Cu^{II}. A backpressure regulator at the end of the system maintained the system pressure close to 25 MPa. At the mixing point, a cold solution of stoichiometric amounts of Cu^{II} and La^{III} acetates (0.01 M each) was rapidly hydrolysed by scH_2O stream. The temperature at the mixing point was in the range of 350 – 400 °C and the residence time was only a few seconds. The hot water and dispersed hydrolysis products (CuO and La(OH)₃) were cooled and collected after the BPR. A gray solid was recovered from the mixture by complete evaporation of water and was annealed at 600 °C for 5 h to form single-phase La_2CuO_4.

Ceramic La_2CuO_4 was synthesized by annealing a stoichiometric mixture of CuO and La_2O_3 at 1100 °C for 48 h with two intermediate grinding sessions.

The phase composition of all the materials was determined by XRD (Phillips XPERT, $Cu_{K\alpha}$ radiation), at a scan rate of 1 min⁻¹ over the range $20 < 2\theta < 60°$. The microstructure of the samples was investigated by SEM (JEOL Winsem JSM-6400, acceleration voltage 10 kV) after the deposition of a gold layer (15 nm thick) on the specimen. The BET surface area was measured by N_2 adsorption at 77 K. TPR profiles were recorded at a heating rate of 10 K min⁻¹; prior to the TPR experiments, the samples were pretreated in an O_2 flow at 600 °C for 1 h and allowed to cool in oxygen until, when at room temperature, the O_2 flow was replaced with an Ar/H_2 flow (95 %/5 %).

The catalytic activity of La_2CuO_4 towards CO oxidation was studied by a pulsed microcatalytic technique over the temperature range 200 – 400 °C.[20] The composition of the gas phase was monitored by an LHM-8MD gas chromatograph (Carbosieve-B column, $l = 1$ m, $\phi = 2$ mm) with a catharometer detector and He carrier gas (70 mL min⁻¹, $P = 1$ atm). The reactant pulse was 1 mL, which contained 7.5 % v/v of the stoichiometric $CO:O_2$ mixture. Before the activity measurements, the catalysts were pretreated in a He flow.

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Evidence for Dangling Bond Mediated Dimerization of Furan on the Silicon (111)-(7 × 7) Surface**

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The binding of organic molecules on silicon surfaces has recently become an increasingly important aspect of surface modification in microelectronics and sensing technology.[1, 2] To gain the control needed for incorporating organic functionalities into existing technologies, there are growing efforts dedicated to the fundamental understanding of molecular adsorption on silicon surfaces.[3, 4] One central focus in this area is the covalent attachment of olefins to the Si dangling bonds at silicon surfaces.[5–7]

Experimental and theoretical results suggest that [4+2] or [2+2] cycloadditions of conjugated dienes with Si=Si dimers proceed by a diradical mechanism on the Si(100) surface.[6, 7] Recently, we showed that the radical nature of the electron-deficient Si dangling bonds plays an essential role in the [4+2] cycloaddition of thiophene to the Si(111)-(7 × 7) surface.[8] These studies implied that the Si dangling bonds can be alternatively viewed as reactive "free radicals" involved in the surface-attachment reactions. On the other hand, organic radical based C−C bond formation[9] was recently shown to be highly selective in enantioselective synthesis[10] or preparation of controlled macromolecular architectures.[11] Therefore, it is of significant interest to investigate whether this radical-based C−C formation is feasible on silicon surfaces in association with Si dangling bonds. Such a study may offer new insight into the covalent attachment of molecular functionalities onto the silicon surface.

We report here on the Si dangling bond mediated dimerization of furan molecules on the Si(111)-(7 × 7) surface. Through the use of thermal desorption spectroscopy (TDS) and vibrational high-resolution electron energy loss spectroscopy (HREELS), the structure and bonding of the adsorbed furan species on Si(111)-(7 × 7) have been investigated. The structure of the Si(111)-(7 × 7) unit cell (Figure 1) is well known,[12] and the unique Si(111)-(7 × 7) surface offers an excellent opportunity to examine the surface chemistry associated with the Si dangling bonds at the silicon surface. Furan was chosen for this study because it is one of the basic building blocks for conducting polymers.[13, 14]

