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Adsorption-state-specific C 1*s* core-level chemical shifts of thiophene on Si(111)7$\times$7 by photoemission spectroscopy at 340 eV

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The room-temperature adsorption of thiophene on Si(111)7$\times$7 has been investigated using photoemission with monochromatic synchrotron radiation at 340-eV photon energy. The presence of two C 1*s* photopeaks at room temperature is consistent with the observation of two molecular-desorption states and with an earlier proposed adsorption model of thiophene on Si(111)7$\times$7 (that involves a surface-parallel π-bonded geometry and a σ-bonded geometry through the sulfur atom). The C 1*s* photoemission spectra have also been collected after annealing the sample to different temperatures. Although the observed core-level chemical shifts and the temperature dependence of the two photopeaks are consistent with the thermal-desorption data in the framework of a simple charge-transfer model, correlation between the photopeaks and thermal-desoprtion data cannot be used to unambiguously identify the nature of the proposed adsorption structures for the adsorption states. Some of the potential difficulties involved in this type of common practice will be discussed.

The studies of cyclic hydrocarbons on Si surfaces have attracted recent attention because of the unexpected surface reactivity observed. In particular, recent studies of Si(111)7$\times$7 carried out in our laboratory[1–3] and of Si(111)2$\times$1 by other groups[4–6] have demonstrated the high reactivity of these semiconductor surfaces towards cyclic olefins. Not only adsorption of a series of homologous five-membered and six-membered cyclic olefins, including thiophene, furan,[1] and benzene[2] has been observed at room temperature (RT), strong evidence of catalytic dehydrogenation surface reactions of cyclohexene and cyclohexadienes as well as their methyl-substituted derivatives has also been obtained for Si(111)7$\times$7.[3] Furthermore, π-conjugated heteroaromatic compounds such as thiophene and pyrrole have attracted practical interest as plausible candidates as the basic building blocks of the so-called conductive polymers,[7] which are found to have valuable technological properties.[8]

Very recently, we reported a thermal desorption spectrometric (TDS) study of the room-temperature adsorption of thiophene and related five-membered cyclic olefins on clean and modified Si(111)7$\times$7 surfaces.[1] By comparing the desorption profiles of these olefins, information about their interactions with the surface has been obtained. This work[1] also provides an interesting comparison with the results of a series of photoemission and electron energy loss studies of Piancastelli *et al.*, who reported desulfurization of thiophene[4,5] and deoxygenation of furan on Si(111)2$\times$1 for room-temperature exposure.[6] At low temperature (85 K), however, no fragmentation was found and two adsorption states were reported.[4–6] It was further proposed that the adsorption states for thiophene at low temperature involved a π-bonded geometry and a σ-bonded geometry resulting from the breakage of a C_α-H bond.[4] In the case of room-temperature adsorption of thiophene on Si(111)7$\times$7, we have found two molecular desorption states which, unlike the proposed adsorption geometries for the 2$\times$1 surface,[4] are thought to involve no C-H bond breakage but rather a σ bonding through the lone-pair electrons of the heteroatom, and a π-bonded geometry.[1] The proposed adsorption structures of thiophene on Si(111)7$\times$7 are found to be quite general and appear to be consistent with the TDS results for furan, cyclopentadiene, cyclopentene, and other related derivatives on clean, sputtered, and oxidized Si(111)7$\times$7 surfaces.[1]

In the present work, we present a C 1*s* photoemission study of the room-temperature adsorption of thiophene on Si(111)7$\times$7 using monochromatic synchrotron radiation at 340 eV photon energy. The temperature dependence of the C 1*s* photopeaks is found to be in qualitative accord with our thermal-desorption results and the proposed model. However, ambiguities exist when detailed correlation between TDS data and photoemission data is attempted.

