# Electrophilic surface sites as precondition for the chemisorption of pyrrole on GaAs(001) surfaces

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We report how the presence of electrophilic surface sites influences the adsorption mechanism of pyrrole on GaAs(001) surfaces. For this purpose, we have investigated the adsorption behavior of pyrrole on different GaAs(001) reconstructions with different stoichiometries and thus different surface chemistries. The interfaces were characterized by x-ray photoelectron spectroscopy, scanning tunneling microscopy, and by reflectance anisotropy spectroscopy in a spectral range between 1.5 and 5 eV. On the As-rich $c(4 \times 4)$ reconstruction that exhibits only nucleophilic surface sites, pyrrole was found to physisorb on the surface without any significant modification of the structural and electronic properties of the surface. On the Ga-rich GaAs(001)-$(4 \times 2)/(6 \times 6)$ reconstructions which exhibit nucleophilic as well as electrophilic surface sites, pyrrole was found to form stable covalent bonds mainly to the electrophilic (charge deficient) Ga atoms of the surface. These results clearly demonstrate that the existence of electrophilic surface sites is a crucial precondition for the chemisorption of pyrrole on GaAs(001) surfaces. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4906117]

## I. INTRODUCTION

Hybrid materials consisting of interfaces between organic layers and solid semiconductors form the basis for a whole new field of applications.[1–4] The understanding of the fundamental properties that determine the interaction between organic materials and semiconductor surfaces, however, is still insufficient and represents a key issue for recent semiconductor research. Several authors have pointed out that semiconductor surfaces need to be understood analogously to organic reagents in order to describe the adsorption processes of organic molecules on semiconductor surfaces.[5–8] In this context, therefore, a central challenge arises from the fact that concepts like, e.g., electrophilicity or cycloaddition reactions that have been established in organic chemistry need to be applied and eventually be adapted for the description of semiconductor surfaces.

Also, it has been shown that the atoms of the Si–Si (Ge–Ge) dimers at the Si(Ge)(100)-$(2 \times 1)$ surface can be regarded as electrophilic (electron deficient) and nucleophilic (electron rich) bonding partners depending on the respective occupation of their dangling bonds.[5–9] In adsorption experiments of the aromatic molecule pyrrole on Si(Ge)(100)-$(2 \times 1)$ surfaces, pyrrole was found to chemisorb at the electron deficient dangling bonds, hence the electrophilic surface sites.

However, the Si(Ge) $(2 \times 1)$ surface always exhibits both nucleophilic and electrophilic surface sites at the same time. A systematic investigation of the influence of the existence of electrophilic surface sites on molecular adsorption

behavior has yet not been performed. In our work, we investigate how far the concept of electrophilicity can also be applied for the description of the reactivity of III-V compound semiconductor surfaces towards the adsorption of organic molecules. GaAs(001) surfaces have been studied extensively over the last decades and provide a large number of well-understood surface reconstructions with different stoichiometries.[10–14] As a consequence, the GaAs(001) surface reconstructions vary particularly in terms of the occupation of their respective surface dangling bonds and thus the number of electrophilic and/or nucleophilic surface sites. The different GaAs(001) surface reconstructions, therefore, form an ideal model system to study the influence of electrophilic and/or nucleophilic surface sites on the adsorption mechanism of organic molecules.

The most As-rich GaAs(001)-$c(4 \times 4)$ reconstruction exhibits a triplet of As–As dimers in the outermost layer bond to As atoms in the second layer. According to the electron-counting rule,[15] the dangling bonds of the surface anions (i.e., the As-atoms) should be fully occupied and hence the $c(4 \times 4)$ reconstruction provides only filled (nucleophilic) dangling bonds at the surface.

For the Ga-rich GaAs(001) surfaces, a $(4 \times 2)$ and a $(6 \times 6)$ reconstructed phases are found which exhibit both surface As atoms with filled dangling bonds as well as surface Ga atoms with empty (electrophilic) dangling bonds in the outermost layer.[14,16–20] The structure models of the three reconstructions investigated here and their respective nucleophilic and/or electrophilic surface sites are depicted in Fig. 1. The Ga-rich and the As-rich surfaces provide surface transitions that contribute to the reflectance anisotropy spectroscopy (RAS) signal and were previously shown to be sensitive to molecular chemisorption.[21,22,25–27]

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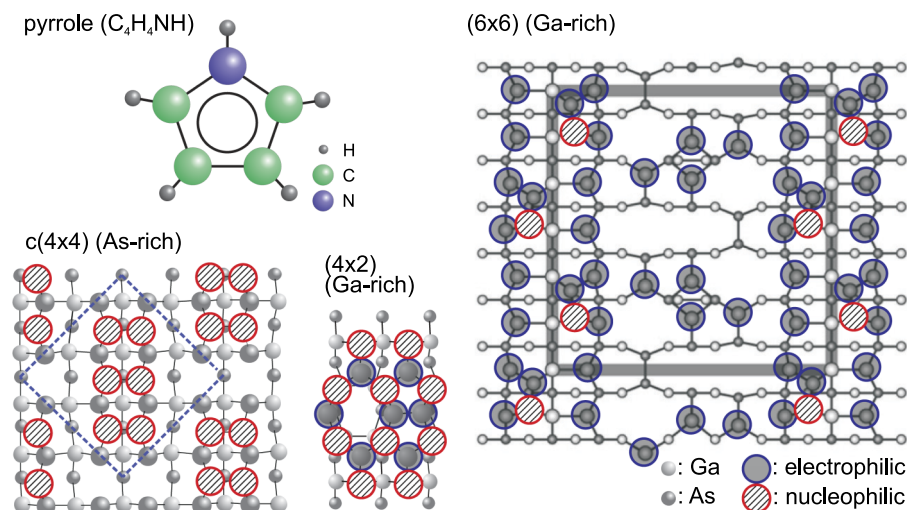b)Electronic mail: patrick.vogt@tu-berlin.de

