

Core to surface excitations on GaAs(110)^{a)}

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We have carried out *ab initio* calculations of surface core excitations on finite cluster models of the GaAs(110) surface. For the Ga core excitation we find a localized excited state involving excitation into the empty Ga-4p orbital and bound with respect to the conduction band minimum (CBM) by 0.7 eV. This is in reasonable agreement with experiment (binding energy ≥ 0.8 eV). This transition, which is not analogous to bulk core excitations, is termed a *core surfaston* to emphasize the character of the state. We find that the As core surfaston is above the CBM by 1.0 eV and hence should be difficult to observe.

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I. INTRODUCTION

A promising experimental approach for examining the detailed atomic character of the surface states of solids is the observation of transitions between core levels and acceptor levels of surface atoms.¹⁻⁴ Such transitions, often referred to as surface core excitons, have been observed in several semiconductors. In this paper we have undertaken a detailed

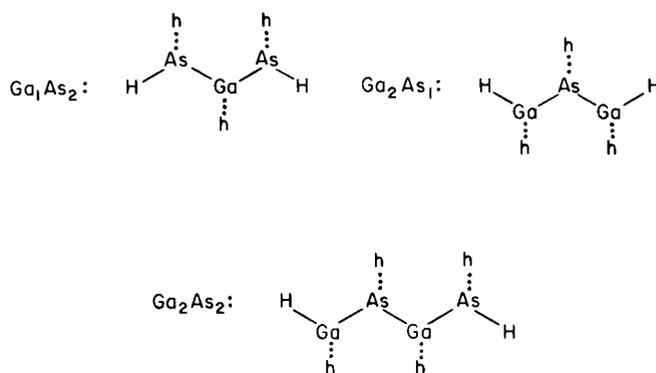


FIG. 2. Clusters modeling the GaAs (110) surface.

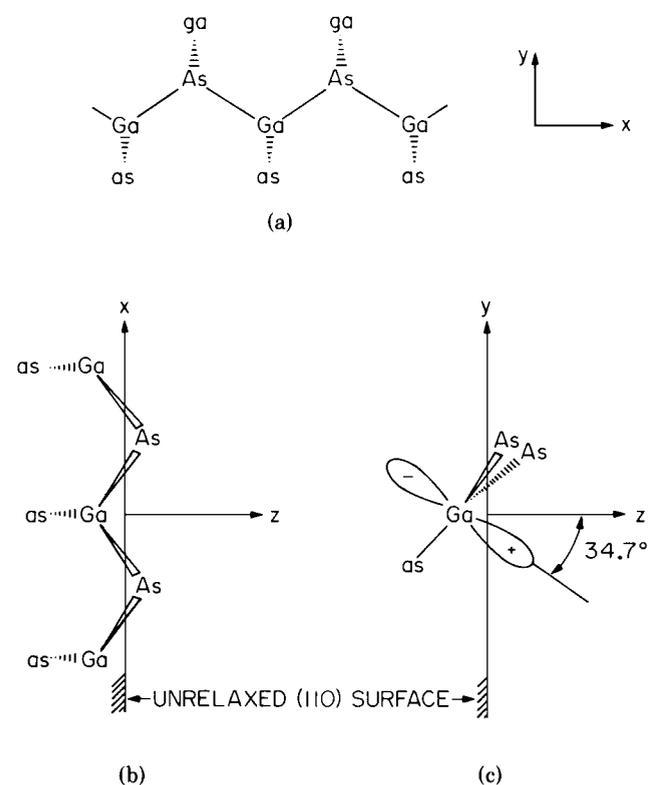


FIG. 1. The (110) surface of GaAs. Lower case characters indicate subsurface atoms. (a) Top view of the unreconstructed surface, (b) side view of the reconstructed surface, projected in the plane through the surface Ga's and normal to the unreconstructed surface, (c) side view of the reconstructed surface, projected in the plane normal to the surface and bisecting the As-Ga-As angle. The empty orbital is shown in the direction perpendicular to the plane through the three ligands of the surface Ga.

theoretical study of these transitions for one system, GaAs(110), in order to provide a basis for interpreting experiments on various systems.

The organization of this paper is as follows: In Sec. II we discuss the calculational details together with the surface models used in these calculations. In Sec. III we give the results of the calculations in which all electrons on the surface atom containing the core hole are treated self-consistently. It will be shown that these calculations lead naturally to a Ga excitation bound with respect to the conduction band minimum (CBM) and an As excitation unbound with respect to the CBM. In Sec. IV we discuss a simplified approach that allows us to treat larger models. Section V contains additional results, while a discussion of the results is given in Sec. VI, and our conclusions are summarized in Sec. VII.

