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# Bond breaking of adatoms on Si surfaces by electronic excitation

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**Abstract.** To understand the mechanism of defect initiated atomic emissions induced by electronic excitation of semiconductors, a semiempirical approach is used to study the nature of the relaxed excited states for an Si adatom on the Si(111) surface. We found an antibonding excited state embedded on the continuum and intermediate excited states, of which the relaxed states show bond weakening. Our results suggest that a series of excitation–relaxation processes can finally lead to the emission of weakly bonded atoms associated with defects on the semiconductor surface.

## 1. Introduction

Desorption induced by electronic transitions (DIET) from solid surfaces is a topic of current interest [1–5]. The desorption induced by excitation of valence electrons of adsorbates on surfaces has been interpreted in terms of the Menzel–Gomer–Redhead (MGR) mechanism [6, 7], which suggests bond breading for the adsorbates by excitation to an antibonding orbital. For DIET from solid surfaces, an additional requirement should be imposed on the MGR mechanism: localization of the electronic excitation energy possessed either by excitons or electron–hole pairs.

It has been suggested [8] that the self-trapping of an exciton on surfaces of alkali halides can induce a localization antibonding state leading to the emission of halogen atoms. For alkali halides, for which extensive studies of desorption [9–12] have been carried out, the emission can be observed by irradiation with conventional ultraviolet light sources and the yield is proportional to the number of excitations [13]. The nature of the emission falls in the category of the MGR mechanism, namely arising from an antibonding excited state. Recent theoretical calculations have shown that formation of an exciton on the top surface layer leads to an emission of a halogen atom leaving an F centre (halogen atom vacancy) on the surface [14, 15]. It has also been shown that self-trapped excitons located between the second and fourth layers are unstable, leading to the emission of the halogen atoms.

The MGR mechanism from solid state surfaces described above is however only effective in solids in which self-trapping of excitons can be induced and cannot be effective in semiconductors and some other insulators including MgO, ZnO and CaO. Indeed recent high-sensitivity measurements of laser induced emission of Si atoms from Si surfaces [16] and Ga atoms from GaAs [17] and GaP [18] surfaces have shown emissions only at high

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laser fluences, the yield being a superlinear function of the fluence. It has also been shown that the emission is originated from defects on surfaces [18].

Because of the absence of self-trapping from semiconductors, the localization of electronic excitation energy can only be induced by the interaction of charge carriers with defects: trapping of either electrons or holes by a defect or recombination of an electron and a hole by a defect. Thus any atomic emission induced by excitation of valence electrons that can be induced from surfaces of semiconductors should be defect related [19, 20]. Moreover, the electronic excited state of semiconductors possesses at most the band gap energy, which is usually smaller than the bonding energy of atoms on the surface. Consequently, a single excitation is considered to be unable to cause bond breaking [19, 20], in accordance with experimental observations. Hattori *et al* [18] suggest that repetition of excitation of a defect on the surface and following relaxation during a laser pulse finally leads to the emission of weakly bonded atoms associated with defects on the semiconductor surface. The present authors [19, 20] have shown that the first electronic excitation of a Ga adatom on the GaP(110) surface induces a relaxed metastable state and further excitation from the relaxed state leads to the antibonding state.

It has been argued also that the bond breaking can be induced by multiple excitation or by two-hole localization [19–25]. The concept is based on the fact that each bond for atoms on the surface possesses two bonding electrons and that removal of them can lead to bond breaking. The situation is not very simple in reality because of the interaction of the bonding electrons with holes in the valence band. It is of importance to examine the nature of the antibonding state that can finally lead to the emission. Without knowing the nature of the defects that are indeed responsible for the emissions, it is not yet possible to carry out qualitative arguments. However, it is worthwhile to discuss semiquantitatively the various processes that can finally lead to bond breaking.

In this paper, we carry out a model calculation of the excited states of a Si adatom on the unreconstructed Si(111) surface (figure 1), which is the simplest singly bonded defect. It is the purpose of the present calculation to clarify the nature of the antibonding state and the types of excitation that can finally yield the antibonding state. The results give a comprehensive picture of the mechanism of atomic emission induced by valence electron excitation of materials in which the self-trapping of excitons is not induced.

