers becomes significant (at 600 to 800 K) and the device goes into thermal-current runaway. In thermal-current runaway, the increasing temperature decreases the device’s resistivity and causes an increased current that further increases the temperature. If this runaway is not halted by stopping power from entering the device, the resulting high temperatures will damage or destroy the semiconductor by creating hot spots and melting the depletion region.

Current-mode second breakdown occurs at higher energy levels. In this mode, the current from avalanche breakdown does not level off at a temporary equilibrium but continues to increase. Normally, the electric field in the depletion region is controlled by the doping density (i.e., the density of the fixed charges) in that region. However, at large applied voltages, the density of charge carriers generated by avalanche breakdown may approach and exceed the doping density before thermal effects can terminate the process. The electric field is then forced out of the center of the depletion region, with resulting higher fields along the edges. These higher fields enhance avalanche generation at the edges, producing so-called “double injection” of carriers into the depletion region. The more charge carriers that are injected into the depletion region, the more of the electric field that is forced to the edges. This increased electric field at the edges, in turn, increases the double injection. The current through the device now increases rapidly, and the device goes into current-mode second breakdown (see Fig. 2). The high current eventually produces damaging hot spots in the depletion region that lead to the degradation or destruction of the semiconductor device.

The use of power transistors and other semiconductor devices is often limited by second breakdown phenomena. Its initiation is manifested by an abrupt decrease in device voltage with an increase in current that is accompanied by the formation of an internal current constriction. This internal current constriction appears to be associated with an instability in the junction area, and it causes the formation of hot spots.

When the temperature of a hot spot reaches about 1000 K, the performance of an electronic device is degraded. At about 1600 K, the semiconductor material melts, permanently damaging...
the device. If the input power is reduced before the occurrence of permanent damage or significant degradation, then a device usually resumes normal operation. Thus, accurate predictions of the threshold power, threshold voltage, and time delay for device failure are essential for defining a safe region of operation.

Theories on Second Breakdown

Various theories and models have been proposed to describe second breakdown. In general, these can be grouped into two categories, thermal and electrothermal models. Most existing models either contain too many simplifying assumptions or neglect too many terms. Consequently, they cannot accurately predict failure conditions in junction devices nor can they predict the mode of second breakdown that will occur. Simple thermal models, for example, neglect all of the transport equations for electrons and holes and thus fail to predict the existence of current-mode second breakdown.

The electrothermal models generally are more sophisticated. One recent study, for example, using an electrothermal model to investigate the second breakdown phenomena for a one-dimensional case, obtained a power-failure curve that agreed rather well with some experimental data. In principle, this approach gives a fair description of the second breakdown phenomena. However, the one-dimensional model described above lacks the ability to describe current and thermal filament formation (hot spots), it has temperature limitations, and it ignores thermal and electrical diffusion.

Our assessment of existing models led us to conclude that none of them is accurate enough to predict failure thresholds in semiconductor junction devices. Any meaningful physical model must take into consideration all the electrical and thermal properties of the device under investigation. This implies that the time-dependent energy-transport equation, Poisson’s equation, and the nonlinear, time-dependent continuity equations for electrons and holes must be solved simultaneously. These equations are complicated, stiff, nonlinear, coupled, partial differential equations that have no analytical solutions. (“Stiff” equations describe phenomena of interest that occur on radically different time scales.) Therefore, they must be solved numerically with some reasonable assumptions and approximations. The object of our work at LLNL is to develop computer models that embody all of these equations and solve them with a reasonable amount of computer time. (Most of our simulations with these models take about 30 minutes, but some may require nearly 30 hours.)

Computer Models

Two one-dimensional computer models in operation at the Laboratory for a year or so have generated a number of significant results. A third model is just starting to give results.

The first model is a cylindrical, azimuthally symmetrical, one-dimensional, time-dependent diode model that represents a p-n junction operating in a strong electric field. It embodies the equations for the cylindrical p-n junction diode shown in Fig. 3a and performs detailed numerical integrations of the thermal effects in the radial direction, using analytical equations for thermal and electrical effects in the axial direction. This code is being used to investigate hot-spot and filament formation.

The second model is a one-dimensional, time-dependent model of the transistor shown in Fig. 3b. It generates detailed, one-dimensional, numerical solutions for all of the electrical and thermal equations in the n region of the device and uses analytical expressions for the other dimensions and the rest of the device. This model is useful for investigating current-mode and thermal-mode breakdown.

