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## Theoretical Study of the Gradual Chemical Transition at the Si-SiO<sub>2</sub> Interface

### II. Electronic Density of States Calculations <sup>2)</sup>

By

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Calculations of the electronic density of states at the Si-SiO<sub>2</sub> interface performed with the help of the cluster-Bethe-lattice method are presented. A cluster is constructed, which realizes the semiconductor-insulator transition between a Bethe lattice of Si atoms and an SiO<sub>2</sub> Bethe lattice within three atomic SiO<sub>x</sub> layers with average  $x$  values of 0.33, 1.17, and 1.67. The resulting densities of states are compared with corresponding results for bulk SiO<sub>x</sub> and the static effective charges of all the cluster atoms are calculated. It is shown that an intermediate-range order (Si-Si chains and rings) strongly influences the position of the valence-band edge and, therefore, the variation of the width of the gap in dependence on the chemical composition  $x$  across the Si-SiO<sub>2</sub> inter-region. The defect levels resulting from dangling bonds of Si atoms with different backbond configurations and from a peroxy bridge and a peroxy radical are investigated. An influence of structural percolation effects on the dangling-bond levels is shown. Further microscopic origins of interface states are discussed.

Es werden Berechnungen der elektronischen Zustandsdichte an der Si-SiO<sub>2</sub>-Interface vorgestellt, die mit Hilfe der Cluster-Bethe-Gitter-Methode durchgeführt werden. Ein Cluster wird konstruiert, der den Halbleiter-Isolator-Übergang zwischen einem Si-Bethe-Gitter und einem SiO<sub>2</sub>-Bethe-Gitter innerhalb von drei atomaren SiO<sub>x</sub>-Schichten mit mittleren  $x$ -Werten von 0,33; 1,17 und 1,67 realisiert. Die erhaltenen Zustandsdichten werden mit entsprechenden Resultaten für Volumen-SiO<sub>x</sub> verglichen, und die statischen effektiven Ladungen aller Clusteratome werden berechnet. Es wird gezeigt, daß eine Zwischenordnung (Si-Si-Ketten und -Ringe) starken Einfluß auf die Position der Valenzbandkante und damit auf die Veränderung der Breite des Gaps in Abhängigkeit von der chemischen Zusammensetzung  $x$  quer durch die Si-SiO<sub>2</sub>-Interregion hindurch besitzt. Die sich durch abgerissene Bindungen von Si-Atomen mit verschiedenen Konfigurationen ihrer rückwärtigen Bindungen und durch eine Peroxybrücke sowie ein Peroxyradikal ergebenden Defektniveaus werden untersucht. Ein Einfluß von strukturellen Perkolationseffekten auf die dangling-bond-Niveaus wird nachgewiesen. Weitere mikroskopische Ursachen für Grenzflächenzustände werden diskutiert.

### 1. Introduction

The structural and chemical transition from the crystalline silicon substrate to its oxide in metal-oxide-semiconductor (MOS) devices is not an abrupt one [1]. It was shown, e.g., by means of photo- [2, 3, 4] and Auger-electron spectroscopy [5] that there is an interregion beginning with a disturbed and/or rough surface of the crystalline silicon substrate, which is followed by an SiO<sub>x</sub> ( $0 < x < 2$ ) layer (called the "Si-SiO<sub>2</sub> interface") and a layer of strongly disturbed amorphous SiO<sub>2</sub> changing over into regular amorphous SiO<sub>2</sub> [1, 4, 6]. A ball-and-sticks model based on these experi-

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mental results was investigated in Part I of this series [7]. The aim of the present paper is to calculate the electronic density of states (EDOS) at the Si-SiO<sub>2</sub> interface (IF). Though, as mentioned above, its gradual character was experimentally proved, in previous theoretical studies either bulk SiO<sub>x</sub> [8 to 12] or an abrupt transition [13 to 16] was used as a structural model for calculations of the IF-EDOS. The only exception is the work of Martinez and Yndurain [17], who investigated a layer structure with the chemical composition Si-SiO<sub>0.5</sub>-SiO<sub>0.5</sub>-SiO<sub>0.5</sub>-SiO<sub>2</sub>, which corresponds to a buried Si layer at the IF. The authors pointed out that the consideration of the two-dimensionality of the IF is necessary for its realistic description. It was shown [17] that localized electronic states in the semiconductor gap can be caused even by the existence of an IF without defects. This conclusion was not confirmed by other authors most of which [8, 9, 10, 12, 13, 15] used a Bethe-lattice (BL) technique [18, 19] for their calculations.

