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Microstructure of local defects in amorphous Si:H: A quantum chemical study

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The mechanism of the Staebler-Wronski effect, which is responsible for the light-induced degradation of photovoltaic devices based on amorphous, hydrogenated silicon (a-Si:H), is still in question. It is, e.g., assumed that a defect precursor A is transformed into the actual, metastable defect B by excitation and subsequent electron trapping. We present calculations on large, distorted silicon clusters containing vacancies/voids of up to three missing atoms. A sophisticated embedding procedure is employed where the atoms surrounding the vacancy/void are treated by means of a density functional (BP86) and the outer atoms are taken into account semiempirically (AM1). Full geometry optimization results in novel and unprecedented structure information. Excitation energies and electron attachment energies are presented. These findings substantiate ideas regarding the nature of A and B.

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I. INTRODUCTION

For application in optoelectronic devices such as, e.g., solar cells, amorphous hydrogenated silicon (a-Si:H) could serve as a cheap and technically more versatile replacement for crystalline silicon. In the following paragraph the characteristic features of this material are summarized in brief.

The hydrogen content of a-Si:H varies between 1 and ~15 at. %. The distribution seems to be inhomogeneous. Hydrogen is mostly bound as Si-H, but variable shares of SiH_2 bonding have been found as well. Under extreme circumstances, even molecular H_2 has been observed, but recent results make it plausible that a certain share of H_2 is present also under usual conditions.[1–9] The material contains up to 5×10^{19} microvoids per cm^3. It has been shown that, by keeping the hydrogen content below 4 at. %, also samples free of larger voids can be produced. Most device-quality a-Si:H, however, is interspersed with cavities. Assuming a spherical structure the *mean* void radius amounts to 3.3–4.3 Å, which corresponds to 16–26 missing atoms. The mean hydrogen content per void is estimated to be 5–9 bonded H atoms, i.e., the inner void surfaces are only slightly hydrogenated.[10–12] a-Si:H contains 10^{18}–10^{20} strained Si-Si bonds and about 10^{15}–10^{16} paramagnetic centers per cm^3. Molecular-dynamics (MD) simulations and measurements of the radial distribution functions of a-Si both with and without hydrogen show[13–17] that the mean Si-Si distance is somewhat longer (0.05–0.10 Å) than in c-Si, whereas the mean bond and dihedral angles do not deviate much from the values of the ideal crystal. Their distribution, however, is relatively broad. Also some fivefold coordinated Si has been found. The facts indicate that the paramagnetic entities are *localized* radical centers of subvalent (threefold coordinated) Si, called *native dangling bonds*. Their distribution depends on the manufacturing conditions. Some of these native dangling bonds may be located in the vicinity of a hydrogen, which could be responsible for the observed shift in the electron-spin resonance hyperfine splitting.[3,18–24] The band gap of a-Si:H depends on the manufacturing conditions and attains values between 1.55 and 1.85 eV.

Unfortunately the practical use of a-Si:H is limited by the so-called Staebler-Wronski effect (SWE).[25,26] Phenomenologically the SWE is a photoelectronic two-step process: During several hours of exposure to sunlight both the photoconductivity and the dark conductivity of a-Si:H decrease significantly. This conductivity loss, however, can be fully reversed by thermal annealing in the dark ($T\geqslant150\,°C$). The well-established facts are as follows: During 1–100 h of light exposure the photoconductivity decreases by about one order of magnitude, which is coupled to a decline in dark conductivity of at least four orders of magnitude.[25,27] At the same time the spin density (the number of paramagnetic centers) increases by about one to two orders of magnitude. These additional paramagnetic centers are called *light-induced* or *metastable* dangling bonds. The saturation value of the spin density is independent of (i) the temperature during exposure, (ii) the initial density, and (iii) the carrier generation rate. It is, however, approximately proportional to the band gap and the hydrogen content.[28] The increase in spin density is qualitatively independent of the photon energy (if $E\geqslant1.2$ eV) and the light intensity (at least in the range 0.1–3.0 W/cm^2). It is obviously coupled to the conductivity loss, but no simple one-to-one correlation has been established.[21,22,27–34] By thermal annealing in the dark at a temperature above 150 °C the original state of the material can be fully restored.[25–27,29,30]

Despite a vast amount of experimental information on both device-quality a-Si:H and the SWE,[1–5,10–39] its mechanism is still in question and discussed controversially.[40–48] New mechanistic proposals emphasize the role of hydrogen,[49–51] but they contradict chemical experience and are put into question by recent experiments.[52] Moreover, resistance noise measurements have shown that H diffusion does not play an important role in both creation and annihilation of the metastable defects.[53,54] Nevertheless there is general agreement that a-Si:H possesses a lot of strained, weakened, and unsaturated Si-Si bonds, and it is therefore supposed that these *localized* entities are the precursors (A) of the light-induced dangling bonds (see, e.g., Refs. 35, 55–57). They can be found at least 0.2 eV above the edge of the valence band. Experimental evidence and some of the differ-

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ent mechanistic conceptions coincide in the following rough idea of an explanation of the SWE, which will be elaborated on in detail in a subsequent paper:

- It is assumed that exposure of A to sunlight enables A to trap an energetically nearby electron from the conduction band. By relaxation of this intermediate the metastable dangling bond B is formed. It is situated at about 0.5 eV above the A level.
- The thermal reformation of A (the annealing process) may be considered the reverse of the photoelectronic formation of B. The threshold for thermal reformation of A amounts to about 1.0 eV.

Recall that both A and B are geometrically localized entities embedded in the amorphous bulk, but neither the nature of A and B nor the reaction path $A \rightarrow B \rightarrow A$ are known up to now. It seems to be improbable that the native dangling bonds act directly as electron traps, since in this case negatively charged closed-shell silicon centers would be generated and accordingly a *decrease* in spin density should be observed.

In view of the fact that a-Si:H is interspersed with an enormous amount of microvoids it seems plausible that the sequence of reactions responsible for the SWE takes place at certain sites of inner void surfaces. This idea has first been proposed by Carlson,[58] who assumed that the first step of $A \rightarrow B$ is the trapping of a hole near a microvoid.

