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STUDIES OF RADIATION DAMAGE
IN SEMICONDUCTORS

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ABSTRACT

The program on the study of radiation damage in semiconductors is described. This work divides into three areas: 1) EPR measurements on silicon and diamond; 2) optical and electrical measurements on silicon and diamond; and 3) theoretical work on these materials and their defect structures, including the nature of the amorphous state. The goals of the total program are the understanding of the physics of the radiation damage process, the identification of the defects created and the determination of the influence these defects play in altering the bulk properties of these materials. This past year saw a number of substantial advances toward these goals; this next year will probably consist of a (hectic) consolidation and extension of these advances.
I. Introduction.

The study of defects created by radiation damage of semiconductors remains an exciting and challenging area of solid state science; in view of the relevance of this work to ion-implantation and amorphous semiconductors and because of the need in many areas for improved radiation tolerance of semiconductor devices, the science has a strong technological motivation as well.

The general background of the problems addressed in our program has been treated elsewhere. The goals of our program are: 1) the understanding of the physics of the damage creation process; 2) the identification of the defects created; and 3) the determination of the influence these defects play in altering the bulk properties of the semiconducting materials. Our emphasis is upon the basic science but we are constantly mindful of the needs of the companion technology.

In this past year we have made a number of substantial advances. These advances are largely theoretical, or better, conceptual; they have come quickly and have considerable promise. We are, of course, diligently carrying out the analysis required by these advances and performing related experiments, but the work has really only begun; we expect this next year to see substantial fruition from these advances.

Briefly the advances are:

1) The interstitial in the diamond lattice. Our theoretical work in diamond and silicon argues that the self-interstitial is a split-
<100> interstitial and that some impurity interstitials have a similar
split character (See Sect. II.);

2) The Bourgoin mechanism for defect migration\textsuperscript{9,10} Our theoretical
work argues that defect migration, especially the self-interstitial
and impurity interstitial migration, can occur via repeated changes
of charge state, i.e., an athermal process (See Sect. II.);

3) Annealing kinetics. Our related theoretical work\textsuperscript{11,12} on
reaction kinetics has given us new insight into the origin of the
third-order kinetics in the annealing of Ge bombarded at low
temperatures;

4) Vacancy clusters and loops. Extending the earlier\textsuperscript{13,14} analysis
of linear vacancy chains to vacancy clusters, vacancy (6-membered)
rings and vacancy "planes" we have found a number of possible
candidates for structures observed in the EPR and have obtained a new
insight into the microscopic structure of dislocation and amorphous
material (See Sect. III.);

5) Silicon. We have observed over ten new EPR spectra in n-
irradiated Si and the work mentioned in 4) has suggested models for a
number of these and other spectra observed earlier\textsuperscript{15,16}; we are
probing these models experimentally now (See Sect. III.);

6) Diamond. We have observed several new EPR spectra and an extension
of Brower's analysis\textsuperscript{14} of linear vacancy chains to diamond together
with the work mentioned in 4) has suggested models for many of the
diamond spectra\textsuperscript{17-24} which we are now probing experimentally (See
Sect. IV.).
II. Theory.

The Kohn-Luttinger\textsuperscript{25} theory of shallow levels in semiconductors is, of course, quite successful but deep levels have remained a problem\textsuperscript{2,3}. The one-electron LCAO-MO treatment of the EPR spectra of radiation defects was quite successful in the hands of Watkins\textsuperscript{26}, embarrassingly so to the theorists in light of the expected deficiencies of such a theory. Recently Messmer and Watkins\textsuperscript{27} have achieved comparable success with an extended \textsc{h}"{u}ckel theory\textsuperscript{28} using the direct computer diagonalization of the secular determinant for an array of atoms (e.g., say thirty atoms) representing a small portion of crystal surrounding a defect. While the extended \textsc{h}"{u}ckel theory has its limitations (e.g., ionicity, the small size of the cluster, etc.), the Messmer-Watkins advance renders a broad class of problems tractable for the first time, and in our view represents a major advance.