Our third model is a one-dimensional diode model that is similar to the first model but contains more complex physics. It numerically solves all of the electronic and thermal
Fig. 3
One-dimensional cylindrical diode model (a), one-dimensional transistor model (b), and one-dimensional diode model with complex physics (c) used in our numerical simulations. These three computer models are being used at LLNL, one for investigating thermal hot-spot formation in a p-n junction diode and two for investigating thermal-mode and current-mode second breakdown in the depletion region of a transistor and a diode. (Note that a transistor has three connections and a diode has only two.) In the transistor model (b), the computational domain covers just the n region, whereas in the diode model with complex physics (c), the computational domain extends over the whole device.

Model Results

Cylindrical Diode Model
Using our first model, the one-dimensional cylindrical diode model, we have investigated hot-spot formation. Figure 4 shows the development of a hot spot. When the electrical overstress arrives at the diode, it immediately goes into avalanche breakdown. For a few hundred microseconds, the device is uniformly heated over the whole junction. When the critical temperature is reached, thermally generated carriers become significant. As a result of thermal diffusion, the center of the device is slightly warmer than the rest. Thus, the center of the device is the first region to go into thermal-mode second breakdown. If any minor imperfection existed in the surface that would cause some minor heating above its surroundings, then that point also could be a nucleating point for current filaments.

As heating continues, the electrical conductivity in the breakdown region increases tremendously. The conductivity becomes so high that all the current passing through the junction is channeled into the breakdown region and forms a current filament. There is a continued increase in temperature in the breakdown region, due to the increased current, while the surrounding region actually cools down a little. Thus, a hot spot is formed.
One-Dimensional Transistor Model

We have used our second model, the one-dimensional transistor model, to investigate current-mode and thermal-mode second breakdown. Figure 5 shows how the current changes with time for a set of voltages applied across the collector-base junction of the transistor. Current-mode second breakdown occurs within a few nanoseconds when the applied voltages are above 206 V. With a slight decrease in the voltage (only 0.1 V), the device goes into thermal-mode second breakdown instead of current-mode second breakdown. Figure 5 also shows how the current-mode and thermal-mode second breakdown delay times change as the applied voltage changes.

One important characteristic that differentiates current-mode from thermal-mode second breakdown is the delay time for initiation. For current-mode second breakdown, the delay time is of the order of nanoseconds; for thermal mode, it is of the order of microseconds.

Current-thermal switching. More recently, we have allowed the transistor-model calculations for second breakdown to continue further. Although Fig. 5 shows the current increasing indefinitely, Fig. 6 indicates that current-mode second breakdown may saturate and then go into thermal-mode second breakdown. This current-thermal switching may be explained as follows.

When a voltage whose magnitude is much higher than the breakdown voltage is applied across a p-n junction, the device immediately goes into current-mode second breakdown. If there is a resistor in the external circuit, the current will saturate and the device will heat up uniformly. The overall temperature increase begins to suppress the current-mode second breakdown by slowing the avalanche process. As the temperature of the device continues to increase, the number of thermally generated carriers also increases. Eventually, the number of thermally generated carriers will exceed the number of avalanche-generated carriers, driving the device into thermal-mode second breakdown. That is, the device first goes into current-mode second breakdown and then switches to thermal breakdown because of the increase in temperature. All of these calculations assume that current...
Variation of the total current through a transistor vs time, calculated with the one-dimensional transistor model described in the text. During the first nanosecond, the device is in avalanche breakdown. At this point, if the applied voltage is high enough, the device goes into current-mode second breakdown. At lower voltages, the current saturates, and the device begins to heat up. Raising the temperature suppresses the avalanche breakdown, and the current decreases a little. Finally, at about one microsecond, the number of thermally generated carriers becomes significant, and the device goes into thermal-mode second breakdown. Only a small change in the collector-base voltage (0.1 V) is required to produce a shift from current-mode to thermal-mode second breakdown. This plot indicates one of the strongest differences between thermal-mode and current-mode second breakdown—the delay time to breakdown. Whereas the delay to breakdown for thermal-mode second breakdown usually is in microseconds, for current-mode second breakdown it is in nanoseconds.