The photoemission experiments were conducted at the Grasshopper beamline of the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center of the University of Wisconsin at Madison. The UHV chamber was pumped by a 500 liters/s ion pump and a titanium sublimation pump to a base pressure better than 7×10^{-10} Torr. The chamber was equipped with an ion sputtering gun and a four-grid reverse-view low-energy electron diffraction (LEED) optics (capable also of retarding field Auger electron spectroscopy). The Si substrate (20×10 mm^2) was cut from a polished *n*-type Si(111) wafer with a resistivity of 10–30 Ω cm. It was attached to a Ta sample plate mechanically by Ta strips spot welded to the sample plate. The Si surface was precleaned by repeated cycles of Ar$^+$ ion sputtering at 500 eV for 30 min followed by annealing to 1150 K for 5 min (which was achieved by electron bombardment of the backside of the sample plate). Subsequent cleaning could be achieved by repeated flashings of the crystal to 1200 K for 1 min until a sharp 7$\times$7 LEED pattern was obtained. The sample could also be annealed radiatively by a heated tungsten filament. The absolute accuracy of the temperature measurement, as provided by *K*-type Chromel-

Alumel thermocouple attached to the front face of the Si sample (using Ta strips spot welded to the sample plate), was generally limited by various constraints in the existing setup and was estimated to be ±30 K. Exposures were controlled by a variable leak valve and were determined by the ambient chamber pressure using an uncalibrated ionization gauge. All exposures were performed with the sample held at room temperature. Thiophene was obtained commercially (Aldrich) at over 99% purity. Dissolved gases such as nitrogen and oxygen were minimized from the liquid sample by repeated freeze-pump-thaw cycles prior to use.

The Mark IV Grasshopper monochromator with a 1800 lines/mm grating for the 50-μm entrance and exit slits provided usable photons from 80 to 400 eV.[9] A Leybold-Heraeus LHS-11 photoelectron spectrometer (of 254 mm mean diameter) was used to record the spectra.[10] The resolving power of this spectrometer was estimated to be 125. Photoemission experiments have been performed at several photon energies and with the surface normal oriented approximately 45° with respect to the polarization vector of the light. The acceptance angle (±10° half angle) of the spectrometer system was too large to allow investigation of angle-dependent and/or polarization effect. Only the valence-band spectra collected at 90 eV photon energy and C 1*s* spectra recorded at 340 eV photon energy will be reported for a saturation coverage of thiophene on Si(111)7×7 at RT and after subsequent annealing to different temperatures. The overall instrumental energy resolutions at 90 and 340 eV photon energy, with the pass energy of the analyzer set at 25 eV, are estimated to be 0.22 and 1.41 eV full width at half maximum (FWHM), respectively.

The TDS profiles of thiophene on Si(111)7×7 measured as a function of RT exposure were given in our earlier work.[1] In Fig. 1, we show a typical TDS profile of 600 L ($1\ \mathrm{L}=1\times10^{-6}$ Torr s) of thiophene exposed to Si(111)7×7 at room temperature, together with the proposed adsorption geometries. Evidently, two adsorption phases were observed for the room-temperature exposure: a (zeroth order) α phase with a desorption maximum at ~360 K, and a (first-order) β phase with a desorption maximum at 420 K.[1] The α phase is believed to involve a near-surface-parallel π-bonded geometry while the β phase corresponds to an upright or tilted geometry involving σ bonding through the sulfur atom.

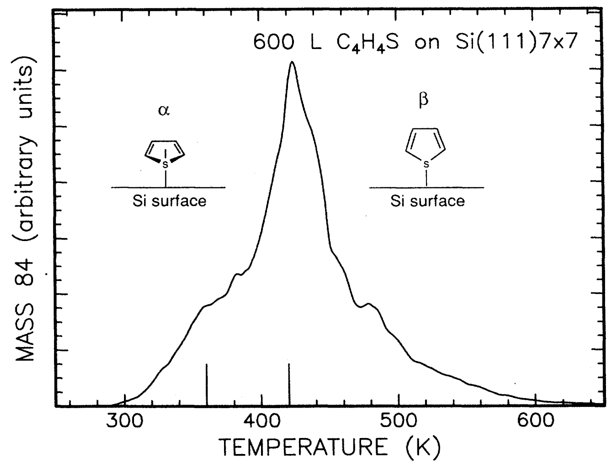

FIG. 1. Thermal-desorption profile of mass 84 (parent mass) for a 600-L room-temperature exposure of thiophene on Si(111)7×7. The desorption maxima for the α phase (at ~360 K) and β phase (at 420 K) are indicated by vertical bars.

