PHYSICAL REVIEW B VOLUME 35, NUMBER 2 15 JANUARY 1987-I

Electronic structure of CF_3 radicals on GaAs(001)

P. K. Larsen and L. F. Feiner
Philips Research Laboratories, NL-5600JA Eindhoven, The Netherlands

P. Friedel
Laboratoires d'Electronique et de Physique Appliquée, 3 avenue Descartes, 94450 Limeil—Brévannes, France

(Received 27 May 1986)

A reconstructed GaAs(001)-2×4 surface, prepared *in situ* by molecular-beam epitaxy, has been exposed to a CF_4 plasma and subsequently studied by reflection high-energy electron diffraction, valence-band photoemission, and core-level photoemission. The exposed surface is crystalline with a 1×1 structure. Valence-band spectra show five plasma-induced peaks in the energy range -16 to -5 eV below the valence-band maximum. The spectra resemble those for gas-phase CF_4 but are shifted 4 eV upwards in energy. The line shape of the core levels, especially the As($3d$) level, has also been modified. We propose that the plasma exposure leads to a bonding of CF_3 radicals on As surface atoms, and results of a Hartree-Fock self-consistent-field calculation for a simple model of this chemisorption system are presented. It is found that the radicals can bond to the surface without significant changes in their internal electronic structure and the calculated and experimental energy positions agree well for all orbitals, except the highest-lying bonding orbital derived from the empty carbon sp_z orbital and the As dangling-bond orbital. An analysis of the core-level data indicates strong electronic charge transfer from the substrate to the chemisorbed radical.

I. INTRODUCTION

The chemisorption and reaction of gas-phase species (atoms, molecules, ions, radicals) with semiconductor surfaces are not only of fundamental interest, but also of technological importance. For GaAs the adsorption of oxygen has been widely studied (see Ref. 1 and references therein) with the interest being at least partly related to problems in passivating the surface using oxidation.[2–5] Uses of other gases in the oxidation processes have also been attempted and the combination of oxygen and CF_4 in plasma exposures has been reported to have beneficial effects on the interface state density.[6,7] Recently, chemisorption of hydrogen on GaAs has attracted some attention[8–17] mainly for two reasons. This system can be considered as a chemisorption model system, and the presence of hydrogen during molecular-beam epitaxy (MBE) might influence the growth.

The experimental investigations of the interaction of hydrogen or oxygen with the surface have largely been carried out by means of surface sensitive electron spectroscopies, exposing the semiconductor surface to the gas-phase species in the UHV chamber which also contains the electron spectrometer. Obviously, such arrangements are only of use for chemisorption of relatively "harmless" species like oxygen, hydrogen, or nitrogen which do not damage the analyzing system. These limitations can be avoided if a dedicated chemisorption-reaction chamber is linked to the main experimental chamber by a UHV sample transfer system. This approach was used in studies of the interaction of hydrogen and nitrogen plasmas with GaAs surfaces[18–20] and it was also used in the present investigation of the interaction of a CF_4 plasma with GaAs(001).

The fluoromethane compounds CF_4 and CF_3H and similarly chlorinated methanes are widely used in dry etching of semiconductors.[6,21–28] The gas-phase species are excited in a plasma to form ions and radicals which then interact with the surface. A precursor state of etching can be chemisorption of the species provided by the plasma on the surface, and studies of the type and position of the chemisorbed species and their energy levels might not only lead to a better insight into dry etching, but would also be of considerable interest from a fundamental point of view. The fluorinated methanes in the gas phase have been studied both experimentally and theoretically and their electronic structures are well understood.[29–32] This is a useful basis for the interpretation of spectra of the chemisorbed species originating from a CF_4 plasma. In the unexcited gas phase this fluoromethane is very inert. In a plasma the CF_4 gas can be converted to contain radicals, e.g., CF_3, $CF_3{}^+$, and F^+ ions[21,22,26] which are strongly reactive and interact with the semiconductor surface.

We have investigated the effects of exposing a clean, reconstructed GaAs(001) surface to a CF_4 plasma using angle-resolved photoemission (ARPES), core-level photoemission, and reflection high-energy electron diffraction (RHEED). The 2×4 GaAs(001) surface, grown *in situ* by molecular-beam epitaxy (MBE), is close to being stoichiometric As-terminated.[33,34] The present results show strong evidence for chemisorption of CF_3 radicals to As dangling bonds with a large electronic charge transfer from the dangling bond towards the radical. A self-consistent calculation of a pseudomolecule CF_3H^* shows excellent agreement with the experiments.

In this paper the experimental technique and the experimental results will be described in Secs. II and III, respectively. In Sec. IV we present the model and results of the self-consistent calculation and the comparison with the experiments. Finally, Sec. V deals with other aspects than those treated by the calculation.

II. EXPERIMENTAL DETAILS

The experiments were carried out in a UHV system consisting of a main chamber and a plasma chamber, linked together by a UHV substrate transfer system. In the main chamber there are provisions for *in situ* growth of GaAs by MBE, and for characterization by RHEED and ARPES.[35] The chamber is connected to a beamline of the ACO storage ring [at Laboratoire pour l'Utilization du Rayonnement Electromagnétique (LURE) Orsay], allowing both photoemission studies of the valence bands and measurements of the Ga(3*d*) and As(3*d*) core levels. The plasma source is a hot cathode discharge combined with multipole magnetic confinement of the electrons. Because of the low voltages used a quiescent plasma free of very energetic particles is created. The plasma-surface interactions are therefore mainly of chemical nature while mechanical effects due to ion bombardment are minimized (the plasma is a few volts negatively biased with respect to the substrate potential). The system has previously been used in the present configuration in the studies reported in Refs. 18–20 where details about the plasma chamber and exposure procedures have been described.