II. STRATEGY AND METHODS

In a first step of our efforts we will concentrate on the nature of the localized reaction centers A and B.

The accurate modeling of chemical and physical systems containing a large number of atoms is still a challenging task. An obvious solution to this problem is the partitioning of the system into two (or more) parts, where the more interesting part (the so-called core) is treated at a higher level of theory, and the rest of the system (the bulk) is described by an approximate and computationally less-demanding method. The crucial aspect, however, is the embedding of the core into the bulk, i.e., the *coupling* of the two parts. For this we have employed the recently developed ONIOM scheme[59] which is implemented in the Gaussian98 program package.[60] The total energy E_{ONIOM} is defined as

$$E_{\mathrm{ONIOM}} = E_3 - E_1 + E_2, \tag{1}$$

where E_3 is the energy of the entire system (core+bulk) calculated at the lower-level method and E_1 and E_2 are the energies of the core determined at the lower and higher level of theory, respectively.

If a system is divided into core and bulk, obviously a lot of bonds are cut so that the surface of the core would be covered with unpaired electrons (dangling bonds), which would cause the formation of totally unrealistic structures. To avoid this, each dangling bond is saturated with a so-called link atom. In most cases (and in this work throughout) H is used. It is seen immediately that the quality of the treatment of the bond between a core atom and the corresponding link atom should be the same for both methods employed, since only then the effect of the artificially introduced link atoms on E_{ONIOM} cancels out. So a reasonable adjustment or selection of the high-and the low-level methods is necessary. During geometry optimization the force acting on a link atom is projected onto the respective core atom and the corresponding atom in the bulk.

The material is modeled by silicon clusters, which represent clippings of c-Si. The outer surfaces are hydrogenated to prevent the formation of unrealistic electronic states, and terminal silyl groups are replaced by H. The overall point-group symmetry of the clusters used is D_{2d} or C_{2v}. Then some silicon atoms are removed from the center of the cluster, and the neighboring atoms are regarded as the core of the system, which is treated by means of a high-level quantum chemical (HQC) method. The influence of the surrounding silicon network is described by embedding the core into a much larger Si frame (the bulk), which is treated semiempirically. Then we allow for *total* geometry relaxation in either a very low symmetry or without any symmetry constraints at all.

Most of the stationary points obtained in this way are characterized by a vibrational analysis to be sure that they are minima indeed and not saddle points on the respective potential hypersurfaces. If the system size is too large for a complete vibrational analysis, the geometry of the stationary point is distorted and then a second geometry relaxation is performed so that the existence of a nearby minimum in C_1 symmetry can be excluded. Finally however, and most important, the bulk dimensions are changed drastically. In this way it is possible to vary the strain exerted by the bulk on the core. If, despite a broad variation in bulk size, the core geometry remains qualitatively the same, then we may be sure that the minimum structure found in fact represents a site that may be present in the actual material.

One could make the objection that an investigation of vacancies/voids in these clusters does not allow for statements regarding *amorphous* silicon, because the cluster structures are derived from *crystalline* Si. However, on a length scale of 5–10 Å the difference between crystalline and amorphous loses its meaning completely. A cluster of, let us say, 100 Si atoms is neither crystalline nor amorphous. The experimental knowledge about amorphous Si is limited to distribution functions, which represent statistics over a large number of bond lengths or angles. These functions do not provide any information on the details of the bonding situation in a localized area confined to a few Angstrom around a certain site. So it is reasonable to proceed in the way described above to characterize the various vacancies/voids, especially since during relaxation more or less severe distortions of the ideal lattice occur anyway. To demonstrate this, the distance matrices of the final structures have been evaluated statistically to obtain distance histograms. These histograms show the typical features of the radial distribution function of amorphous silicon: With respect to the unperturbed clusters,

- the peaks are shifted towards longer distances, and
- the distribution is broadened significantly.

We do all calculations deliberately *without* periodic boundary conditions, since they would simulate a certain long-range correlation of subunits, which by definition is not present in an amorphous material. Note, however, that the bulk size may not exceed a limit of, let us say, roughly 200–300 atoms, because in case of significantly larger systems the peripheral area of the bulk could retain its crystalline character during geometry optimization so that finally the system would represent an unrealistic mixture of amorphous and crystalline parts.

In the following we will present results obtained by applying the above-described procedure to systems with up to three adjacent silicon atoms missing. The respective vacancies/voids are not hydrogenated. Corresponding results on the role of H will be presented in a forthcoming paper.

The HQC method has to provide reliable geometries and relative total energies of strained and defective Si clusters with or without hydrogen atoms present. Also hydrogen migration should be described correctly. Moreover, it should allow for reasonable electron affinities for both closed- and open-shell systems. In a previous article[61] we have examined whether customary density functionals meet with these requirements. Five combinations of exchange and correlation functionals have been tested, which represent the three possible ways to improve the local spin-density approximation: inhomogeneity correction, modeling of exchange and correlation holes, and hybrid exchange. It has been shown that the combination of Becke's 1988 exchange[62] and Perdew's 1986 correlation functional[63] is best suited for our purposes. This finding is supported by recent results of Ahlrichs *et al.*[64,65] In all calculations presented in this article the $6-31G^*$ standard basis set has been used.

As the lower-level method, we have chosen the semiempirical method AM1,[66,67] because in test calculations on hydrogenated silicon clusters up to $Si_{17}H_{36}$, it has proven to be superior to other semiempirical approaches.

At the local minima of the potential hypersurfaces vertical excitation energies and oscillator strengths are calculated by means of the single-excitation configuration-interaction (CIS) method[68] based on the corresponding Hartree-Fock (HF) orbitals. In cases of interest vertical electron attachment energies and/or singlet-triplet splittings have been computed as well. Open-shell cases have been handled by use of the unrestricted Kohn-Sham and Hartree-Fock schemes, respectively.

In the following all energy values given refer to the BP86 treatment of the core plus link atoms only. Recall that the core describing the localized reaction center is the essential part of the total system, and the function of the bulk is to provide for a reasonable arrangement of the core atoms by simulating the restrictive effect of a surrounding silicon network.

