In Situ UPS Study of the Formation of FeSi Films from *cis*-$Fe(SiCl_3)_2(CO)_4$[†]

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The chemical vapor deposition (CVD) reaction of *cis*-$Fe(SiCl_3)_2(CO)_4$ to form iron silicide, FeSi, has been investigated by *in situ* photoelectron (PE) spectroscopy in the surface-controlled regime up to 600 °C. The experimental data provide evidence for $SiCl_4$ elimination. The reaction is assumed to occur at the surface via adsorbed silylene complex intermediates. A density functional theory (DFT) calculation approximated for the gas phase shows the elimination of $SiCl_4$ to be endothermic by 15.0 kcal mol^{-1}. The mechanism considered in the calculations involves Cl transfer from Si1 to Si2 of *cis*-$Fe(SiCl_3)_2(CO)_4$ accompanied by Fe−Si2 bond fission and formation of $[Fe({=}SiCl_2)(CO)_4]$ (calculated energy of activation 47 kcal mol^{-1}, Fe=Si bond dissociation energy 52 kcal mol^{-1}).

Introduction

The iron silicides FeSi and $FeSi_2$ have gained considerable interest recently because of their optoelectronic properties.[1] For instance, cubic FeSi ($a = 4.49$ Å) has a band gap of 0.55 eV, $\rho = 250\ \mu\Omega$ cm, and the orthorhombic phase β-$FeSi_2$ ($a = 9.86$ Å, $b = 7.79$ Å, $c = 7.83$ Å) is a direct band gap (0.87 eV) semiconductor.[2] Both materials appear to be most promising candidates for use as light detectors or sources in the near-infrared region and for applications in optical fibers.

In the search for a convenient route to FeSi/Si and $FeSi_2$/Si heterostructures, we developed a low-temperature metal organic chemical vapor deposition (MOCVD) process which uses *cis*-$Fe(SiCl_3)_2(CO)_4$ as a single-source precursor. Depending on the substrate, polycrystalline FeSi was obtained on glass, and (100) oriented β-$FeSi_2$ was obtained on (100) Si.[3] β-$FeSi_2$ was previously deposited by Aylett *et al.* from $Fe(SiH_3)_2(CO)_4$ on silica substrates at higher temperatures, ~700 °C.

MOCVD from (trichlorosilyl)metal carbonyls has successfully been employed to obtain films of Co_2Si, CoSi, $CoSi_2$, and MnSi.[4,5] Aylett *et al.* have provided fundamental studies of the silicide formation process from $M(SiH_3)_x(CO)_y$ (M = Mn, $x = 1$, $y = 5$; M = Fe, $x = 2$, $y = 4$; M = Co, $x = 1$, $y = 4$) as well as from $Mn_2(CO)_{10}$-(μ-SiH_2).[6,7] CVD generally offers important advantages over alternative techniques such as molecular beam epitaxy (MBE) or sputtering, since it allows more conformal coverage of structured surfaces and a stepwise growth of crystalline films by a chemical self-assembling mechanism.[8]

Results

An important prerequisite for the formation of uniform and defect-free films is a selective decomposition channel of the precursor. To gain better insight into the deposition mechanism of FeSi films on glass from *cis*-$Fe(SiCl_3)_2(CO)_4$,[9] we investigated its CVD reaction *in situ* in a pyrolysis reactor. The pyrolysis chamber was connected to a photoelectron spectrometer (He I photoionization), and the temperature of the substrate was varied between 30 and 600 °C. All volatile reaction products were monitored continuously by PE spectroscopy. The CVD reaction was done at the very low pressure of 10^{-6} bar in the surface-controlled rather than the diffusion-controlled regime. The heterogeneous reaction was assumed to take place in the following

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sequence of steps: diffusion/adsorption/surface diffusion/surface reaction and nucleation/product desorption/product effusion.