II. CALCULATIONAL DETAILS

To study the surface core excitations we use the methods of quantum chemistry,⁵⁻⁷ which have been successfully applied in previous studies of (i) the reconstruction of the (110) surface of GaAs,⁸⁻¹⁰ (ii) the initial steps in the oxidation of this surface,^{8,9,11} and (iii) the initial steps in the chemisorption of Al on this surface.^{11,12} These methods require that the infinite surface be modeled by a finite cluster of atoms. Figure 1 shows several views of the GaAs (110) surface, and in Fig. 2 we give

the models used to mimic this surface. In order to describe the Ga core excitations, we use the Ga_1As_2 model, where all Ga electrons are treated self-consistently and an effective potential is used to describe the As core electrons. To describe an excitation from an As core orbital, we use the Ga_2As_1 model, where now all As electrons are treated self-consistently and an effective potential is used to describe the Ga core. We also carried out simplified calculations using the Ga_2As_2 model, which makes a direct comparison of the results for Ga and As excitations possible (see Sec. IV).

As is well known,^{10,13,14} the free GaAs (110) surface undergoes a (1×1) reconstruction (Fig. 1), in which the Ga atom moves towards the subsurface, leading to three nearly coplanar covalent bonds to the neighboring As atoms, with an empty Ga valence orbital ($4p$ -like) perpendicular to this plane. Also, during the reconstruction the As atom moves away from the subsurface (Fig. 1), leading to three pyramidally oriented (average bond angle of 95°) covalent bonds to the neighboring Ga atoms, with a $4s$ lone pair pointing away from the surface. These reconstruction effects have been incorporated in our models.

With the Ga_1As_2 and Ga_2As_1 models we carried out fully self-consistent *ab initio* calculations, using a double zeta basis set (two contracted basis functions for each valence atomic orbital; in addition, we used two contracted basis functions for the Ga- $3d$, As- $3p$, and As- $3d$ orbitals).^{6,15} Proper open-shell methods were used for the open-shell wave functions.⁷ Excitation energies and ionization potentials were obtained from differences in the total energies of the corresponding self-consistent wave functions.

In exciting an electron from a core d orbital, there are five possible states that will, in general, have different energies due to the asymmetry in the environment. For the surface As we find the total splitting in these d orbitals to be 0.19 eV, whereas for Ga it is 0.22 eV. In solving the wave functions for the core-ionized and core-excited states, we have averaged over all five d -substates and report only the average excitation energy. In addition, we have ignored spin orbital coupling effects (0.5 eV for Ga) in solving for the orbitals.

III. RESULTS

A. Ga core excitations

The lowest state arising from excitation out of the $3d$ core orbital of the surface Ga leads to the excited electron in the empty $4p$ -like orbital on the Ga site, as shown in Fig. 3(a). This orbital has 95% p -character and is oriented at $\sim 37^\circ$ with respect to the normal to the unreconstructed surface. (The normal to the plane through the three ligands of the surface Ga makes an angle of 34.7° with the normal to the unreconstructed surface.) The calculated excitation energy is 19.45 eV, which compares well with the experimental value of 19.85 eV.² This indicates that the cluster used to describe this excitation is adequate.

Experimentally, it is found that the Ga- $3d$ level is 20.1 eV below the Fermi level for n -type GaAs(110).¹⁶ Thus we conclude that our calculations place the Ga core excitation ~ 0.7 eV below the CBM. This is again in good agreement with