Vacancies in silicon have attracted the interest of several other authors, too.[69–80] Most of their work makes use of density-functional theory in the local-density approximation (LDA) with simple energy functionals and either an optimization algorithm or molecular dynamics. In most cases also pseudopotentials are employed. Sometimes the results are complemented by semiempirical calculations on the partial retention of diatomic differential overlap (PRDDO)[81] level and single-point *ab initio* HF. Supercells containing from 32 to 216 atoms are used. Either periodic boundary conditions are applied, or the outer shell of the silicon aggregate is kept fixed during geometry relaxation. Some authors also make use of MD based on the Stillinger-Weber force field.[73,79] However, faced with the facts that (i) BP86 is a much more sophisticated density functional than any LDA version, and that (ii) AM1 is a better semiempirical method than PRDDO, it is obvious that our methodical approach is significantly superior to what has been done before. Moreover, it must be emphasized that the force fields employed so far are not able to describe the formation of a new bond starting from two radical centers (dangling bonds). (It should be mentioned that other attempts employ a developed force field[82] or the local spin-density approximation based on the simple Perdew-Zunger exchange-correlation functional,[83] but this does not change the above conclusion regarding the predictive power of our approach.)

III. RESULTS

A. The monovoid (monovacancy)

If one central Si atom is removed from the cluster, a vacancy (monovoid) is generated. Its local point-group symmetry is T_d because of the tetrahedral arrangement of the four silicon atoms with dangling bonds. These four electrons can be distributed to four orbitals. One of them is totally symmetric (a_1) and the other three are degenerate (t_1 or t_2). Therefore the electronic state of the core is degenerate in any case, and in consequence a Jahn-Teller distortion will reduce the local symmetry to C_s or C_2. So the starting geometry of the monovoid optimizations has been reduced accordingly by slight distortion. A subsequent vibrational analysis of the stationary points on the potential hypersurface showed that in this way true minima are obtained.

Independent of the cluster size *one* set of qualitatively equivalent structures is obtained. At the beginning of the optimization all core atoms have a distance approximately 3.82 Å from each another, and the Si-Si-Si angle amounts to about 109.5° (deviations are due to the above-mentioned small input distortion). During relaxation of the total system the core atoms rearrange in pairs in such a way that now two more or less strained Si-Si single bonds perpendicular to one another are formed (see Fig. 1). Atoms 1 and 2, as well as atoms 3 and 4, get closer to each other so that the distances R_a and R_b reduce from 3.82 to 2.4–2.5 Å, i.e., by more than $\frac{1}{3}$. These two new bonds have nearly equal bond lengths. The corresponding angles, which, in the projection of Fig. 1, are bisected by R_a and R_b, respectively, decrease from 60° to about 40°. The other Si-Si distances, however, are not very much affected by the contraction of the void. Thus, the diameter of the void shrinks by about 10%.

In the case of the C_2 minima there is only a small difference between R_c (R_c') and R_d (R_d'), indicating that the two new bonds are twisted towards one another by a few degrees only. With the C_s structures, where obviously R_c (R_c') must be equal to R_d (R_d') but $R_c \neq R_c'$ and $R_d \neq R_d'$, we find $R_c \approx R_d$ and $R_c' \approx R_d'$. So in both cases there is a slight deviation from the common higher point-group symmetry C_{2v} only. To sum up, if a single Si atom is removed, the cluster will relax to dispose of the vacancy, or to put it into other words, a

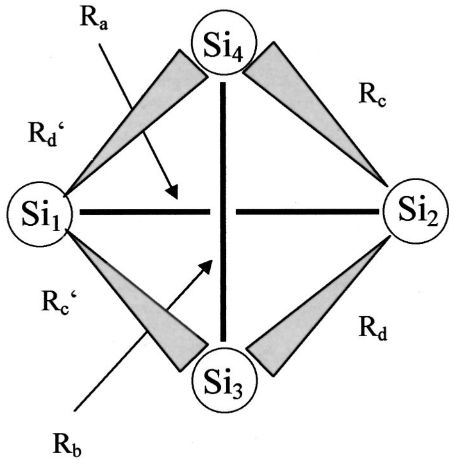

FIG. 1. Result of the total geometry relaxation of the monovoid/monovacancy.

monovoid with four dangling bonds *does not exist* if the system is allowed to rearrange.

Values for bond lengths and angles of clusters up to Si_{121} can be found in Table I. One can see that the newly formed Si-Si bonds become longer as the cluster size increases. Based on previous experience we infer that the maximum bond length will be found near 2.6 Å. This is due to the fact that a larger bulk is less deformable than a small one and therefore prevails against the tendency to form short unstrained bonds. So one would expect that the energy of the core (including the link atoms) rises with increasing cluster size. This is the case indeed: The total energy of the core of the Si_{33} cluster amounts to $-1164.121\,48$ Hartree, whereas we obtain $-1164.095\,92$ Hartree for the core of the Si_{121} cluster, i.e., the energy increases by 0.17 eV per bond elongated by 0.125 Å.

The above results differ significantly from previous works of other authors (see, e.g., Refs. 70 and 72), who found in relaxed structures distances of the vacancy-surrounding atoms of at least 3.0 Å. We assume, however, that these findings are methodic artifacts (see the discussion in Sec. II). This assumption is supported by the fact that the vanishing of the vacancy is reproduced correctly even if only a less sophisticated quantum chemical method such as AM1 is employed to describe the total system.

Finally it should be emphasized that already predictions of the geometry relaxation obtained by relatively small clusters are in qualitative agreement with the outcomes of large-scale systems. This is very comforting knowledge with respect to the treatment of larger voids.