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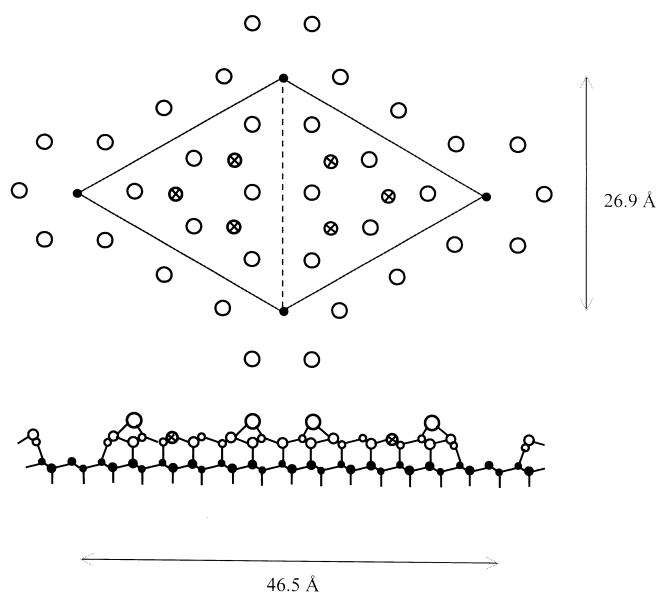
Figure 1. Schematic diagram of the Si(111)-(7 × 7) unit cell (one unit cell is within the borders; only the adatoms (first layer) and the rest atoms (second layer) with dangling bonds along the surface normal are shown). Open circles (12 per unit cell) represent the adatoms. Crossed circles (6 per unit cell) represent the rest atoms with dangling bonds that are located one atomic layer below the adatoms. The small solid circles (1 per unit cell) represent the corner-hole rest atoms at two atomic layers below the adatoms.

The temperature-programmed desorption (TPD) spectra of furan (m/z 68; see the Experimental Section), collected for various initial exposures of furan at 300 K, are displayed in Figure 2a. At low exposures, a single desorption peak with a slight tailing at the high temperature side is observed at about
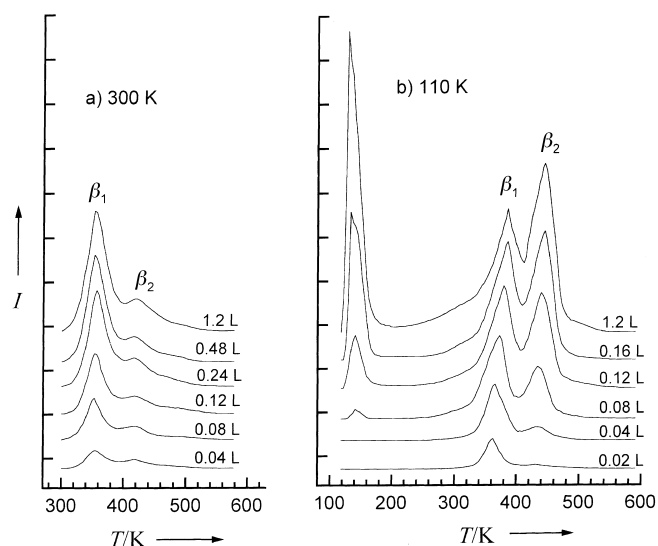
maximum at an exposure of about 1.2 L. In contrast, the population of the β_2 peak remains very low even at this saturation exposure.

Figure 2b shows the TPD spectra collected as a function of furan exposure at a low adsorption temperature (110 K). An increased desorption yield is observed after dosing furan at 110 K, compared to the same exposure at 300 K, implying that the chemisorption of furan on Si(111) is precursor-mediated. At low exposures, the desorption profiles (Figure 2b) are identical to those for exposure at 300 K (cf. Figure 2a), with the β_1 state being the predominant state. With increasing furan exposure, a physisorbed state at about 120 K appears. In addition, the population of the β_2 state grew much faster than that of the β_1 state. Upon saturation of the β_1 peak, the β_2 peak becomes the predominant state, as shown in the thermal desorption spectrum corresponding to an exposure of 1.2 L. This surprising change in the relative intensities of the β_1 and β_2 peaks as a function of adsorption temperature implies the formation of a unique chemisorbed state (see below).

