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The multi-hole localization mechanism for particle emission from semiconductor surfaces

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Abstract. We have investigated the consequences of multi-hole localization at defect sites on the GaP(110) surface: the relaxation of the lattice and the emission of atoms due to bond breaking. It is shown that the combination of localization of two-hole states on a defect with cascade excitation results in emission of an atom from the defect. The results support the mechanism suggested by Hattori *et al* of defect-initiated emission of Ga atoms under laser irradiation, of which the yield is a superlinear function of laser fluence.

1. Introduction

The study of desorption of atoms and molecules from surfaces has attracted great scientific interest this past decade [1–4]. This is mainly due to its immediate relevance and practical importance in technology and industries such as materials science, corrosion prevention and catalytic sciences as well as its applications in biological science involving laser irradiation of matter. Knowledge gained from experimental studies of surface processes involving electronic excitation of surface species by ion or photon (including laser) bombardment has provided the impetus for the development of theoretical models to explain such desorption phenomena [5–8].

Basically, two types of model have been suggested to explain desorption induced by two different types of excitation: the Menzel–Gomer–Redhead (MGR) model [5] for excitation of valence electrons and the Knotek–Feibelman (KF) mechanism [6] for excitation of core electrons. In the MGR model, a Franck–Condon excitation of valence electrons yields an antibonding potential surface which leads to ejection of an atom from the surface. The KF mechanism explains the desorption processes induced by core-electron excitation, and assumes that localized two-hole states formed within 10^{-15} s in the valence band, due to Auger transition to a core hole, often result in emission of an ion or an atom. The two-hole state produced after core-electron excitation is not stable against the repulsive interaction between the two holes if the two-hole state is located within the valence band, that is, the on-site Coulomb repulsion energy U is smaller than the width W of the valence band. Even if $U > W$ (Cini–Sawatsky criterion [7]), the tunnelling process separates the two holes, and hence emission occurs only when the lifetime of the two-hole localized state is

smaller than the inverse of the characteristic lattice frequency. Thus, the KF two-hole localized state is generated only by the core excitation and it is unlikely that it is generated in a dense electron–hole plasma produced under laser irradiation.

A two-hole localized state of a completely different nature is that induced by Anderson negative-U localization [8]: if the value of U is smaller than the lattice relaxation energy E_{LR}, the two-hole state is stabilized by virtue of the lattice relaxation. The negative-U state once generated is stable with respect to Coulomb repulsion because of the lattice relaxation. Such a two-hole localized state may be called a phonon-mediated two-hole localized state. Itoh and Nakayama [9] have suggested that the lattice relaxation of a negative-U state on the surface could be the one in which an atom is eliminated from the surface. In this case the negative-U interaction forms an anti-bonding state, leading directly to particle emission; the emission by this mechanism is not the MGR process since multiple excitation is involved. Recently, on the basis of the results of high-sensitivity measurements of Ga atoms emitted by laser irradiation from GaP surfaces, of which the yield is a superlinear function of the fluence, Hattori *et al* [10] suggested that a series of cascade excitations of defects on a surface leads to desorption. The relaxed excited state reached after cascade excitation of a defect can be regarded as a phonon-mediated multi-hole localized state.

It is the purpose of this paper to elucidate possible mechanisms for formation of antibonding states for atoms on the surface of semiconductors. Semiconductors are of particular interest since they exhibit superlinear emission, indicating that the one-hole–one-electron (1h1e) excited state does not induce emission. Since the laser-induced emission can be a possible means of elimination of surface defects [10, 11], it is beneficial to clarify the conditions by which an atom is emitted from a specific defect site on the surface. At the present stage, we consider it most useful to choose specific defects and to compare the potential energy surfaces induced by several types of multi-hole localization: the KF-type multi-hole and phonon-mediated multi-hole localized states. It will be shown that not only the KF-type but also the phonon-mediated two-hole localized state on defects on surfaces can induce particle emission or weaken the bond.