B. The doublevoid

By removal of the central atom and one adjacent Si atom a doublevoid (also called a "simple divacancy") is created. Based on the experience with monovoids, four clusters have been selected to examine the relaxation behavior of the doublevoid. The cluster size covers the range from 75 up to 167 silicon atoms. The core consists of the six next neighbors of the removed centers. Before geometry relaxation these atoms are arranged in two staggered equilateral triangles yielding D_{3d} symmetry. The Si-Si distances within the triangles amount to 3.82 Å, where the intertriangular distances attain values of 4.48 and 5.89 Å, respectively. The latter one may be considered the diameter of the void. The electronic state of six dangling bonds in the D_{3d} arrangement is again orbitally degenerate, because the three electrons of each triangle have to be distributed to one totally symmetric orbital and two degenerate orbitals of e symmetry. So the system will undergo a Jahn-Teller distortion allowing for two local minima with local C_s symmetry. In the first case one can expect the formation of one new bond within each triangle leaving one electron per triangle unpaired (I), whereas in the second case two new bonds will be formed (II).

Previous work[72,75,78] yielded lowest-energy configurations quite similar to the primary structure obtained by just removing the two Si atoms, i.e., Si-Si distances of still more than 3.0 Å and overlap populations of at best 0.20 are found. It is, however, hard to believe that an agglomeration of six dangling bonds does not find a way to stabilize itself by the formation of new real bonds as described above.

Despite the fact that the clusters we had used differ significantly from one another, we obtain *one* kind of doublevoid structure (Fig. 2) only, which corresponds to result II of the Jahn-Teller distortion: The six radical centers rearrange within the two groups of three atoms each. Said three atoms of each group now form an isosceles triangle with a lateral side length of a little bit more than 2.5 Å and an angle of slightly smaller than 90°. The two triangles are twisted by about 180° towards one another. What has happened? The diameter of the void decreased by more than 1 Å from 5.89 to 4.70 Å. The other intertriangular distance, however, remained more or less constant, i.e., the essential step in the

TABLE I. Monovoid geometries (distances are in angstrom, angles in degrees). The meaning of the atom labels is explained in Fig. 1.

N(Si)	Local core symmetry	R_a	R_b	R_c	R_d	∢ 1-3-2	∢ 3-2-4	∢ 1-3-2-4
33	C_s	2.382	2.381	3.749	3.749	36.9	37.1	83.6
36	C_2	2.398	2.398	3.783	3.762	38.0	37.2	84.5
43	C_2	2.413	2.413	3.760	3.733	37.6	37.6	81.6
65	C_2	2.445	2.445	3.722	3.678	38.6	38.6	80.1
89	C_2	2.455	2.455	3.703	3.652	39.0	39.0	79.6
121	C_s	2.506	2.505	3.580	3.580	41.0	41.0	81.9

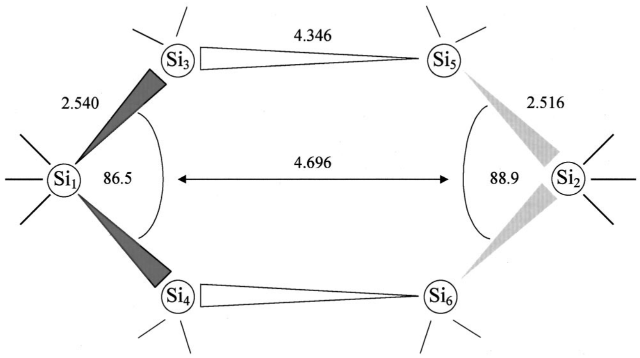

FIG. 2. Doublevoid structure. Mean values of bond lengths (in angstrom) and angles (in degrees).

relaxation process was the movement of the atoms 1 and 2 towards one another (see Fig. 2) leading to the formation of new bonds between 1 (2) and 3,4 (5,6). The values for bond lengths and angles given in Fig. 2 are the means of the respective values of the four clusters, which can be found in Table II. There are *no* significant differences in going from one cluster to the other!

Also in the case of the doublevoid a contraction of the vacancy takes place, but in contrast to the monovoid situation the doublevoid does not disappear during relaxation. Instead it is stabilized by a rearrangement of the atoms. In this context it is a noteworthy fact that the vertices Si_1 and Si_2 of each triangle become *fivefold* coordinated (see Fig. 2). The bond lengths to the three outer silicon atoms amount to 2.40–2.45 Å. Recall that the existence of fivefold coordinated silicon (often referred to as ''hypervalent'') is discussed in the context of *a*-Si.

The unusual structure of the doublevoid has encouraged us to calculate the excitation energy from the ground state to the lowest excited singlet state (S_1). It should be mentioned that silicon has a distinctive tendency to favor the lowest-possible spin states. We therefore exclude that triplet states play any role in the processes of interest unless diradicals are present. The results can be found in Table II where also the oscillator strengths are reported, which are a measure of the transition probability. Recall that the dimensionless oscillator strength f is a function of the transition moment and the transition frequency. It may take on values between 0 and 1. If $f \rightarrow 1$ the corresponding transition is allowed and intense. If, on the other hand, f decreases below about 0.1, then the transition is more or less forbidden.

Irrespective of the cluster size, $\Delta E(S_0 \rightarrow S_1)$ amounts to about 1.36 eV. With $f \approx 0.67$ these transitions are obviously allowed. They are characterized by a quite pure highest occupied molecular orbital (HOMO)→lowest unoccupied molecular orbital (LUMO) excitation. With respect to the HOMO, the LUMO possesses an additional nodal plane between the two triangular substructures so that the wave function changes its sign if we go from atom 3 to atom 5 or from 4 to 6 (see Fig. 2). It is worth noting that, in the model of the SWE reported in Sec. I, this energy would be sufficient to surmount the gap between the defect precursor *A* and the edge of the conduction band.

