

Exchange of deeply trapped and interstitial hydrogen in silicon

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Using *ab initio* density-functional calculations, we examine possible exchange mechanisms between an interstitial hydrogen atom and a deeply bound H at a silicon-hydrogen bond. We determine a low-energy pathway for exchange, which involves an intermediate, metastable $\equiv\text{SiH}_2$ complex with both hydrogen atoms strongly bound to the silicon atom. The energy barrier for the exchange process is $E_{\text{ex}} < 0.2$ eV, consistent with observations of hydrogen-deuterium exchange in *a*-Si:H(D) films. [S0163-1829(99)04507-5]

I. INTRODUCTION

Hydrogen plays an important role in many technologically relevant processes in silicon.¹ Introduction of hydrogen can result in passivation of shallow acceptor and donor states, as well as of electrically active deep levels.¹⁻⁴ The latter are often found at silicon surfaces, grain boundaries, interfaces, and in amorphous silicon (*a*-Si), and are usually associated with the presence of silicon dangling bonds. The formation of Si-H bonds, via hydrogen passivation of electrically active silicon defects, is crucial for device fabrication. However, hydrogen is also involved in the *creation* of electronic defects. Hydrogen-induced extended defects (referred to as “platelets”) have been observed in *c*-Si,⁵ and hydrogen is commonly accepted to play a role in the light-induced degradation (the Staebler-Wronski effect) in hydrogenated amorphous silicon (*a*-Si:H).^{6,7} Determining the relationships of hydrogen to electronic defects requires a fundamental understanding of H-H interactions and of the mechanisms for H diffusion.

Let us briefly review what is known regarding the atomistic mechanisms for H diffusion in silicon-based materials. *Ab initio* calculations have been performed for hydrogen interstitials in bulk crystalline silicon (*c*-Si).^{4,8,9} The results indicate that for neutral- and positive-charge states the lowest energy position for hydrogen is at the bond-center site (BC), whereas in the negative charge state the lowest energy site is at the tetrahedral interstitial site. Neutral hydrogen at the BC site is ~ 1.1 eV lower in energy than a neutral H atom in free space.⁴ The barrier for H interstitial diffusion is low, between 0.2 and 0.5 eV.⁸⁻¹⁰ Hydrogen interacts strongly with other impurities as well as with defects in the crystal. The strongest of these interactions is with silicon dangling bonds, where Si-H bonds are formed with bond strengths up to 3.6 eV,^{4,11,12} similar to those in silane. Silicon dangling bonds thus form deep traps for hydrogen. In *a*-Si:H hydrogen diffusion is understood to occur by the dissociation of Si-H bonds, producing interstitial hydrogen; the latter diffuses rapidly along interstitial sites until trapped at a dan-

gling bond or other defect site. The measured activation energy for hydrogen diffusion in *a*-Si:H is about 1.5 eV.¹³

Hydrogen exchange between deeply trapped and mobile states plays an important role in the diffusion process.¹⁴ If such exchange takes place by first dissociating a Si-H bond and subsequently placing another H at the dangling bond, the activation energy would be high. Although hydrogen exchange has not, to our knowledge, been studied experimentally in crystalline silicon, exchange is known to proceed very efficiently in amorphous silicon.¹⁵⁻¹⁷ Similarly, efficient exchange has been observed at the Si/SiO₂ interface.¹⁸

The goal of the present paper is to study atomistic mechanisms for a neutral interstitial hydrogen to exchange with a deeply trapped hydrogen. We specifically focus on hydrogen trapped at an isolated Si-H bond in bulk crystalline silicon. Our main result is that H-H exchange can proceed with an energy barrier of less than 0.2 eV. The first part in the process consists of an interstitial H atom approaching the Si-H bond, resulting in a hydrogen in a bond-center site next to the Si-H bond. The H-H exchange then proceeds via an intermediate, metastable state, in which *both* H atoms are equally bonded to the Si atom, a configuration, which we label $\equiv\text{SiH}_2$. In this configuration the two atoms can easily rotate; the H atom that was originally deeply bound can then jump to a BC position and diffuse away, completing the exchange.

After we present our results, we will discuss whether our model of the Si-H bond is sufficiently generic to describe the general features of hydrogen-hydrogen exchange, and applicable to other situations where hydrogen passivates deep defects. The H-H exchange mechanism examined here for bulk *c*-Si should also be representative of hydrogen exchange in *a*-Si:H, grain boundaries, surfaces and at interfaces such as the Si/SiO₂ interface.