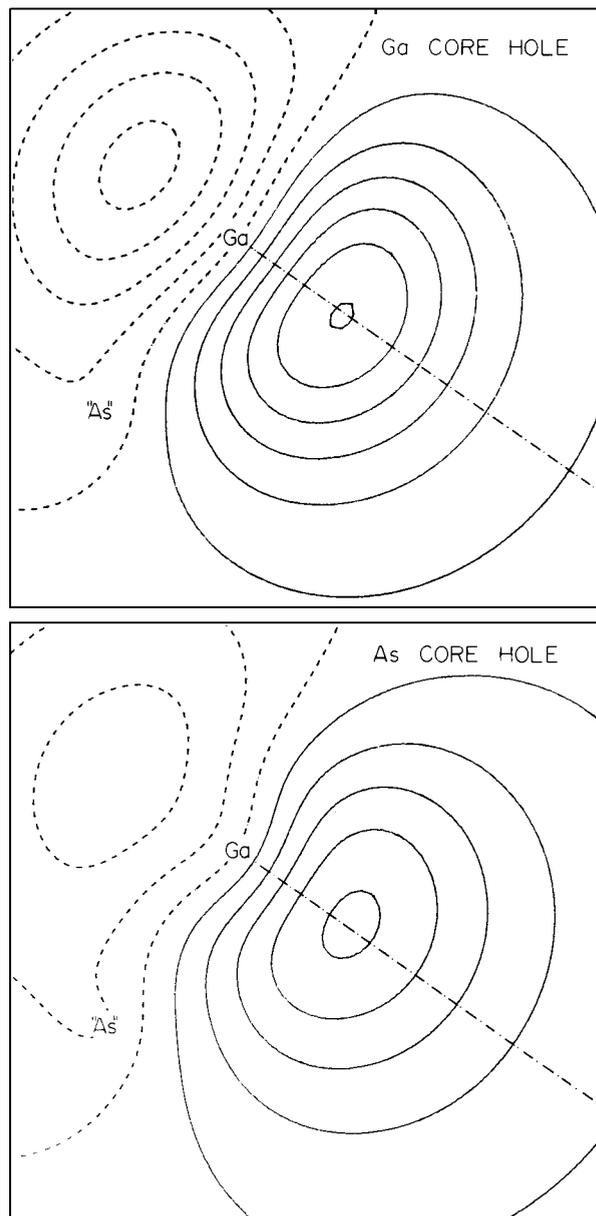


FIG. 3. Excited orbital for the Ga core excitation (top) and the As core excitation (bottom). The orbitals are plotted in the plane normal to the unreconstructed surface bisecting the As-Ga-As angle. The normal to the unreconstructed surface is along the abscissa. The dash-dot line indicates the direction normal to the plane through the three ligands of the surface Ga [compare Fig. 1(c)]. Solid lines represent contours of positive amplitude, dashed lines represent contours of negative amplitude. The increment between successive contours is 0.03. "As" indicates the H atom representing a subsurface As.

experiment; early partial yield photoemission experiments by Eastman and Freeouf¹ yielded a binding energy (BE) of 0.7 eV with respect to the CBM, while recent experiments (detecting the shift of the surface Ga- $3d$ levels relative to the bulk) give a BE of ≥ 0.8 eV.⁴

This surface core excitation is usually referred to as a surface core exciton. However, we believe that this name is inappropriate and may lead to confusion. In semiconductors, bulk excitons involve excited orbitals that are very large (~ 100 Å) and correspond to Rydberg orbitals of atoms or molecules. Thus bulk Ga core excitons are bound by ≈ 0.2 eV²³ with re-

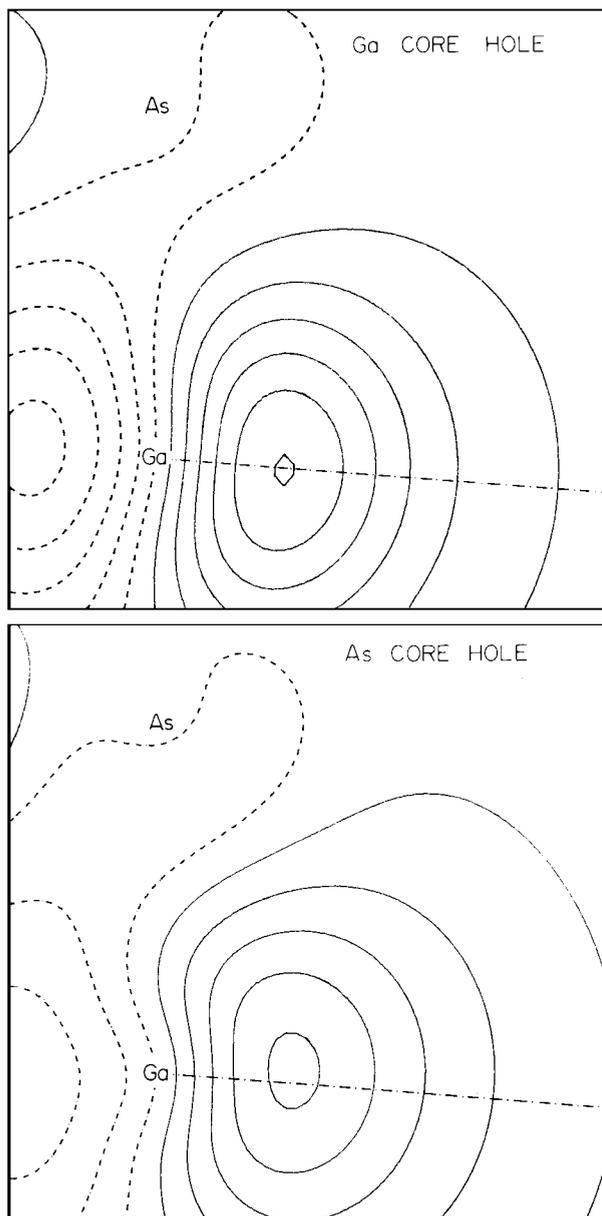


FIG. 4. Excited orbital for the Ga core excitation (top) and As core excitation (bottom). The plane of the plot passes through a surface Ga and a surface As and contains the normal to the plane through the three ligands of the surface Ga (dash-dot line).

spect to the conduction band. On the other hand, the excited orbital in Fig. 1(a) is a *valence* orbital having the same size and principal quantum number ($n = 4$) as the bond orbitals and is bound by 0.7 eV. For tetrahedrally bonded Ga (four bonds), this valence excited state disappears since this orbital is used in the bonds. For surface Ga, the other two valence $4p$ orbitals are involved in the three bonds (sp^2) and hence excluded as excited states (Pauli principle). Consequently, there is only one level associated with this excitation at the surface rather than the usual three. In order to distinguish this valence core-surface excitation from normal core excitons, we will refer to the former as *core surfastons*. In addition to the Ga surfaston, there could be normal Ga core excitons associated with the surface Ga atoms. For these exciton states the excited orbital would extend over many atoms and the binding energy

would be less than that of the bulk Ga core exciton (i.e., less than ~ 0.2 eV).

