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We have developed a cyclic-cluster program to compute the structure and properties of defects in crystalline solids. We have found the semi-empirical electronic structure method MINDO/3 to give the best account of the structure, stability and states near the gap for defects in silicon. We have applied the cyclic cluster program to describe the chemistry and physics of hydrogen and oxygen in a silicon crystal. We have concluded that a di-ylid is a promising candidate for the core of the 450° oxygen thermal donor in silicon. We have discovered that a four-member ring containing two oxygen atoms is likely to diffuse much faster than interstitial oxygen in silicon. We have applied pertubation theory to give a qualitative explanation of the ladder of effective mass states associated with oxygen clusters in silicon and germanium.

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THEORETICAL STUDIES OF THE CHEMISTRY AND PHYSICS OF OXYGEN IN SILICON

FINAL REPORT

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THEORETICAL STUDIES OF THE CHEMISTRY AND PHYSICS OF OXYGEN IN SILICON

THE PROBLEM STUDIED

Broadly stated, we have attempted to describe the chemistry and physics of oxygen in a silicon crystal. To do this we have combined the semi-empirical electronic structure methods developed by chemists with the cyclic cluster methods developed by physicists. Our tools are of general applicability, and may be used with previously developed parameters to describe various defect structures in silicon containing oxygen, hydrogen, and other elements.

Our interest has centered on elucidating the nature of the core of the thermal donors which are formed when crystalline silicon containing dispersed interstitial oxygen is annealed at 450°C. A series of thermal donors appears to be formed by the sequential addition of oxygen atoms. They have been studied using infrared (IR) spectroscopy, electron spin resonance (ESR), and electron-nuclear double resonance (ENDOR). These tools show that the thermal donors are shallow double donors with a pair of electrons in effective-mass states. The kinetics for thermal donor formation have often been interpreted to require an enhanced diffusion rate for interstitial oxygen or an oxygen dimer. For this reason we have studied the mechanism and energetics of diffusion of oxygen.

We are also interested in relatively well understood defects containing oxygen in silicon: these include interstitial oxygen, oxygen in a vacancy, and two oxygen atoms in a vacancy. These systems provide a test of any methods we develope.

Properties of defects of interest include structure, thermodynamic stability, location of electronic states relative to the gap, vibrational frequencies, and potential surfaces for structural changes.

Because of the increasing interest in the role of hydrogen in silicon, we have undertaken studies of the structures by which hydrogen is bound to the crystal and the diffusion path for hyrogen.

SUMMARY OF THE MOST IMPORTANT RESULTS

We have developed a cyclic-cluster program to compute the structure and properties of defects in crystalline solids [1]. We incorporated several semiemperical electronic structure methods in cyclic cluster and molecular cluster programs and found the Modified Intermediate Neglect of Differential Overlap (MINDO/3) to give the most satisfactory description of defect electronic states close to the gap in silicon [2]. We found the original MNDO method was not rotationally invariant with a resulting loss of degeneracy of energy levels of cyclic clusters. We proposed a solution to this problem [3].

Application of the cyclic cluster program to describe the bonding of hydrogen in silicon showed the most stable bonding to be at a bond centered position [4]. We have reviewed related experiments which appear to support this conclusion [5]. The potential surface for the diffusion of hydrogen in silicon was also explored in paper [6]. Cyclic cluster calculations were made to decribe the passivation by hydrogen of substitutional sulfur in silicon. This work showed the hydrogen to bond to the silicon atoms neighboring the sulfur atom [7]. Major results of our hydrogen related work are summarized in two review articles [8,9].

A copy of the MINDO/3 cylic cluster and molecular cluster programs has been given to Dr. Arthur Edwards of the Electronics Device and Technology Laboratory at Fort Monmouth.

We believe that oxygen becomes trivalent in its bonding to silicon to form the oxygen thermal donor. The silicon oxygen-ylid [10,11,12] was the first such structure proposed by us for the core of the oxygen thermal donor. A single ylid is of C_{2v} symmetry and would have an oxygen atom on the rotation axis of the defect. This disagrees with the conclusion from ENDOR spectra that although the thermal donor contains oxygen, none is on the rotation axis. For this reason we have explored a di-ylid, four-member rings, and other models for the core of the thermal donor. These calculations showed that a vacancy model favored by ENDOR spectroscopists is thermodynamically unstable [13]. We examined the location of gap states and qualitative ENDOR splittings for these models and

concluded that a di-ylid model for the thermal donor core is promising and should be studied further [14].

Our studies of various bonding structures in of oxygen in silicon lead us to the surprizing conclusion that a four-member ring containing two oxygen atoms is stable with respect to dissociation into two interstitial oxygen atoms and that the four member ring may be a fast diffusing species in silicon [15,16]. This has lead us to undertake a systematic study using the cyclic cluster method of one- and two-oxygen defects in silicon [17].

We have found a simple application of perturbation theory to be helpful in understanding the ladder of effective mass states in silicon associated with a postulated series of donor cores with an increasing number of oxygen atoms [18]. It has been used to explain a new shallow donor series in silicon [19] as well as spectra of thermal donor series in germanium [20,21,22].

We have had success in fitting the observed kinetics of formation of the thermal donor series by assuming that the smallest electrically active species contains five oxygen atoms [23]. We find our model to predict an oxygen depletion rate which is in excellent agreement with experimental findings [24,25]. Some of our findings were summarized in an invited review paper [26].

We have explored the application of the concept of fractals to ion cascades [27,28] and disordered impurities in solids [29].

We published four additional papers more distantly related to the main thrust of our research [30,31,32,33].

RESEARCH OPPORTUNITIES

We believe that molecular cluster and cyclic cluster calculations can be profitably be used to study the etching of silicon by hydrogen [34] and other species. We also intend to approach the study of the structure and electronic states of surfaces and interfaces using these tools.

We have modified our programs to compute the vibrations of subsets of atoms moving in the potental provided by the remaining atoms of the cluster. This program has given very encouraging results in describing the infrared spectra of interstitial oxygen and

other oxygen defects in silicon. We believe a large research opportunity exists here.

I have been funded by the National Research Council to join Dr. Arthur Edwards of the U. S. Army Electronics and Technology Lab. in Fort Monmouth in developing MINDO/3 parameters for gallium, arsenic, aluminum, and nitrogen for application of the methods we have developed here to new materials. That collaboration may lead to a proposal to study defects in gallium arsenide and related materials.

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