II. METHODOLOGY

Our *ab initio* self-consistent total-energy calculations are based on density-functional theory in the local density

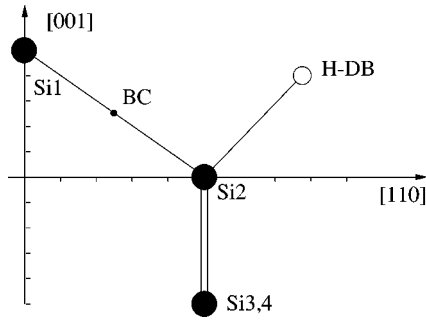


FIG. 1. Schematic illustration of a dangling bond at atom Si2 passivated by a H atom (H-DB). The small-open circle represents a hydrogen atom; the large-filled circles represent silicon atoms. The solid lines represent bonds in the plane of the page [the $(11\bar{0})$ plane]; the double lines indicate bonds to the Si3 and Si4 atoms, which lie in front of, respectively behind, the plane of the page.

approximation,^{19,20} using norm-conserving pseudopotentials.²¹ The pseudopotential core radii are 1.2 Å for Si and 0.2 Å for H. Integrations over the first Brillouin zone are replaced by summations using a $2 \times 2 \times 2$ sampling which reduces to 2–4 high-symmetry $\mathbf{k}$ -points in the irreducible wedge.²² We use a plane-wave basis set with an energy cutoff of 20 Ry. Tests at 24 Ry show that total energy differences changed by less than 0.05 eV. Similar implementations of density-functional theory have been widely used to investigate hydrogen interactions with Si.^{4,8,12,23}

We employ a supercell geometry, based on a 32-atom supercell. To create an isolated Si-H, we follow the procedure outlined in Ref. 24. We first remove one Si atom, creating a vacancy and focusing on one of its dangling bonds. Then the Si atoms corresponding to the other three dangling bonds are removed, creating nine new dangling bonds; all of the latter are passivated by hydrogen atoms. These H atoms are more than 3 Å away from the H atom on the Si-H bond under study. The geometry of this isolated Si-H bond in a small void is illustrated in Fig. 2 of Ref. 24. Two shells of silicon atoms are allowed to relax around the central Si-H bond. Test calculations showed that relaxing more shells does not measurably affect the relative total energies. The silicon atoms are relaxed until each component of the atomic forces is less than 0.1 eV/Å. To avoid spurious relaxations, all calculations were carried out at the theoretical lattice constant (5.38 Å). Zero-point energies are not included in the values reported. Since these energies are similar for all the hydrogen configurations discussed here,⁴ we do not expect our conclusions to be affected. Overall, we estimate the uncertainty on our calculated energy barrier to be ± 0.1 eV.^{4,8}

III. RESULTS

Figure 1 shows a schematic of hydrogen passivating the dangling bond. Note that Fig. 1 includes neither all the atoms of the supercell nor all the atoms relaxed in our simulations. We use the following notation: hydrogen at a bond-center site is labeled H-BC; for the isolated dangling bond we use DB, and if it is passivated by hydrogen we use H-DB or Si-H, interchangeably; for hydrogen in a BC site next to a DB site, we use (H-BC,H-DB); finally, if H-BC is far from a DB site we use (H-BC)+(H-DB).