2. Theoretical method

We used the CNDO (complete neglect of differential overlap) method [12] whereby the matrix elements of the Hamiltonian are systematically approximated via the introduction of three semiempirical parameters: the orbital exponent (ξ), the ionization potential (I) and the bonding parameter (β). The CNDO parameters were fitted to the experimental values of the cohesive energy, the lattice constant and the width of the valence band. The basis set includes the 4s and 4p orbitals of Ga and the 3s and 3p orbitals of P. The calculated bulk properties are in good agreement with experimental data. This set of parameters has been used to investigate interstitial H in crystalline GaP [13], and to investigate the energy required to eject atoms from defects on surfaces [14]. In our work, we implemented the Harwell MOSES code [15] and the calculations were performed on a 75-atom GaP(110) surface cluster, similar to the one used elsewhere [11]. The dangling bonds at the edges of this cluster were saturated by hybrid atoms of Ga or P (Ga* or P*) at locations representing the next shell of neighbours. The parameters of these hybrid atoms were chosen to give a

constant charge to the surface and inner atoms of the cluster as well as to reflect their relative charges of about 0.75 for Ga* and 1.25 for P*.

The bond angle tilt in the perfect surface reconstructed configuration attained using the CNDO methods was 24.4°, slightly smaller than the experimental value of 27.5° determined from low-energy electron diffraction (LEED) experiments [16] (figure 1(*a*)). Two kinds of defect were chosen in the present calculation. In system A, a Ga adatom (Ga_D) is attached to a surface P atom (P_S) (figure 1(*b*)) and in system B, one of the P atoms in the second layer of the surface cluster is replaced by a Ga atom (Ga_A) (figure 1(*c*)). For both systems, we obtained the adiabatic potential energy surfaces (APESS) at several excited states by calculating the total energy of the cluster at various configurations.

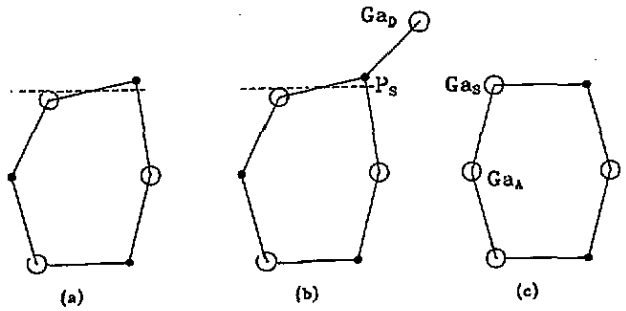

Figure 1. Schematic diagrams for atomic configurations for the GaP lattice near the (110) surface denoted by dashed lines: (*a*) perfect surface, (*b*) surface with a Ga adatom (Ga_D) attached on a P atom (P_S) on the surface and (*c*) surface with an antisite Ga(P) defect (Ga_A) in the second layer beneath a Ga atom (Ga_S) on the surface.

We simulated two different types of two-hole localization on a defect, one closer to the KF-type two-hole (2h) localization and the other the phonon-mediated two-hole localized state (2h2e) or (2h1e). To generate a hole on a defect, we used two procedures: to change the occupancy of the one-electron orbitals to excite an electron to a higher state, and to ionize the cluster by assigning a charge +1 [17–19]. Phonon-mediated multi-hole localized states were obtained by repeating or combining the procedures of creating a hole followed by lattice relaxation. In the multi-hole localized states obtained by these procedures, the holes are not localized exclusively on a specific atom but distributed over a few atoms on or around the defect. In order to simulate the KF-type two-hole localized state, in which the holes are localized on a specific Ga or P atom to a greater extent, we apply a localizing potential by shifting the ionization potentials (I) of a Ga or P atom at the site of the defect. The procedure is analogous to the one adopted by Itoh *et al* [20] for alkali halides.

3. Results and discussion

3.1. Adatom site

For system A, the phonon-mediated multi-hole localization was simulated by exciting the electron in the topmost occupied orbital of a relaxed positively charged cluster to

the next higher orbital. The equilibrium Ga_D–P_S distance in the ground state is found to be nearly the same as the equilibrium Ga–P distance of 2.36 Å in the bulk. In the ground state, the highest half-occupied orbital A and the next fully occupied orbital B are in the forbidden gap. After ionizing the cluster, the APES minimum was obtained by changing the Ga_D–P_S distance. As shown in table 1, the Mulliken charges on Ga_D and P_S after ionization followed by relaxation are lower than those before ionization, indicating that a hole is partly localized on these atoms. Then, we excited an electron in orbital A to B and, as can be seen from table 1, hole localization on Ga_D and P_S is enhanced by excitation. The APES for this excited state shows an antibonding character, as illustrated by curve a in figure 2.