At a pyrolysis temperature of 30 °C[10] the PE spectrum of pure *cis*-$Fe(SiCl_3)_2(CO)_4$ was recorded (9.20 eV ($3d_{xz}$), 10.12 eV ($3d_{xy}$, $3d_{yz}$), 11.71 eV (Cl 3p (integral intensity 6)), 12.52 eV (Cl 3p (4)), 13.37 eV (Cl 3p (2)) and assigned by a DFT calculation using Slater transition state theory.[11] The signals gradually disappeared with higher temperature, giving space to new ones arising from CO (14.01 eV, n-CO, 16.91 eV, ν 1610 Hz, π-CO) and $SiCl_4$ (12.015 eV ($1t_1$), 12.863 eV ($3t_2$), 13.452 eV (1e), 15.221 eV ($2t_2$), 18.020 eV ($2a_1$), appearance temperature 190 °C).[12] At temperatures of 100−200 °C, occasionally also traces of H_2O and HCl (12.75 eV, 12.85 eV, n-Cl, spin−orbit coupling, 16.5 eV, ν 1610 Hz, σ-H−Cl) were detected; the latter one seemed to be a secondary product of partial hydrolysis.

The spectra at pyrolysis (surface) temperatures of 400−600 °C showed ionizations from the CO n- and π-orbitals and—with higher integral intensity— ionizations from the $SiCl_4$ $1t_1$, $3t_2$, 1e, $2t_2$, and $2a_1$ orbitals. In addition, a small peak at 18.08 eV was recorded resulting from the n-bonding electrons of CO_2, which is formed from CO via the Boudouard equilibrium (Figure 1).[13] No further products were observed in the entire temperature range, particularly not $SiHCl_3$,[14] $Cl_3SiSiCl_3$, Cl_2, Cl, $COCl_2$, or COClH. The selective elimination of $SiCl_4$ and CO was confirmed by an independent pyrolysis experiment in a mass spectrometer which—besides a CO-elimination signal— showed a $SiCl_4$ molecular peak and fragmentation pattern at an appearance temperature of 190 °C.

These results suggest a decomposition pathway of *cis*-$Fe(SiCl_3)_2(CO)_4$ via elimination of $SiCl_4$ and formation of multiply bonded highly reactive intermediate silylene species such as $[Fe(CO)_4{=}SiCl_2]$.[15] It has to be pointed out that under the chosen conditions the reaction is most likely to take place at the surface. An intermediate such as $[Fe(CO)_4{=}SiCl_2]$ will remain adsorbed and, after further elimination of CO and Cl_2, undergo nucleation to finally give polycrystalline FeSi. The FeSi has been identified by EDX, XRD, SEM, AFM, and ESCA. Deposition and properties of the films are described elsewhere.[3]

The nucleation process of $[Fe(CO)_4{=}SiCl_2]$ may include dimeric silylene complexes and iron silicon cluster