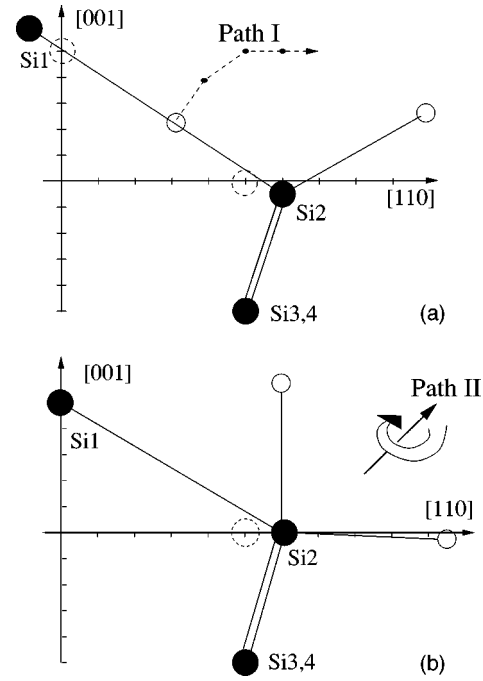


FIG. 2. Hydrogen-hydrogen exchange takes place via a three-step process. (a) The bond-centered H atom moves by the path labeled I towards the dangling-bond region, resulting in a metastable $\equiv\text{SiH}_2$ complex. The dotted circles represent the initial position of the silicon atom. The solid circles show the position of the Si atoms in the (H-BC,H-DB) complex. (b) In the $\equiv\text{SiH}_2$ complex the two H atoms can “rotate” around the $[111]$ direction, as schematically illustrated by path II. To complete the exchange, the originally deeply bound H atom moves to a new BC position, along a path that is the equivalent of path I. The energetics for the exchange are reported in Fig. 3.

Figure 2(a) is a schematic of the fully relaxed (H-BC,H-DB) complex which is the starting point for the exchange. The Si1 and Si2 atoms relax by 0.39 and 0.50 Å, respectively, primarily along the Si1-Si2 bond direction. The relaxation of Si2 is 10–20% larger than for an isolated bond-centered H in c-Si,^{8,12} presumably due to the greater freedom enjoyed by atom Si2, which is lacking a Si-Si bond. Somewhat surprisingly this greater freedom does not translate into a lowering of the energy of the (H-BC,H-DB) complex with respect to (H-BC)+(H-DB). As shown in Table I, (H-BC,H-DB) is actually 0.15 eV higher in energy, i.e., it is less stable than (H-BC)+(H-DB). We find that the Si-H bond length in the (H-BC,H-DB) complex is 2.0% larger than an isolated Si-H. This result indicates that the Si-H bond is weakened by the neighboring H-BC, explaining why the (H-BC,H-DB)

TABLE I. Energies of various configurations involving two H atoms. The reference state is (H-BC)+(H-DB) (i.e., one H at a BC site plus one H at an isolated DB site). Abbreviations are explained in the text.

Site	Energy (eV)
(H-BC)+(H-DB)	0.00
(H-BC,H-DB)	+0.15
$\equiv\text{SiH}_2$	+0.14

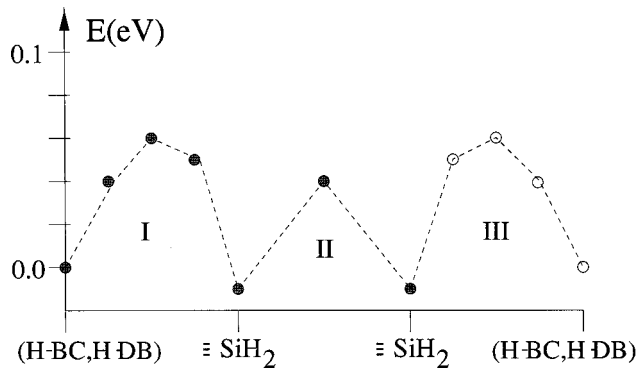


FIG. 3. Calculated energies for H-H exchange, proceeding by the mechanism illustrated in Fig. 2. The energetics for paths I and III are the same by symmetry. Solid circles represent our calculations; open circles are results determined by symmetry. Note that the (H-BC,H-DB) configuration is 0.15 eV higher in energy than (H-BC)+(H-DB), with H-BC far away from H-DB.

complex is higher in energy than (H-BC)+(H-DB). Still, this modest increase in energy (0.15 eV) does not constitute much of a barrier for an interstitial H atom to approach the Si-H bond.

Taking the (H-BC,H-DB) configuration as our starting point we now investigate the mechanism by which the H-BC may exchange with the H-DB. This process involves a concerted motion of the two H atoms, along with relaxations of all the Si atoms. A full exploration of the multidimensional adiabatic energy surface would be computationally prohibitive. In our search for a low-energy exchange path we have therefore fixed the position of one hydrogen atom, allowing the other H as well as the Si neighbors to relax. Once a low-energy path was discovered, several calculations, with both H atoms fixed, were performed to verify the initial results. The energy barrier identified in this fashion should be an upper limit to the true barrier.