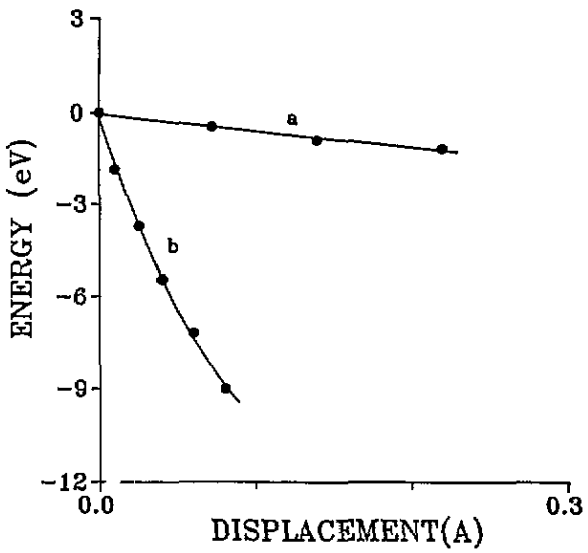

Figure 2. The adiabatic potential energy as a function of the displacement of the Ga adatom (Ga_D): after excitation of the outermost electron of the ionized Ga adatom (curve a) and after two-hole localization (curve b). The displacement for curve a is with respect to the equilibrium configuration of the ionized Ga adatom, while that for curve b is with respect to the equilibrium configuration of the neutral Ga adatom.

Table 1. Mulliken charge on a Ga atom (Ga_D) attached to a P atom (P_S) on the GaP (110) surface at the ground state, at a phonon-mediated two-hole localized state and at a KF-type two-hole localized state. The phonon-mediated two-hole localized state is simulated by combination of the processes of ionization, relaxation and then excitation.

		Phonon-mediated multi-hole localized state		
Atom	Ground state	after ionization + relaxation	after further excitation	KF-type multi-hole localized state
Ga_D	2.85	2.54	2.47	2.52
P_S	5.22	5.14	5.06	4.71
Total	8.07	7.68	7.53	7.23

In order to see the consequence of two-hole localization at a higher degree, the ionization energy of P_S in the positively charged cluster, without relaxation, is changed by various values ranging from 2 to 12 eV. When the ionization energy of P_S is reduced, the total energy of the cluster increases and, at the same time, the charge on P_S reduces. The optimum hole localization is attained by changing the value of I by 12 eV, where the coefficients of the basis functions of Ga_D are dominant on the lowest unoccupied orbital. The Mulliken charge in this optimum condition is shown in table 1. The charge reduction of the P atom is about 0.45 and is larger than that for the phonon-mediated two-hole localized state. Unlike the latter state, there is no guarantee for the absence of instability against separation of two-hole states due to Coulomb repulsion between the holes. Because of the smaller Mulliken charge, we consider that the hole-localized state thus obtained is more likely the KF-type two-hole localized state.

To confirm whether desorption of a Ga atom occurs from the hole-localized state obtained above, the Ga_D adatom was displaced slightly outwards from the surface along the bonding direction, away from the hole-localized site. The resultant total energy variation of the cluster as Ga_D is displaced outwards is compared with that for the phonon-mediated two-hole localized state in figure 2. It is clear the APES for desorption of a Ga atom is steeper for the two-hole localized state obtained by reducing the ionization energy than for the phonon-mediated two-hole localized state.