## 2. Method of calculation

We employ a semiempirical molecular orbital method, the complete neglect of differential overlap (CNDO) method [26], to investigate the possible excited states corresponding to valence electron excitation of an Si adatom on the Si(111) surface. In this method, we systematically approximate the matrix elements of the Hartree–Fock–Roothaan equations by introducing three semiempirical parameters, namely, the orbital exponent, the electronegativity and the bonding parameter. From these approximations, the method yields self-consistent solutions similar to Hartree–Fock solutions [26, 27]. In this work, we implement the Harwell MOSES code [28] and the Si parameters used here are from Harker and Larkins [29], who fitted the bulk properties of Si to their theoretical predictions by using a 16-atom periodic large unit cell. Using the same method, we have recently investigated the effects of halogen adsorbates on the energies for atomic emissions from defect sites on the Si surfaces [30]. The parameters have also been used successfully in the study of Si surfaces [31–33]. Our calculations are performed on a 35-atom Si(111) surface cluster (the edges of the cluster are saturated by Si hybrid pseudoatoms, details of which have

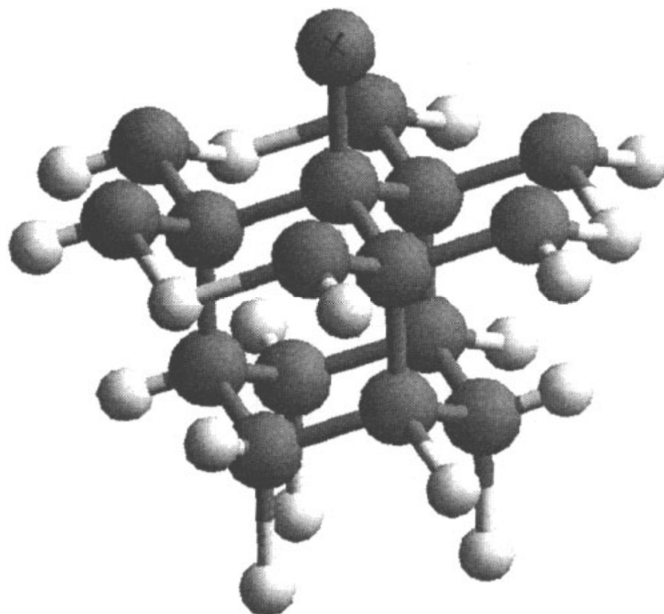

**Figure 1.** A diagram of the 35-atom Si(111) surface cluster with the Si adatom (marked with a cross) attached. The hybrid atoms saturating the edges of the cluster are shown in white. The cluster is constructed using Cerius[2] (Molecular Simulations Inc., Burlington MA).

previously been given in [27] and [30]), with an Si adatom attached as shown in figure 1. Excited states of interest are investigated by changing the occupancies of the orbitals around the top of the valence band and the bottom of the conduction band. Figure 2 depicts the levels of interest for which we simulate the possible transitions.

## 3. Results and discussion

We consider first the ground state of the Si/Si(111) system. The Si adatom on the Si(111) surface provides four localized levels, due to the symmetrically split dangling bond, bonding and antibonding levels. We calculate the equilibrium configuration of the adatom by taking the total energy minimum. The distance between the Si adatoms ($Si_A$) and the surface of Si atom ($Si_H$) to which the adatom is bonded is varied until the total energy of the system is minimum. This equilibrium distance is found to be 2.35 Å, compatible with the Si–Si bondlength in the bulk [34]. $Si_H$ is also found not to be displaced from its original lattice point.