On the GaAs(001) substrate a fresh GaAs layer was first grown under As-stable conditions ($T_{\text{sub}} \simeq 830$ K, Ga:As_2 fluxes $\simeq$1:3), corresponding to a 2×4 structure. RHEED and photoemission studies were carried out to ensure that the layer and surface grown were of high quality. The substrate was then transferred to the plasma chamber and exposed in a CF_4 plasma under the following conditions: CF_4 pressure $\sim 6\times10^{-4}$ torr, filament bias -60 V, discharge current 14 mA, exposure time 5 sec. From Langmuir probe characteristics for oxygen and oxygen+CF_4 plasmas we estimate the density of the plasma under these conditions to be in the range 10^8–10^9 cm^{-3}. On the basis of earlier experiments with N_2 and H_2 plasma exposures[18–20] and the (expected) larger reactivity of a CF_4 plasma compared to a N_2 or H_2 plasma, these conditions were assumed to lead to a significant but not excessive surface modification. In the following only results from this exposure are reported. The CF_4 gas used was research grade (99.99%).

Winters, Coburn, and Kay have discussed the dissociation of CF_4.[22] These authors conclude that both for dissociation of this molecule into ionic fragments and for dissociation into neutral fragments the probability for formation of CF_3 and F radicals is $\sim$80%. For electronic excitation of CF_4 there is a threshold energy of $\sim$12.5 eV for dissociation and up to an energy of $\sim$16 eV only neutral fragment are formed. At an energy of $\sim$70 eV the cross sections for dissociation into neutral and ionic fragments are of the same order. We would therefore expect for the present experimental conditions that the major components of the plasma are CF_3 and F radicals ($\sim$80%) and that both neutrals and ions are present. A crude calculation of the number of radicals impinging on the surface during the exposure can be made on the basis of the experimental parameters (plasma density, etc.). We estimate an upper limit in the order of a few tenths of a monolayer.

Immediately after the exposure, the plasma chamber was pumped down to its base pressure (below 10^{-8} torr) followed by transfer of the substrate back to the main chamber for characterization by RHEED and photoemission. The overall energy resolution in the photoemission measurements was 0.2–0.4 eV in the valence-band studies and 0.23 eV in core-level measurements at the photon energy $h\nu = 72.7$ eV.

III. EXPERIMENTAL RESULTS

The exposure of the GaAs(001)-2×4 surface to the CF_4 plasma has a dramatic effect on the surface properties. RHEED measurements show a change of the diffraction pattern from a 2×4 to a streaky 1×1 structure with a rather high background. The 2×4 reconstruction of the clean, As-terminated GaAs(001) surface is closely connected with the formation of asymmetric As-As dimers[34] and the RHEED results therefore indicate that the dimer bonds have been broken by the CF_4 plasma exposure, but that the surface remains crystalline. This is in agreement

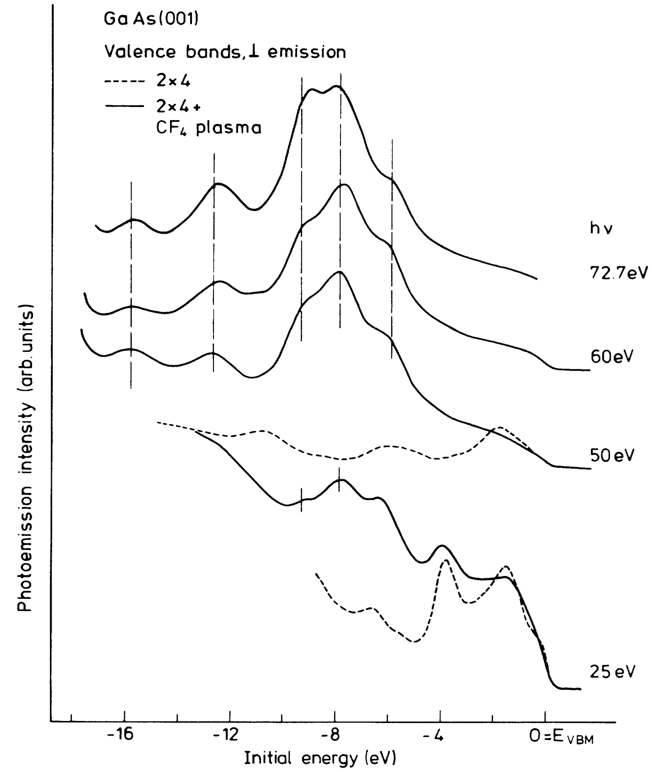

FIG. 1. Photoelectron-energy spectra taken at normal emission for a number of photon energies of the clean GaAs(001)-2×4 surface and of this surface after an exposure to a CF_4 plasma. The vertical dashed lines indicate the energy positions of CF_4-induced features.

with our estimate that the total exposure of the surface during the plasma treatment corresponds to considerably less than one monolayer.