It has already been mentioned in the Introduction that the primary step of the SWE is likely to be the trapping of a conduction-band electron by a defect precursor *A*. The resulting defect *B* must be a radical anion if *A* is neutral. Recall, however, that the electron to be trapped is the result of an excitation where a hole (cation) is left over, which is more or less localized somewhere in the silicon lattice. So in fact we obtain an anion-cation pair separated by, say, five to seven atom layers, i.e., by at least on the order of 10 Å. In terms of molecules and clusters a charge arrangement such as this is called a *zwitterion* (see the Appendix). It is well known that in systems with low polarity such as, e.g., the silicon clusters under investigation, the zwitterion is an *excited* electronic state. Now, seen from a quantum chemist's point of view, if this zwitterion is located energetically *below* the edge of the conduction band, then it is stabilized with respect to the combination of hole plus delocalized electron vs excited precursor. In this case trapping is favored and we finally obtain a metastable state, which corresponds to the actual defect. If, on the other hand, the energy of the zwitterion is above the conduction-band edge, trapping will not result in an energy gain, and in consequence no metastable defect is formed. So, assuming that *B* can be represented by the anionic part of the zwitterionic state belonging to *A*, the relation of the energy difference $E(B) - E(A)$ to the band gap decides whether a defect is obtained or not.

Unfortunately, however, zwitterionic states are extremely difficult to realize in calculations on large systems with low symmetry or no symmetry at all, but the vertical electron attachment energies $E_{A,v}$ of the precursor ground states allow for a rule of thumb regarding the energy of the zwitte-

TABLE II. Doublevoid geometries and parameters of the $S_0 \rightarrow S_1$ transition (distances are in angstrom, angles in degrees, and ΔE in eV). The meaning of the atom labels is explained in Fig. 2.

N(Si)	75	89	139	167
R(1-3,4)	2.517	2.531	2.566	2.546
∢ 3-1-4	87.5	86.8	85.3	86.5
R(2-5,6)	2.499	2.489	2.548	2.528
∢ 5-2-6	90.9	90.1	87.8	86.7
R(1-2)	4.704	4.685	4.686	4.708
$R(3\text{-}5)=R(4\text{-}6)$	4.357	4.390	4.297	4.338
Excitation energy ΔE	1.37	1.34	1.37	1.37
Oscillator strength f	0.688	0.663	0.652	0.672

TABLE III. Zwitterionic states and vertical electron attachment energies of several Si_nH_m molecules (energies are in eV).

Molecule	E(zwitterion)- E(ground state)	$E_{A,v}$
2,6-disilyl-heptasilane, Si_9H_{20}	5.37	+0.20
2,6-dehydro-2,6-disilyl-heptasilane, Si_9H_{18}	1.62	−2.74
2-dehydro-2,6,6,6-tetrasilyl-heptasilane, $Si_{11}H_{24}$	1.25	−2.57
2,8-disilyl-nonasilane, $Si_{11}H_{24}$	4.91	−0.22
2,8-dehydro-2,8-disilyl-nonasilane, $Si_{11}H_{22}$	1.22	−3.59

rion. The reason for this is shown in Table III. There we compare $E_{A,v}$ to the actual excitation energy from the ground state to the zwitterionic state. It is seen immediately that high anion stabilization corresponds to an in-gap zwitterion while low anion stabilization (and destabilization) corresponds to a zwitterion energetically far above the edge of the conduction band in a-Si:H. So, $E_{A,v}$ is a good indicator for whether a system is able to form a metastable defect or not.

The vertical electron attachment energy $E_{A,v}$ of the Si_{75} cluster attains the remarkably high value of 3.25 eV ($\langle \mathbf{S}^2 \rangle = 0.752$), i.e., the anion is stabilized versus the neutral system to a significant extent. Because of the enormous similarity of all examined clusters this value may be considered representative for all doublevoids.

C. The triplevoid

Eight atoms form the boundary of the triplevoid, which is obtained if three adjacent silicon atoms are removed. The situation is shown in Fig. 3. The eight "black" atoms envelop the vacancy. The electronic structure again consists of two triangles of local C_3 symmetry, but now they are separated by two additional dangling bonds. Nevertheless we have to expect local-orbital degeneracy yielding to a Jahn-Teller stabilization of the triplevoid by distortion, and again, in complete analogy to the doublevoid case, there are two possibilities for the system to relax.

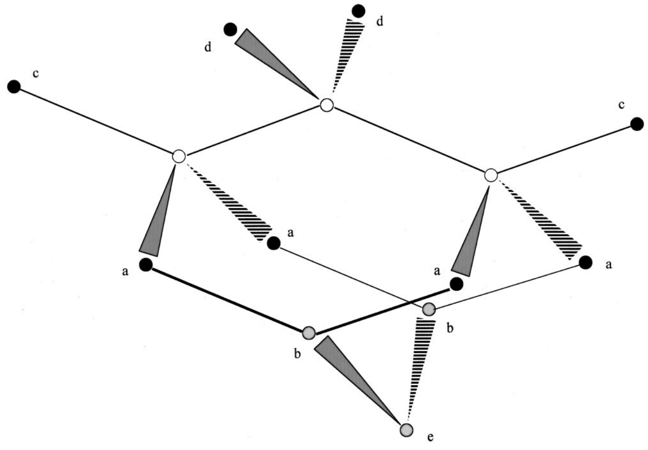

FIG. 3. Scheme of the triplevoid.

Usually one would identify the "black" atoms with the core of the system. Here, however, a difficulty arises that is not found for the smaller voids, because two pairs of these "black" atoms, denoted by "a," are bound to one and the same atom of the bulk each (denoted by "b"). It is obvious that the type-b atoms, which are divalent with respect to the core, cannot be substituted by a monovalent link atom like hydrogen. So one either has to employ other kinds of link atoms or the core has to be extended. The results of our study on divalent link atoms will be presented elsewhere. Here we report the possibility to extend the core by adding the two type-b atoms and the atom labeled "e" to the core so that $N(\mathrm{Si,core}) = 11$.

Unfortunately, by extending the core in the way described above, the "black" atoms are not treated equally. Each of the four atoms labeled "a" is bound to one other core Si (labeled "b"), whereas the other four atoms (labeled "c" and "d") are not. Note that the distance a-b amounts to 2.34 Å at the beginning of the optimization, whereas c-a is 3.82 Å. The type-d atoms are even more far apart. There is some risk that an unbalanced core like this will cause unrealistic effects. In consequence the core should be extended further so that also atoms adjacent to c and d are included. Since we do not want divalent bulk atoms we finally arrive at a core consisting of 22 Si atoms. In the ONIOM calculations the outer surface of the core is saturated with 32 H. The symmetry of the entire system is C_2. We have concentrated on singlet states (as usual).