B. As core excitations

For the surface As atom we have calculated the energies for both the As- $3p$ and As- $3d$ core excitations, which we find to be at 145.25 and 42.88 eV, respectively. The excited electron occupies an essentially identical valence orbital in both cases, and in both cases we obtain a BE of 4.43 eV for the excited state with respect to vacuum. Thus the calculated separation between the As- $3p$ and As- $3d$ core levels is 102.4 eV, in reasonable agreement with the experimental value¹⁷ of 103.2 eV (bulk As). Thus the As core excitations are seen to be well described by our model.

Experimentally it is found that the As- $3d$ level is 42.0 eV below E_F for n -type GaAs (110).¹⁶ Thus we conclude that the As- $3d$ (and As- $3p$) core surfaston is *unbound* with respect to the CBM by ~ 0.9 eV.

For the As core surfaston we find excited orbitals very similar to the Ga core surfaston orbital. Namely, the excited electron goes into the empty orbital on the *adjacent* surface Ga (there are two such surface Ga atoms adjacent to each surface As, leading to two core surfastons), as indicated in Fig. 3(b). Another view is shown in Fig. 4 where the plot plane passes through both the surface Ga and the surface As. This plane is oriented to pass through the optimum direction for the empty valence orbital on the Ga site (dash-dot line). We see that for both the Ga and As core surfastons the excited orbital is essentially the empty valence orbital on the Ga site, although the As core surfaston has slightly larger amplitude near the surface As, due to the core hole on that atom. It is now also clear why the As core surfaston has a higher energy (lower binding energy) than the Ga core surfaston even though the orbitals for the two cases are the same. For the Ga core surfaston the core hole is on the *same* center as the excited orbital, leading to a large stabilization of this orbital, while for the As core surfaston the plus charge in the As core is removed from the location of the excited orbital (centered on Ga), leading to a smaller stabilization of this orbital. The energy diagram for the Ga and As core excitations is given in Fig. 5, where comparison is made with the position of a localized surface orbital not stabilized by a core hole. The latter level is estimated to be ~ 3 eV above the VBM.

Since the As core surfaston is well above the CBM, it can mix with the continuum of excited states arising from excitation of As core levels into the conduction band. The result would be a broad absorption transition (a surfaston resonance) out of the surface As- $3d$ level and a lifetime that is probably too short for observation by partial yield photoemission. Thus it should be quite difficult to detect the As core surfaston (resonance). Indeed, excitation of As- $3d$ levels does not lead to observed As core surfastons.³ There is a report³ suggesting an As- $3p$ core surfaston bound with respect to CBM (by ~ 1.4 eV). However, there were experimental uncertainties with these studies. Our results predict conclusively that excitation of the As core levels ($3d$ or $3p$) should *not* lead to bound surfaston states (below the CBM). These results are for the perfect surface; defects (for example, a Ga vacancy adjacent to the surface As) could lead to As core surfastons bound with respect

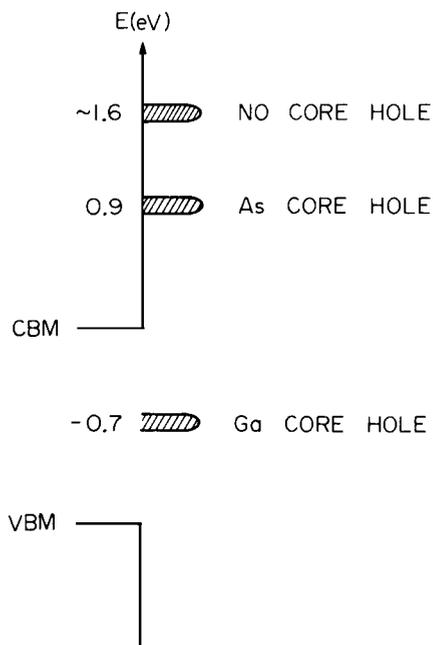


FIG. 5. Energy diagram for the various core excitations on GaAs (110). The energy position of the empty surface orbital when no core hole is present is estimated to be ~ 1.6 eV above the CBM.

to the CBM. In addition to the As surfaston resonance, there could conceivably also be surface core excitons involving diffuse excited orbitals and slightly bound with respect to the CBM.