We have begun a collaboration with Messmer and Watkins on some of these calculations. We have completed calculations on the carbon-interstitial in diamond\textsuperscript{7,8} and on the boron - and the nitrogen-interstitial\textsuperscript{8} in diamond. We have begun calculations on the silicon-interstitial in silicon. These results indicate that the interstitial is not in the tetrahedral or "hexagonal" site as has been previously assumed\textsuperscript{29-34} but is in a split-interstitial configuration, i.e., two atoms sharing a substitutional site, with the split axis along the $\langle 100 \rangle$ direction; this is true for the self-interstitial and for the impurities, though the latter are asymmetrical.
Identifying the interstitial is a major problem in radiation damage in semiconductors. We feel these theoretical results are very useful, since they suggest new ways of approaching the identification problem, e.g., suggest that certain EPR spectra in diamond and silicon may be interstitial related.

In addition these EHT calculations obtain, en passant, the interatomic potential, e.g., the potential of the carbon atom vs the diamond lattice. This potential is not a universal two-body potential as is often assumed, but depends upon the electronic bonding experienced by the two atoms. This potential is the foundation upon which dynamic calculations of the damage production process could be based, such as those calculations performed for metals.\textsuperscript{35,36}

Much work needs to be done on this problem, but already we find that the potential well for displacement damage is to first-order isotropic; this differs from earlier (to be sure, qualitative) treatments\textsuperscript{37,38} which assumed there would be an anisotropy due to the bonding; the isotropy does agree with experiment on the orientation dependence of the displacement threshold in Ge\textsuperscript{39} and Si\textsuperscript{40}.

In addition this collaboration has impelled us to begin work on amorphous materials. Specifically, the point is that the computer program only requires that the location of the atoms be specified, then the electronic and total energies may be evaluated. Hence if locations of atoms in an array corresponding to an amorphous structure can be specified, information on the electronic structure of amorphous materials (including with impurities and defects) can be obtained.
While amorphous structures by definition have no regular lattice sites, there is information on possible arrays of atoms with amorphous structures. For example, Polk has carried out modeling of amorphous structures of silicon and germanium similar to early directly comparable work on fused silica. These approaches simply showed, using tetrahedrally coordinated models, that large (e.g., 450 units) models of glasses could be built. Our approach goes considerably beyond this. We are analyzing the structural elements of tetrahedrally coordinated crystals, such as in cubic and hexagonal diamond (wurtzite), quartz and water structures. Of course, the "boat" and "chair" puckered six-membered rings are well known, but we have found less well-known elements such as the planar hexagonal ring made of tetrahedrally coordinated atoms (not like the planar cyclo-hexane ring). The extended Hückel program is admirably suited to evaluate the relative energy differences between structural elements such as the "boat", the "chair" and the planar hexagonal ring mentioned above, and combinations of such elements. From such studies we hope to find an Markovian algorithm for the generation of amorphous structures in a computer; in any event we will achieve prototype structures for the extended Hückel program, in which we can treat the intrinsic structure or the added impurities or defects.

We have also begun the consideration of the properties of the sequence: sulfur, selenium and tellurium. These materials can form helical structures as well as amorphous material. In our view their
"one-dimensional" nature readily lends itself to the study of the fundamental aspects of the amorphous state in these materials.

Our consideration of the charge-state dependence of radiation damage phenomena lead one of us to suggest a new mechanism for defect migration, which we call the Bourgoin mechanism. The mechanism is simple. It arises when the equilibrium site of a defect depends significantly on the defect charge state. The mechanism was implied by Weiser's calculations on impurity interstitial mobility (although unrealized by him), so we will discuss it in those terms. Suppose an impurity interstitial in one charge state has its equilibrium site at the tetrahedral site and in another charge state the equilibrium charge state is the "hexagonal" site; then a change of charge state will cause a motion through the lattice - an athermally induced motion. Of course, subsequent motion requires another change in charge state, but that can readily arise in an ionizing flux or in thermodynamic equilibrium if the Fermi level is at the electronic level in question. The mechanism can apply to impurities as well as radiation defects. There are a number of implications of this mechanism, which we are now exploring; some of the technological ones we will mention in Section VII. Extending the Weiser calculations we would argue that Cu and Li diffusion should be quite sensitive to ionization. The Bourgoin mechanism is also a natural explanation for the 4K migration of interstitials observed in Si and in Ge; indeed our calculations suggest that the equilibrium configurations are
charge-state dependent.

The Bourgoin mechanism remains to be confirmed experimentally.