Although the presence of the antibonding APES is the sufficient condition for desorption for the phonon-mediated two-hole localization, this is not the case for the KF-type two-hole localized state. Because of Coulomb repulsion between the holes, the Cini–Sawatsky criterion [7] must be satisfied. The hole-localization or correlation energy (U) at this point is calculated to be 13.4 eV. For our cluster, the valence bandwidth (W) is also calculated, yielding a value of 12.4 eV, in good agreement with the experimental value of 11.8 eV [21]. Since $U > W$, we expect that an adatom is emitted by the KF mechanism.

3.2. Antisite defect

In order to compare further the KF-type and phonon-mediated multi-hole localizations, we carried out CNDO calculations on another GaP(110) surface cluster, but this time with a surface Ga_S atom having a Ga_A antisite atom as one of its nearest neighbours in the layer immediately below the surface instead of a P atom (see figure 1(*c*)). In this antisite configuration, Ga_S is displaced slightly outwards by 0.5 Å from its original perfect reconstructed position at the equilibrium situation. In addition, this configuration exhibits hole localization on Ga_A via examination of the lowest unoccupied orbital. The Ga_A antisite atom has four Ga nearest-neighbour atoms (Ga_S is one of them) and this configuration can be thought of as

(i) a molecular excited state of the Ga_2 molecule with localized holes (Ga_2^{2+}) on the surface or

(ii) an embedded Ga_5 molecule with hole localization on the central Ga (antisite) atom near the surface with tetrahedral configuration (Ga_2–Ga_A^{2+}–Ga_2), with Ga_A in a threefold-coordinated configuration trapping two holes in the broken bond between Ga_S and Ga_A.

In either case, the geometric configuration of the antisite defect may act to isolate this substructure on the GaP(110) surface, thereby reducing this group's

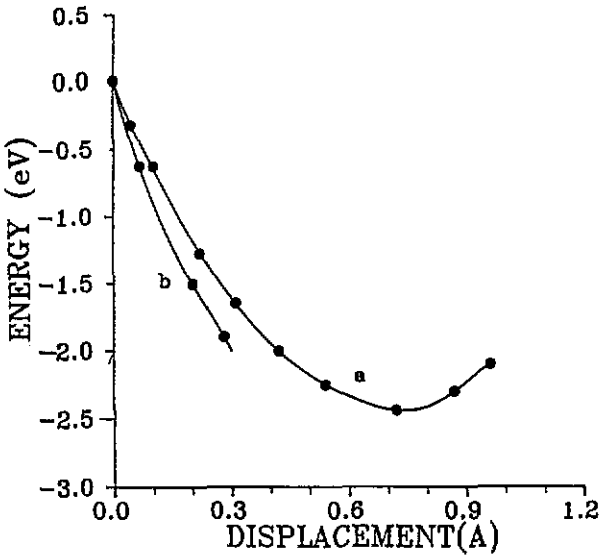

Figure 3. The adiabatic potential energy for the antisite defect in the second layer, as a function of displacement of the Ga atom (Ga_S) on the surface outwards in the direction perpendicular to the surface, after excitation of one of the outmost electrons and (curve a) after two-hole localization on Ga_S (curve b).

interaction with its neighbours [22] and hence making the situation more conducive to localization. The presence of the localized (or trapped) holes as a result of the introduction of the antisite defect (Ga_A) atom may play a role in aiding desorption, perhaps similar to the role the self-trapped exciton plays in the desorption of halogen atoms from alkali halides upon excitation [23]. But of more importance, the initial deposition of energy necessary for hole localization is already present when the Ga antisite atom is introduced into the perfect cluster replacing a P atom. The energy of formation of this defect structure is 7.7 eV [24]. The relaxation of the bond between Ga_A and Ga_S reflects the high energy of this hole-localized state.

In a similar way to the adatom case, we investigated whether the cascade excitation of the antisite defect can create the negative-U state. We have carried out calculations of the adiabatic APESs for the ground and excited states of the antisite defect cluster in which an electron on the highest occupied orbital is excited to the lowest unoccupied orbital. As shown by curve a of figure 3, the minimum for the adiabatic APES of the excited state is displaced by as much as 0.6 Å, but no desorption is induced by this excitation. The Mulliken charges on Ga_A and Ga_S before and after excitation, as shown in table 2, indicate that a hole is practically transferred from Ga_A to Ga_S by excitation while keeping the total charge the same. It has been argued that the transfer of the hole to Ga_S weakens the bond to Ga_S and hence the atom displaces outwards [24]. The bond weakening, however, is still not enough in this excited state to cause emission. The calculations of the excited states reached after cascade excitation from this relaxed configuration failed because of a convergency problem.