The energy level scheme of an Si adatom on the Si(111) surface is shown in figure 2. Figure 2 is implemented in the following manner. Since the eigenvalue spectrum derived from the CNDO calculations overestimates the band gap by a consistent factor of 2.4 [29], the difference between the eigenvalues of the highest occupied level (level B, top of the valence band) and the lowest unoccupied level (level D, bottom of the conduction band) is scaled by this factor to the experimental band gap energy of 1.1 eV. The half occupied dangling bond level ($C_1$) is found to be in the gap. Its location in the gap is determined by multiplying 1.1 eV by the CNDO results of the ratio of the separations of the eigenvalues between B

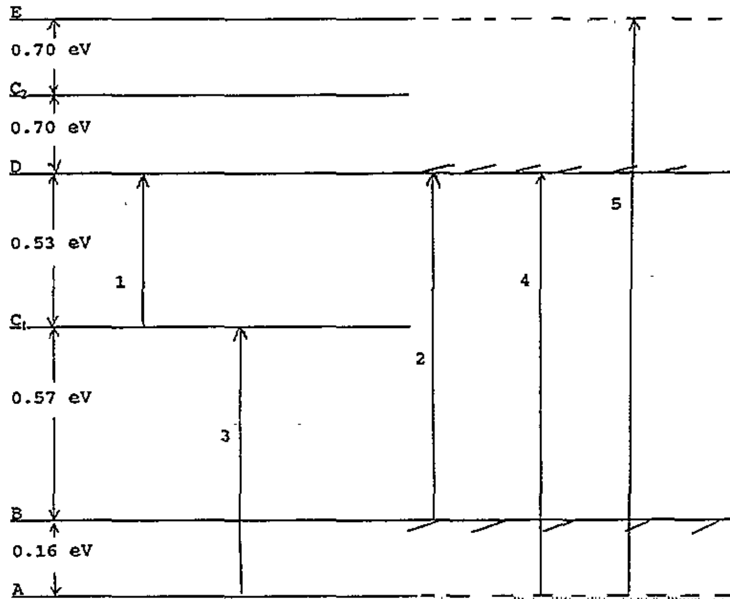


**Figure 2.** A schematic diagram of the energy level scheme illustrating the levels of interest and the transitions involved in the valence excitation of the Si/Si(111) system. Further details can be found in the text.

and $C_1$ to that between B and D. The locations of the bonding level (A) and those of the antibonding level (E) and the dangling bond level ($C_2$) embedded in the conduction band are also calculated accordingly from the separations of the corresponding eigenvalues. The centre of the bonding and antibonding orbitals and the average position of the dangling bond levels are shifted upwards from the midgap; this is accounted for by the lower coordination of the adatom compared with the bulk atoms. The separation of 2.7 eV between the bonding and antibonding levels is slightly bigger than the binding energy 2.32 eV of the Si–Si bond in the Si lattice [34].

Based on the energy diagram shown in figure 2, we then calculate the eigenvalues and eigenfunctions of the Franck–Condon excited states and the energy change by lattice relaxation at each excited state. We investigate the nature of the possible transitions 1–5 (single excited states) depicted in figure 2; transition 1 is from $C_1$ to D, 2 from B to D, 3 from A to $C_1$, 4 from A to D and 5 from A to E. The configuration coordinate curves for each excited state as well as the ground state (curve (a)) are shown in figure 3. Electrons can be excited from bonding orbitals as well as from non-bonding orbitals. Transitions 1 and 2 do not involve the bonding orbital, while transitions 3–5 involve the bonding orbital. We first consider those from non-bonding orbitals.

Excitation 1, corresponding to the transition from $C_1$ to D, results in a charge transfer excited states and a slight contraction of the Si–Si bond between the adatom and the surface atom; the Si adatom loses charge by $0.3e$. At the excited state, $Si_A$ displaces along the $\langle 111 \rangle$ direction towards the surface, and at the relaxed equilibrium excited state, there is a contraction of the $Si_A$–$Si_H$ bond by 0.13 Å (see curve (b) in figure 3). This shortening of the adatom bond can be ascribed to the attraction of the image charge [35]. On the other hand, excitation 2, corresponding to a transition from the top of the valence band (B) to the bottom of the conduction band (D) changes the equilibrium configuration only slightly