Figure 2 shows the valence-band photoemission spectra of 600 L of thiophene exposed to Si(111)7×7 at RT and after annealing to 370 and 1100 K, which were obtained at a photon energy of 90 eV. It should be noted that the sample was allowed to cool back to RT after each annealing before the photoemission spectra were recorded. In particular, five dominant features with maxima at 4, 7, 10, 17, and 26 eV, with the peak at ~7 eV being the most intense one, are observed. Interpretation of the constituent molecular-orbital characters of these bands is usually made by comparison with the gas-phase valence-shell photoelectron data.[11] The observed features are found to be similar to those observed for condensed thiophene on metal surfaces, including, for example, a Pt electrode,[12] Pt(111),[13] and Mo(100) surfaces.[14] Furthermore, valence-band photoemission spectra of thiophene on Si(111)2×1 at 60 K and RT obtained at 40 eV photon ergy have been reported by Piancastelli *et al.*[5] In particular, the small difference in the sharpness of the observed features in the photoemission spectra recorded at 60 K and RT for the 2×1 surface has been used by Piancastelli *et al.* as evidence for the desulfurization of thiophene at RT. However, the reported RT valence-band spectrum for thiophene on the 2×1 surface is found to be very similar to that for the 7×7 surface observed in the present work [Fig. 2(a)]. The two molecular-desorption phases found in our earlier TDS data[1] (Fig. 1) clearly indicate that decomposition of thiophene is not possible for the 7×7 surface. We therefore conclude that the valence-band photoemission data of Piancastelli *et al.* may not be particularly discriminative to allow identification of surface species with sufficient sensitivity;

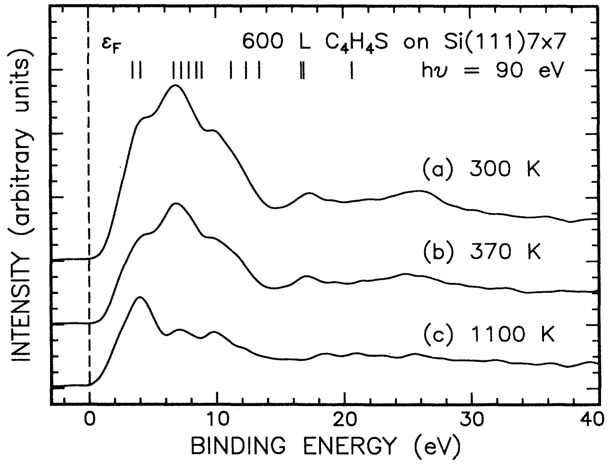

FIG. 2. Valence-band photoemission spectra of a 600-L room-temperature exposure of thiophene on Si(111)7×7 collected with a photon energy of 90 eV at (a) room temperature and after subsequent annealing to (b) 370 K and (c) 1100 K. The vertical bars correspond to vertical ionization potentials of the valence shell of gas-phase thiophene (Ref. 11) red shifted by 5.4 eV.

however, the apparent core-level energy shifts found in their S 2*p* and C 1*s* photoemission data obtained at two different temperatures could indeed be used to indicate the possible presence of different adsorbed (molecular or fragmented) species on the 2×1 surface.[5] Figure 2(b) shows marginal changes in the special intensities of the observed features after the sample has been annealed to 370 K. There are, however, substantial changes in the photoemission spectrum for the sample after annealing to 1100 K [Fig. 2(c)]. In particular, the peak at 4 eV becomes the most intense peak. There is also evidence of a weak shoulder at 2 eV, which corresponds to one of three well-known surface states (S_3) of a clean 7×7 surface.[15] It should be noted that the sharp 7×7 LEED pattern of the clean Si(111)7×7 surface generally became diffuse after RT exposure to thiophene. The high-temperature anneal to 1100 K restored the diffuse LEED pattern to a sharp 7×7 pattern, indicative of complete desorption of the adsorbed thiophene and regeneration of the clean Si(111)7×7 surface.