FIG. 1. Structure model of pyrrole and structure models of the different GaAs(001) reconstructions according to Schmidt *et al.*[28] and Ohtake *et al.*[14,18] The $c(4 \times 4)$ surface provides only nucleophilic surface sites while the $(4 \times 2)$ and the $(6 \times 6)$ surfaces exhibit both nucleophilic and electrophilic surface sites.

For the adsorption experiments, we used pyrrole, a five-membered aromatic ring molecule consisting of four carbon atoms and one NH group. Together with the electron lone pair of the N atom, the $\pi$-electrons of the four carbon atoms form a highly stable aromatic ring.[29,30] A structure model of pyrrole is shown in Fig. 1. Several authors have shown that pyrrole acts as an electron donor when adsorbing on Si or Ge surfaces and adsorbs to electrophilic (electron deficient) surface sites.[6,9,31–33]

## II. EXPERIMENTAL

For the experiments, As-capped GaAs(001) samples were used, grown by molecular beam epitaxy (MBE) with a nominal Si-doping below $n = 1 \times 10^{17}$ cm$^{-3}$. The GaAs samples were thermally decapped, prepared, and analyzed under ultrahigh vacuum (UHV) conditions with a base pressure below $2 \times 10^{-10}$ millibars throughout the experiments.[34] As-rich c(4×4) surfaces were obtained at annealing temperatures of approximately 350 °C. For the preparation of Ga-rich surfaces, the samples were annealed at 540 °C. After this annealing, the Ga-rich surfaces revealed a mixed phase of (4×2) and (6×6) reconstructed areas as discussed in Sec. III. The preparation process was monitored by RAS, and the chemical and structural surface quality was checked by low energy electron diffraction (LEED) and Auger-electron spectroscopy (AES) which particularly proved no detectable C contamination of the sample before molecule deposition.

Pyrrole (Aldrich, purity 98%) was introduced into the chamber from gas-phase through a variable gas-inlet valve. During the deposition of pyrrole, the GaAs(001) surface was kept at room temperature and all filaments inside the chamber were switched off in order to prevent decomposition of the molecules. All deposition amounts are given in Langmuir ($1L = 1.33 \times 10^{-6}$ millibars s). In order to prepare sub-monolayer coverages of pyrrole, the deposition process was monitored *in-situ* by RAS transient measurements as described elsewhere.[23,24,37]

For the RAS measurements, a standard RAS setup was used according to Aspnes *et al.*[35,36] operating between 1.5

and 5 eV. The STM measurements we performed using a RT-Omicron STM1 and electro-chemically etched tungsten tips. All images show filled states and the bias values refer to the sample voltage with respect to the STM tip.

For the XPS measurements, we used a monochromatic Al K$\alpha$ x-ray source ($h\nu = 1486.87$ eV) and a hemispherical PHOIBOS 100 detector (SPECS). The experimental resolution of the XPS apparatus amounted to 450 meV and was determined by measuring the Fermi edge on a molybdenum sample holder being in ohmic contact with the sample. Measurements of the Fermi edge were also used to calibrate the binding energy scale of all XPS spectra. The XPS spectra were measured with an angle of 80° between surface normal and detector. For the identification of bulk and surface components, the As(Ga) *3d* spectra were also measured in normal emission. In Sec. III, only the spectra measured at 80° emission are depicted. The numerical line shape analysis was realized with the help of the software UniFIT 2006 using convoluted Voigt-profiles. For the As/Ga *3d* spectra, we used a Gaussian broadening of $0.58 \pm 0.05$ eV, whereas for the N/C *1s* spectra, the Gaussian broadening amounted to $1.2 \pm 0.05$ eV.