In contrast to the doublevoid situation, we obtain *both* predicted minima on one and the same potential hypersurface. (In the following this situation is discussed using the results found for the Si_{107} cluster.) The structure of the first minimum (I) is shown in Fig. 4(a) (only the eight inner core atoms are presented). The d atoms, initially 3.82 Å apart, moved towards one another and formed a strained single bond with a length of 2.561 Å, which is comparable to what has been found with the monovoids. Also the two pairs of type-a atoms came close to each other, starting from a distance of 3.82 Å, so that additional new single bonds are produced ($R = 2.464$ Å). The type-c atoms, however, did not rearrange significantly. Their distance did increase only negligibly (from 7.64 to 7.71 Å), and no other atoms moved towards them during the optimization process. So three new single bonds have been formed, but the type-c atoms preserved their radical character, i.e., two of the initially eight dangling bonds survived and the total system is a *diradical* now. The a-b distances became inconsiderably longer (from 2.34 to 2.358/2.359 Å).

The electronic structure is characterized by the Kohn-Sham HOMO and LUMO. Both orbitals are localized at the radical centers c with the HOMO (symmetry type b) being the antibonding orbital, whereas the LUMO (symmetry type a) represents the bonding combination of the atomic orbitals. The orbital gap, however, is very small (0.02 eV) due to the fact that the two dangling bonds are coupled only slightly because of their long distance. In a simple Hartree-Fock picture (see below) one would expect the contrary, but recall that the density functional contains electron correlation to a

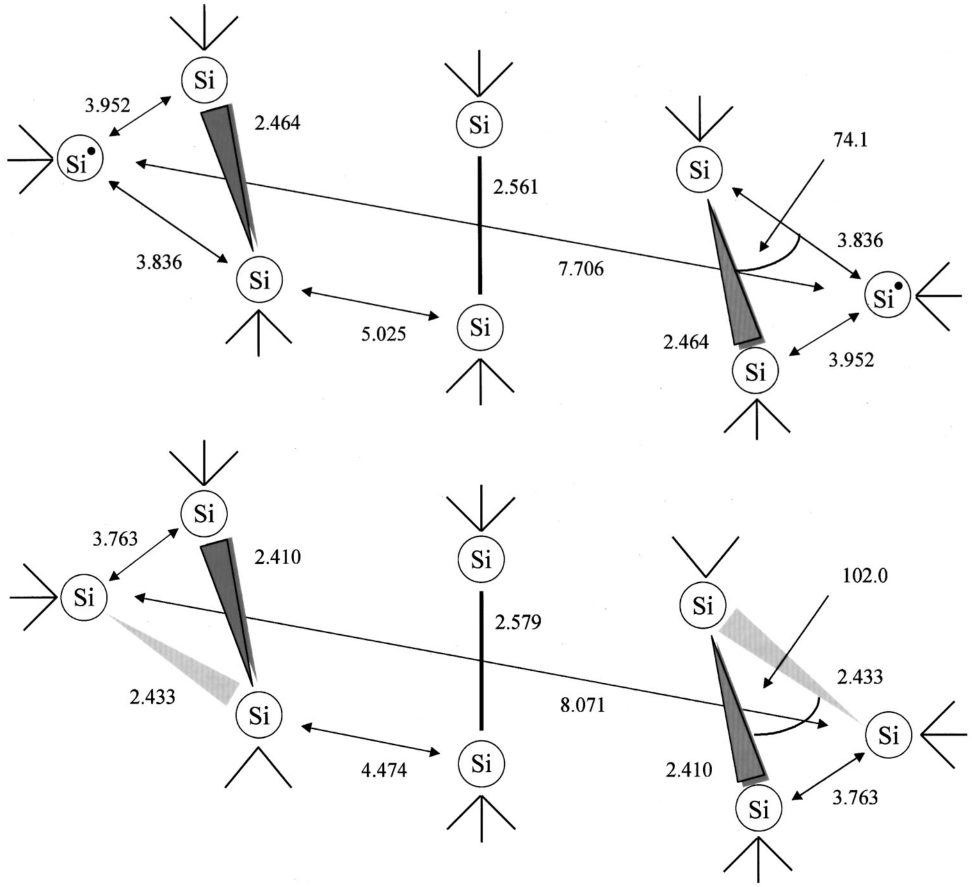

FIG. 4. (a) Si_{107} cluster. Triplevoid minimum I. Bond lengths and distances are given in angstrom, angles in degrees. (b) Si_{107} cluster. Triplevoid minimum II. Bond lengths and distances are given in angstrom, angles in degrees.

certain degree too so that a nodal plane between two faraway radicals could be the energetically better solution.

Roughly speaking, the structure of the second minimum (II), shown in Fig. 4(b), is a combination of two approximately isosceles triangles and one isolated single bond. The triangles, with a lateral side length of about 2.42 Å and including an angle of 102°, may be interpreted as the result of the incorporation of each of the dangling bonds into the respective nearest single bond and the regrouping of the atoms of the next shell. This in principle corresponds to the only realized doublevoid minimum, but now the vertices of both triangles, which have a distance of 5.474 Å, are fourfold coordinated only. Here the a-b distances amount to 2.330/3.542 Å, i.e., the b-b axis is significantly twisted with respect to the d-d bond so that, differently from what has been found with I, the lower part of the core is distorted considerably.

Both Kohn-Sham HOMO and LUMO are localized at the type-b atoms (see Fig. 3). The HOMO (b) is σ bonding and π antibonding with respect to a plane perpendicular to both b-e-b and c-e-c (see Fig. 3), whereas the LUMO (a) is σ antibonding and π bonding. The gap amounts to 0.26 eV.