Figure 3 shows the C 1*s* photoemission spectra of 600 L of thiophene exposed to Si(111)7×7 at RT and after annealing to 370 and 1100 K. These spectra were recorded at a photon energy of 340 eV, which corresponds approximately 50 eV above the ionization threshold where the electron mean free path is believed to be minimal (~3 atomic layers).[16] By fitting two Gaussian line shapes, with individual widths (2 eV) and an energy separation (2.2 eV) determined empirically, to the photoemission spectra, we could identify two photopeaks with maxima at 287.5 and 289.7 eV. The photoelectron work of Gelius *et al.* reported a single peak at ~290.4 eV for gas-phase thiophene and further showed that the C 1*s* core levels are separated by 0.34±0.12 eV, which corresponds to an "intrinsic" chemical shift between the binding energies of two pairs of C atoms with equivalent chemical environments (i.e., C_α's and C_β's) in a thiophene molecule.[17] On the other hand, the photoemission study of condensed thiophene thin films ("bulk") by Clark and Lilley reported a binding energy value of 285.0±0.2 eV for the two pairs of C atoms in thiophene.[18] The difference between the C 1*s* binding energy values for the gas phase and condensed phase has been attributed to relaxation effect.[19] Evidently, the chemical shift between the two C_α and C_β atoms of thiophene is found to be small in both gaseous (<0.5 eV) (Ref. 17) and condensed phases (<0.2 eV).[18] Each of the broad C 1*s* photopeaks observed in the present work may therefore be regarded as consisting of two narrower profiles corresponding to the different chemical environments of C_α and C_β atoms in an adsorbed thiophene molecule. The experimental widths (2 eV FWHM) for these photopeaks are found to be in good accord with the instrumental width (~1.4 eV FWHM) and the contribution from an "intrinsic" chemical shift similar to those determined by the previous studies.[17,18] The two broad photopeaks, separated by an "extrinsic" chemical shift, therefore correspond to thiophene in two different adsorption geometries, which are consistent with the presence of two molecular-desorption phases as shown in our TDS results (Fig. 1).[1] It is of interest to note that photoabsorption studies on a monolayer coverage of thiophene on Pt(111) appear to indicate that the C 1*s* edge of thiophene in the monolayer phase occurs between the bulk (i.e., multilayer) and gas-phase values.[20] Furthermore, the photoemission spectrum for a 100 L RT exposure of thiophene on Si(111)2×1 reported by Piancastelli *et al.*[5] shows the presence of a photopeak at ~289.5 eV with a width of 2.2 eV FWHM. This RT spectrum was found to be different from the photoemission spectrum for 50 L of thiophene exposed at 50 K at the same surface but allowed to warm to RT. In particular, the small decreases in the energy position (0.4) and width (0.7 eV) of the C 1*s* photopeak observed in the latter case led Piancastelli *et al.* to hypothesize further fragmentation of the adsorbed C_4H_4 fragment.[5]

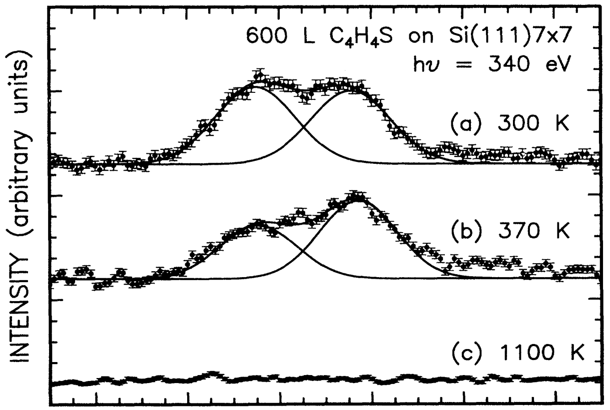

FIG. 3. Core-level C 1*s* photoemission spectra of a 600-L room-temperature exposure of thiophene on Si(111)7×7 collected with a photon energy of 340 eV at (a) room temperature and after subsequent annealing to (b) 370 K and (c) 1100 K.