## III. RESULTS

### A. Adsorption configuration of pyrrole on Ga-rich GaAs(001) surfaces

Fig. 2 shows the LEED patterns and the RAS spectra recorded before and after the adsorption of pyrrole on the Ga rich GaAs(001) surface. The LEED pattern shows a (4×2) symmetry. In STM measurements, however, the surface was shown to exhibit also significant (6×6) reconstructed areas. For reasons of convenience, we label this mixed (4×2)/(6×6) phase as Ga-rich (4×2) dominant surface. After the deposition of approximately $2 \times 10^5$ L pyrrole, the LEED pattern shows only (1×1) bulk spots but no reflexes from the initial surface symmetry. In the RAS spectra, significant changes can be observed at the surface transitions S2 (2.2 eV) and S3 (3.5 eV) which are reduced and essentially vanish upon the adsorption of pyrrole. The same changes were also observed
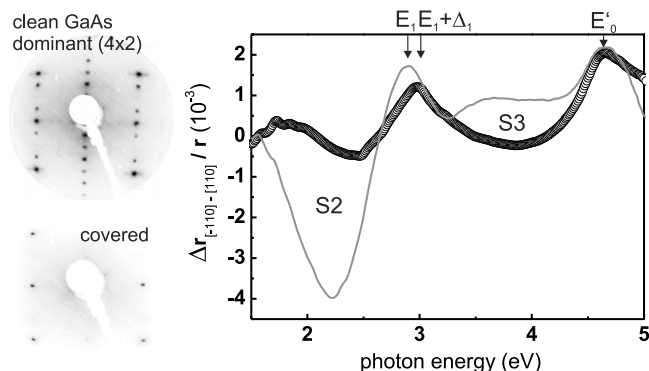
FIG. 2. Left: LEED patterns before and after adsorption of pyrrole on the Ga rich GaAs(001) surface. Right: RAS spectra before (solid line) and after (open circles) the adsorption of pyrrole.
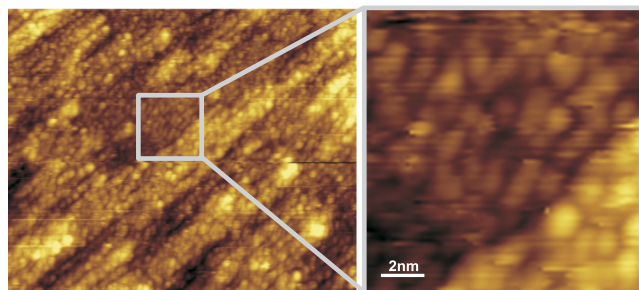


FIG. 3. STM image $U_{gap} = -8.6$ V and $I = 117$ pA after the adsorption of pyrrole on the Ga rich GaAs(001) surface. The image shows a complete layer of bright protrusions of approximately 1.1 nm diameter. On the large scale image (left), also the terrace steps of the GaAs surface can be recognized.

upon the adsorption of cyclopentene molecules on the GaAs (4×2) surface and indicate a chemisorption of the molecules involving a modification or destruction of the surface states contributing to these anisotropies.[21,37]

Fig. 3 shows a STM image of the Ga-rich surface covered with pyrrole molecules. The image clearly shows a complete layer of bright protrusions (1.1 nm diameter each) that originate from the adsorbed molecules as discussed previously.[37] On the large scale STM image (left in Fig. 3), also the terrace structure of the Ga-rich GaAs surface can be recognized. The STM measurements, therefore, show a molecular coverage of around 1 monolayer. The STM images also indicate that the molecules are stably bond to the surfaces within the adsorbed layer so that stable tunneling conditions can be realized. The XPS spectra of the As 3d, Ga 3d, N 1s, and C 1s core levels are depicted in Fig. 4. In the line shape analysis of the Ga 3d core level of the clean surface, three surface components could be identified additional to the bulk component. The most prominent surface component is shifted by $-0.36$ eV relative to the bulk component. This component agrees with the surface component $S_2$ from earlier publications, which is attributed to Ga atoms of the surface Ga–Ga dimers.[38] The other surface Ga atoms of the Ga-rich phase are present in $sp^2$-like condition. The respective surface components shifted to higher binding energies are, therefore, labeled $Ga_{sp^2}$.

In the line shape analysis of the As 3d core level of the clean surface, two surface components could be identified additional to the bulk component. The surface component shifted to lower binding energies is well known to stem from As atoms of the (4×2) reconstructed phase and is, therefore, labeled $As_{4\times2}$.[38–40] The surface component B shifted to higher binding energies is usually not observed at the (4×2) reconstructed phase. In our experiments, we could observe this component only when we observed a significant ($n\times6$) symmetry in LEED. We, therefore, conclude that this surface component B stems from surface As atoms of the (6×6) phase.

After the adsorption of pyrrole, the analysis of the As 3d core level shows a small new component which is shifted by $+0.9$ eV to higher binding energies relative to the bulk component. Such a component was also observed after the adsorption of cyclopentene on the GaAs(001)-$c$(4×4) and can be attributed to As atoms that are involved in a covalent bond to carbon atoms of the adsorbed molecules.[25]

A significant change can also be observed in the Ga 3d core level after adsorption of pyrrole. The surface component related to the Ga atoms of the Ga–Ga dimers is reduced by approximately 70% upon adsorption of pyrrole. Additionally, up to three new components can be identified in the Ga 3d line shape after adsorption of pyrrole. The most pronounced one of these new components is shifted to higher binding energies by $+0.27$ eV relative to the bulk component and can be attributed to Ga–N bondings involving a charge transfer from nitrogen to gallium. This significant modification of the Ga 3d line shape shows that the Ga atoms of the Ga–Ga dimers are involved in covalent bondings to the adsorbed molecules. Altogether, the spectra of the Ga 3d and As 3d core levels indicate the formation of four different bondings between the adsorbed molecules and the surface. For the exact attribution of the new components to specific bondings, the N 1s and C 1s core levels are analyzed in detail.