The reaction path I→II is characterized by the transition state T, which is a first-order saddle point on the potential hypersurface. Its structure is not the result of a mere superposition of I and II. The approach of the two dangling bonds at the type-c atoms to the respective nearest single bond is advanced widely. The distance has decreased already from 3.836 to 2.641 Å, a value expected for a strained single bond. At the same time all of the three void-surmounting bonds became longer by up to 0.1 Å. Now, however, the vertices of the two newly formed triangles are *fivefold* coordinated. Recall that the corresponding atoms are normal (fourfold) coordinated in both I and II, but in I they are bound to three atoms of the next sphere each, whereas in II only two of these three atoms remain connected [see Figs. 4(a) and 4(b)]. So T just represents the situation where the approach of the dangling bond is more or less completed although the change in coordination has not taken place yet.

The diradical minimum I is energetically favored with respect to the bistriangular minimum II by 0.19 eV. T is located 0.76 eV above I and 0.57 eV above II.

With both minima, the $S_0 \rightarrow S_1$ transition is characterized by the HOMO→LUMO excitation. In the case of II the Hartree-Fock orbitals are similar to the corresponding Kohn-Sham orbitals described above. With the diradical, however, the Hartree-Fock HOMO is the bonding combination and the Hartree-Fock LUMO the antibonding one. For I we obtain an excitation energy of 1.10 eV and a high oscillator strength of 0.866. In the case of II the transition to S_1 needs a little bit more energy (1.26 eV), but f amounts to 0.119 only, which means that this excitation is not very likely although not impossible to occur.

To our methodic approach one could object that a diradical is a typical multireference case, because the bonding and the antibonding orbitals can be superimposed to yield two equivalent and nearly degenerate orbitals, allowing for two nearly degenerate Hartree-Fock determinants to be constructed. In consequence, one Hartree-Fock determinant would not be enough to provide a reasonable description. Recall that also a density-functional approach is *a priori* unable to deal with a real multireference situation. We therefore have reexamined the energy ratio and the excitation energies of both minima at the complete active space self-consistent-field (CASSCF) level of theory with two electrons distributed in an active space of two to four orbitals. For this purpose we performed single-point calculations of the core (plus corresponding link atoms) at the respective minimum conformation of the total system.

First the energy relation of I and II has been reexamined. In very satisfactory agreement with the density-functional finding we obtain a difference $E(\mathrm{II})-E(\mathrm{I})$ of 0.39 eV (small active space) and 0.81 eV (larger active space), respectively, but this result is not a surprise, because it is a well-known fact that even curious silicon structures can be described quite well by wave functions based on a single determinant. However, excitation energies, in contrast to pure ground-state properties, are much more difficult to compute. In the case of the larger active space the vertical excitation energy to S_1 is 0.92 eV (I), whereas the corresponding value of II amounts to 0.85 eV. In comparison to the above-reported results, and in view of the enormous computational effort caused by a multireference treatment, the results obtained by the relatively simple CIS method may be considered as reasonable estimates of the true values.

It cannot be excluded that a triplet state of I plays a role in processes relevant to the SWE. We have therefore determined the energy of the vertical transition from the ground state to the lowest triplet state. At the geometry of the S_0 minimum, T_1 is 1.35 eV higher in energy. Subsequent total optimization of T_1 leads to a minimum structure very similar to the one of the singlet ground state. The adiabatic energy difference $E(T_1)-E(S_0)$ still amounts to 1.15 eV ($\langle \mathbf{S}^2 \rangle = 2.006$). Faced with the fact that the spin-orbit coupling of molecules containing silicon and hydrogen only is extremely small—in $^3\mathrm{SiH}_2$, e.g., the spin-orbit coupling amounts to 1.9×10^{-4} eV—it is unlikely that this triplet state will exert any influence.

It is important to know whether any of the two minima is able to stabilize a negative charge. The vertical electron attachment energy of I is 1.24 eV, i.e., the anion is stabilized versus the neutral system by 1.24 eV. The $\mathbf{S}^2$ expectation value of the unrestricted Kohn-Sham determinant amounts to 0.754, indicating that the system is described correctly as a doublet state. Compared to what we have seen in the case of the doublevoids the stabilization energy is quite low. Therefore, in view of the rule of thumb regarding the energy of the zwitterion, it is doubtful whether the zwitterionic state is located in gap. In contrast to this the bistriangular minimum II allows for a significant anion stabilization (3.01 eV, $\langle \mathbf{S}^2 \rangle = 0.759$).

We have checked the consistency of the results obtained for the Si_{107} cluster by examining the much larger system consisting of 227 Si atoms and using the same extended core as described above. There is a reasonable agreement of the data showing that (i) the two minima are not artifacts caused by an insufficient cluster size but realistic entities, and (ii) the properties of I and II are predicted correctly. Detailed data will be presented, in connection with the analysis of the role of H, in the forthcoming paper already mentioned in Sec. II.

IV. SUMMARY AND OUTLOOK

We have tried to elucidate the character of the entities *A* (stable defect precursor) and *B* (metastable defect), which play the crucial role in the mechanistic description of the SWE. For this purpose a model of *a*-Si:H has been developed consisting of a void generated by removing one to three adjacent Si atoms in the center of a hydrogenated Si cluster. Then the total system is allowed to relax to a minimum of the respective potential-energy hypersurface. The calculations make use of an embedding procedure where the inner part of the total system (the core) is described by means of a suitable density functional (BP86). The remaining and much larger outer part (the bulk) is treated by means of the semiempirical method AM1. The coupling of the inner and outer parts is achieved by the ONIOM scheme. This procedure is superior to previous approaches to vacancies/voids in silicon.

The following results have been obtained:

- A monovoid/monovacancy in the sense of an actual hole inside the silicon framework does not exist. If one atom is removed, the surroundings rearrange in a way that finally the vacancy disappears. So monovacancies can be present in systems large enough to prevent complete relaxation only. This is the case for crystalline silicon but not for the amorphous material.
- In contrast to this, doublevoids are actual cavities. Geometry optimization yields a structure of the inner six atoms that can be described by two isosceles triangles, which are rotated and shifted towards one another. Two fivefold coordinated Si atoms are found.
- Triplevoids can exist in two different configurations. I is a real diradical with a distance of the isolated radical centers of about 8 Å. So I represents a pair of only slightly interacting dangling bonds and may serve as a model of the naturally occurring native dangling bonds. It therefore seems to be improbable that I is an appropriate candidate for the defect precursor A, since then, by trapping an electron, a decrease in spin density should be observed.
- The triplevoid configuration II is a bistriangular arrangement of atoms with one Si-Si single bond in the projected center of the void. Neither unpaired (isolated) electrons nor hypervalent silicon atoms are present in II, but, in spite of this, II is energetically unfavorable with respect to I by 0.19 eV.
- In the transition state *T* between I and II, two fivefold coordinated core atoms are present. *T* lies 0.76 eV above I and 0.57 eV above II.