C. Comparison of the two models

So far we have compared the results for our two models separately with experimental results and have found that the Ga core excitation is bound by 0.7 eV with respect to the CBM, whereas the As core excitation is unbound by 0.9 eV with respect to the CBM; i.e., the separation between the two levels is ~ 1.6 eV. In this section we will compare the results of the two models with each other, without reference to experiment, to examine consistency.

To compare the two models we must have a common reference level, and the only level that is available is the vacuum level. Therefore we have calculated the ionization potential (IP) for ionization out of the core levels of interest. By comparing the IP with the excitation energy of the corresponding core surfaston we obtain a BE of this core surfaston with respect to vacuum, which can then be compared for the various models. Unfortunately the use of a finite cluster to calculate IP's requires large corrections (1 to 2 eV) because the final

state is charged. For the real surface this positive charge is shielded by a semi-infinite dielectric medium, but for the cluster this positive charge is shielded only by a finite collection of atoms. Therefore the use of a finite cluster leads to too large an IP. However, the correction to the IP should be similar for both clusters, in which case the corrections cancel out in a comparison of the BE's. To see how well this cancellation works, we compare the various IP's again with experiment. Our calculations lead to an IP of 26.11 eV for the Ga-3d level and 47.31 eV for the As-3d level, so that

$$\text{IP}(\text{As-}3d) - \text{IP}(\text{Ga-}3d) = 21.2 \text{ eV.}$$

Experimental values for this difference are 22.0 eV (Skeath *et al.*¹⁶) and 21.7 eV (Bachrach¹⁸). Thus we conclude that the results of the two models can be compared, but that errors of the order of 0.8 eV can occur. [The difference between the two BE's will be too large because there is a larger correction to IP (Ga-3d) than to IP (As-3d)]. We find a BE of 6.67 eV for the Ga-3d core surfaston with respect to vacuum, whereas for the As-3d core surfaston we find a BE of 4.43 eV with respect to vacuum. This leads to an energy separation of 2.24 eV between the two levels. If we assume that the Ga-3d core surfaston is bound with respect to the CBM by ~ 0.7 eV, we find once again that the As core surfastons are unbound with respect to the CBM. However, the energy separation is now ~ 0.7 eV larger than found previously (2.24 eV vs 1.6 eV). The value of 1.6 eV for the energy separation is believed to be more accurate since it was obtained by calculating excitation energies only, in which case there are no large dielectric corrections, the cluster being neutral.

In order to treat the electrons on both Ga and As consistently, we have used the larger Ga₂As₂ cluster of Fig. 2. To reduce the computational costs connected with considering core excitations on more than one center, we have developed the simplified approach discussed in the next section.

IV. SIMPLIFIED APPROACH

A limitation in the above calculations is the necessity of including all the core electrons on the Ga or As in order to study excitations out of these core orbitals. In order to reduce the effort (and to increase the size of system that can be considered) we have tested the following simplified approach: (i) The core electrons are replaced by an effective potential. (ii) A core hole on an atom is represented by placing one additional plus charge on the nucleus whose core electron is ionized. (iii) Two calculations are carried out: (a) core-ionized state: no electron in surface orbital, and (b) core-surfaston: electron is included in surface orbital. (iv) The difference in energy between calculation (a) and calculation (b) is the binding energy of the core surfaston.

The results of this simplified approach for the small models of Fig. 2 are given in Table I, where they are compared with the rigorous results of Sec. III. The simplified approach leads to errors of 0.36 eV or 5% for Ga and 0.04 eV or 1% for As, satisfactory for our purposes.

In order to obtain BE's for the Ga and As core surfastons that can be compared directly, we have also applied the simplified approach to the Ga₂As₂ model of Fig. 2. The results

TABLE I. Binding energies (eV) with respect to vacuum for Ga and As core surfastons.

	Simplified model	Rigorous model
Ga (Ga ₁ As ₂ model ^a)	7.03	6.67
As (Ga ₂ As ₁ model ^b)	4.47	4.43

^aThe ground state total energy for this model is -1937.9182 hartrees.

^bThe ground state total energy for this model is -2240.8045 hartrees.

TABLE II. Comparison of binding energies (eV) for various models.