Figure 3(b) shows that annealing the sample to 370 K gave rise to a reduction in the intensity of the photopeaks at 287.5 eV while the intensity of the photopeaksat 289.7 eV remained essentially unchanged. Further annealing the sample to 1100 K removed the C 1*s* features entirely, indicating complete desorption of the adsorbed thiophene [Fig. 3(c)]. The preferential removal of the photopeaks at 287.5 eV after the 370 K anneal appears to be consistent with the TDS result of thiophene on Si(111)7×7. In particular, the temperature dependence of the photopeaks suggests that the π-bonded α phase at ~360 K corresponds to the photopeak at 287.5 eV while the β phase, which involves σ bonding through the sulfur atom, corresponds to the photopeak at 289.7 eV.

A comprehensive review of core-level chemical shifts at surfaces and in solids has been given by Egelhoff.[21] For the present purpose, the observed C 1*s* chemical shift can be understood qualitatively by simple consideration of charge transfer.[22] In particular, we can consider the effect of surface bonding of the Si surface on a "free" thiophene molecule. The charge transfer from the dangling bond of a Si surface atom to the π bond of an adsorbed thiophene molecule in the α phase results in negatively charged C atoms in the five-membered ring. A more negatively charged C atom, relative to that of free thiophene, tends to have a higher (i.e., less stable) electronic (C 1*s*) energy level, which in turn leads to a correspondingly smaller binding energy as observed. In the case of thiophene in the β adsorption phase, the charge transfer from the Si dangling bond to the heteroatom (the σ bond) causes a negatively charged S atom, which could in turn induce charge transfer to the C atoms due to the aromaticity of the heterocycle. However, the σ bonding through the heteroatom is expected to be more localized than the direct interaction involving the π electrons of the five-membered ring as for the α adsorption phase. Apparently, the smaller core-level chemical shift (with respect to free thiophene) observed for the β phase is consistent with the above proposal, that the negative charge transfer to the C atoms for the β phase is less than that for the π-bonded α phase.

While the above simple argument may offer some qualitative understanding on the observed core-level chemical shifts, many important questions remain. For instance, the 2.2 eV difference found for the "extrinsic" chemical shifts between the two proposed adsorption phases is of considerable magnitude, which suggests quite different chemical environments for the proposed adsorption phases. A more quantitative theory (involving the proposed charge-transfer model) that could explain the observed difference is clearly of interest. Furthermore, the connection between the presently observed core-level chemical shifts to our earlier reported thermal-desorption results should be viewed with due caution. In particular, the correlation between the temperature dependence of the C 1*s* photopeaks and that of the thermal-desorption peaks is not well understood and requires further theoretical and experimental investigations. The difficulty is largely due to the fundamental differences in the information provided by the two techniques. It is important to emphasize that thermal desorption itself is a complex process, which probes not only the nature of statically adsorbed species and evolved surface intermediates but also the transition pathways involved in the dynamics of desorption.[23] Core-level photoemission, on the other hand, is a relatively straightforward probe of the local chemical environment specific to the atoms of interest within the adsorbed species. It is therefore a more direct tool for the chemical analysis of local electronic structure of the adsorbates. In our thermal-desorption work, the proposed α and β adsorption configurations are based primarily on the premise that the desorption peaks at ~360 and 420 K correspond to statically adsorbed species, without consideration of dynamics-related effects (such as surface migration).[23] The validity of such a simple assumption can be tested in greater detail by recording sequential core-level photoemission spectra as a function of the annealing temperature. Like temperature-dependent electron energy loss studies, this kind of experiment may offer more direct information on the adsorbates. Finally, other surface-structure-sensitive techniques such as high-resolution electron-energy-loss spectroscopy and photoelectron diffraction can provide further insight into RT adsorption configuration of thiophene on Si(111)7×7.