Lannoo and Allan [8] and Martinez and Yndurain [9] constructed special SiO<sub>x</sub>-BL's for the composition sets  $x = 0, \frac{2}{3}, \frac{4}{3}, 2$  and  $x = 0, 0.5, 1, 1.5, 2$ , respectively. It was shown [9] that the intermediate-range order (chains of Si-Si bonds) in SiO<sub>x</sub> is of great importance for the transition of the valence-band EDOS of silicon to the one of SiO<sub>2</sub>. Furthermore, a dependence of the angle  $\vartheta$  of an Si-O-Si bridge in SiO<sub>x</sub> on  $x$  must be taken into account, since for  $\vartheta = 120^\circ$  to  $125^\circ$  the calculated EDOS of SiO<sub>4/3</sub> [8] and SiO [9] corresponds best to experimental results, whereas the mean value of  $\vartheta$  for amorphous SiO<sub>2</sub> is  $144^\circ$  [7]. Strehlow and Lamfried [10] developed a BL method for calculating the EDOS of SiO<sub>x</sub> not only for any chemical composition between the values  $x = 0$  and  $x = 2$ , but also for different distributions of oxygen atoms within the Si matrix. Therefore, the authors were able to compare the EDOS curves of random-bonding SiO<sub>x</sub> (randomly distributed Si-Si and Si-O bonds) and mixture SiO<sub>x</sub> (randomly distributed small spheres of Si and of SiO<sub>2</sub>) and they showed that with decreasing  $x$  the formation of the EDOS structure of silicon occurs for the random-bonding SiO<sub>x</sub> for smaller  $x$  values than for the mixture SiO<sub>x</sub>. This follows from the influence of sufficiently long Si-Si chains in mixture SiO<sub>x</sub> on the electronic structure as already mentioned in [9]. Quite another approach was chosen by Ching [11], who used large unit cells of amorphous silicon and distributed oxygen atoms according to the average compositions  $x = 0, 0.5, 1, 1.5$ , and 2 within these cells. The author pointed out that the localization of the electronic states at the conduction-band edge increases with increasing  $x$  until the value  $x = 1.5$  is reached and that the static effective charges at the oxygen and Si atoms in SiO<sub>x</sub> vary between  $-1.54$  and  $-1.67$ , and  $+3.07$  and  $+0.59$ , respectively (in units of the elementary charge). Recently, Grafe and Strehlow [12] investigated the influence of Si-Si bonds on the local EDOS of SiO<sub>2</sub>. One of the results is that the electronic states occurring in the local EDOS of the central Si atom of an Si-O<sub>y</sub>Si<sub>4</sub> tetrahedron ( $y = 1, \dots, 4$ ) and within the SiO<sub>2</sub> gap can also be found in the valence-band tail of SiO<sub>x</sub> with  $x$  values near two.

Models of abrupt Si-SiO<sub>2</sub> interfaces were constructed by Laughlin, et al. [13] and Herman and Kasowski [14] by coupling together corresponding BL's and crystalline networks, respectively. It was shown [13] that variations of the bond length and of the bond angle at the IF cause localized electronic states at the band edges within the silicon gap, whereas the Si dangling bond (db) on the silicon side of the IF causes a localized state around midgap. A similar conclusion was drawn by Sakurai and Sugano [15].

In the present paper we consider for the first time a realistic gradual chemical transition at the Si-SiO<sub>2</sub> IF, namely that this semiconductor-insulator transition occurs within approximately three atomic layers [7], and calculate the EDOS at the Si-SiO<sub>2</sub> IF with the help of the cluster-Bethe-lattice method (CBLM) [18, 19]. The choice of

a corresponding cluster is discussed in Section 2. The results of the EDOS calculations for the Si-SiO<sub>2</sub> IF without and with defects are given in Section 3. Some conclusions are drawn in Section 4.

## 2. Model and Method

For the calculation of the EDOS with the help of the CBLM at first a cluster of atoms is needed, which is representative for the system under investigation. The unsaturated bonds at the boundary of the cluster are connected with BL's. A BL is an infinite, tree-like network without closed loops of chemical bonds. All the atoms of a BL have the same short-range order, i.e. the same coordination number, bond length, and bond angle. Due to limited computer capability we are not able to use the cluster discussed in Part I [7] of this work. Therefore, a new cluster [20] is constructed, which is much smaller but still representative for the atomic arrangement at the Si-SiO<sub>2</sub> IF.

Starting with a chain of Si atoms, oxygen and Si atoms are successively added until reaching the stoichiometry of SiO<sub>2</sub> after three layers in accordance with the experimental and theoretical experience discussed in [7]. To ensure lateral periodicity the ends of the chains are linked together yielding the ring-like structure shown in Fig. 1. A ring size of six atoms is chosen, since it is typical for the structure of the common forms of crystallin esilicon as well as of non-crystalline SiO<sub>2</sub> [21]. Ascribing the oxygen atoms located between two neighbouring rings with half weight to each of them, the model reveals the average chemical compositions SiO<sub>0.33</sub>, SiO<sub>1.17</sub>, and SiO<sub>1.67</sub> in ring I, II, and III, respectively, and, therefore, a quasi-gradual transition from silicon to silicon dioxide.

For the determination of the dependence of the value  $x$  on the distance  $d$  from the silicon surface (oxygen-concentration profile  $x(d)$ ) we assume the bond lengths at the IF to be the same as in the corresponding bulk materials, i.e. 0.235 and 0.161 nm for the Si-Si and the Si-O bond, respectively (see [7]). Since the variation of the bond angle  $\vartheta$  of oxygen across the Si-SiO<sub>2</sub> transition is not known, the values  $\vartheta_1 = 116^\circ$ ,  $\vartheta_2 = 124^\circ$ ,  $\vartheta_3 = 134^\circ$ , and  $\vartheta_4 = 145^\circ$  of the Si-O<sub>*y*</sub>Si<sub>4</sub> tetrahedra of reactively sputtered SiO<sub>*x*</sub> films [22] and corresponding arithmetic means for oxygen atoms belonging to two tetrahedra with different values of  $y$  are used. The shape of the resulting  $x(d)$

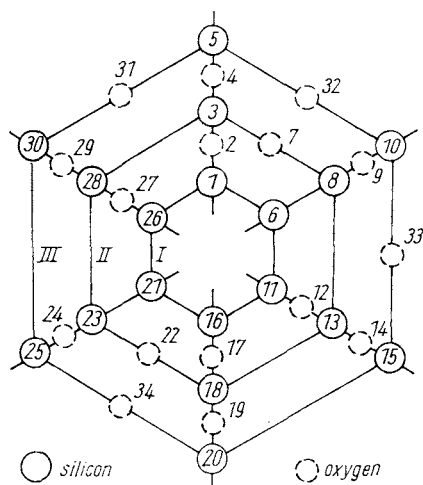


Fig. 1. 34 atom cluster as a model for the gradual change of the chemical composition across the Si-SiO<sub>2</sub> interregion. The sixfold rings appearing in the cluster are marked with Roman numerals