The photoemission results also demonstrate that the plasma treatment has a large influence on the surface electronic properties. This is seen in Fig. 1, in which ARPES spectra taken at normal emission at different photon energies are shown for the exposed surface and for comparison also for the clean reconstructed surface. At low photon energies (25 eV) the GaAs valence-band structure can still be recognized for the exposed surface, but the shoulder seen for the 2×4 surface near the top of the valence bands is reduced in intensity. This shoulder is related to dangling-bond-like surface states[34] and at polar angles where it is a strong peak for the 2×4 surface it appears also for the exposed surface, but again with a much reduced intensity. At initial energies below ~ -5 eV the $h\nu=25$ eV spectrum shows several features induced by the CF_4 plasma. At higher photon energies these features are dominating compared to the GaAs valence-band structure, showing five major peaks or shoulders at $E_i < -5$ eV and rather little structure for $E_i \geq -5$ eV. The energy positions of these features which we have indicated by vertical dashed lines (eye fit) are independent of the photon energy (no energy dispersion with $k_\perp$) which is in agreement with their surface nature. (The apparent disagreement in energy position of lower and higher photon energies for the feature at $E_i \simeq -5.9$ eV is due to the presence of a bulk GaAs feature at $E_i \simeq -6.5$ eV which dominates at lower photon energies.) The increase in intensity of the plasma-induced features with increasing photon energy is related to a higher surface sensitivity (smaller electron escape depth) and to the energy dependence of the cross section for photon excitation.

It is interesting to compare these spectra with those of gas-phase CF_4 (see, e.g., Refs. 29–32): They appear to be quite similar, but with a considerable change in binding energies towards smaller values. This is shown in Table I (lower five rows), where results for gas-phase CF_4 are given together with the present results. The binding energies and assignments for $(CF_4)_{gas}$ have been determined by He II photoelectron measurements.[29] The present results are those indicated by the vertical dashed lines in Fig. 1, which are referenced to the vacuum level by adding the photoelectric threshold E_{th}, of GaAs ($\simeq 5.4$ eV) to the binding energy of Fig. 1 ($= -E_i$). For the observed levels there seems to be a one-to-one correspondence with a rather uniform energy shift of ~ 3.9 eV, except for the highest-lying level.

TABLE I. Energy levels for gas-phase CF_4, E_{CF_4} (after Refs. 29 and 32), and for the present measurements GaAs(001) + CF_4 plasma, E_{plasma}. The energy difference $\Delta E = E_{CF_4} - E_{plasma}$ is also given. The energies are binding energies referred to the vacuum level, $E_{vac}=0$. The symmetry labels for the CF_4 levels are also indicated. The results in brackets refer to very weak features; see the text.

E_{CF_4} (eV)	Symmetry	E_{plasma} (eV)	ΔE (eV)
43.8	$3a_1$	(38.7)	(5.1)
40.3	$2t_2$	(36.1)	(4.2)
25.1	$4a_1$	21.2	3.9
22.1	$3t_2$	18.0	4.1
18.5	$1e$	14.7	3.8
17.4	$4t_2$	13.3	4.1
16.2	$1t_1$	11.3	4.9

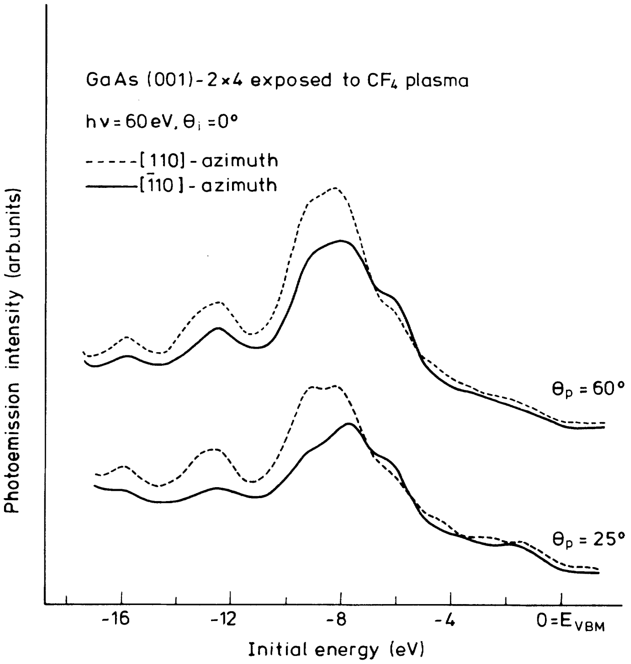

FIG. 2. Photoelectron-energy spectra taken at $h\nu=60$ eV at two polar angles (θ_p) of the GaAs(001)-2×4 surface after an exposure to a CF_4 plasma. The incident radiation was s polarized (normal incidence, $\theta_i=0°$), with the vector potential **A** directed along the [110] azimuth (dashed line) and the [$\bar{1}$10] azimuth (full line).

Photoemission spectra taken at off-normal polar angles show peaks or shoulders at almost the same energies as observed for normal emission, but the intensities depend markedly on the polar angle and the polarization of the incoming electromagnetic radiation. This is seen in Fig. 2 where spectra are shown for s-polarized light (normal incidence) with the vector potential **A** parallel to the [110] and the [$\bar{1}$10] azimuthal directions. For p-polarized radiation ($\theta_i=45°$) it is also found that spectra with **A** parallel to the [110] azimuth display more intense peaks than for the [$\bar{1}$10] azimuth.