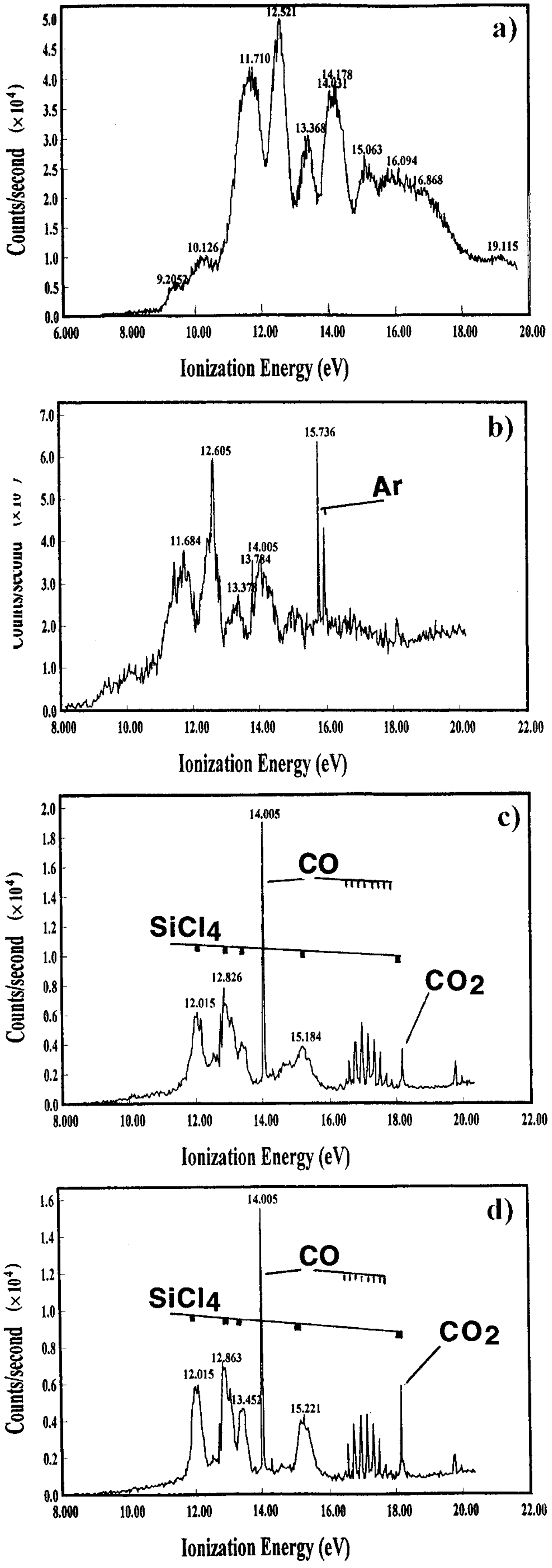

Figure 1. UPS spectra of the pyrolysis products of *cis*-$Fe(SiCl_3)_2(CO)_4$ at (a) 30 °C (starting material, $p \approx 10^{-3}$ bar), (b) 150 °C ($p \approx 10^{-6}$ bar), (c) 400 °C, and (d) 600 °C (see text).

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(10) A Pyrex glass tube was placed in a pyrolysis oven (20 cm length) connected to the PE spectrometer with a capillary. The background pressure was 10^{-7} bar (dynamic vacuum). A Schlenk tube with the sample was connected to the pyrolysis tube, and 330 mg of *cis*-$Fe(SiCl_3)_2(CO)_4$ was continuously sublimed into the pyrolysis oven. From there, residual gases were pumped into the spectrometer. A detailed description will be published elsewhere.

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compounds at a later stage of the reaction, which unfortunately escape detection. To suppress cluster formation, the overall pressure of the reaction vessel was kept as low as possible (10^{-6} bar).

Alternative pathways considering elimination of CO from *cis*-Fe(SiCl$_3$)$_2$(CO)$_4$ as the first step followed by subsequent migration of Cl to Fe also involve reactive silylene complex intermediates such as [Fe(Cl)(CO)$_3$-(SiCl$_3$)=SiCl$_2$] but are energetically highly endothermic (~30 kcal mol^{-1} compared to the value for the starting material).

Finally, decomposition reactions involving the elimination of species such as Si$_2$Cl$_6$ and SiCl$_2$ clearly are not supported by our experimental data.

The mechanism of SiCl$_4$ elimination was modeled by DFT calculations with a double-ζ valence pair DZVP/(A1) basis set. For the sake of simplicity the reaction was assumed to occur in the gas phase. *cis*-Fe(SiCl$_3$)$_2$-(CO)$_4$ adopted a C_s-symmetric ground state with a coplanar Fe−Si1−Cl···Si2 arrangement. The calculated distances were Si1−Cl = 2.05 Å (bonding) and Si2···Cl = 3.51 Å (nonbonding). The overall reaction energy for the assumed SiCl$_4$ elimination (*cis*-Fe(SiCl$_3$)$_2$(CO)$_4$ → [Fe(CO)$_4$=SiCl$_2$] + SiCl$_4$) was calculated to be 15.2 kcal mol^{-1} endothermic with respect to the starting material. The product [Fe(CO)$_4$=SiCl$_2$] adopted a C_{2v} structure with the silylene ligand in an equatorial position and both Cl substituents parallel to the axial CO's. This conformation allows optimal π-back-bonding from energetically high d_{xy} and $d_{x^2-y^2}$ orbitals in the equatorial plane of the tbp iron to the silicon atom. The calculated Fe−Si bond distance amounted to 2.11 Å (2.33/2.35 Å in Fe(SiCl$_3$)$_2$(CO)$_4$). The Si atom has an almost perfectly trigonal planar geometry (Fe−Si−Cl = 128.5°, Cl−Si−Cl = 102.95°, Si−Cl = 2.06 Å), and the axial CO's are slightly inclined toward the Si atom (2°).