In the N 1s core level, three components could be identified, one of which can be attributed to N atoms of unmodified adsorbed molecules ($N_{CC}$). The other two components must stem from N atoms that are involved in covalent bondings to the surface. The component which is shifted to higher binding energies can be attributed to N atoms that have lost charge due to the adsorption process most probably due to a dative bonding to the charge attracting (electrophilic) empty dangling bonds of the surface Ga atoms ($N$-$Ga_{dat}$). The larger component that is slightly shifted to lower binding energies ($-0.27$ eV relative to the $N_{CC}$ component) must, therefore, stem from N atoms that have gained charge after the adsorption. We attribute this component to N atoms that have undergone N–H dissociation after the adsorption to the surface Ga atoms.

In the C 1s core level, two components can be identified resulting from C atoms that are not involved in covalent bonds to the surface ($C_{CC}$ and $C_{NC}$). Additional to these components, two more components are found that must result from C atoms that are involved in bondings to the surface. The component shifted to higher binding energies stems from C atoms that have lost charge after the adsorption. We, therefore, attribute this component to C atoms that bonded to the electrophilic surface Ga atoms ($C$-$Ga$). The second component is shifted to lower binding energies and stems from C atoms that have gained charge after the adsorption. We, therefore, attribute this component to C atoms that bonded to the electron rich (nucleophilic) surface As atoms ($C$-$As$).
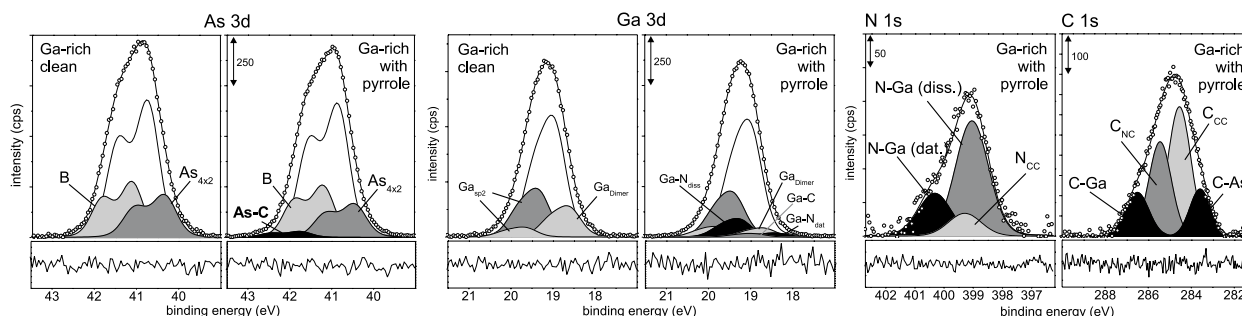
FIG. 4. XPS spectra of the As *3d* (left), Ga *3d* (middle), N *1s*, and C *1s* core levels (right). The As *3d* and Ga *3d* spectra show several new components after the adsorption of pyrrole, which evidences the formation of covalent bonds between the molecules and the GaAs surface.

In principle, the central maximum of the C *1s* spectrum could be fitted with only one component which would then reveal a broadening of 1.6 eV. Such large broadening, however, would be much larger than for the other components and the broadening observed for the C *1s* emission line for the measurements of pyrrole adsorbed on As-rich surfaces (Fig. 8(b)) and is also in good agreement with the values obtained on Si.[9] Hence, a minimum number of four components are required for fitting the C *1s* core level line shape with all components showing a broadening of 1.2 eV, in agreement with the other above mentioned results.

From the XPS spectra, we conclude pyrrole to adsorb preferentially to the electrophilic empty dangling bonds of the surface Ga atoms, particularly of the Ga–Ga dimers. The molecules form dative bondings via the electron lone pair of the N atom to the surface Ga atoms. After this dative bonding, most molecules undergo N–H dissociation as similarly observed for the adsorption of pyrrole on Si(Ge)(100)-(2×1) surface.[9,31]

Additionally, we found indications for C–As and C–Ga bonds. We, therefore, conclude that a minor but significant amount of the adsorbed molecules forms covalent bonds from the carbon atoms to the As and/or Ga atoms of the surface.

We expect these bondings to be formed from the metastable dative bonded adsorption state before the dative bonded molecules undergo N–H dissociation. This conclusion agrees well to recently published observations by Bae *et al.*[41] who investigated pyridine molecules adsorbed on Ge(100) surfaces and found a dative N–Ge bonding which is followed by C–Ge bondings.

Our suggestion for the resulting adsorption configuration is schematically illustrated for the (4×2) phase in Fig. 5. The same reactions as illustrated in Fig. 5 are expected to take place on the (6×6) reconstructed phase. Here, the dissociated $H^+$ atoms can be expected to saturate the occupied dangling bonds located at the As atoms of the mixed Ga–As dimers of the surface.