In addition to the levels discussed above two more levels are experimentally observed for gas-phase CF_4 using XPS. These levels of symmetries $3a_1$ and $2t_2$ have strong F $2s$ character and are observed at binding energies of 43.8 and 40.3 eV, respectively. If similar levels are present here they should be observed in the energy range between the As($3d$) level ($E_b \simeq 46$ eV) and the Ga($3d$) level ($E_b \simeq 24$ eV), irrespective of whether they have been shifted by ~ 3.9 eV towards lower binding energies or not. We have measured the photoemission spectra for the energy range between the As(3*d*) and Ga(3*d*) levels at $h\nu=72.7$ eV for both the clean surface and the surface exposed to the CF_4 plasma. By subtracting the former signal from the latter the background signal due to inelastically scattered electrons could partly be eliminated. The difference spectrum shows the presence of two weak and broad features at binding energies of 36.1 ± 0.4 eV and 38.7 ± 0.4 eV. The peak heights are of the order of 5—10% of the background signal and ~1% of the Ga(3*d*) peak height. The binding energies are 4—5 eV lower than those of the F(2*s*) derived levels of CF_4 having $2t_2$ and $3a_1$ symmetry character[32] (see Table I, upper two rows). The relative weakness of the two levels observed here will be discussed in Sec. V.

Photoemission spectra of the As(3*d*) and Ga(3*d*) core levels measured before and after the exposure of the GaAs(001)-2×4 surface to the CF_4 plasma are shown in Fig. 3. The line shape of the As(3*d*) has changed a great deal, while the Ga(3*d*) spectrum shows a broadening towards higher binding energies. The changes are seen more clearly in the difference spectra, also shown in Fig. 3, obtained after normalizing the As and Ga spectra, respectively, to the same peak height. (A better way of analyzing the spectra would be to deconvolute these into the different components but we were not able to do so in a satisfactory, unambiguous way; see below.)

We shall first discuss the As(3*d*) spectra. The difference spectrum shows a large component shifted towards higher binding energies. This plasma-related component is broadened to such an extent that it is not possible to observe any spin-orbit splitting. The high background observed in RHEED points in the direction of a less well-ordered surface, and the absence of spin-orbit splitting might therefore be related to the presence of more than one component and possibly a distribution rather than an intrinsic broadening of the level. At lower binding energies (~40 eV) the difference curve shows a sign reversal. It is well known from deconvolution of As(3*d*) spectra for GaAs(001)-2×4 that in addition to a bulk doublet (*B*) there is a surface doublet (S_L) shifted ~0.3 eV towards lower binding energies (see, e.g., Ref. 33 for details). The negative peak in the difference curve indicates that the surface contribution S_L has decreased as a result of the plasma exposure. We have attempted to deconvolute the As(3*d*) spectrum for the exposed surface and, in addition to the two doublets mentioned, the presence of a doublet S_H at 0.9 ± 0.1 eV higher binding energy than the bulk doublet is found in the curve-fitting procedure. Due to the broadening of the line shape at the high binding energy side it was not possible to obtain an unambiguous best fit with these three doublets (nor with more) and the relative intensities of the various doublets can only be qualitatively estimated. It is found, however, that the plasma treatment leads to a large reduction of the intensity of the surface component S_L (by more than 50%) and as is directly seen from Fig. 3 to the appearance of the component S_H.

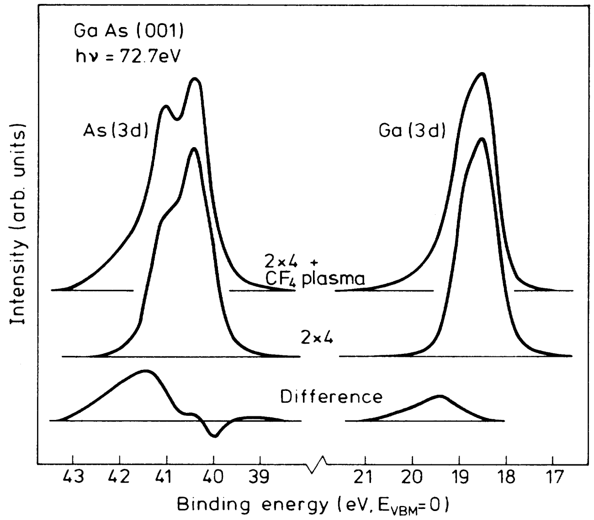

FIG. 3. As(3*d*) and Ga(3*d*) core-level spectra measured at normal emission and $h\nu=72.7$ eV of the GaAs(001)-2×4 surface and of this surface after an exposure to a CF_4 plasma. Difference spectra between the exposed and the clean surface are also shown.

Turning to the Ga(3*d*) results, the changes in line shape induced by the plasma exposure are much less prominent, although observable, than for the As(3*d*) level. The main effect is seen as a broadening towards higher binding energies. The difference spectrum in Fig. 3 shows a peak shifted ~0.9 eV towards higher binding energies than the bulk doublet. In Sec. V we shall discuss further the core-level results.

IV. MODEL CALCULATIONS

The results presented in Sec. III give strong indications in support of the hypothesis that the exposure of the GaAs(001)-2×4 surface to the CF_4 plasma leads to bonding of CF_3 radicals to the surface atoms. This is suggested by the similarity between the valence-band spectra presented here and CF_4 gas-phase spectra and by the fact that CF_3 radicals are a main constituent of the plasma. One would also expect an interaction between fluorine atoms and ions and the surface atoms, but the observable effects seem to be dominated by CF_3 radicals. Because the starting surface was As-terminated, the total exposure is considerably lower than corresponding to one monolayer and the As(3*d*) level is more modified by the exposure than the Ga(3*d*) level, it is natural to assume that the CF_3 radicals are bonded primarily to As surface atoms. The possibility of bonding to Ga atoms cannot be excluded, however, and we will return to this point in Sec. V.