Löwdin charges allow an insight into the molecular charge distribution and were calculated for the silylene complex as −0.81 (Fe), 0.51 (Si), and −0.04 (Cl) and as −1.06 (Fe), 0.37/0.38 (Si), and 0.38 (average, Cl) for *cis*-Fe(SiCl$_3$)$_2$(CO)$_4$. For both the silylene and the disilyl complex, the M−Si bonds are very polar (dipole moment 0.209 D for [Fe(CO)$_4$=SiCl$_2$]). The dissociation energy of the FeSi bond ([Fe(CO)$_4$=SiCl$_2$] → *eq*-Fe(CO)$_4$ + SiCl$_2$) was calculated to be 52 kcal mol^{-1} (uncorrected). As a matter of fact, bond energies of M−Si double bonds often are lower than bond energies of M−Si single bonds (80−90 kcal mol^{-1}) because of considerable repulsive electronic interaction between M and Si. This trend increases for Ge, Sn, and Pb and has been discussed in the literature.[16]

In Figure 2 a 2D cross-sectional view orthogonal to the Fe−Si bond is displayed for the HOMO of the silylene complex, which shows significant π-bonding interrelations between Si and Fe.[17] The LUMO is predominantely located at the Si atom (Figure 3).

For simulation of the SiCl$_4$ elimination, a reaction coordinate was defined, transferring Cl1 of the Si1Cl$_3$ group in *cis*-Fe(SiCl$_3$)$_2$(CO)$_4$ gradually from Si1 to Si2 of the Si2Cl$_3$ group, with the distance Cl1···Si2 constrained to the following values: Cl1···Si2 = 2.38, 2.20, 2.10, 2.09, and 2.08 Å. Furthermore, starting from the structure Cl1···Si2 = 2.08 Å, the Fe−Si2 distance was fixed to 2.80 and 3.00 Å, and the rest of the molecule was subjected to a full geometry optimization. Several different structures were calculated along the reaction coordinate (Figure 4), with their total energies reaching as high as 47 kcal mol^{-1} with respect to the starting material (**A**). This energy of activation has to be viewed as an upper estimate, which in fact could be drastically lower for an adsorbate bound to the surface. With migration of the Cl1 atom proceeding from Si1 to Si2, the four-membered ring Fe−Si1−Cl1−Si2− showed a twist of as much as 16.79° (**C**). The loss of a Cl atom at Si1 induced a shortening of the Fe−Si1 bond to 2.21 Å, indicating increased back-bonding (**C**). Concomitantly, the coordination geometry at Si1 was planarized. The single bond Fe−Si2 was gradually elongated to 2.44 Å (**D**) and was finally disrupted. At this stage, eliminated SiCl$_4$ still exerted a weak contact to the silylene ligand in the sense of a donor adduct, Fe(CO)$_4$=SiCl$_2$←SiCl$_4$ (**D**). As expected, the donor complex bore the "silylene" ligand in an axial position.[18] This adduct turned out not to be a minimum on the potential hypersurface but dissociated spontaneously into the products SiCl$_4$ and [Fe(CO)$_4$=SiCl$_2$] (**E**). The doubly bonded silylene com-

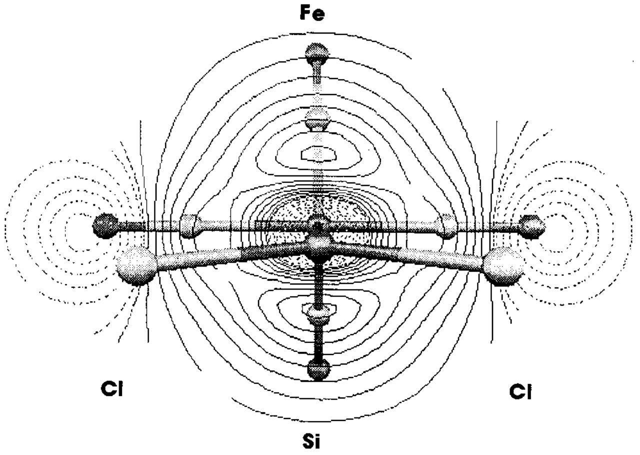

Figure 2. Cross-sectional view of the Fe−Si π-bond in Fe(=SiCl$_2$)(CO)$_4$ at half-bond length.