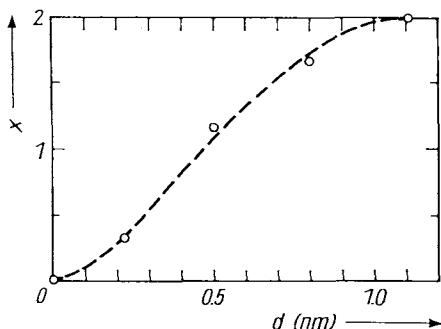


Fig. 2. Oxygen-concentration profile  $x(d)$  of the cluster shown in Fig. 1. The determination of the profile begins at the silicon surface (Si Bethe lattice,  $d = 0$ ) and is continued across ring I, II, and III to the  $\text{SiO}_2$  Bethe lattice in a distance of  $d = 1.1$  nm from the silicon surface

curve shown in Fig. 2 is very similar to this one obtained from a statistical model for the oxygen distribution in a thermally grown  $\text{SiO}_2$  film on the surface of a silicon single crystal [23].

Of course, our gradual IF model (GIM) is a very simple one, since it represents a chain-like, one-dimensional IF. Nevertheless, it turns out to be a very useful tool to examine theoretically the EDOS at the Si-SiO<sub>2</sub> IF [20] and the influence of Si-Si chains and rings as well as of various defects. Finally, it should be mentioned that we use the version of the CBLM introduced by Yndurain [19] and also used by Strehlow and Lamfried [10] for their investigations of the EDOS of bulk  $\text{SiO}_x$ . The interaction and self-energy parameters for the Si-Si and Si-O bonds are taken from [10] assuming that they are valid for the IF as well as for the BL's. Two different BL's are needed to saturate the dangling bonds of the Si atoms in the first (I) and third (III) ring, i.e. one of them for the silicon substrate and another one for the  $\text{SiO}_2$  layer.

### 3. Results and Discussion

#### 3.1 Interface without defects

With the help of the CBLM all the local densities of states of the 34 atoms involved in the cluster described above are computed simultaneously by the inversion of a complex  $(136 \times 136)$  Green's function matrix and composed in the same manner as for calculating the values of  $x$ . Accordingly, we get three EDOS curves for the three "layers" of the GIM with  $x = 0.33, 1.17$ , and  $1.67$ . These curves as well as the local EDOS of the seven topologically different Si atoms in the especially interesting energy region between the  $\text{SiO}_2$  and Si valence-band edges were already discussed elsewhere [20]. Therefore, in Fig. 3 a comparison between our results (b, d, f) and those obtained for bulk  $\text{SiO}_x$  (a, c, e) [10, 24] is shown. For this end and in distinction to [20] the EDOS in Fig. 3 b, d, and f is computed with all the Si-O-Si bridging angles at the oxygen atoms of the GIM being equal to  $144^\circ$ , since the bulk- $\text{SiO}_x$  EDOS was calculated under the same assumption.

Obviously, the most interesting energy region for the intended comparison is between the valence-band edges of  $\text{SiO}_2$  and silicon at  $-2$  eV and  $3.2$  eV, respectively. There, the EDOS of the GIM exhibits a structure, which is more distinct than the one of bulk  $\text{SiO}_x$ . This result becomes evident, if one regards the cluster as a finite defect embedded into two different BL's. Therefore, this structure is a defect-induced one, which correlates with the existence of Si-O<sub>3</sub>Si<sub>4</sub> tetrahedra and their interconnection. This interpretation is supported by the results of Grafe and Strehlow [12], who showed that Si-O<sub>3</sub>Si<sub>4</sub> defects in  $\text{SiO}_2$  produce electronic states above the  $\text{SiO}_2$  valence-band edge at  $0.4$  eV ( $y = 3$ , see Fig. 3b), at  $-0.7$  eV and  $1.5$  eV ( $y = 2$ , see Fig. 3d), at  $-1.7$  eV and  $1.5$  eV ( $y = 1$ ), and at  $1.5$  eV ( $y = 0$ ). A more detailed investigation