For the analysis of single adsorbed molecules on the differently reconstructed surface phases, a sub-monolayer coverage of pyrrole was prepared on the Ga-rich GaAs(001) surface by the help of RAS transients, as described in a previous publication.[27] Fig. 6 shows STM images (13×13 nm) of (4×2) and (6×6) reconstructed areas of the Ga rich surface after the deposition of 2000 L of pyrrole. The images of the
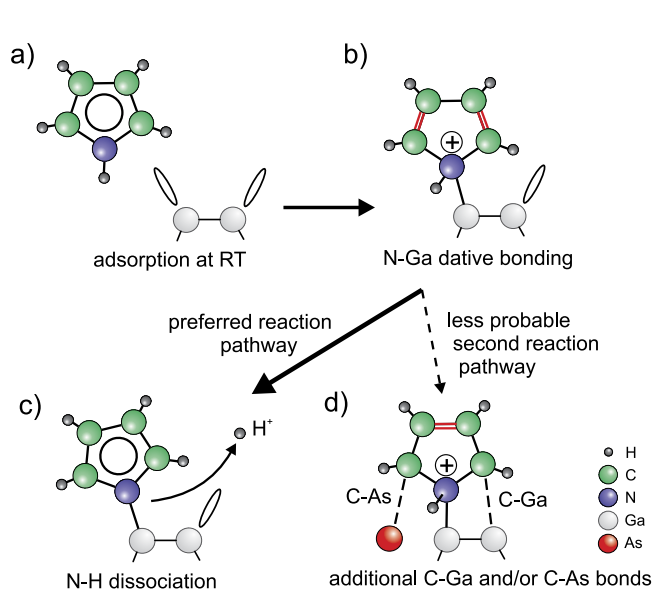


FIG. 5. (a) Structure suggestion for the adsorption configuration of pyrrole on the Ga rich GaAs(001) surface. After dative N–Ga bonding (b), most molecules undergo N–H dissociation (c) while some molecules instead of N–H dissociation form additional C–Ga and/or C–As bonds (d).
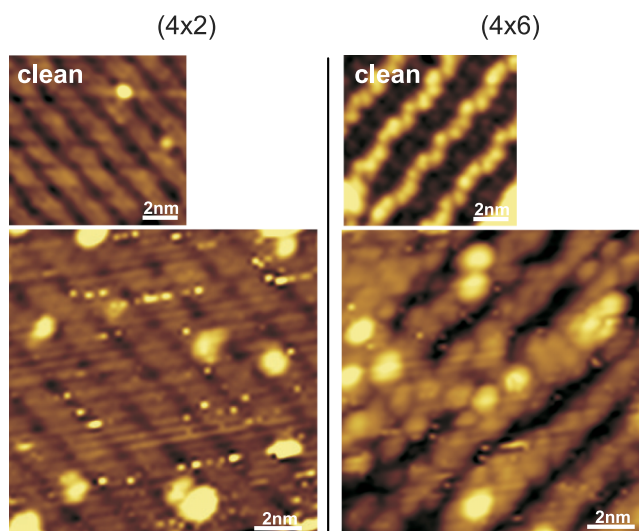


FIG. 6. STM images before (small images, $U_{gap} = -3.4$ V, $I = 131$ pA) and after the adsorption of pyrrole on the Ga rich GaAs(001) surface. The images after pyrrole adsorption (13 × 13 nm; $U_{gap} = -4.15$ V, $I = 149$ pA) show single bright protrusions on the surface. On the (4 × 2) reconstructed area (left), we identified 8 adsorbed molecules; on the (6 × 6) reconstructed area (right), we counted at least 12 adsorbed pyrrole molecules.

clean surface (small images) showing rows along the [110] direction ((6×6)) and [−110] direction ((4×2)) as they are typical for the Ga rich GaAs(001) reconstruction.[13,17] After pyrrole deposition, the single adsorbed molecules can be identified as bright protrusions on top of these rows.

On the (4×2) reconstructed area (left), 8 molecules can be observed as bright protrusions on top of the dimer rows. On the (6×6) reconstructed area (right), an identification of the adsorbed molecules is more difficult than on the (4×2) area because the bright protrusions are also located between the dimer rows and cannot always be distinguished from the structural elements of the clean surface with certainty. We counted at least 12 adsorbed pyrrole molecules on the (6×6) reconstructed area which is 50% more molecules than on the (4×2) reconstructed area.

The fact that significantly more molecules are adsorbed on the (6×6) reconstructed area, which exhibits more electrophilic surface sites, indicates that the amount of electrophilic surface sites determines the probability of the adsorption of pyrrole. At present, we cannot provide a statistical analysis to derive more detailed conclusions about this particular aspect but the general trend seems clear.

## B. Adsorption configuration of pyrrole on As-rich GaAs(001)-$c$(4×4)

After deposition of pyrrole on the $c$(4×4) reconstructed GaAs(001) surface, all performed measurements show a significantly different behavior compared to the previously described (4×2) reconstruction.

In Fig. 7(a), the RAS spectra are depicted of the GaAs(001)-$c$(4×4) surface before (solid line) and after (open circles) the deposition of pyrrole. It can clearly be seen that the spectrum is not modified significantly upon pyrrole adsorption. Particularly, the anisotropies S1 (below 2 eV) and S2 (4 eV) related to transitions between surface states localized at the As–As dimers are not changed upon molecule adsorption. Also the LEED pattern after pyrrole deposition still shows the $c$(4×4) symmetry of the clean surface.