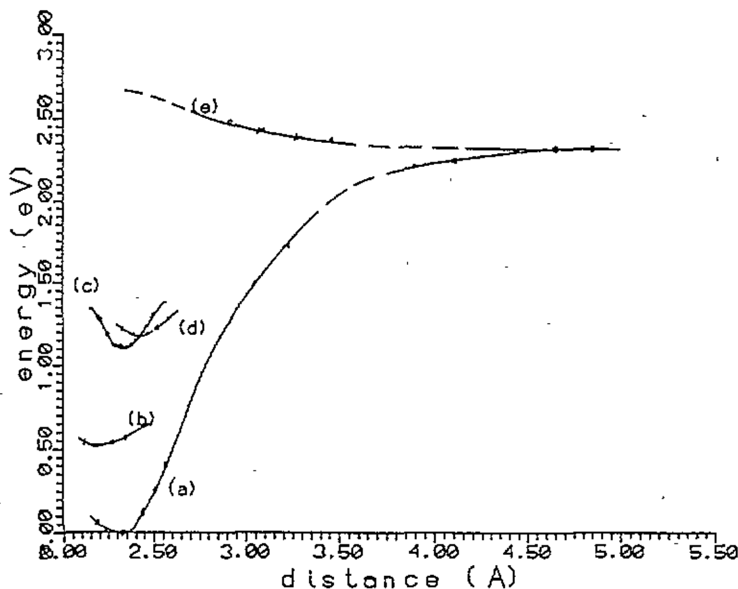


**Figure 3.** The configuration coordinate curves for the various transitions represented in figure 2. Curves (b)–(e) represent the outcomes after transitions 1, 2, 4 and 5 respectively.

(curve (c) in figure 3). This result is easily understood since the transition merely results in the formation of a localized electron–hole pair. Excitations 1 and 2 have the smallest transition energies and are simulated from non-bonding levels. From our results, they do not lead to any appreciable bond weakening, since the adatom bond after both excitations does not lengthen, and are considered not to cause bond weakening.

Next, we consider excitations from the bonding orbital. A: excitations 3, 4 and 5. We do not succeed in obtaining convergence results from the CNDO calculations for the excited state reached by excitation 3, an intra-atomic transition, between the bonding and dangling orbitals. On the other hand, excitation 4 is apparently a charge transfer transition from the bonding orbital to the conduction band, but we found that the dangling bond is filled after excitation; the Mulliken charge of $Si_A$ is converted from 3.98 to 4.30 by the excitation. This is regarded as a consequence of electronic relaxation, since the orbital $C_1$ due to the dangling bond is located below the conduction band. In spite of the charging of $Si_A$, it is displaced forward away from the surface by 0.04 A. The bondlength of $Si_A$–$Si_H$ is thus elongated upon excitation, albeit only slightly (curve (d)). This suggests that the bond weakening effect due to excitation has overcome the image charge effect. We also find that, after relaxation at the excited state reached by excitation 4, the bonding orbital is still occupied but shifts upwards, closer to the top of the valence band. The upward shift of the bonding orbital can be ascribed to the bond weakening. It implies that the electron in the bonding orbital of the relaxed state after excitation 4 can be excited again by photons having the same energy as those that have caused excitation 4. Furthermore, we find that the wavefunction at the relaxed excited state is localized more on the $Si_A$–$Si_H$ bond, suggesting that the second excitation of the electron from the bonding orbital will be further efficient for bond breaking.

We then implement excitation 5, between the bonding orbital A and the antibonding orbital E. According to our evaluation of the location of this level in the energy diagram,

as described above, the transition energy is 2.6 eV and is larger than the bond strength, 2.3 eV, of the Si–Si bond [34]. Convergence difficulties in CNDO calculations prevent us from obtaining total energy values near the Franck–Condon excited state. However, we are able to obtain the transition energies of excitation 5 at larger separations between $Si_A$ and $Si_H$ (above 3.8 Å) and the excited state appears to be antibonding: the total energy at the excited state plotted as a function of the $Si_A$–$Si_H$ bond length decreases as the bond length is increased (curve (e) in figure 3). Examination of the eigenfunctions after the excitation shows a reduction in the coefficients of the basis functions associated with the bonding level. Thus, we conclude that the excited state reached by excitation 5 is antibonding and we interpolate backwards the configuration coordinate curve obtained at large $Si_A$–$Si_H$ distances as depicted in figure 3.