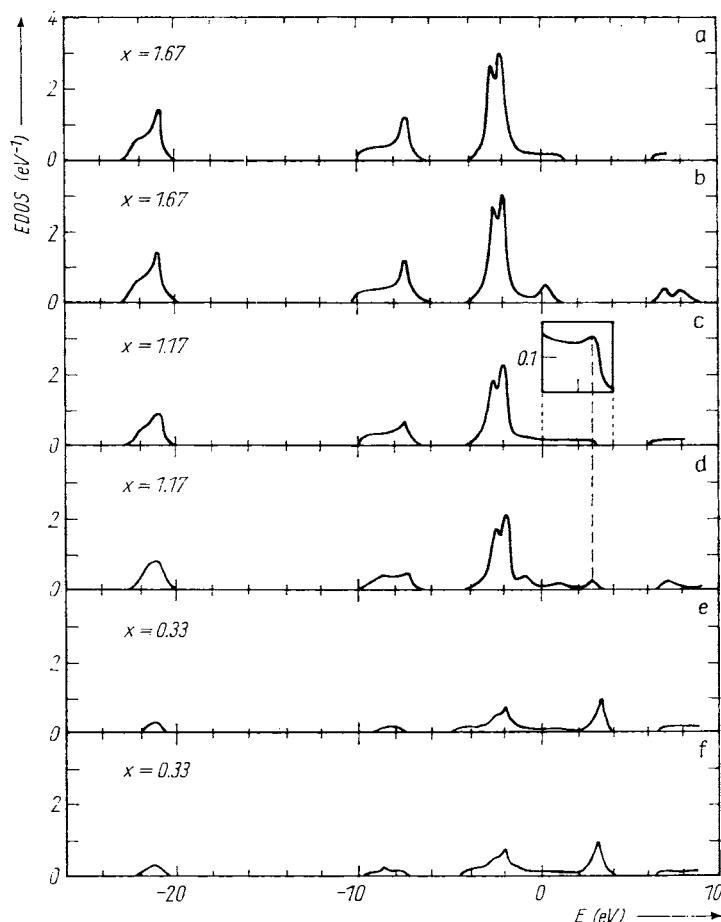


Fig. 3. Comparison between the EDOS of bulk SiO<sub>x</sub> [10, 24] (a, c, e) and the EDOS at the gradual Si-SiO<sub>2</sub> interface with a value of the angle of all the Si-O-Si bridges of 144° (b, d, f)

is needed with regard to the peak at 1 eV (Fig. 3d) which has shoulders on both sides (see Fig. 3 of [20] and Fig. 5b and Fig. 6b of this paper). With the help of a calculation with a reduced damping (an imaginary part of the energy of 0.05 eV instead of 0.2 eV) this peak can be resolved into three peaks at 0.5, 1.0, and 1.5 eV, two of which are already known from [12] for the cases  $y = 3$  and  $y = 2$ . To find the origin of the 1.0 eV peak we place the oxygen atom 27 (Fig. 1) between the Si atoms 6 and 8. Then, there is only the 1.5 eV peak in the local EDOS of the Si atoms 8, 13, and 18, which is caused by the Si atom 13 with  $y = 2$ . Therefore, we conclude from the comparison with isolated Si-O<sub>y</sub>Si<sub>4</sub> defects in SiO<sub>2</sub> [12] that there are additional effects at the Si-SiO<sub>2</sub> IF, which are caused by the formation of Si-Si chains throughout the SiO<sub>x</sub> layer. On the other hand, there is a close correspondence between the EDOS of bulk SiO<sub>x</sub> [24] and the EDOS at the Si-SiO<sub>2</sub> IF as far as the upper valence-band edge is concerned. Particularly, for both the models the Si 3p-like peak, which determines this band edge, can be found for  $x = 1.17$  at an energy of 2.8 eV (Fig. 3 c, d) instead of 3.2 eV (Fig. 3 e, f), which is typical for the EDOS of bulk silicon (within the frame of the parameter set used). Therefore, and since the conduction-band edge changes

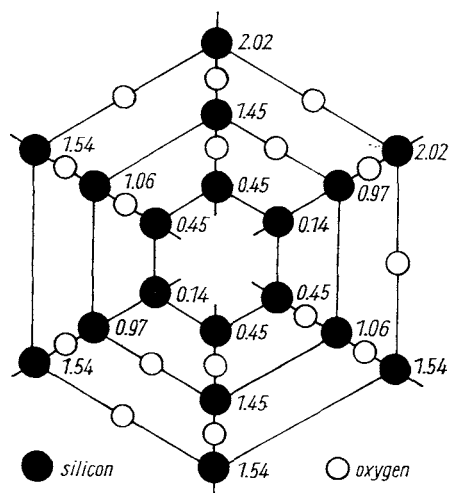


Fig. 4. Static effective charges (in units of the elementary charge) of the Si atoms of the cluster computed by an integration of the corresponding local EDOS curves. The charges at all the oxygen atoms are equal to  $-1$

only slightly with  $x$  it follows that the width of the gap between the valence band and the conduction band in bulk SiO<sub>*x*</sub> and at the Si-SiO<sub>2</sub> IF behaves in a similar manner. Namely, it increases only slightly until the structural percolation threshold of SiO<sub>*x*</sub> [25] at  $x = 1.25$  to  $1.33$  is reached and then much stronger until a value of about  $9$  eV is reached for SiO<sub>2</sub> in correspondence with measurements of the optical absorption coefficient in SiO<sub>*x*</sub> [26, 27]. However, this does not mean that charge carriers could not reveal a reverse trend in their barrier behaviour, i.e. a fast opening of the electrical gap across the Si-SiO<sub>2</sub> IR [28] as predicted in [29].

From an integration of the local EDOS curves we get the static effective charges of all the cluster atoms. In Fig. 4 only the positive Si charges are given because the charges of all the different oxygen atoms are equal to  $-1$  (in units of the elementary charge). However, it is noteworthy that the static effective charges of Si atoms with an equal number of oxygen neighbours (equal  $y$  value of the corresponding Si-O<sub>*y*</sub>Si<sub>4</sub> tetrahedra) differ by an amount of about  $0.1$ . This means that the charge of an Si atom depends on its intermediate-range order and not only on the kind of its nearest neighbours. This fact should be taken into consideration, when, e.g., a decomposition of Si 2p core-level spectra is performed.

For a further investigation of the role of the intermediate-range order (Si-Si chains and rings) at the Si-SiO<sub>2</sub> IF we test several redistributions of oxygen atoms within the GIM. This means that an Si-Si bond is created, where an oxygen atom was removed and placed between two other Si atoms, which were connected by an Si-Si bond hitherto. Two examples are given in Fig. 5 a, c and Fig. 6 a, c with the new positions of the oxygen atoms shown in the upper part (compare Fig. 1) in comparison with the EDOS curve obtained before the redistribution of oxygen atoms (Fig. 5 b, d and Fig. 6 b, d). In this way a five-membered chain of Si atoms in the second "layer" of the GIM with  $x = 1.17$  (Fig. 5a), a three-membered chain in the third "layer" with  $x = 1.67$  (Fig. 5c), and a fourfold ring between the second and the third "layer" (Fig. 6 a, c) are created. It can be seen from Fig. 5 and 6 that such structural irregularities produce electronic states between the SiO<sub>*x*</sub> and Si valence-band edges. Small rings of Si-Si bonds have a particularly strong influence on the EDOS at the Si-SiO<sub>2</sub> IF. They are able to fix the Si valence-band edge up to relatively high  $x$  values, if they are present in a sufficiently high concentration. On the other hand, a lower concentration of Si-Si chains and rings can be thought to be the origin of hole traps at the Si-SiO<sub>2</sub> IF.