	Simplified model			Rigorous model		
	Ga ₂ As ₂	Ga ₁ As ₂	Ga ₂ As ₁	Ga ₂ As ₂	Ga ₁ As ₂	Ga ₂ As ₁
Ga core surfaston	6.78	7.03			6.67	
As core surfaston	4.49		4.47			4.43
Δ BE	2.29	2.56		1.97 ^a		2.24

^aThis number was estimated from the other results (see text).

are given in Table II. The Ga₂As₂ model gives a separation between the two levels of 2.29 eV, whereas the same approach applied to the Ga₁As₂ and Ga₂As₁ models gives an energy separation of 2.56 eV. This means that the energy separation obtained by comparing the Ga₁As₂ model with the Ga₂As₁ model must be corrected by 0.27 eV (due to corrections on the IP's). If we apply this correction to the rigorous results for the Ga₁As₂ and Ga₂As₁ models, we obtain an energy separation of 1.97 eV, in reasonable agreement with the value of 1.6 eV obtained in Sec. III. B. Therefore we conclude that the calculations lead to a consistent picture of a Ga core surfaston bound by ~ 0.7 eV with respect to the CBM and an As core surfaston (*3d* or *3p*) unbound by ~ 1.0 eV with respect to the CBM.

Using the simplified approach for the Ga₂As₁ model, we have also examined the effect on the As core surfaston of adding additional basis functions on the As site, which may allow the As core surfaston to delocalize more onto the As site. We have added sets of *4d*, *5s*, and *5p* basis functions, obtained by scaling the *3d*, *4s*, and *4p* basis functions.¹⁹ Results of these calculations are given in Table III.

The extra basis functions lead to a slight change in the excited orbital (see Fig. 6), which still remains a *4p*-like orbital on the Ga site. The increase in basis set leads to a *decrease* in the BE of the As core surfaston by 0.10 eV. Thus the additional basis functions help the ground state more than the excited state!

V. ADDITIONAL RESULTS

In the case of an As core surfaston, the excited electron occupies the surface orbital on an adjacent Ga site. There are two such sites, leading to various choices for the excited state. First of all, the excited state can be the surface state localized on one Ga atom; the results given in the previous section apply

TABLE III. Effect of additional basis functions on the binding energy (eV) of the As core surfaston for the H₂Ga₂As₁ model.

	Extra functions	BE
Rigorous	none ^a	4.43
	<i>5s, 5p</i>	4.41
Simplified	none ^a	4.47
	<i>4d</i>	4.37
	<i>5s, 5p</i>	4.43
	<i>4d, 5s, 5p</i>	4.37

^aNormal double zeta basis.

TABLE IV. Comparison of final states for the As core surfaston.

Core hole	Excited state	Excitation energy (eV)	BE with respect to vacuum (eV)
As- <i>3p</i>	Localized on one Ga atom	145.25	4.43
	Symmetric	145.47	4.21
	Antisymmetric	145.57	4.11
As- <i>3d</i>	Localized on one Ga atom	42.88	4.43
	Symmetric	43.11	4.20
	Antisymmetric	43.20	4.11

to this case. Secondly, the excited state can be a linear combination of the states localized on the two Ga atoms adjacent to the As atom that contains the core hole. In this case there are two possibilities, namely, symmetric or antisymmetric with respect to the reflection plane through the surface As atom. Results for the above three states for both an As-*3d* and an As-*3p* hole are given in Table IV. We see that the state localized on one Ga atom has the lowest energy (0.22 eV lower than the symmetric state), whereas the symmetric and antisymmetric states are separated by 0.10 eV. Since the symmetric and antisymmetric states are so close in energy, it follows that the electron does not gain an appreciable amount of kinetic energy from this delocalization, and that the state localized on one Ga atom will lead to a lower energy since it allows more relaxation of the valence electrons.

In order to determine the dependence of intensity of the core surfaston transition upon the symmetry of the core level, we have calculated the transition matrix elements for the various core levels. This was done in an approximate way as follows: Using the orbitals of a particular excited state (say Ga-*3d* hole, excited electron in surface orbital), we have calculated the dipole matrix elements $\langle cm | r_i | s \rangle$ between the various components (*m*) of the core states $|cm\rangle$ and the surface orbital $|s\rangle$. These matrix elements are then used to calculate the oscillator strength f_{cs} for the transition from a group of core levels (summed over *m*) to the surface orbital,

$$f_{cs} = \frac{2}{3} \frac{m_0}{\hbar} \sum_m \sum_i |\langle cm | r_i | s \rangle|^2 (E_s - E_{cm}).$$

The results are given in Table V. Since the surface orbital is mostly *p* character, we expect transitions from *p* core states to be weaker than from *d* (or *s*) core states. Indeed, this is the case, with the Ga-*3d* core surfaston calculated to be 17 times stronger than the Ga-*3p* core surfaston. This is in agreement with the fact that only the Ga-*3d* exciton has been observed experimentally. The Ga-*3p* transition is only possible if the surface state has an appreciable amount of *s* (or *d*) character. In the present case, the surface has only 2.4% *s* character.