Preliminary explorations of the energy surface allowed us to focus on the path depicted in Fig. 2. First, we move the H atom from BC towards H-DB, fixing this H at a number of positions along a path labeled “Path I” in Fig. 2(a); the corresponding energies are shown in Fig. 3. Path I leads to an intermediate $\equiv\text{SiH}_2$ configuration, as shown in Fig. 2(b). For this configuration, an additional atomic relaxation was performed in which both H atoms were allowed to relax; this established that $\equiv\text{SiH}_2$ is actually a metastable configuration (i.e., a local minimum in the energy surface). Figure 3 shows that the energy barrier along path I is ~ 0.06 eV.

The energy of the $\equiv\text{SiH}_2$ complex is 0.01 eV lower than the (H-BC,H-DB) complex, as reported in Table I and Fig. 3. The Si-H bond lengths of the complex are 4% longer than the isolated Si-H bond length, consistent with weaker bonding. The Si-Si bonds are also lengthened particularly the Si1-Si2 bond length. An investigation of the electronic structure reveals that along path I the highest occupied eigenlevel descends from near the conduction-band edge to near mid-gap, at which point the eigenstate is localized on the central (Si2) silicon and both hydrogens.

We find that the H atoms in the $\equiv\text{SiH}_2$ complex can “rotate” with relative ease around the [111] direction of the original Si-H bond. The H atoms “rotate” out of the (110) plane as sketched in Fig. 2(b). As a first guess, we simply

moved the H atoms along straight lines to a symmetrically equivalent position with the $\equiv\text{SiH}_2$ lying in the $(01\bar{1})$ plane instead of the (110) plane. The H atoms were moved at 0.3 Å intervals, and the Si atoms were allowed to relax at each step. The barrier at the midpoint of this path was found to be 0.11 eV. Near the saddle point for the reorientation the forces on the H atoms should be near zero; however, at the midpoint of step II, the forces on the H atoms are 0.5 eV/Å and nearly perpendicular to the respective path vectors suggesting that the simple linear path is not the minimum-energy pathway. The energy barrier of 0.11 eV thus represents an upper limit. A more realistic estimate of the barrier for “rotation” of the $\equiv\text{SiH}_2$ complex was obtained as follows: for the midpoint of path II, after the silicon atoms were fully relaxed, we also allowed one H to relax. The ensuing atomic relaxation (by ~ 0.1 Å) provided a further energy gain of 0.07 eV. From these calculations we estimate the energy barrier for the reorientation of the $\equiv\text{SiH}_2$ complex to be smaller than 0.04 eV (see Fig. 3).

To complete the exchange, the original H-DB moves into a BC site along a path which, by symmetry, is the reverse of path I, with the same energy barrier (see Fig. 3). In order to consider the full exchange process, the energies in Fig. 3 need to be combined with other relevant energies. The energies in Fig. 3 are referenced to (H-BC,H-DB), which is 0.15 eV higher in energy than (H-BC)+(H-DB), in which the H atoms are widely separated. The activation energy of the exchange process is therefore dominated by the energy gain of 0.15 eV needed to place the interstitial (transport-level) hydrogen in a (H-BC,H-DB) state. However, one should keep in mind that an interstitial H must migrate between BC sites in order to reach the (H-BC,H-DB) site. Since the migration barrier for interstitial H is between 0.2 and 0.5 eV,⁸⁻¹⁰ no additional energy barriers are presented for the interstitial H to reach the (H-BC,H-DB) site. The local barriers of 0.06 eV to actually exchange the two hydrogens, depicted in Fig. 3, are smaller than the barrier for interstitial migration and therefore easily overcome at temperatures for which interstitial migration can occur.

In the course of our investigations we explored a number of possible paths and exchange mechanisms other than the one reported in Fig. 2. For instance, we examined the possibility that as the H-BC moved towards the dangling bond region, the H-DB would simultaneously move to one of the two neighboring BC sites. We found that such a process would encounter energy barriers over 0.8 eV. We conclude that having at least one H to passivate the dangling bond at any time is essential to a low-energy exchange. Only mechanisms that consistently maintain at least one H passivating the dangling bond will be competitive with those reported in Figs. 2 and 3. In addition, we found large energy barriers for a hydrogen to move from the $\equiv\text{SiH}_2$ complex into an open interstitial site. These results suggest that for neutral hydrogen the path described in Fig. 2 is the most likely path for hydrogen exchange.