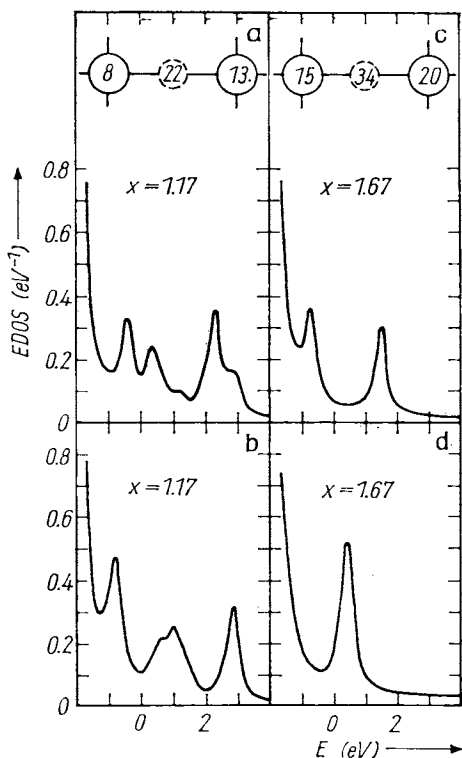


Fig. 5

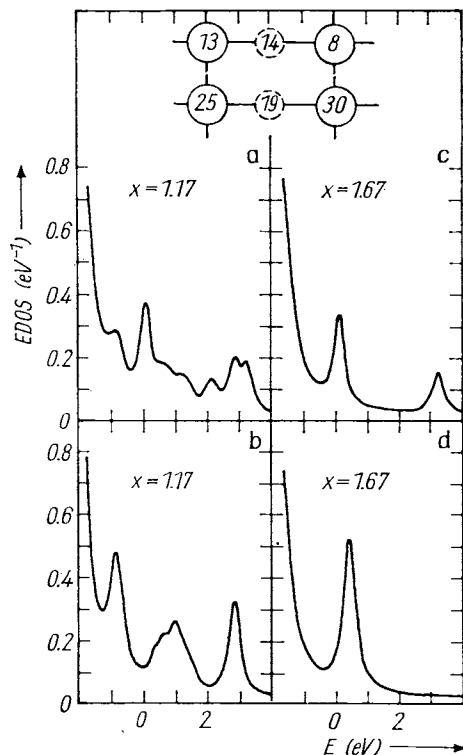


Fig. 6

Fig. 5. EDOS resulting from a redistribution of an oxygen atom (a, c) as shown in the upper part (cf. Fig. 1) in comparison to the interface EDOS from Fig. 3b, d

Fig. 6. EDOS resulting from a redistribution of two oxygen atoms (a, c) as shown in the upper part (cf. Fig. 1) in comparison to the interface EDOS from Fig. 3b, d

### 3.2 Defects at the Si-SiO<sub>2</sub> interface

The dangling bond (db)  $\equiv \text{Si} \cdot$  of an Si atom at the Si-SiO<sub>2</sub> IF is a defect, the existence of which is unambiguously proved by electron-spin resonance (ESR) measurements [30]. It is one of the main origins of the interface density of states  $N_{\text{ST}}$ , which strongly affects the quality and reliability of corresponding microelectronic devices [1]. For a theoretical investigation of the db the GIM is especially suitable, since a lot of different backbond (bb) configurations are possible. For this end we perform several EDOS calculations with the help of the GIM with one broken Si-Si bond, e.g. two generally different bb configurations, in each case (see Fig. 7) simply assuming that the interaction parameter between the two fixed Si atoms is equal to zero and no relaxation is taken into account. A separate problem arises from the change of the self-energy of the db hybrid, which is, of course, necessary. The values of 6 and 7 eV used here for the Si  $\text{sp}^3$  hybrid in silicon and SiO<sub>2</sub>, respectively, are fitted to experimental information in such a way that the value of the SiO<sub>2</sub> gap is 9.6 eV ( $-2$  eV to 7.6 eV) and that the energetic distance between the Si valence-band edge at 3.2 eV and the SiO<sub>2</sub> conduction-band edge is 4.4 eV [31]. Then, it follows from the value of the interaction parameter  $\Delta = -2.2$  eV between two  $\text{sp}^3$  hybrids at one and the