Since the relative intensity of the Ga-*3p* and Ga-*3d* core surfastons provides a measure of the hybrid character of the surface orbital, experimental observation of the Ga-*3p* exciton, as well as the ratio of the *3p:3d* strength, would provide experimental data about the amounts of *s* and *p* character in the surface orbital. These amounts depend on the geometry and electronic configurations of the surface atoms and hence such

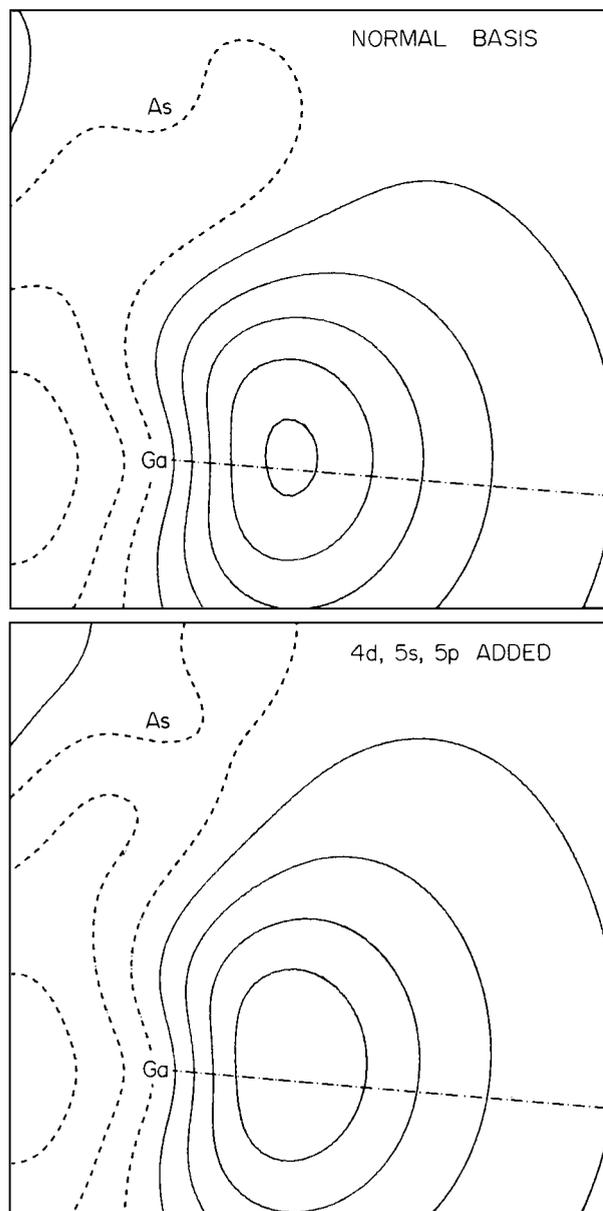


FIG. 6. Effect of extra basis functions on the excited orbital for the As core excitations. Top: normal double zeta basis set; bottom: As-4*d*, -5*s*, and -5*p* basis functions added. As in Fig. 3.

measurements will provide information about the surface geometry.

For the As core excitons, the transitions from the 3*d* level are much weaker than for the Ga-3*d* levels, because we are now dealing with states on different centers. On the other hand, the transitions from the As-3*p* levels have about the same strength as those from the As-3*d* levels, because in this case there is no selection rule.

VI. DISCUSSION

In order to provide additional insight concerning the core surfaston, it is useful to consider the spectra of excited states of a trivalent Ga system [e.g., GaH₃ or Ga(CH₃)₃]. There is a series of excited states whose orbitals are large compared with the size of Ga bonds. These orbitals are closely related

to hydrogenic states and are referred to as Rydberg orbitals with the notation 5*s*, 4*d*, 5*p*, etc., denoting approximate atomic character but with the five 4*d* orbitals and the three 5*p* orbitals split somewhat by interactions with the various ligands. In addition to these Rydberg orbitals, there is one valence excited state, corresponding to exciting an electron into the empty 4*p_z* orbital (where *z* is perpendicular to the molecular plane). There is no corresponding 4*p_x* or 4*p_y* transition, since these orbitals are used in bonds (and hence excluded due to the Pauli principle).

Thus one cannot view the 4*p_z* level as one of the three levels of a 4*p* state (with the *x* and *y* levels higher). Rather, the 4*p_z* level is the state that is available because the Ga is only trigonally bonded. If the Ga has four tetrahedral bonds, as in the bulk, there is no longer an empty 4*p* orbital into which to excite an electron, and the transition disappears (excluded by the Pauli principle). The Rydberg transitions remain for tetrahedrally bonded cases, but they get distorted and destabilized, leading to the rather extended exciton orbitals for the bulk.