To gain further insight into the adsorption behavior of furan on Si(111), a vibrational HREEL spectrum was taken after exposing furan to the silicon surface at 300 K (Figure 3a). Two separate vibrational features at 2886 and 3080 cm^{-1}, corresponding to sp^3 and sp^2 C–H stretching modes, respectively,

Figure 2. TPD spectra of furan (m/z 68) as a function of exposure to Si(111)-(7 × 7) at a) 300 K and b) 110 K. The heating rate for all spectra was 2 K s^{-1}.
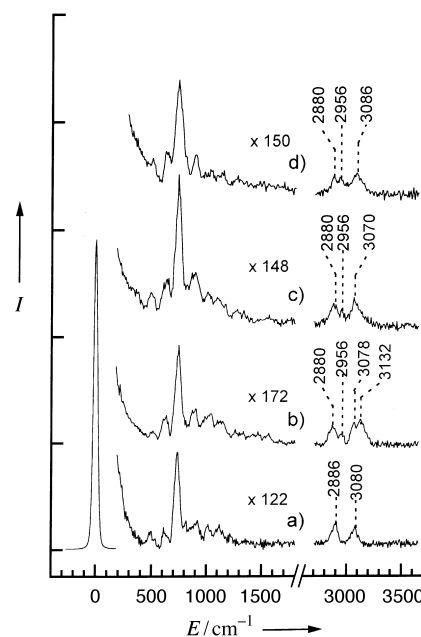

Figure 3. HREEL spectra obtained after exposing 1.20 L of furan to the Si(111)-(7 × 7) surface a) at 300 K, b) at 110 K, c) after annealing the sample from b) to 300 K, and d) after annealing the sample from b) to 360 K. The primary electron beam with an energy of 5.0 eV impinges on the surface at 60° from the surface normal. The scattered electrons were detected at the specular direction. The resolution of the spectrometer (FWHM) is 6 – 7 meV. E indicates energy loss.

360 K, which is labeled as β_1 and corresponds to molecular desorption of chemisorbed furan. Increasing the furan exposure causes the gradual development of a weak feature at 420 K, labeled as β_2. The intensity of the β_1 peak reaches a

indicate rehybridization in the chemisorbed furan.[16] This is in good agreement with the [4+2] cycloaddition reaction of thiophene[8] on the Si(111) surface. Considering that the β_1 state is the predominant state at 300 K, the features in Figure 3a are mainly attributed to the vibrational structure of the β_1 furan. The electronic structure of furan is similar to that

of thiophene.[17] In addition, it is well documented that furan easily undergoes cycloaddition reactions in the solution phase.[18] Thus, the β_1 state observed in our experiment is assigned to the [4+2] cycloadduct formed upon the bonding of the C2 and C5 carbon atoms in furan to a pair of adjacent adatom and rest atoms on the Si(111)-(7 × 7) surface.

The HREEL spectrum corresponding to exposure of 1.20 L of furan at 110 K is shown in Figure 3b. Four overlapping, but still resolvable features associated with C–H stretching modes can be identified. The loss feature at 3132 cm^{-1} is associated with the molecular furan[19] physisorbed on the chemisorbed monolayer, which is in good accordance with the results for thermal desorption (Figure 2b). The additional three peaks at 3078, 2956, and 2880 cm^{-1} are attributable to the chemisorbed furan on Si(111). To focus our study on chemisorbed furan, physisorbed molecules were desorbed from the surface by annealing to 300 K. Figure 3c shows the combined vibrational features contributed from the β_1 and β_2 states of chemisorbed furan. Three vibrational loss features at 3070, 2956, and 2880 cm^{-1} associated with C–H stretching motions can be resolved. Compared to the spectrum obtained for the sample in Figure 2a, in which the β_1 state predominates, it is concluded that the additional weak feature at 2956 cm^{-1} arises from the β_2 state.

Upon a progressive annealing to 360 K, only the β_2 state of chemisorbed furan is retained on the Si(111) surface (Figure 3d). Three loss bands at 3086, 2956, and 2880 cm^{-1} corresponding to C–H stretching modes are observed; these bands have comparable peak intensities. The presence of two loss features at 2956 and 2880 cm^{-1} corresponding to sp^3 C–H stretching suggests that there are two kinds of sp^3-hybridized carbon atoms in the more strongly bonded β_2 state of chemisorbed furan. In the temperature range studied, no energy losses around 2055 cm^{-1} (Si–H) were observed,[20] suggesting the nondissociative nature of furan adsorption.