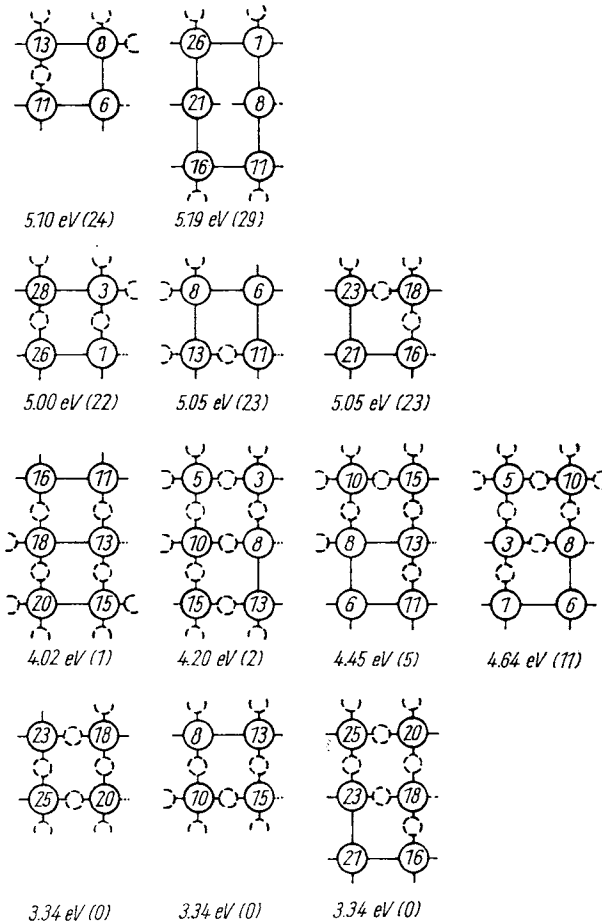


Fig. 7. Defect levels within the silicon gap between 3.2 and 6.3 eV created by Si dangling bonds (dashed lines) with different backbond configurations. The numbers given in parantheses denote the number of Si-Si bonds connected among each other and with the dangling-bond atom up to its second-nearest neighbour

same Si atom that the Si 3s and Si 3p energies are  $-0.6$  and  $8.2$  eV, respectively. Since the self-energy of the O 2p state has a value of  $-2$  eV, this means that the self-energies of Si are shifted by about  $1.4$  eV relative to the free-atom levels, for which it was shown by means of Hartree-Fock calculations [32] that the orbital energies of Si 3s and O 2p are nearly equal. This shift becomes necessary, because of the demand for orthogonality of the atomic basis (Si 3s, Si 3p, O 2s, O 2p) used for the EDOS calculations [33]. Concerning the db hybrid it can be argued that its self-energy shift must be much smaller, because it overlaps only very weakly with orbitals of other atoms. Therefore, we reduce the self-energy shift at the db hybrid and use a value of  $4.6$  eV. This approximation is a little bit crude, but better than a calculation without any change of the db self-energy, which yields for bulk silicon a db level at  $6$  eV, i.e. at the upper boundary of the silicon gap, which ranges from  $3.2$  to  $6.3$  eV. Instead of this level we get an energy of  $5.19$  eV for the db at the Si atom number 6 (Fig. 7), which is



closer to the experimental value for an Si db at the Si-SiO<sub>2</sub> IF (detected below midgap by C-V and ESR measurements [30]).

In Fig. 7 the dependence of the db levels on the bb configurations of the db atoms is shown. Note that the db level of an Si atom on the SiO<sub>2</sub> side of the IF with three Si-O-Si backbonds lies below the one of an Si atom on the silicon side of the interface with three Si-Si backbonds. The question, whether this result also obtained in [33] or the contrary one [34, 35] is true, is still unsolved and with the help of the simple version of the CBLM used in this paper we cannot contribute to its solution. It should be noted, however, that the energetic distance between the db level and the valence-band edge increases within the Si-SiO<sub>2</sub> interregion with increasing oxygen content, i.e., with increasing distance from the silicon surface (see Fig. 8, which follows from Fig. 2, 3, and 9) in agreement with some recent experimental observations [45].

Therefore, we will direct our attention to another interesting observation, which can be made by considering all the Si-Si bonds being linked among each other and with the db atom. We sum up to the second-nearest neighbours of the db atom, where, in some cases, it becomes necessary to continue with the counting process into the very Si BL. The resulting numbers  $N$  of such cluster-forming Si-Si bonds in the environment of the db atom are given in parentheses in Fig. 7. Fig. 9 shows the dependence of the energetic positions of the db peaks in eV relative to the Si valence-band edge and of their Si 3s parts on  $N$ . This dependence can be understood in terms of dielectric screening. With increasing oxygen content (decreasing  $N$ ) the dielectric screening decreases and, therefore, the db level moves downward in the gap and its sphericity increases. The slopes of both curves change substantially at  $N = 3$  to 4, i.e. just the values of  $N$  at the structural percolation threshold (see Section 3.1) of a BL and a network of atoms (both fourfold coordinated). This means that not only

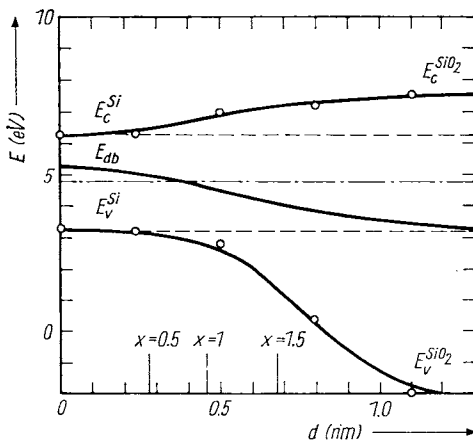


Fig. 8

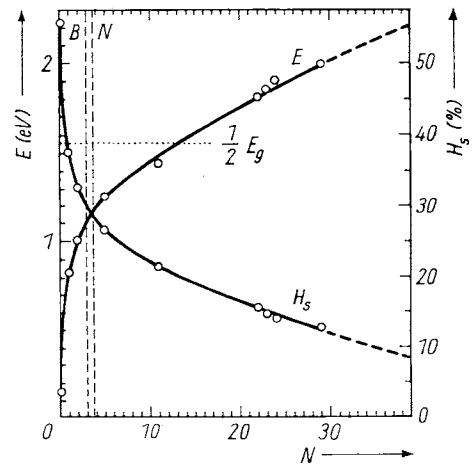


Fig. 9

Fig. 8. Energetical position of the dangling-bond (db) level within the SiO<sub>x</sub> gap in dependence on the distance  $d$  from the silicon surface