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[1] D. Q. Hu, C. D. MacPherson, and K. T. Leung, Solid State Commun. **78**, 1077 (1991); C. D. MacPherson, D. Q. Hu, and K. T. Leung, Surf. Sci. **276**, 156 (1992).

[2] C. D. MacPherson, D. Q. Hu, and K. T. Leung, Solid State Commun. **80**, 217 (1991).

[3] D. Q. Hu, C. D. MacPherson, and K. T. Leung, Solid State Commun. **82**, 55 (1991); Surf. Sci. **273**, 21 (1992).

[4] M. N. Piancastelli, M. K. Kelly, G. Margaritondo, D. J. Frankel, and G. J. Lapeyre, Phys. Rev. B **34**, 3988 (1986).

[5] M. N. Piancastelli, R. Zanoni, M. K. Kelly, D. G. Kilday, Y. Chang, J. T. McKinley, G. Margaritondo, P. Perfetti, C. Quaresima, and M. Capozi, Solid State Commun. **63**, 85 (1987).

[6] M. N. Piancastelli, M. K. Kelly, G. Margaritondo, D. J. Frankel, and G. J. Lapeyre, Surf. Sci. **211/212**, 1018 (1989).

[7] *Handbook of Conducting Polymers,* edited by T. Skotheim (Dekker, New York, 1986).

[8] A. Tsumura, H. Koezuka, and T. Ando, Appl. Phys. Lett. **49**, 1210 (1986).

[9] K. H. Tan, G. M. Bancroft, L. L. Coatsworth, and B. W. Yates, Can. J. Phys. **60**, 131 (1982).

[10] B. W. Yates, K. H. Tan, L. L. Coatsworth, and G. M. Bancroft, Phys. Rev. A **31**, 1529 (1985).

[11] P. J. Derrick, L. Åsbrink, O. Edqvist, B. Ö. Jonsson, and E. Lindholm, Int. J. Mass Spectrom. Ion Phys. **6**, 177 (1971).

[12] G. Tourillon and Y. Jugnet, J. Chem. Phys. **89**, 1905 (1988).

[13] T. A. Land and J. C. Hemminger, Surf. Sci. **268**, 179 (1992).

[14] J. P. Fulmer, F. Zaera, and W. T. Tysoe, J. Phys. Chem. **92**, 4147 (1988).

[15] G. V. Hansson and R. I. G. Uhrberg, Surf. Sci. Rep. **9**, 197 (1988), and references therein.

[16] B. Feuerbacher, B. Fitton, and R. F. Willis, in *Photoemission and the Electronic Properties of Surfaces,* edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, New York, 1978), p. 12.

[17] U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, Phys. Scr. **3**, 237 (1971).

[18] D. T. Clark and D. M. J. Lilley, Chem. Phys. Lett. **9**, 234 (1971); S. Pignataro, R. Di Marino, G. Distefano, and A. Mangini, *ibid.* **22**, 353 (1973).

[19] See, for example, C. B. Duke, in *Extended Linear Chain Compounds,* edited by J. S. Miller (Plenum, New York, 1982), Vol. 2, p. 99.

[20] J. Stohr, J. L. Gland, E. B. Kollin, R. J. Koestner, A. L. Johnson, E. L. Muetterties, and F. Sette, Phys. Rev. Lett. **53**, 2161 (1984); A. P. Hitchcock, J. A. Horsley, and J. Stohr, J. Chem. Phys. **85**, 4835 (1986).

[21] W. F. Egelhoff, Jr., Surf. Sci. Rep. **6**, 253 (1986).

[22] F. J. Himpsel, in *Chemistry and Physics of Solid Surfaces VI,* edited by R. Vanselow and R. Howe (Springer-Verlag, Berlin, 1986), p. 435.

[23] H. Froitzheim, P. Schenk, and G. Wedler, J. Vac. Sci. Technol. A **11**, 345 (1993).