- Both the doublevoid and the two triplevoid ground states can be excited by light of an energy within a range relevant for the SWE.
- Because of its vertical electron attachment energy $E_{A,v}$ of more than 3 eV, the doublevoid will possess an in-gap zwitterionic state. Also the triplevoid structure II is able to stabilize a negative charge considerably ($E_{A,v} \approx 3$ eV). With I, however, this ability is much less developed ($E_{A,v} \approx 1.2$ eV).

There are two prerequisites for an entity to play a decisive role in the mechanism of the SWE: First it must be excitable within the accessible energy range, i.e., the transition to a state just below the band gap must be possible *both* energetically and regarding the oscillator strength. These requirements are clearly met by the doublevoid and the triplevoid I. The corresponding excitation of triplevoid II is not so likely to occur, although not impossible, because of the low oscillator strength of 0.119. Secondly, since *B*, in the quantum chemist's point of view, is assumed to be represented by an in-gap zwitterion, the entity in question should possess a corresponding excited state. The ability of the ground state to stabilize an excess electron may serve as a rule of thumb for the existence of a proper zwitterionic state. In the case of the doublevoid this ability is very high. In contrast to this, triplevoid I is able to stabilize an excess electron by 1.24 eV only. So we assume that the corresponding zwitterionic state will not be an in-gap state. Triplevoid II, however, again allows for a significant anion stabilization. Therefore, regarding the voids investigated in the present paper, *the doublevoid is the most plausible candidate for the defect and its precursor*. Future work will clarify the role of hydrogen and extend the size of the examined systems up to the hexagonal hexavoid.

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APPENDIX

Assume two dangling bonds at atoms *A* and *B* where the electrons are placed in atomic orbitals a and b, respectively. Taking into account the fact that electrons are indistinguishable, we arrive at the singlet wave function

$$\Phi^{\mathrm{cov}} = a(1)b(2) + a(2)b(1).$$

(The negative linear combination represents a triplet state which, however, is not relevant for our further considerations.) If both electrons are put in one and the same atomic orbital, the two following linear combinations can be constructed:

$$\Phi_{\pm}^{\mathrm{zwitt}} = a(1)a(2) \pm b(1)b(2).$$

$\Phi_{+}^{\mathrm{zwitt}}$ and $\Phi_{-}^{\mathrm{zwitt}}$ are the in-phase and out-of-phase zwitterionic wave functions, respectively, which describe the cation-anion pair $A^{-}B^{+} \pm A^{+}B^{-}$.

In molecular-orbital (MO) theory one first has to form two MO's via linear combination of the atomic orbitals according to

$$\psi_{\pm} = a \pm b,$$

which are called the bonding and the antibonding MO, respectively. With these MO's we can construct three singlet wave functions with the spatial parts

$$\psi_{+}(1)\psi_{+}(2),$$

$$\psi_{+}(1)\psi_{-}(2) + \psi_{+}(2)\psi_{-}(1),$$

and

$$\psi_{-}(1)\psi_{-}(2).$$

$\psi_{+}(1)\psi_{+}(2)$ describes the double occupation of the bonding MO, i.e., it represents the ground state as long as there is any bonding interaction between A and B.

Now, the correct wave functions within this two atomic-orbital model are obtained if the electron correlation is taken into account. This is done by combining linearly the functions given above [configuration interaction (CI)] where, however, only functions of the same symmetry may be superposed. We obtain

$$\Psi_1 = \psi_{+}(1)\psi_{+}(2) - \lambda\psi_{-}(1)\psi_{-}(2),$$

$$\Psi_2 = \psi_{+}(1)\psi_{-}(2) + \psi_{+}(2)\psi_{-}(1),$$

and

$$\Psi_3 = \lambda\psi_{+}(1)\psi_{+}(2) + \psi_{-}(1)\psi_{-}(2)$$

with $\lambda > 0$, where Ψ_1 represents the ground state and $\Psi_{2,3}$ excited states.

If we express these correct wave functions in terms of the original atomic orbitals a and b we obtain

$$\Psi_1 = (1+\lambda)\Phi^{\mathrm{cov}} + (1-\lambda)\Phi_{+}^{\mathrm{zwitt}},$$

$$\Psi_2 = \Phi_{-}^{\mathrm{zwitt}},$$

and

$$\Psi_3 = (1-\lambda)\Phi^{\mathrm{cov}} + (1+\lambda)\Phi_{+}^{\mathrm{zwitt}}.$$

So the ground-state wave function is dominantly covalent with an in-phase zwitterionic admixture. The first excited state is purely zwitterionic, determined solely by the out-of-phase function, and the second excited state is of in-phase zwitterionic character mainly.

The farther *A* and *B* are apart, the more will ψ_{+} and ψ_{-} come closer to each other energetically. In case of degeneration, λ becomes equal to 1 so that the ground state attains a solely covalent character, i.e., it represents a diradical. Ψ_3 in turn will lose its covalent admixture and finally attain a solely zwitterionic character. Ψ_2, however, is always purely zwitterionic.

Note that these considerations are valid only if A and B do not differ too much in electronegativity. In the case of *doped* *a*-Si:H e.g., where atoms such as boron or phosphorous are present, we would have to form the MO's according to

$$\psi_+^d = a + \chi b$$

and

$$\psi_-^d = \chi a - b$$

with $\chi > 0$. This, however, would result in other CI wave functions where the ground state could turn out to be of dominantly zwitterionic character.

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