Fig. 9. Energetic position  $E$  relative to the valence-band edge of silicon and s-part  $H_s$  of the dangling-bond (db) peaks within the silicon gap in dependence on the number  $N$  of Si-Si bonds being linked among each other and with the db atom up to its second-nearest neighbour. Vertical dashed lines characterize the structural percolation threshold in a Bethe lattice (B) and in a network of atoms (N)

structural [36] and optical [6, 25] properties, but also defect properties of  $\text{SiO}_x$  are influenced by percolation effects. This can be proved as follows. An Si atom in random-bonding  $\text{SiO}_x$  participates on the average in  $n = 4 - 2x$  Si-Si bonds with its nearest neighbours. Therefore, a db atom is participating in  $\frac{3}{4}n$  Si-Si bonds, and its nearest and next-nearest neighbours attainable via Si-Si bonds are part of  $(\frac{3}{4}n)^2$  and  $(\frac{3}{4}n)^3$  Si-Si bonds, respectively. Accordingly, a db atom has

$$N = -3.375x^3 + 22.5x^2 - 51x + 39 \quad (1)$$

cluster-forming Si-Si bonds in its environment up to the second-nearest neighbours. On the other hand, it is known [37, 38] that the critical percolation probability  $p_c$  of a  $z$ -fold coordinated BL and a network of the same kind can be calculated from  $p_c^B = 1/(z - 1)$  [37] and  $p_c^N \approx 1.5/z$  [38], respectively, whereas from a Monte-Carlo calculation for the diamond lattice it follows  $p_c^D = 0.39$  [37]. The meaning of  $p_c$  in percolation theory is to express the probability for finding an unblocked bond, e.g. an Si-Si bond in  $\text{SiO}_x$ , which is equal to  $(2 - x)/2$  for a random-bonding structure. Therefore, we obtain

$$x_c^B = 1.33, \quad x_c^N \approx 1.25, \quad x_c^D = 1.22$$

and from (1)

$$N^B = 3, \quad N^N \leq 3.8, \quad N^D = 4.1.$$

(A prediction of the existence of a structural percolation threshold in silicon oxynitride  $\text{SiO}_x\text{N}_y$  can be made in a similar manner, see Appendix.) The value of  $N^N$  is given by an inequality, because the bond-counting process is carried out for a BL with  $x = x_c^N$ . However, a network atom has fewer second-nearest neighbours than a BL atom if there are small closed rings of chemical bonds in the network.

Two adjacent dangling bonds of Si appear in amorphous  $\text{SiO}_2$  if there is an oxygen vacancy. This so-called E' centre and the peroxy bridge (PB)  $\text{O}_3 \equiv \text{Si}-\text{O}-\text{O}-\text{Si} \equiv \text{O}_3$  can be regarded as complementary members of a Frenkel-defect pair in  $\text{SiO}_2$ . The PB, on the other hand, can be converted by hole trapping into the paramagnetic peroxy radical (PR)  $\text{O}_3 \equiv \text{Si}-\text{O}-\text{O} \dots \text{Si} \equiv \text{O}_3$ . This defect was detected by ESR experiments in heavily irradiated amorphous  $\text{SiO}_2$  [39] and both the PB as well as the PR in  $\text{SiO}_2$  were studied theoretically [33, 40, 41]. To investigate their influence on the EDOS at the Si-SiO<sub>2</sub> IF we use again the possibility of a redistribution of oxygen atoms within the GIM yielding the PB configuration shown in Fig. 10 b. The orbital

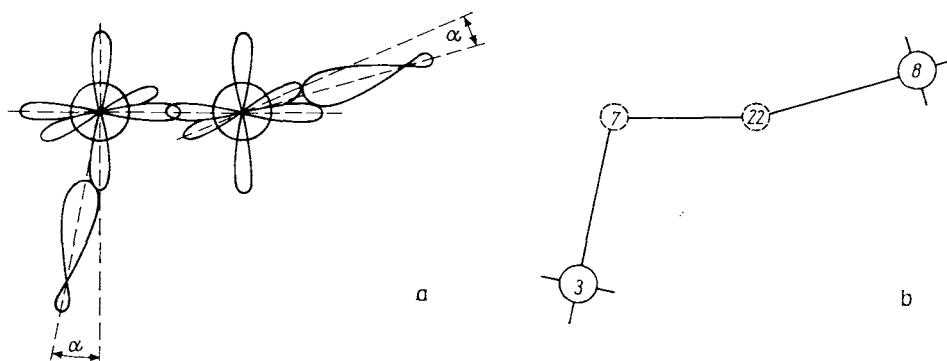


Fig. 10 a) Orbital arrangement and b) schematic representation of a peroxy-bridge configuration. The angle  $\alpha$  was taken to be equal to  $5^\circ$  and  $26^\circ$  for the peroxy bridge and the peroxy radical, respectively. The peroxy radical is formed by breaking the bond between atoms with number 22 and 8