Wang and Joannopoulos²⁰ have carried out tight binding calculations for the Ga core excitations on GaAs(110). For the interaction between the excited electron and the core hole, these authors use a contact potential, the strength of which is determined from the binding energy of the *bulk* core exciton. Since the bulk core exciton has a large radius, the use of a contact potential may lead to incorrect results. Subsequently they used this contact potential for calculations on the surface excitations of *unrelaxed* (tetrahedral) GaAs(110). Such calculations on the unrelaxed surface should substantially overestimate the binding energy of the surfaston. (We find that changing the surface structure from the relaxed to the tetrahedral geometry increases the binding energy of the surfaston by ~1.7 eV. Therefore the binding energy obtained by these authors for the Ga-3*d* excitation (0.6 eV with respect to the CBM) would have been substantially smaller if the relaxed surface had been used. Since the core-to-surface excitations are intimately tied to the existence of an empty orbital on the surface Ga and have no analog in the bulk, it is not surprising that transfer of bulk parameters (i.e., the contact potential) to surface calculations lead to incorrect results. Indeed, these authors find that the excited orbital contains a large amount of As character, whereas our calculations indicate that the excited orbital is located on the Ga site (≥95% Ga character).

TABLE V. Oscillator strength f_{cs} for transitions from a set of core levels $|cm\rangle$ to the surface orbital $|s\rangle$.

Core level	As core surfaston		Ga core surfaston
	As-3 <i>p</i> ^a	As-3 <i>d</i> ^a	Ga-3 <i>d</i> ^a
1 <i>s</i>	6.4×10^{-6}	6.4×10^{-6}	4.9×10^{-4}
2 <i>s</i>	3.5×10^{-5}	3.4×10^{-5}	2.2×10^{-3}
3 <i>s</i>	1.8×10^{-4}	1.4×10^{-4}	4.7×10^{-3}
2 <i>p</i>	2.4×10^{-4}	2.4×10^{-4}	6.4×10^{-5}
3 <i>p</i>	1.9×10^{-3}	1.6×10^{-3}	1.4×10^{-3}
3 <i>d</i>	1.6×10^{-3}	4.1×10^{-3}	2.34×10^{-2}

^aThe orbitals for calculating the matrix elements were obtained from this core surfaston state.

TABLE VI. Character of the excited orbital.

Model	Approach	Basis	Core hole	% Ga-4s	% Ga-4p	% As-4d	% As-5s	% As-5p
H ₅ Ga ₁ As ₂	rigorous	normal	Ga-3d	2.43	94.76			
H ₅ Ga ₁ As ₂	simplified	normal	Ga	2.02	95.50			
H ₆ Ga ₂ As ₂	simplified	normal	Ga	2.28	95.40			
H ₅ Ga ₂ As ₁	rigorous	normal	As-3p	6.48	91.38			
H ₅ Ga ₂ As ₁	rigorous	normal	As-3d	6.40	91.50			
H ₅ Ga ₂ As ₁	rigorous	+5s,5p	As-3d	5.08	90.07		2.78	0.77
H ₅ Ga ₂ As ₁	simplified	normal	As	7.27	90.84			
H ₅ Ga ₂ As ₁	simplified	+4d	As	7.19	85.36	5.38		
H ₅ Ga ₂ As ₁	simplified	+5s,5p	As	5.93	89.53		2.87	0.56
H ₅ Ga ₂ As ₁	simplified	+4d,5s,5p	As	5.78	83.02	5.29	3.07	1.77
H ₆ Ga ₂ As ₂	simplified	normal	As	7.68	89.68			

Our calculations are in agreement with recent tight binding calculations by Daw *et al.*,²¹ who find that the Ga core excitation is bound by 0.9 eV with respect to the CBM, whereas the As core excitation could not be observed. Furthermore, these authors determine the excited orbital to have 2.9% s character and 97.1% p character, in good agreement with our results. We find (see Table VI) from the rigorous calculations that the excited orbital for the Ga core hole has 2.4% Ga-4s and 94.8% Ga-4p character. The excited orbital for the As core excitation has 6.4% Ga-4s and 91.5% Ga-4p character. The difference between the two orbitals is due to the different locations of the core hole.

VII. CONCLUSIONS

Our conclusion is that localized core-to-surface excitations (core surfastons) do exist on semiconductor surfaces; however, the largest binding energy requires an empty surface orbital on the center whose core electron is ionized. For GaAs we find that the Ga core surfaston is bound by ~ 0.7 eV with respect to the CBM, allowing it to be observed easily, but that the As core surfaston is ~ 1.0 eV above the CBM, making it difficult to observe. Systems with larger band gaps (e.g., GaP and ZnO) might lead to anion core surfastons that are bound with respect to the CBM.

The excited orbital of the core surfaston is localized and hence experimental probes of such orbitals could provide detailed data concerning the geometry and electronic configuration of the surface atoms.

Similar localized transitions can also exist at vacancy sites. Thus studies of the core surfastons at vacancies could yield detailed information about the geometry and electronic configurations of the vacancy. An As adjacent to a vacancy might lead to core surfastons bound with respect to the CBM and hence such transitions might be studied easily. These experiments would be most sensitive to vacancies at or near the surface; however, such studies would be valuable since there is evidence that such sites are responsible for Fermi-level pinning and Schottky barrier formation.²²

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