In order to gain insight into the bonding of CF_3 radicals to the GaAs surface we have performed Hartree-Fock self-consistent-field (SCF) calculations for a model in which we assume that the radicals are bonded to As surface atoms.

A. Model

In Fig. 4(a) we show the asymmetric dimer of the GaAs(001)-2×4 surface with two dangling bonds and a dimer bond. The initial energies of the dangling bonds are

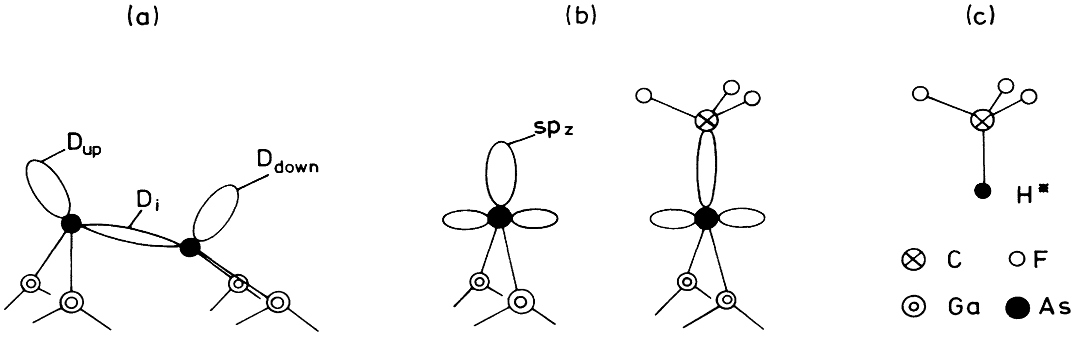

FIG. 4. Schematic diagrams of (a) the asymmetric dimer model for the reconstructed As-terminated GaAs(001) surface, showing the dimer bond (D_i) and dangling bonds (D_{up} and D_{down}); (b) the unreconstructed As-terminated GaAs(001) surface showing a dehybridized dangling bond (sp_z) and a CF_3^+ radical chemisorbed to such a dangling bond; (c) the pseudomolecule CF_3H^* where the pseudohydrogen atom H^* represents the surface.

in the range from -0.5 to -1.6 eV and for the dimer bond ~ -3.5 eV.[34] The RHEED results show that the dimer bond has been broken (the 2×4 pattern has changed to an unreconstructed 1×1 pattern) and the suggested situation after the chemisorption of a CF_3 radical to the surface is that shown schematically in Fig. 4(b). A new bond has been formed between the As surface atom and the carbon atom of the CF_3 radical and its orbital is derived from an sp_z-like As dangling orbital and the similarly unsaturated orbital of the CF_3 radical stretching out from the carbon atom.

We have taken an extremely simple model for the clean As-terminated GaAs(001) surface: Only the unpaired electron in the As dangling-bond orbital is included explicitly, the rest of the surface being represented by an attractive potential that keeps the electron bound. For simplicity we take for the potential that of a positive point charge Z^*e and the dangling orbital is represented by an s-orbital centered at the charge. So the surface is actually modeled as a pseudohydrogen atom H^* with a fractional "nuclear" charge Z^*e. One might think of Z^*e as the effective charge of the surface As atom as seen by the dangling-bond electron, i.e., screened by all other, core and valence, electrons. The value of Z^* is chosen so as to produce the appropriate electron binding energy corresponding to that of the dangling bond, i.e., $(Z^*)^2\,\mathrm{Ry}=E_b=E_{\mathrm{th}}-E_i\simeq6$ eV or $Z^*=0.67$, and accordingly the effective Bohr radius of the s orbital becomes $a^*=a_0/Z^*\simeq0.80$ Å. Note that H^* is fractionally negatively charged by $-0.33e$.

We then take the molecule CF_3H^* shown in Fig. 4(c) to serve as a cluster model for a CF_3 radical chemisorbed onto the GaAs surface. In doing so we tacitly assume that any changes brought about by the adsorption in the surface itself (as, e.g., the disappearance of the reconstruction) are so small that the same model potential, i.e., the same value of the effective charge, can still be used after chemisorption has taken place. For our purposes this is a reasonable assumption since the energy associated with the reconstruction is of the order of a few tenths of an eV, whereas we are interested here in shifts in the spectra of the order of several eV.

B. Hartree-Fock SCF calculations for CF_4, CF_3H^*, and $CF_3H_2^*$

The Hartree-Fock SCF calculations were carried out with the program MOLECULE-ALCHEMY,[36] using atomic basis sets of contracted Cartesian Gaussian functions. The primitive basis sets were those given by Huzinaga:[37] $(9s,5p)$ for C and F, $(4s)$ for H; they were contracted to $[3s,2p]$ and $[2s]$, respectively.[38] For H^* the basis set of hydrogen was used, but with the exponents scaled down by a factor $(Z^*)^2\simeq0.45$; it was verified that this scaling led to reoptimization. The geometries used all had tetrahedral bond angles, with atomic distances $R(\mathrm{C{-}F})=1.32$ Å, $R(\mathrm{C{-}H})=1.09$ Å as in CF_4 (Ref. 39) and CH_4,[40] respectively, and $R(\mathrm{C{-}H^*})=1.17$ Å. The last value was obtained by minimizing the total energy of CH_4^*. Further geometry optimization affects, in particular, the C—H^* distance, but changes the orbital energies by less than 0.1 eV, which is irrelevant for our purposes.