Temporal behavior of the current of a transistor in a common-emitter-base configuration (see Fig. 3) showing how current-mode second breakdown can switch to thermal-mode second breakdown. The external series resistance is 300 Ω.
filaments have not yet formed. If current filaments do form, then we expect the curves to be qualitatively similar, although things will happen in a shorter time frame.

Figure 7 shows some experimental results\(^4\) that indicate the existence of current-thermal switching. (Note that Fig. 7 gives voltage vs time, whereas Fig. 6 shows current vs time. The voltage through a device is inversely proportional to the current.) Although Figs. 6 and 7 are plotted for different transistors and therefore can be compared only qualitatively, these figures illustrate the need for both experimental and theoretical studies; the experimental data in Fig. 7 indicate the existence of switching, and the calculation in Fig. 6 shows that switching does indeed occur.

**Effect of pulse shape.** Almost all the experiments that have tried to determine the failure power or energy threshold for a semiconductor device have used square-wave input voltages or currents, with pulse widths in the microsecond region. For such a long pulse, the rise time of the pulse is not very important. However, for pulses of 10 ns or less, the exact pulse shape, including rise time, must be used in the calculation in order to simulate the exact experimental conditions.

Recently, we used the transistor model to investigate the temporal behavior of the current during second breakdown when the input voltages have different pulse shapes. The results of our investigation are shown in Fig. 8.

![Fig. 7](image1)

Experimental results\(^4\) showing the current-thermal mode switching in a transistor. The device initially breaks down with current-mode second breakdown; subsequent heating causes it to switch to thermal-mode second breakdown.

![Fig. 8](image2)

The theoretical temporal behavior of the current in a p-n junction for step-voltage and ramp-voltage input pulses.

![Fig. 9](image3)

Temporal behavior of the current in a p-n junction device. Experimental results reported by (a) the Russians\(^5\) and (b) LLNL.\(^6\) The rise time of the current is very fast (less than a nanosecond) when the input voltage is a ramp, as shown by the curve on the left in (b).

One of the most important results obtained from these calculations is the indication that the rise time of the current is different for different input-voltage pulse shapes. The rise time (above currents of \(10^{-3}\) A) is much slower for step-voltage excitation than for ramped input voltages. This fast current rise time (of the order of less than a nanosecond) with a ramped input voltage has been observed experimentally by the Russians\(^5\) and duplicated at LLNL.\(^6\) Figure 9 compares the two sets of experimental results. Our calculation shows essentially the same behavior.
Diode Model with Complex Physics

Using our third model, the diode model incorporating more complex physics, we can show in great detail the physical events taking place inside a diode during the application of a high-voltage transient and subsequent breakdown of the device. Figure 10 illustrates segments of the sequence of events calculated by this new model.

In Fig. 10a, we show the doping profile of the diode used in this calculation. The steady-state results obtained with zero applied voltage show the initial carrier densities and

(a) Doping density, cm⁻³

(b) Charge density, cm⁻³

(c) Voltage, V, and temperature, K

<table>
<thead>
<tr>
<th>Theoretical</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 0.97 μm 0.99 μm</td>
<td></td>
</tr>
<tr>
<td>B 0.24 V 0.23 V</td>
<td></td>
</tr>
<tr>
<td>C 0.71 V 0.73 V</td>
<td></td>
</tr>
<tr>
<td>D 0.12 V 0.13 V</td>
<td></td>
</tr>
</tbody>
</table>

Position in device, μm

A = 0.4 ns, punch-through
B = 0.8 ns, avalanche begins
C = 1.5 ns, carrier density at 10¹³ cm⁻³
D = 3.4 ns, at equilibrium
E = 10 ns, thermal-suppressed avalanche
F = 28 μs, thermal generation increases
DEFENSE PROGRAMS

Figures 10c through 10e detail the phenomena of second breakdown. Initially, the diode is in the state described by Fig. 10b, with no applied voltage and no current flow. The external circuit consists of a voltage source in series with a 50-Ω resistor. The voltage source delivers a linear,