It is well known that the surface RAS signature is modified significantly if covalent bonds are formed between adsorbed molecules and the substrate surface.[21,25,42] The RAS spectra, therefore, indicate that pyrrole physisorbs on the $c$(4×4) surface but does not form covalent bonds to the surface.
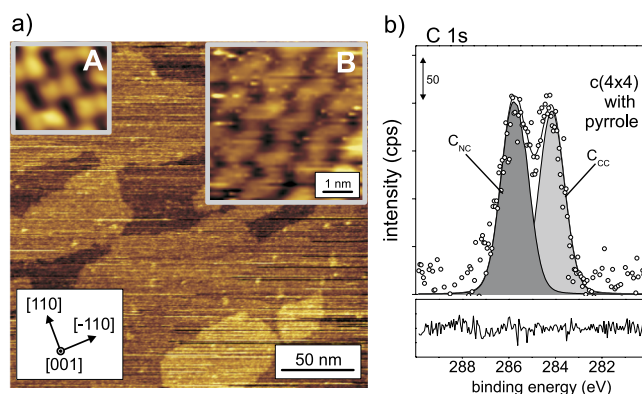


FIG. 8. (a) STM measurements $U_{gap} = -5.37$ V and $I = 95$ pA at the $c$(4×4) surface after deposition of pyrrole. Inset A shows a small scale image of the clean surface for comparison. The images after pyrrole deposition (inset B) only show structural features of the GaAs surface but not the adsorbed molecular layer. Although not visible in the image themselves, the adsorbed molecules have an effect on the STM measurements by causing less stable tunneling conditions. (b) XPS spectrum of the C $1s$ core level after pyrrole deposition on the As-rich GaAs surface. Two species of carbon could be identified related to the two different bonding configurations ($C_{NC}$ and $C_{CC}$) within the adsorbed pyrrole molecules.

A line shape analysis of the As $3d$ spectra before and after the deposition of pyrrole (not depicted but discussed elsewhere[23]) revealed that the As $3d$ spectrum does not experience any significant changes upon the adsorption of pyrrole. This indicates that no covalent bonds are formed between pyrrole and the As-rich GaAs surface.

Fig. 8(b) shows the C $1s$ core level after deposition of pyrrole. In the spectrum, two species of carbon can be identified, which stem from the two different bonding configurations ($C_{NC}$ and $C_{CC}$) of carbon atoms within the adsorbed pyrrole molecules. In the N $1s$ spectrum (not depicted), only one component could be resolved. These observations within the XPS spectra clearly show that there are no indications for covalent bond formation between the adsorbed molecules and the As-rich GaAs(001) surface. Still, the C $1s$ and N $1s$ spectra reveal that a layer of pyrrole molecules is present on the surface. It can be seen that the energetic positions of the $C_{NC}$ and $C_{CC}$ are different here as compared to the respective components in Fig. 4. This shift indicates that the electronic states of the C atoms of the molecules adsorbed on the Ga-rich surface are modified as a consequence of the covalent bond formation between the molecule and the GaAs surface.

Fig. 8(a) shows STM images of the As-rich GaAs surface after the deposition of pyrrole (400×400 nm, $U_G = -6$ V (large image) and $U_G = -5.4$ V (inset B)). The large scale image shows the terraces which are typical for $c$(4×4) reconstructed surfaces.[12,13] Also in the small scale STM image (inset B) of the surface after pyrrole adsorption, the typical "brickstone-like" structures of the As–As dimer triplets (inset A) can be observed. Besides these features of the GaAs surface (terraces and dimer triplets), the adsorbed molecular layer itself could not be imaged. This behavior has been described and discussed in detail elsewhere[23] and creates the impression that the molecules were either moved around by the tip during the STM measurements or that the images were obtained by tunneling through the adsorbed molecular layer.
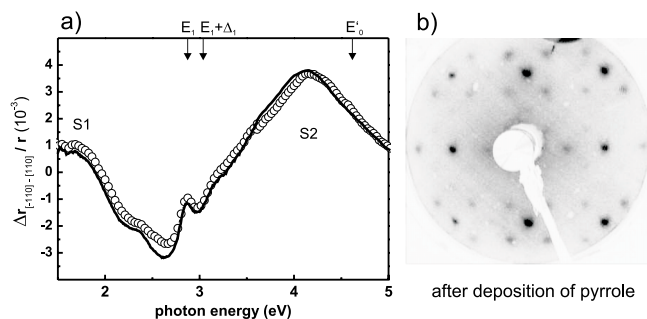


FIG. 7. (a) RAS spectra before (solid line) and after (open circles) the deposition of pyrrole on the GaAs(001)-$c$(4 × 4) surface. (b) LEED pattern (47 eV) of the $c$(4 × 4) surface after the adsorption of pyrrole.

All observations with RAS, STM, and XPS clearly show an adsorption behavior of pyrrole on the As-rich surface which is significantly different from the adsorption of pyrrole on the Ga rich $(4 \times 2)$ reconstructed surface. The fact that the RAS signature does not change upon pyrrole adsorption reveals that the surface states and related optical transitions which are located at the topmost As dimers remain intact after pyrrole adsorption. This could not be the case if covalent bonds were formed between the adsorbed pyrrole molecules and the GaAs surface.

In conclusion, our measurements show that pyrrole physisorbs on the $c(4 \times 4)$ surface and does not form any covalent bonds to the surface atoms as similarly observed by Chen et al. for the adsorption of ethylene molecules $(C_2H_4)$ on As terminated GaAs(100) surfaces.[43]

## C. Discussion

The experiments performed on the adsorption behavior of pyrrole on the As-rich and the Ga-rich GaAs(001) surfaces show remarkable differences between the $c(4 \times 4)$ surface and the $(4 \times 2)$ surface.