According to the stepwise, diradical mechanism proposed for the [4+2] cycloaddition of thiophene on Si(111)-(7 × 7),[8] the initial molecular adsorption of furan would lead to the formation of a mono-σ-bonded surface complex involving a linkage between the electron-rich α-carbon atom in furan and the electron-deficient Si dangling bond at an adatom site. Apparently, the short-lived radical-like mono-σ-bonded complex can serve as the precursor for the subsequent chemisorption reaction. At room temperature, the radical-like precursor state readily reacts with a nearby dangling bond at a rest atom site, leading to the predominant formation of the β_1 state corresponding to a [4+2] cycloadduct. Owing to the short residence time of the precursor at room temperature, the surface concentration of this species remains very low during the adsorption process, which prohibits dimerization to form the β_2 state.

However, for furan adsorbed at 110 K, our TPD and HREELS results strongly suggest the formation of a dimer complex in addition to the [4+2] cycloadduct on the Si(111)-(7 × 7) surface. At a cryogenic temperature of 110 K, the mono-σ-bonded precursor state is thermally stablized and a high population of the state can be built up on the silicon surface. Two radical-like mono-σ-bonded species resting on two adjacent adatom sites can readily recombine to form a C–C bond; the dimensions of two furan molecules[21] are comparable with the distance between two nearest (6.9 Å) and next nearest (7.7 Å) Si atoms on the Si(111)-(7 × 7) surface.[12] This combination reaction would lead to the formation of a covalently C–C-linked, dimerlike furan adsorption complex through C_α–C_α coupling. This state of chemisorbed furan is more stable than the corresponding [4+2] product due to the formation of an additional C–C linkage between two mono-σ-bonded species. In addition, the chemical environment of the two C–C-linked α carbon atoms is clearly different from that of carbon atoms directly bonded to the silicon atoms.

The formation of the more strongly bound dimer complex for furan adsorption on Si(111) has been further supported by a PM3 semiempirical calculation using the Spartan 5.1.1 program.[22] A five-layer $Si_{51}H_{40}$ cluster containing two adatoms, two rest atoms, and three dimers as proposed by Takayanagi et al.[12] was employed in the calculation. Because of the large number of atoms involved, it was not possible to perform the calculation at a higher level. The results indicate that the proposed dimerized state (β_2) is about 93 kJ mol^{-1} more stable than the β_1 state corresponding to the [4+2] cycloadduct associated with a single furan molecule.

In summary, we have demonstrated the dimerization of adsorbed furan on the Si(111)-(7 × 7) surface. This facile reaction is attributed to the recombination of pairs of adjacent mono-σ complexes at low temperature. The clarification of the microscopic molecular mechanism involved in the chemisorption of furan on Si(111)-(7 × 7) as well as the nature of the radical precursor state during the chemisorption process can provide further insight into the attachment of molecules on semiconductor surfaces. Moreover, the present approach may open up new routes for the creation of molecular species with novel structures on silicon surfaces by organic radical based reactions.
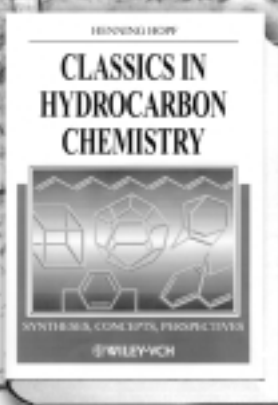
Experimental Section

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[16] Additional losses at 1220, 1112, 1017, 920, 818, 737, 620, and 500 cm^{-1} are assigned to C−C stretching, C−H bending, C−H rocking, ring deformation, C−O stretching, C−H bending, ring torsion, and C−Si stretching modes, respectively.

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[21] A planar furan molecule is about 2.2 Å in width (spacing between two α carbon atoms). If the formation of an additional C−C bond between adjacent mono-σ precursors is considered, the overall dimension of the dimer complex is comparable to the distance between two neighboring Si adatoms.

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