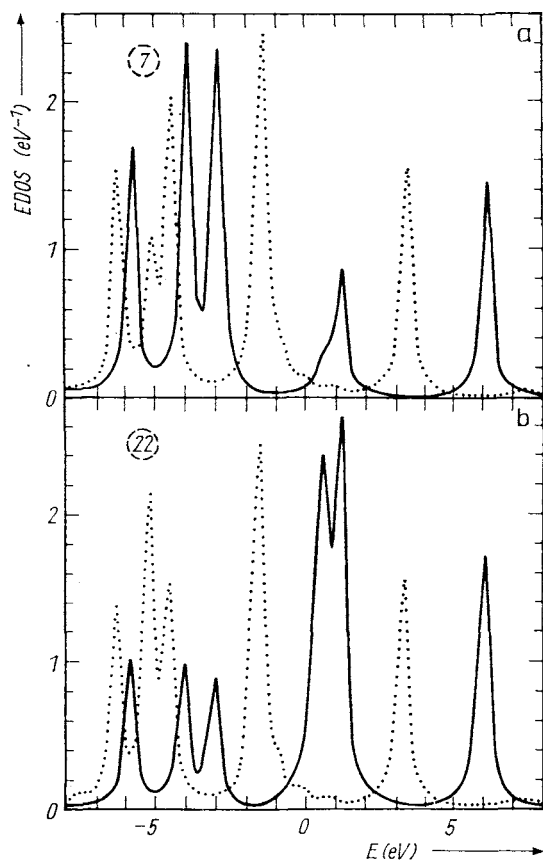


Fig. 11. Local EDOS at the oxygen atoms with number a) 7 and b) 22 of the peroxy bridge (dotted line) and the peroxy radical (full line)

arrangement (Fig. 10a) is that of H<sub>2</sub>O<sub>2</sub> and is taken from [33] together with the interaction parameters between the two oxygen atoms. Then, a PR is created by breaking one of the two Si-O bonds of the PB. First of all, the resulting EDOS curves (Fig. 11) show that the 3:1 asymmetry of the unpaired spin density at the two peroxy oxygens deduced from the <sup>17</sup>O hyperfine structure of an isotopically enriched sample [39] is reproduced correctly by the ratio of the EDOS peak heights at 1 eV. Besides, the shape of the EDOS curves in Fig. 11 resembles that given in [33] and is discussed there extensively. From a variation of the angle  $\alpha$  (Fig. 10a) and the investigation of different positions of the PB and the PR at the Si-SiO<sub>2</sub> IF we can draw the following

conclusions: (1) The PB at the IF can contribute to the interface density of states  $N_{ST}$  near the Si valence-band edge if it is strongly distorted, i.e., if the Si-O-O angle is only slightly greater than 90°. On the other hand, a more stretched PB creates a number of electronic states between the SiO<sub>2</sub> and Si valence-band edges. (2) The nearer the PR is located at the silicon surface, the deeper are its electronic states created at the Si conduction-band edge. (3) The nearer the PR is at the silicon surface and the less its Si-O-O angle differs from 90°, the larger is the splitting between the two defect states in the lower half of the SiO<sub>2</sub> gap at 1 eV.

The valence-alternation pair (VAP) O<sub>3</sub><sup>+</sup>/O<sub>1</sub><sup>-</sup> consisting in a pair of over- and under-coordinated oxygen atoms (lower index) being less and more negatively charged (upper index) than the twofold coordinated oxygen atom is another important defect at the Si-SiO<sub>2</sub> IF [1, 42]. EDOS calculations for the VAP with the help of the GIM were already published elsewhere [42]. There, it was shown that owing to their weak additional (third) bond with Si atoms of the silicon surface and within the SiO<sub>x</sub> transition O<sub>3</sub><sup>+</sup> centres induce interface states within the semiconductor gap. Details of the electronic structure of VAP defects were investigated in [43]. Finally, it should be mentioned that distorted Si-Si bonds lead to interface states near the band edges within the silicon gap [28, 44], as shown with the help of the methods discussed in the present paper.

#### 4. Conclusions

A new model of the Si-SiO<sub>2</sub> interface was investigated, which considers for the first time that the semiconductor-insulator transition occurs within a region of about three atomic layers. The particular advantage of this gradual interface model is that defects as well as chains and rings of Si-Si bonds can be studied for different positions within the interregion. It was shown that different backbond configurations convert the defect levels known from bulk silicon (broken Si-Si bonds) and bulk SiO<sub>2</sub> (oxygen vacancy and peroxy defects) into a broad spectrum of electronic states over the entire range of the SiO<sub>2</sub> gap including the energetical range of the silicon gap. An influence of the structural percolation threshold of the SiO<sub>x</sub> transition on the dangling bond level of Si atoms was shown. Additionally to the indirect influence of oxygen on the Si dangling bond, there is a direct influence of oxygen on the interface states due to the O<sub>3</sub><sup>+</sup> constituents of valence-alternation pair defects.

#### Appendix

##### *Structural percolation threshold in silicon oxynitride*

Assuming that in SiO<sub>x</sub>N<sub>y</sub> with  $M$  Si atoms all the chemical bonds are saturated and that there are no Si-Si bonds we will find in this material  $2M - 1.5yM$  h-O-h bridges (h stands for Si sp<sup>3</sup> hybrid), since  $1.5y$  Si-O-Si bridges are substituted by the admixture of N atoms. Then, the probability  $W_{\text{h-O-h}}$  for finding an h-O-h bridge in random-bonding SiO<sub>x</sub>N<sub>y</sub> can be calculated according to the expression

$$W_{\text{h-O-h}} = \frac{2M - 1.5yM}{2M} = \frac{2 - 1.5y}{2}.$$

Considering an h-O-h bridge as an unblocked path (in the sense of the percolation theory [32]) we can use the critical percolation probability

$$p_c = \frac{1.5}{4}$$

for a fourfold coordinated network [38]. From the relation  $W_{\text{h-O-h}} = p_c$  it follows  $y = \frac{5}{6}$ . Therefore, the structural percolation threshold in silicon oxynitride is predicted for a chemical composition which corresponds to SiO<sub>3/4</sub>N<sub>5/6</sub>.

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