All measurements show a weak physisorption of the pyrrole molecules on the GaAs $c(4 \times 4)$ surface but give no evidence for covalent bonds between pyrrole and the GaAs surface. Neither is the RAS signature affected by the pyrrole adsorption nor do we find any modification of the As $3d$ line shape upon adsorption of pyrrole on the $c(4 \times 4)$ surface.

At the Ga-rich GaAs(001) surface, the anisotropies from surface transitions are significantly reduced upon the adsorption of pyrrole. In the XPS spectra of the As $3d$, Ga $3d$, N $1s$, and C $1s$ core levels, we found clear evidence for the formation of covalent bonds between the adsorbed pyrrole molecules and the surface atoms. The preferred bonding sites are the empty dangling bonds of the Ga–Ga dimer atoms. For the adsorption configuration, we suggest that pyrrole undergoes dative bonding via the electron lone pair of the N atom. After this dative bonding, most molecules experience N–H dissociation. Those molecules that do not experience N–H dissociation can additionally form covalent bonds from the C atoms to the As and/or Ga atoms to the surface as similarly reported by Bae et al. for the adsorption of pyridine on the Ge(100)-$(2 \times 1)$ surface.[41]

As described above, the GaAs surface reconstructions differ in terms of the occupation of the respective dangling bonds as a consequence of their different stoichiometries. At the As-rich phase, the GaAs(001) surface provides only filled dangling bonds which are to be regarded as nucleophilic sites. At the Ga-rich phase, the GaAs(001) surface provides (nucleophilic) filled dangling bonds as well as empty dangling bonds which are electrophilic. All experiments on the adsorption of pyrrole on Si(100)-$(2 \times 1)$ show that pyrrole always chemisorbs at the electrophilic down atom of the Si–Si dimer.[6,9,31,32] In agreement with these observations at Si(Ge) surfaces, our investigations show that pyrrole can only chemisorb at the Ga-rich GaAs surface, while the exclusively filled dangling bonds at the As-rich $c(4 \times 4)$ surface prevent a chemisorption and lead to a weak interaction between pyrrole and GaAs(001)-$c(4 \times 4)$. These findings are summarized in Fig. 9.
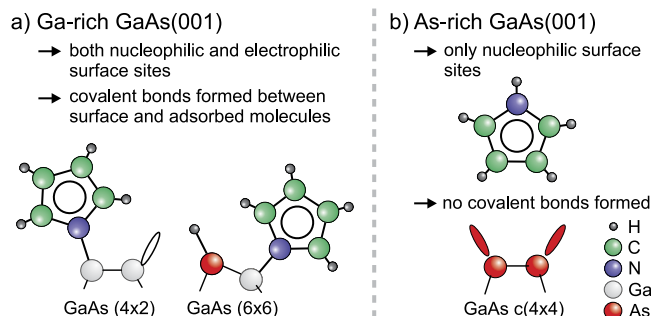


FIG. 9. Overview over the results obtained in this work about the adsorption of pyrrole on GaAs surfaces. (a) At Ga-rich surfaces with electrophilic surface sites, pyrrole was found to chemisorb preferredly at the surface Ga atoms. (b) At As-rich GaAs surfaces with only nucleophilic surface sites, it was found that no covalent bonds are formed between pyrrole and the GaAs surface.

From the comparison of the pyrrole adsorption on the Ga-rich $(6 \times 6)$ phase to the adsorption on the $(4 \times 2)$ phase, we found that the adsorption probability of pyrrole is higher the more electrophilic surface sites exist at the surface. We, therefore, conclude that the existence of electrophilic surface sites is a crucial precondition for the chemisorption of pyrrole on III-V surfaces. These results can, therefore, provide an important contribution to the controlled junction of molecular layers on III-V semiconductors.

## IV. SUMMARY

We have compared the adsorption behavior of pyrrole on the As-rich and on the Ga-rich phase of GaAs(001). Our results show the formation of stable covalent bonds between pyrrole and the Ga-rich GaAs(001) surface. At the As-rich GaAs(001)-$c(4 \times 4)$ reconstruction, all observations show a weak physisorption of the adsorbed pyrrole molecules without any structural modification of the underlying GaAs surface. The adsorption mechanism of pyrrole on GaAs(001) surfaces was, therefore, found to be crucially dependent on the stoichiometry of the surface because of the existence of empty dangling bonds that can be regarded as electrophilic surface sites.

[1]R. J. Hamers, Nature **412**, 489 (2001).
[2]C. Joachim, J. K. Gimzewski, and A. Aviram, Nature **408**, 541 (2000).
[3]C. Sanchez, B. Julian, P. Belleville, and M. Popall, J. Mater. Chem. **15**, 3559 (2005).
[4]M. Stutzmann, J. A. Garrido, M. Eickhoff, and M. S. Brandt, Phys. Status Solidi A **203**, 3424 (2006).
[5]S. F. Bent, Surf. Sci. **500**, 879 (2002).
[6]M. Filler and S. F. Bent, Prog. Surf. Sci. **73**, 1 (2003).
[7]R. J. Hamers, Annu. Rev. Anal. Chem. **1**, 707 (2008).
[8]F. Tao, S. L. Bernasek, and G.-Q. Xu, Chem. Rev. **109**, 3991 (2009).
[9]X. Cao, S. K. Coulter, M. D. Ellison, H. Liu, J. Liu, and R. J. Hamers, J. Chem. Phys. B **105**, 3759 (2001).
[10]J. Falta, R. M. Tromp, M. Copel, G. D. Pettit, and P. D. Kirchner, Phys. Rev. Lett. **69**, 3068 (1992).
[11]A. Ohtake, P. Kocán, K. Seino, W. G. Schmidt, and N. Koguchi, Phys. Rev. Lett. **93**, 266101 (2004).
[12]D. K. Biegelsen, R. D. Bringans, J. E. Northrup, and L.-E. Swartz, Phys. Rev. B **41**, 5701 (1990).
[13]Q.-K. Xue, T. Hashizume, and T. Sakurai, Appl. Surf. Sci. **141**, 244 (1999).
[14]A. Ohtake, Surf. Sci. Rep. **63**, 295 (2008).
[15]M. D. Pashley, Phys. Rev. B **40**, 10481 (1989).