IV. APPLICATION TO HYDROGENATED AMORPHOUS SILICON

Our calculations were for a *c*-Si based model of an isolated Si-H bond. We now discuss to what extent our results

are applicable to other environments, in particular to amorphous silicon. We have examined several atomistic α -Si:H models, which have been reported in the literature in order to compare their Si-H bonding environments to the one employed here. (See Ref. 11 for a review of various α -Si:H models.) The local environment of our present model, including the open void above the Si-H bond, is similar to the environment of deeply trapped, isolated Si-H bonds in the α -Si:H models. Recent *ab initio* total energy calculations also indicate that for isolated Si-H bonds, the Si-H bond strengths in α -Si:H are similar to those in our c -Si model.¹² In addition, the interactions governing the energetics of the exchange process seem to be fairly localized in nature (as illustrated by the insensitivity to relaxations beyond second-nearest neighbors); we therefore suggest our results would apply to an amorphous environment as well.

Detailed experimental information about the exchange process in amorphous silicon was obtained in hydrogen-deuterium tracer diffusion experiments in α -Si:H(D).^{15,16} A solution of the tracer diffusion equations¹⁶ was fit to the experimental profiles of Ref. 15. Consistency with all available data was obtained only when deep trap levels, in addition to shallow traps and a transport level, were taken into account; in addition, it was found necessary that (1) there is significant exchange between the transport level and the deeply trapped hydrogen and (2) the energy barriers for H-H(D) exchange are much smaller than the barriers for long-range diffusion. The latter criterion can be written as $E_{\text{ex}} \ll 1.5$ eV, where E_{ex} is the energy barrier for exchange and 1.5 eV is the activation energy for long-range diffusion. Kemp and Branz¹⁶ proposed that H-D (or H-H) exchange occurs via an intermediate state with two H atoms bonded to a Si atom, i.e., where the Si atom is overcoordinated. They also noted that the energy of this intermediate state has to be nearly degenerate with the energy of an isolated Si-H plus a transport-level hydrogen. The properties of the $\equiv\text{SiH}_2$ emerging from our calculations are entirely consistent with the mediatory complex suggested by Kemp and Branz.¹⁶ We find an energy difference of 0.14 eV between $\equiv\text{SiH}_2$ and (H-BC)+(H-DB). The consistency of our present results with the experimentally based constraints for hydrogen exchange suggests that we have captured important features of the exchange mechanisms for H in α -Si:H.

Disorder in the α -Si network may affect some details of the exchange mechanisms. Static and dynamical simulations in realistic models of α -Si:H would indeed be useful to test the mechanisms proposed here. We also note that our calculations apply to *neutral* interstitial H exchanging with a deeply bound H. Interstitial hydrogen can occur in different charge states.^{4,8} In the positive charge state H still prefers the BC site, and we expect only minor modifications to the exchange path described above. In the negative charge state, H prefers to sit in open interstitial positions, and the exchange mechanism (if present) may be quite different.

V. DISCUSSION AND SUMMARY

Finally, we discuss some generalizations and consequences of the present study. First, we note that the H-H

exchange mechanism presented here may be active not just in bulk c -Si or α -Si, but also at surfaces, grain boundaries, or interfaces such as the Si/SiO₂ interface—although at surfaces or in large voids the presence of free H (not bound to the lattice) may complicate the picture.

In this study, we have examined the $\equiv\text{SiH}_2$ complex, which involves a five-fold coordinated silicon atom. Overcoordination defects are known to be present in bulk silicon; in *amorphous* silicon, these have been suggested to be the dominant intrinsic defect.^{12,25} The present complex differs in some respects from over-coordinated defects found in bulk silicon. In the $\equiv\text{SiH}_2$ complex, the underlying silicon defect is a three-fold coordinated atom. The over-coordinated silicon complex only occurs upon introducing two hydrogen atoms into the dangling-bond region. A similarity between the five-fold coordination defect studied in the context of α -Si and the $\equiv\text{SiH}_2$ complex is that both result in a deep level, which is rather localized on several atoms.^{12,26,25}

One might expect that the $\equiv\text{SiH}_2$ complex will be a precursor for H₂ thermal desorption in bulk silicon, at interfaces or at surfaces, e.g., the hydrogenated Si(111) surface. A full determination of the desorption barrier is beyond the scope of the present study. However, preliminary investigations suggest the barrier is greater than 1.0 eV.²⁷

We also propose that the locally stable $\equiv\text{SiH}_2$ complex may play a role in defect formation. Since the complex is electrically active, light or free carriers could enhance the dissociation of the complex which may lead to formation of a dangling bond and an H₂ molecule. This H₂ molecule can then diffuse away leaving behind a dangling bond, i.e., an electrically active defect. Such processes may occur in silicon-based solar cells and transistors where hydrogen is used to passivate deep centers.