Fig. 10

Sequence of events calculated by the diode model with complex physics. The diode is doped as shown in (a) and has the initial carrier densities and electric field distribution (zero applied bias) as shown in (b). The voltage is applied as a ramp to -170 V in 1 ns, through a 50-Ω resistor. The resulting voltage, current, and temperature time histories are given in (c). As the applied voltage increases, the width of the depletion region expands until it achieves punch-through (d), which is the point at which the depletion region extends completely across the n region. Once this occurs, higher applied voltages can only increase the electric field in the depletion region, until avalanche breakdown fills the depletion region with charge carriers. This produces the distribution shown in (e). At this point, the breakdown can go either to thermal-mode or current-mode second breakdown. At a lower applied voltage (here, less than 170 V), the current in the device stabilizes, causing the device to heat up until it goes into thermal-mode second breakdown. At a higher applied voltage, the carrier density increases until it is greater than the doping density in the depletion region. This drives the field out of the center of the depletion region to the edges; the resulting avalanche breakdown at the edges causes double injection, and the device goes into current-mode second breakdown.

potentially distribution (Fig. 10b). Figure 10b also compares the model depletion width and built-in voltages with those calculated with the theoretical, abrupt junction approximations from Ref. 7. These comparisons indicate that the model works well at low voltages.
ramped voltage from 0 to $-170$ V in 1 ns, and thereafter delivers a constant voltage of $-170$ V. The time histories of the current, voltage, and junction temperature for the diode during second breakdown are given in Fig. 10c.

Figure 10d shows that as the external voltage becomes more negative, the depletion region widens. At 0.4 ns (A on Fig. 10c), the depletion region spans the whole n region of the diode, and the diode has achieved punch-through. When punch-through has been reached, the depletion region can no longer expand in response to the increasing applied voltage (although it can expand into the p region and the n$^+$ region to some extent). The electric field in the depletion region continues to increase, but the carrier densities change only slightly. At 0.8 ns (B on Fig. 10c), the electric field has reached avalanche strength, and the depletion region begins rapidly to fill with charge carriers. At 1.5 ns (C on Fig. 10c), when the carrier density reaches about $10^{13}$ cm$^3$ (1% of the doping density in the n region), the current begins to increase rapidly.

Figure 10e reveals that at 4.0 ns (D on Fig. 10c), an equilibrium has been reached between avalanche generation and recombination in a zone and current flow out of a zone. We can see, here, that the electric field takes on a double-peaked structure that is characteristic of the so-called “double injection” phenomenon, where charge carriers are injected into the depletion region from the edges.

At this point, the breakdown can go in either direction, to thermal-mode or to current-mode second breakdown. As the current and voltage remain relatively constant (D on Fig. 10c), the device begins to heat up. This heating begins to suppress avalanche generation, and the current decreases as the charge carrier density decreases to a value below the doping density in the n region (E on Fig. 10c). As avalanche generation is suppressed by the increasing temperature, thermal generation increases and becomes significant (F on Fig. 10c), and the device goes into thermal-mode second breakdown. Once this point has been reached, the current and temperature increase rapidly and the device is degraded or destroyed.

If, in contrast, the temperature increases very rapidly (at higher applied voltage), the carrier density and the current are only slightly depressed. Thus, the carrier density increases until it is greater than the doping density in the depletion region. This drives the field out of the center of the depletion region to the edges. The resulting avalanche breakdown at the edges causes double injection, which sends the device into current-mode second breakdown. When this happens, the current remains relatively constant at the equilibrium level until device failure, which occurs very close to point D on Fig. 10c.

**Conclusion**

Many models have been proposed previously to investigate the second breakdown phenomena. The theoretical results obtained from earlier models do not agree well with the experimental results. The discrepancies arise mainly because many assumptions are made in those models and because the influence on device performance of many parameters—such as doping density, inhomogeneities, and surface conditions—are not accurately known.

The three models developed at LLNL have greatly helped us to understand the physical mechanisms of second breakdown. The cylindrical diode model has provided some insight into the behavior of these devices in the thermal mode. The transistor model and the new diode model have confirmed the existence of the current and the thermal modes of second breakdown as well as the delay time associated with each mode. The new diode model also has greatly enhanced our knowledge of the physical phenomena taking place in a semiconductor device during a large electrical overstress.

Our results, to date, are largely qualitative. However, we are in the process of improving our models to make them quantitatively accurate. We
also plan to extend our codes to more dimensions and to perform a systematic study of the various parameters. Once we know the effects of each parameter on the performance of an electronic device in an EMP environment, we can evaluate the survivability of that device during an EMP-induced transient. Use of these models should result in design rules for semiconductor devices and circuits that will enhance circuit survival during an EMP.

Key Words: electromagnetic pulse (EMP), p-n junction—breakdown, semiconductor; computer modeling.

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