It does offer, however, a solution to a major problem in radiation
damage, namely, the extreme low-temperature mobility.
III. Silicon.

We can briefly summarize the state of the knowledge of radiation defects in silicon. Prior to the time of the introduction of floating-zone silicon, most of the measurements were macroscopic in character, e.g., electrical resistivity, Hall effect, lifetime, and optical absorption. About that time EPR experiments were begun which resulted in the identification of a number of vacancy-related defects. The virtue of the EPR is that it is a "microscopic" measurement (i.e., reveals the defect symmetry) and can facilitate defect identification. Since these defect-identifications there have been frequent attempts to relate the macroscopic (or bulk) measurements to them. These attempts have had varying degrees of success because the macroscopic measurements frequently give indecisive and confused results, e.g., electrical measurements indicate an energy level at $E_c - 0.4$ eV and the EPR reveals at least two different defects with levels in that vicinity. Our approach to remedy this difficulty has been, and is, to convert the macroscopic measurement techniques so that they give microscopic information; the approach has been to exploit the ability to align the defects under the influence of a uniaxial stress and thereby achieve a macroscopic anisotropy in the sample. This was achieved first in vibrational infrared bands and next in electronic infrared bands. The next step in the program was to apply the same techniques to photo-conductivity as has been
achieved by Cheng\textsuperscript{49} and Kalma and Corelli\textsuperscript{50}.

There have, of course, been many other silicon measurements: electrical properties,\textsuperscript{51-67} optical properties,\textsuperscript{68-74} and photo-conductivity.\textsuperscript{73} We do not mean to imply that these other measurements are without value for they certainly are, and indeed have resulted in exciting new results, e.g., the temperature dependent damage production rate.\textsuperscript{63,72} We rather hold that until these measurements are directly related to an identified defect, the work is incomplete, and further that our approach provides a way to achieve such a direct relationship.

Clearly now that "microscopic" measurement techniques have been developed in EFR, optical absorption and photo-conductivity, much work should be done to exploit these techniques on silicon. The research program described below is directed, in part, at that need; the research program, however, also is directed at extending the microscopic measurement approach to the measurement of parameters related to minority carrier lifetime.

Both exploiting and extending are needed (and go hand in hand). That exploiting is needed can be seen from the fact that we know next-to-nothing about the interstitial and its related defects; that extending the technique to lifetime measurements is needed is obvious from the importance of this parameter to device technology.

Our experimental work on silicon is divided into two parts:
1) EPR measurements and 2) electrical and optical measurements. Briefly EPR measurements are being used to try to identify the defects created in neutron irradiation. It has been recently shown\cite{74} that many of the defects that are already identified are created in neutron-damage, but many dominant defects\cite{1,15,16} although there has been speculation\cite{13,14} on their identity, remain unidentified. We have begun studying the response of these defects to stress and to light of various wave-lengths. The stress experiments are designed to reveal the local symmetry of the defect and its motional energies; these techniques have proven quite incisive in identifying defects in the past. The study of the influence of light on the EPR spectra is designed to associate the EPR spectra with energy levels in the forbidden gap; and thus correlate with electrical measurements; by measuring the transient and steady state response of the EPR signal to light we can also obtain lifetime and capture cross-section information - information uniquely associated with the defect associated with that EPR spectra, as opposed to conventional electrical lifetime measurements which average over all defects.

In the course of the EPR studies in neutron-irradiated silicon we have observed ten new spectra, some of them major spectra judging from the intensity. These, added to the thirty-two previously identified spectra, bring the total number of known spectra in irradiated Si to forty-two; of these only fourteen have been
identified with models, in some cases several spectra for the same defect. As mentioned before we had speculated earlier\textsuperscript{13} that some of the spectra observed in neutron-irradiated Si were due to several vacancies along a $\langle 110 \rangle$ in a $\{110\}$ plane. Brower\textsuperscript{14} carried this suggestion further analyzing the D-tensor to be expected for the spin-one state of various multi-vacancies. He arrived at a tentative association of a spectrum with the 4-vacancy defect and of other spectra with multi-vacancies associated with oxygen. Following these lines we have begun the consideration of the molecular orbital models of other forms of multi-vacancies. This analysis has suggested models for several spectra. (In all cases a given model assignment has to be confirmed by stress and other experiments.) Our analysis has also caused us to reconsider the microscopic models\textsuperscript{75,76} of dislocations in the diamond structure; we feel this analysis will also lead to further understanding of the amorphous state and its defects.