In summary, we have used *ab initio* density-functional calculations to determine a low-energy exchange mechanism between interstitial and deeply bound hydrogen. We find that the activation energy for the exchange is dominated by the energy it takes to place the interstitial H near the Si-H bond (0.15 eV); additional barriers for exchange are very low. The microscopic mechanism involves an intermediate $\equiv\text{SiH}_2$ complex. The exchange mechanism discussed here should be relevant not only for hydrogen (and deuterium) exchange in α -Si:H but also at grain boundaries, surfaces, and interfaces such as the Si/SiO₂ interface.

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- ¹*Hydrogen in Semiconductors and Semimetal*, edited by J. Pankove and N. M. Johnson (Academic Press, Boston, 1991), Vol. 34.
- ²R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge, 1991).
- ³R. Helms and E.H. Poindexter, Rep. Prog. Phys. **57**, 791 (1994).
- ⁴C.G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).
- ⁵N.M. Johnson, F.A. Ponce, R.A. Street, and R.J. Nemanich, Phys. Rev. B **35**, 4166 (1987).
- ⁶J. Kakalios, in *Hydrogen in Semiconductors and Semimetal* (Ref. 1), p. 381.
- ⁷Z. Yiping, Z. Dianlin, K. Guanglin, P. Guanglin, and L. Xianbo, Phys. Rev. Lett. **74**, 558 (1995).
- ⁸C.G. Van de Walle, P.J.H. Denteneer, Y. Bar-Yam, and S.T. Pantelides, Phys. Rev. B **39**, 10 791 (1989).
- ⁹F. Buda, G.L. Chiarotti, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 294 (1989).
- ¹⁰A. Van Wieringen and N. Warmoltz, Physica (Utrecht) **22**, 849 (1956).
- ¹¹B. Tuttle, Ph.D. thesis, University of Illinois at Urbana-Champaign (Urbana), 1997; B. Tuttle and J.B. Adams, Phys. Rev. B **53**, 16 265 (1996).
- ¹²B. Tuttle and J. Adams, Phys. Rev. B **57**, 12 859 (1998).
- ¹³R.A. Street, C.C. Tsai, J. Kakalios, and W.B. Jackson, Philos. Mag. B **56**, 305 (1987).
- ¹⁴C.G. Van de Walle and R.A. Street, Phys. Rev. B **51**, 10 615 (1995).
- ¹⁵H.M. Branz, S.E. Asher, B.P. Nelson, and M. Kemp, J. Non-Cryst. Solids **164-166**, 269 (1993).
- ¹⁶M. Kemp and H.M. Branz, Phys. Rev. B **52**, 13 946 (1995).
- ¹⁷R.A. Street, in *Amorphous Silicon Semiconductors—Pure and Hydrogenated*, edited by A. Madan, M. Thompson, D. Adler, and Y. Hamakawa, MRS Symposia Proceedings No. 95 (Materials Research Society, Pittsburgh, 1987), p. 13.
- ¹⁸J.W. Lyding, K. Hess, and I.C. Kizilyalli, Appl. Phys. Lett. **68**, 2526 (1996); K. Hess (private communications).
- ¹⁹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B869 (1964); W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
- ²⁰D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- ²¹N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991); **43**, 8861 (1991).
- ²²D.J. Chadi and M.L. Cohen, Phys. Rev. B **8**, 5747 (1973).
- ²³Y. Zhou, R. Luchsinger, and P.F. Meier, Phys. Rev. B **51**, 4166 (1995).
- ²⁴C.G. Van de Walle and R.A. Street, Phys. Rev. B **49**, 14 766 (1994).
- ²⁵S.T. Pantelides, Solid State Commun. **84**, 221 (1992).
- ²⁶R. Biswas, C.Z. Wang, C.T. Chan, K.M. Ho, and C.M. Soukoulis, Phys. Rev. Lett. **63**, 1491 (1989).
- ²⁷B. Tuttle (unpublished).