[16]S.-H. Lee, W. Moritz, and M. Scheffler, Phys. Rev. Lett. **85**, 3890 (2000).

[17]P. Kocán, A. Ohtake, and N. Koguchi, Phys. Rev. B **70**, 201303(R) (2004).

[18]A. Ohtake, P. Kocán, J. Nakamura, A. Natori, and N. Koguchi, Phys. Rev. Lett. **92**, 236105 (2004).

[19]A. Ohtake, Phys. Rev. B **75**, 153302 (2007).

[20]K. Seino, W. G. Schmidt, and A. Ohtake, Phys. Rev. B **73**, 035317 (2006).

[21]R. Passmann, M. Kropp, T. Bruhn, B. O. Fimland, F. L. Bloom, A. C. Gossard, W. Richter, N. Esser, and P. Vogt, Appl. Phys. A **87**, 469 (2007).

[22]A. Ohtake, J. Nakamura, S. Tsukamoto, N. Koguchi, and A. Natori, Phys. Rev. Lett. **89**, 206102 (2002).

[23]T. Bruhn, B. O. Fimland, N. Esser, and P. Vogt, Phys. Rev. B **85**, 075322 (2012).

[24]T. Bruhn, B. O. Fimland, N. Esser, and P. Vogt, Surf. Sci. **617**, 162 (2013).

[25]R. Passmann, T. Bruhn, T. A. Nilsen, B. O. Fimland, M. Kneissl, N. Esser, and P. Vogt, Phys. Status Solidi B **246**, 1504 (2009).

[26]T. Bruhn, R. Passmann, B. O. Fimland, M. Kneissl, N. Esser, and P. Vogt, Phys. Status Solidi B **247**, 1941 (2010).

[27]T. Bruhn, B. O. Fimland, M. Kneissl, N. Esser, and P. Vogt, Phys. Rev. B **83**, 045307 (2011).

[28]W. G. Schmidt, F. Bechstedt, K. Fleischer, C. Cobet, N. Esser, W. Richter, J. Bernholc, and G. Onida, Phys. Status Solidi A **188**, 1401 (2001).

[29]U. Nygaard *et al.*, J. Mol. Struct. **3**, 491 (1969).

[30]B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, J. Chem. Phys. **24**, 720 (1956).

[31]M. H. Qiao, F. Tao, Y. Cao, and G. Q. Xu, Surf. Sci. **544**, 285 (2003).

[32]M. H. Qiao, Y. Cao, J. F. Deng, and G. Q. Xu, Chem. Phys. Lett. **325**, 508 (2000).

[33]G. T. Wang, C. Mui, J. F. Tannaci, M. A. Filler, C. B. Musgrave, and S. F. Bent, J. Chem. Phys. B **107**, 4982 (2003).

[34]U. Resch-Esser *et al.*, Surf. Sci. **352**, 71 (1996).

[35]D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, Appl. Phys. Lett. **52**, 27 (1988).

[36]D. E. Aspnes, J. P. Harbinson, A. A. Studna, and L. T. Florez, J. Vac. Sci. Technol. A **6**, 1327 (1988).

[37]T. Bruhn, B. O. Fimland, M. Kneissl, N. Esser, and P. Vogt, J. Nanopart. Res. **13**, 5847 (2011).

[38]G. Le Lay, D. Mao, A. Kahn, Y. Hwu, and G. Margaritondo, Phys. Rev. B **43**, 14301 (1991).

[39]I. M. Vitomirov, A. Raisanen, A. C. Finnefrock, R. E. Viturro, L. J. Brillson, P. D. Kirchner, G. D. Pettit, and J. M. Woodall, Phys. Rev. B **46**, 13293 (1992).

[40]K. Ono, T. Mano, K. Nakamura, M. Mizuguchi, S. Nakazono, K. Horiba, T. Kihara, H. Kiwata, I. Waki, M. Oshima, N. Koguchi, and A. Kakizaki, in *Proceedings of the 25th International Conference on the Physics of Semiconductors*, *Osaka*, *2000* (Springer, 2000), Vol. 293.

[41]S. S. Bae, S. Kim, and J. W. Kim, Langmuir **25**, 275 (2009).

[42]Y. Borensztein, O. Pluchery, and N. Witkowski, Phys. Rev. Lett. **95**, 117402 (2005).

[43]Y. Chen, J. Schmidt, L. Siller, J. C. Barnard, and R. E. Palmer, Phys. Rev. B **58**, 1177 (1998).