The results above suggest that the excited state reached by excitation 5 is antibonding while the other excited states are bonding. Kanasaki *et al* [16] have previously obtained a yield–fluence relation with power indices 4–6 using 2.5 eV nanosecond laser pulses. Evidently, a single excitation cannot cause bond breaking but multiple excitation within nanosecond laser pulses is required for bond breaking, agreeing with our evaluation that 2.6 eV is required for excitation to the antibonding state. Furthermore, as we shall discuss later, the direct excitation to the antibonding state, which is a resonant state embedded in the continuum, cannot necessarily lead to bond breaking because of autoionisation.

In view of the results of the present calculation, we can depict the bond breaking process by multiple excitation within a nanosecond laser pulse as follows. Since each atom near the surface can be excited $n$ times during a laser pulse with $n = \sigma F$, where $\sigma$ is the cross-section for photon absorption (taking the cross section to be $10^{-18}$ cm$^2$) and $F$ is the fluence and is typically $10^{19}$ cm$^{-2}$, we can expect that the defects on surfaces can be excited several times during a laser pulse. Since the time required for the relaxation from the unrelaxed to the relaxed excited state configuration is of the order of 1 ps, the next excitation will be induced only from the relaxed configuration. As we have explained, if the first excitation is excitation 4, photons of the same energy can cause excitation of another bonding electron. Further excitation should lead to elongation of the $Si_A$–$Si_H$ distance and, hence, further shift of the bonding orbital upwards. We expect excitation 3 to have almost the same character and we consider that the series of excitation–relaxation involving the bonding orbital is the most efficient path to reach the bond breaking stage. Excitation 1, involving the dangling bond, and excitation 2, an interhost transition, may not be as effective in the bond breaking. Thus, if the cross-section for these excitations is high, the number of excitations before the bond breaking occurs will be higher.

Further remarks may be made on the resonant state embedded in the continuum, as the excited states reached by excitations 4 and 5. These states can undergo the lattice relaxation and the phonon mediated de-excitation of the electron in these cases to the bottom of the conduction band. The competition may be governed by two energies, the $\langle\psi_L|H|\psi_k\rangle$ and the lattice relaxation energy, where $\psi_L$ is the wavefunction of the localized orbital and $\psi_k$ is the wavefunction for the continuum. For defects on the surfaces, a relatively large spatial separation of the localized state from the bulk may make the magnitude of the matrix element for the coupling with the bulk continuum small, favouring the lattice relaxation. The matrix element for the coupling with the surface continuum will be large. The enhancement of the laser induced emissions when the photon energy crosses the band gap energy, observed for GaAs [17], may be ascribed to this mechanism.

## 4. Conclusion

In the present paper, we emphasize the existence of the excitation to the antibonding state. The concept is analogous to the two-hole or multihole localization [19–25], since multiple excitation involving the bonding orbital should occur before the bond is broken. The wave function for a hole on defects on surfaces will be delocalized and does not necessarily mean a hole strictly located on the bond. We have shown that the antibonding orbital for an Si adatom on Si(111) is energetically located in the continuum and excitation to the antibonding orbital can be accomplished by multiple excitation.

In conclusion, the present study has revealed to a certain extent a microscopic picture of the excitation process of defects on semiconductor surfaces. The concept can be applied to other defects, not only in Si, but also in other semiconductors, including compound semiconductors. Since the experimental studies carried out so far are measurements of emitted atoms, which can originate from several types of defect on the surface, any spectroscopy study cannot give insight into the electronic structure of the defects. Spectroscopic studies of the destruction of defects using the STM will give further insight into the electronic structure of defects on surfaces.

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