We first carried out calculations for the fluoromethane series ($CF_4, \ldots, CH_4$) for which experimental ionization energies are well known. The calculated values of the Koopmans's theorem ionization potentials were found to agree very well with those given by Brundle *et al.*,[29] i.e., the rates at which the experimental ionization energies decrease upon hydrogenation are reproduced well in the calculations. However, the calculated binding energies are uniformly too high by about 3 eV. This is a common experience in *ab initio* SCF calculations, and may be ascribed to the imperfect cancellation of the reorganization energy and correlation energy errors. In Fig. 5(a) we show the results of the calculations for CF_4, CF_3H, and CF_2H_2 together with the orbital assignments. Here and in the following we only discuss the calculated valence orbitals corresponding to the strong observed features (see lower five rows of Table I).

Turning to the results of the calculation for the series

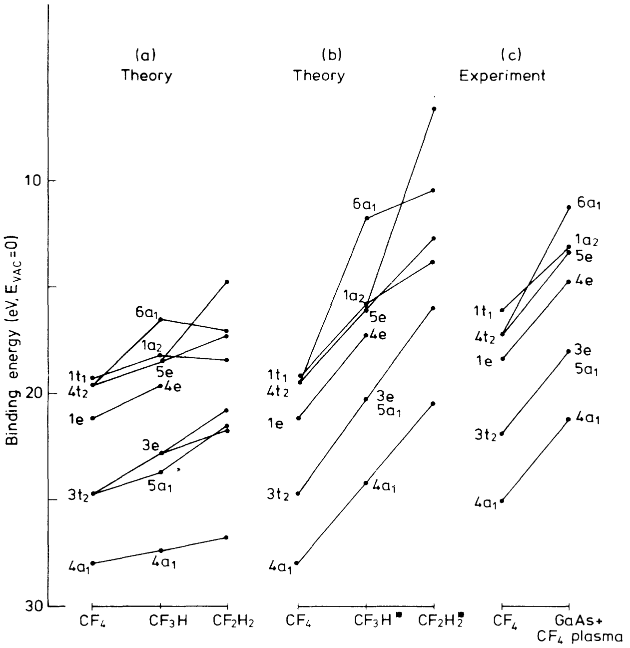

FIG. 5. Hartree-Fock SCF calculations of the binding energies for (a) CF_4, CF_3H, and CF_2H_2; (b) CF_4, CF_3H^*, and $CF_2H_2^*$ (see text). In (c) the experimental values of binding energies are given for gas-phase CF_4 (from Ref. 29) and for GaAs(001)-2×4 exposed to a CF_4 plasma.

with H replaced by H^*, shown in Fig. 5(b), we find that successive substitution of F by H^* instead of by H leads to a much larger and, with the exception of the highest level, more uniform upward energy shift. This may be qualitatively understood as follows. Owing to the weakness of the H^* nuclear potential the deeper levels are determined by the C and F nuclear potentials. Mulliken population analysis indeed shows that these orbitals change much less upon H^* substitution than upon hydrogenation: They remain very much CF_4-like, i.e., behave as internal molecular orbitals. The weaker attraction of electrons by the H^* potential (as compared to that by an H nucleus) therefore acts, as a pure potential effect, rather indiscriminately on all these orbitals. The situation is quite different for the highest ($6a_1$) orbital where bonding effects are dominant. As it turns out, this single orbital, which has large contributions from the H^* $1s$ and the C $2s$ and $2p_z$ orbitals, accounts for nearly all of the C—H^* bond, and at the same time has become strongly C—F antibonding.

Finally we compare the calculated orbital energies for CF_3H^* with the experimental results for GaAs(001) after CF_4 plasma exposure, shown in Fig. 5(c). If we add 3 eV to the calculated energies to correct for the systematic error in SCF calculations discussed above, there is quite good agreement between theory and experiment: Not only the uniformity but also the magnitude (about 4.0 eV) of the level shifts with respect to CF_4 are reproduced well. For the uppermost level the agreement is somewhat less good, but one should note that a similar though slightly smaller discrepancy occurs for CF_3H as well. In addition, precisely this highest bonding level will be most sensitive to the less adequate representation of the sp_z-like As dangling orbital by a spherical s orbital. In conclusion, the calculations support our hypothesis that CF_3 radicals are chemisorbed on the As site without significant changes in their internal electronic structure and all of the bonding effects taking place in a bond formed from the sp_z-like As dangling orbital and the carbon sp_z orbital.

V. DISCUSSION

In Sec. IV a model was used in which the substrate was reduced to a pseudohydrogen atom H^*. This simplification seems justified insofar as it provides a good general agreement between experimental and calculated orbital energy positions of the chemisorbed molecule. However, the limitations of the model are also obvious since the electronic structure of the substrate is not properly accounted for. This is reflected in the disagreement between the experimental and theoretical binding energies for the bonding orbital as discussed at the end of Sec. IV B, and in addition the model obviously cannot deal with the observation of an angular anisotropy as shown in Fig. 2. This latter result shows that the surface must have an ordering effect on the chemisorbed molecules. It is possible to calculate the photoemission intensity from localized orbitals on solid surfaces[41,42] and by comparison with experiments to determine the geometry. This is outside the scope of this paper, however, and would require more systematic measurements than are presented here.