In order to see the consequence of hole localization to a greater extent on such an antisite defect, we reduce the ionization energy of Ga_S. In this case, we obtained the optimal hole localization, where the coefficients of the basis functions belonging to the surface Ga atom dominate on the lowest unoccupied orbital, by reducing the

Table 2. Mulliken charge on an antisite Ga atom (Ga_A) located in the second layer of the GaP(110) surface and on the Ga atom (Ga_S) on the surface atop Ga_A: at the ground state, at an electronically excited state and at a KF-type two-hole localized state.

		Electronically excited state		
Atom	Ground state	after excitation	after excitation + relaxation	KF-type multi-hole localized state
Ga_S	3.14	2.95	2.74	2.55
Ga_A	2.60	2.95	3.15	2.76
Total	5.74	5.90	5.89	5.31

ionization energy of the surface Ga atom by about 1 eV. As seen from table 2, in which the Mulliken charges on both Ga_S and Ga_A are shown, reducing the ionization energy aids hole localization on Ga_S. We calculated the APES for our antisite defect cluster by moving the Ga_S atom away from the surface at this optimal hole-localized state. The total energy variation of the cluster as the Ga atom is displaced outwards is illustrated by curve b of figure 3. As can be seen, the total energy reduces as the Ga atom moves away from the surface, more strongly than for the phonon-mediated hole localization.

We calculated the energy E_{LR} to remove the Ga_S atom to infinity and the hole-localization energy U and found that $E_{LR} = 6.72$ eV and $U = 4.57$ eV. Since $E_{LR} > U$, we expect that the surface Ga atom is desorbed if two holes are localized on it. Thus, it is likely that the two-hole localized state on the surface Ga atom described above forms a negative-U state, in which the lattice relaxation is the one that breaks a bond on the surface and brings an atom into the vacuum, causing desorption. Because of the large U, this negative-U state cannot be produced by combination of two hole states in the valence band.

We note that the excited state reached by photo-excitation is a non-negative-U state, an intermediate between two negative-U states: one with two holes on Ga_A and the other with two holes on Ga_S. As stated above, the relaxed configuration of the latter negative-U state is that in which the surface atom is removed from the surface. It has been argued that the intermediate state in which only a hole is transferred from Ga_A to Ga_S can be stable at a lower energy than the negative-U state, if the relaxation energy for the two negative-U states differ significantly; this condition can be satisfied easily for atoms on the surface [24] unlike the situation in the bulk where the 'enclosed' bulk environment stifles the relaxation of a normal Ga at a substitutional site. Since there is only vacuum above the surface Ga atom, this lack of symmetry gives it a greater propensity to undergo lattice distortion. This lattice distortion can make the resultant intermediate state stable.

We found also that the two half-occupied levels of the intermediate state are located within the forbidden gap. The intermediate state can absorb photons. Thus, it is conceivable that a series of cascade excitations of this defect can effectively bring a greater fraction of holes to Ga_S and ultimately break the bond, similarly to what is found in the adatom case.

4. Conclusion

We have investigated the consequence of two-hole localization: KF type and phonon

mediated. The former, which can be attained through Auger transition to a core hole, has two localized holes almost exclusively on a single atom, while in the latter, the hole is delocalized over a few atoms around the defect. The APES formed by the former is steeper, and hence the emitted atoms or ions acquire a higher kinetic energy. The steep repulsive APES is not the sufficient condition for desorption in this case, because of the Coulomb repulsion between the two holes. On the other hand, the APES for the phonon-mediated two-hole localized state does not produce such a steep antibonding APES, yet desorption can be induced in this case, since the Coulomb repulsion energy is compensated by the lattice relaxation energy. The results of the present investigation indicate that a series of cascade excitations of defects on surfaces produces a phonon-mediated localized state, from which emission can be induced.

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