Related to this work we have begun electron irradiations at elevated temperatures, e.g., 300-500°C, to see if we can create these multi-vacancies and dislocation loops via vacancy agglomeration.
IV. Diamond.

While the main thrust of our program is on silicon, special circumstances have risen recently which have caused us to broaden our program to include measurements on diamond. Of course, it has been some time since the G. E. scientists (at the nearby Research and Development Center) showed that they could convert graphite to diamond by use of a catalyst, and even directly without a catalyst; semi-conducting (p-type only thus far) diamonds can also be made. They recently announced that gem-size and quality diamonds can be made. These scientists have agreed to collaborate with us in a study of some problems on radiation-induced defects in their man-made diamonds. The purity of these diamonds is still not comparable to silicon, but the impurities can be varied in type and concentration, a development that is revolutionizing diamond science. While there have been many measurements on radiation-induced defects in diamond relatively little in the way of firm defect identification has been achieved and "microscopic" measurement techniques used in silicon should prove readily applicable. In short, this collaboration provides us a unique and important opportunity to study defects in diamond. The study of defects in diamond is, of course, of substantial interest in itself. In addition, the theory of defects is much more tractable and advanced in diamond and hence it is imperative that the experimental groundwork be well established, so that the insights obtained in diamond may be carried over into the other semiconductors.
We have begun EPR measurements on diamond. We have performed electron- and neutron-irradiations on both natural and man-made diamonds, the latter including those doped with boron, with nitrogen and with carbon-13. (For EPR purposes the nuclear hyper-fine interaction due to $^{13}\text{C}$ we expect will be especially helpful.) We observe many new resonance lines and have already sorted out several new spectra.

We have also applied the Brower-type analysis to the diamond spectra and find two of our spectra to be strong candidates for a 3-vacancy and a 4-vacancy center, resp., and, more importantly, two of the spectra observed sometime ago to be probably associated with two different charge states of the split-$<100>$ interstitial! We are, of course, pursuing these identifications experimentally.

We have found, for the first time, EPR spectra in heavily-doped boron-containing diamond which we identify with free-and bound-holes.

We have performed ion-implantation experiments on diamond (courtesy of Air Force Cambridge Research Laboratories) and have found, for the first time, the EPR spectrum associated with the amorphous layer in diamond. We are now studying this layer as a function of implanted ion, fluence and annealing.

Using heavily doped diamonds (boron) we have carried out preliminary measurements of the energy dependence of damage production in diamond at liquid nitrogen temperature. As of this writing, the
energy calibration is not firm, but an onset of damage was observed.
Moreover, contrary to the results of others, we observed substantial recovery upon annealing to room temperature.
V. Summary of Program.

Our program on the study of radiation damage in semiconductors and related problems consists of several inter-related efforts:

1) Theory. This work ranges from the Extended Hückel treatment of the electronic and total energy of defects and defect structures to the simple molecular orbital similar structures. Our emphasis is on using the theory as an aid in defect identification and in understanding defect processes. We are presently concerned with interstitials, multi-vacancies, dislocation loops and amorphous material, as well as with the mechanisms for defect-production and -migration.

2) Experiment. Our primary orientation is experimental. We are performing EPR, electrical and optical measurements on silicon and diamond irradiated with ions, neutrons and with electrons, the latter irradiations being performed at room temperature, high temperatures (e.g., 300°C) and low temperatures (e.g., liquid nitrogen). We are trying to identify the defects responsible for the various defect processes.
References.


4. For recent summaries of the field see the reports of the conferences at Santa Fe (Ref. 5) and Albany (Ref. 6).


13. See Ref. 1 p. 81.


32. K. H. Bennemann, Phys. Rev. 137, A1497 (1965) and ibid., 139, A482 (1965).


42. K. Weiser, Phys. Rev. 126, 1427 (1962).
46. See the summary in Ref. 1.


83. Y. M. Kim and J. W. Corbett, to be published.

84. J. C. Bourgoin, P. R. Brosious, Y. M. Kim, J. W. Corbett, R. X. Chrenko and H. M. Strong, to be published.