In Sec. III we reported the presence of two levels of binding energies of ~36.1 and ~38.1 eV. The levels are very weak and difficult to observe which can be related to a small photoionization cross section. We first note that Banna and Shirley[32] have compared spectra for CF_3H measured using Mg $K\alpha$ radiation (1253.6 eV) and yttrium M_ζ radiation (132.3 eV). The relative intensity of the peaks having $5e$ ($E_b=16$ eV) and $2e$ ($E_b=39$ eV) symmetry characters changes from 1:4 at $h\nu=1253.6$ eV to 1:0.4 at $h\nu=132.3$ eV, indicating that strong photoionization cross-section effects are present. We have therefore compared the expected peak intensities on the basis of calculated atomic photoionization cross sections σ and experimental widths w, setting $I=\sigma/w$. Using the Hartree-Fock-Slater dipole length approximation, Yeh and Lindau[43] calculated σ for all elements up to $Z=103$. Taking the photon energy of 80 eV as representative for the energy used here (72.7 eV) one has $\sigma[\mathrm{F}(2s)]=0.67$ Mb and $\sigma[\mathrm{Ga}(3d)]=8.39$ Mb. The linewidths of the Ga($3d$) level in GaAs is ~1 eV (including both spin-orbit split components). In the adsorbed CF_3 radical (i.e., CF_3H^*) the F($2s$) level is expected to split into two levels of $3a_1$ and $2e$ symmetry having intensity ratios 1:2. The experimental linewidths are ~2 eV. Assuming equal numbers of Ga and F atoms one finds $I[\mathrm{F}(2s,2e)]$ to be about 2% of the Ga($3d$) intensity. The observed signal (see Sec. III) is in the order of 1% of $I[\mathrm{Ga}(3d)]$ which is quite reasonable in view of the estimate that the concentration of chemisorbed radicals is in the submonolayer range.

Considering the effects of the CF_4 plasma exposure upon the substrate surface ample evidence has been found for a strong modification of this, e.g., a change of reconstruction and a decrease of the surface state emission. This can be understood directly in the model of bonding of CF_3 radicals to As surface atoms because the dimer bond will be broken and the dangling bonds will disappear. The core-level results also suggest this model. We note that for the As(3*d*) level the surface contribution S_L is reduced while a new component S_H appears at higher binding energy. Using a simple electrostatic model proposed by Brennan *et al.*,[44] which has been applied to GaAs(001) in a study of the $c(4\times4)$ reconstruction,[45] one may relate a core-level shift to a charge transfer (see Ref. 45 for details). Using a value of 1.9 eV/electron and an energy shift between the bulk component and S_L of $\sim$0.9 eV this implies a charge transfer of $\sim$0.45 electron/surface atom from the surface As atom to the chemisorbed radical. If the energy shift between S_L and S_H ($\sim$1.2 eV) is considered more appropriate an even higher charge transfer ($\sim$0.6 electron/atom) is calculated. Both values are rather large, in agreement with what would be expected on the basis of the electronegative character of the CF_3 radical.

The Ga(3*d*) core-level results also show a large charge transfer, but the number of atoms involved is relatively small when judged on the basis of changes in line shapes. This could be explained by assuming that the bonding of the CF_3 radicals is felt also in the second layer of the substrate changing the charge distribution in that layer too. Another explanation, which we consider more plausible, is that the surface stoichiometry has been changed during the plasma exposure by desorbing some As atoms. A bonding of CF_3 and/or F radicals to the Ga surface atoms formed in this way would lead to the observed strong charge transfer. Because only few Ga surface atoms have been created the change in the Ga(3*d*) line shape is small. With respect to the CF_3 radical-induced valence-band structure for a Ga-terminated GaAs surface we would not expect a very different structure compared to the As-terminated surface, since the energy levels of As and Ga dangling bonds are both close to the top of the valence bands.

In conclusion, the present investigations have demonstrated that photoemission and reflection electron diffraction can be fruitfully used to investigate the effects of a fluoromethane plasma exposure to a semiconductor surface, and the experimental results have largely been explained on the basis of an SCF calculation for a simplified chemisorption model.

ACKNOWLEDGMENTS

We are grateful to S. Gourrier for experimental advice and to M. Schuurmans for valuable discussions. We want to thank the technical staff of Laboratoire pour l'Utilization du Rayonnement Electromagnétique (LURE) and of the Laboratoire de l'Accélérateur Linéaire (Orsay, France) for their help in operating the storage ring. We are indebted to P. S. Bagus for permission to use the MOLECULE-ALCHEMY program package.

---

[1] F. Bartels, L. Surkamp, H. J. Clemens, and W. Mönch, J. Vac. Sci. Technol. B 1, 765 (1983); W. Mönch, in *Festkörper Probleme XXIV*, edited by P. Grosse (Vieweg, Braunschweig, 1984), p. 229.

[2] A. Y. Cho and J. R. Arthur, Prog. Solid State Chem. **10**, 157 (1975).

[3] G. Weimann, Thin Solid Films **56**, 173 (1978).

[4] N. Suzuki, J. Hariu, and Y. Shibata, Appl. Phys. Lett. **33**, 761 (1978).

[5] H. H. Wieder, J. Vac. Sci. Technol. **15**, 4 (1978).

[6] R. P. H. Chang, J. J. Coleman, A. J. Polak, L. C. Feldman, and C. C. Chang, Appl. Phys. Lett. **34**, 237 (1979).

[7] S. Gourrier, A. Mircea, and M. Bacal, Thin Solid Films **65**, 315 (1980).

[8] H. Lüth and R. Matz, Phys. Rev. Lett. **46**, 1652 (1981).

[9] J. Beyer, P. Krüger, A. Mazur, and J. Pollmann, J. Vac. Sci. Technol. **21**, 358 (1982).

[10] F. Manghi, C. M. Bertoni, C. Calandra, and E. Molinari, J. Vac. Sci. Technol. **21**, 371 (1982).

[11] R. D. Bringans and R. Z. Bachrach, J. Vac. Sci. Technol. A **1**, 676 (1983).

[12] F. Antonangeli, C. Calandra, E. Colavita, S. Nannarone, C. Rinaldi, and L. Sorba, Phys. Rev. B **29**, 8 (1984).

[13] P. K. Larsen and J. Pollmann, Solid State Commun. **53**, 277 (1985).

[14] T. Carette, M. Lannoo, G. Allan, and P. Friedel, Surf. Sci. **164**, 260 (1985).

[15] A. R. Calawa, Appl. Phys. Lett. **33**, 1020 (1978).

[16] R. D. Bringans and R. Z. Bachrach, Solid State Commun. **45**, 83 (1983).

[17] K. Kondo, S. Muto, K. Nanbu, T. Ishikawa, S. Hiyamizu, and H. Hashimoto, Jpn. J. Appl. Phys. **22**, L121 (1983).

[18] S. Gourrier, L. Smit, P. Friedel, and P. K. Larsen, J. Appl. Phys. **54**, 3993 (1983).

[19] P. Friedel, P. K. Larsen, S. Gourrier, J. P. Cabanie, and W. M. Gerits, J. Vac. Sci. Technol. B **2**, 675 (1984).

[20] S. Gourrier, P. Friedel, and P. K. Larsen, Surf. Sci. **152/153**, 1147 (1985).

[21] J. W. Coburn, H. F. Winters, and T. J. Chuang, J. Appl. Phys. **48**, 3532 (1977).

[22] H. F. Winters, J. W. Coburn, and E. Kay, J. Appl. Phys. **48**, 4973 (1977).

[23] J. W. Coburn and E. Kay, Solid State Technol. **22**, April 117 (1979).

[24] R. K. Ahrenkiel, L. L. Kazmerski, P. J. Ireland, O. Jamjoum, P. E. Russell, D. Dunlavy, R. S. Wagner, S. Pattillo, and J. Jervis, J. Vac. Sci. Technol. **21**, 434 (1982).

[25] Y. Yamane, K. Yamasaki, and T. Mizutani, Jpn. J. Appl. Phys. **21**, L537 (1982).

[26] R. E. Klinger and J. E. Greene, J. Appl. Phys. **54**, 1595 (1983).

[27] S. W. Pang, G. A. Lincoln, R. W. MacClelland, P. D. De Graff, M. W. Geis, and W. J. Piacentini, J. Vac. Sci. Technol. B **1**, 1334 (1983).

[28] R. H. Burton, C. L. Hollien, L. Marchut, S. M. Abys, G. Smolinsky, and R. A. Gottscho, J. Appl. Phys. **54**, 6663 (1983).

[29] C. R. Brundle, M. B. Robin, and H. Basch, J. Chem. Phys. **53**, 2196 (1970).

[30] A. E. Jones, G. K. Schweitzer, F. A. Grimm, and T. A. Carl-

son, J. Electron. Spectrosc. **1**, 29 (1972/73).

[31] M. S. Banna, B. E. Mills, D. W. Davis, and D. A. Shirley, J. Chem. Phys. **61**, 4780 (1974).

[32] M. S. Banna and D. A. Shirley, Chem. Phys. Lett. **33**, 441 (1975).

[33] J. F. van der Veen, P. K. Larsen, J. H. Neave, and B. A. Joyce, Solid State Commun. **49**, 659 (1984).

[34] P. K. Larsen, J. F. van der Veen, A. Mazur, J. Pollmann, J. H. Neave, and B. A. Joyce, Phys. Rev. B **26**, 3222 (1982).

[35] P. K. Larsen, J. H. Neave, and B. A. Joyce, J. Phys. C **14**, 167 (1981).

[36] MOLECULE: J. Almlof (University of Oslo, Oslo, Norway). ALCHEMY: P. S. Bagus and B. Liu (IBM Laboratories, San Jose, California, USA). Interfacing: U. A. Wahlgren (University of Stockholm, Stockholm, Sweden) and P. S. Bagus.

[37] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

[38] Th. H. Dunning and P. J. Hay, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1970), Vol. 3.

[39] C. G. Thorton, Diss. Abstr. **14**, 604 (1954).

[40] D. R. J. Boyd and H. W. Thompson, Trans. Faraday Soc. **49**, 1281 (1953).

[41] B. W. Holland, Surf. Sci. **68**, 490 (1977).

[42] N. V. Smith, in *Photoemission in Solids I*, edited by M. Cardona and L. Ley (Springer-Verlag Berlin, Heidelberg, 1978), Chap. 6, p. 237.

[43] J. J. Yeh and I. Lindau, Data Nucl. Data Tables **32**, 1 (1985).

[44] S. Brennan, J. Stöhr, R. Jaeger, and J. E. Rowe, Phys. Rev. Lett. **45**, 1414 (1980).

[45] P. K. Larsen, J. H. Neave, J. F. van der Veen, P. J. Dobson, and B. A. Joyce, Phys. Rev. B **27**, 4966 (1983).