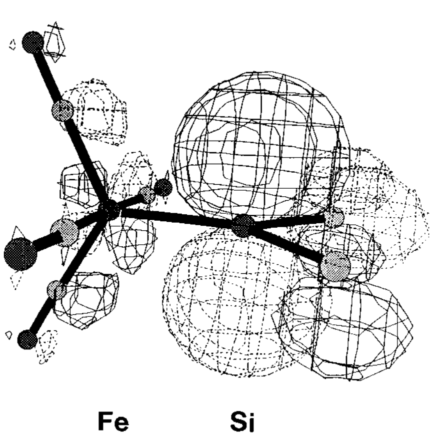

Figure 3. View of the LUMO of Fe(=SiCl$_2$)(CO)$_4$.

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[17] One should be aware of the fact that this orbital is dependent upon the Kohn Sham orbitals implemented in the basis set.

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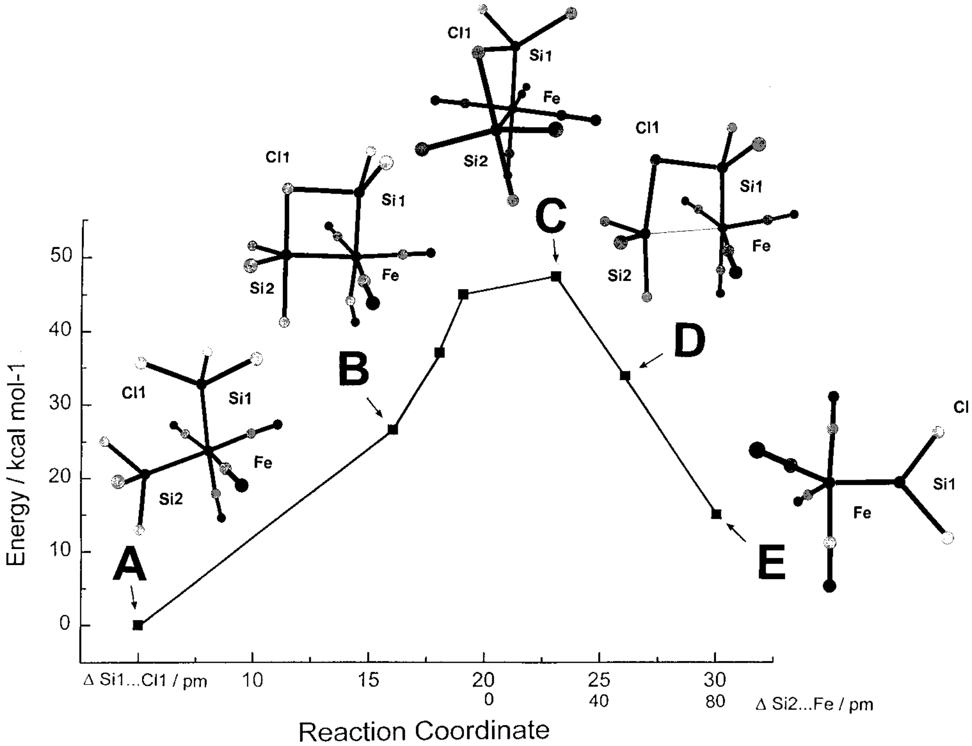

Figure 4. Calculated molecular structures and energies along the reaction coordinate transferring Cl1 from Si1 to Si2.

plex was first formed in its axial geometry,[19] from which it relaxed into its thermodynamically more stable equatorial ground state.[20]

The calculations suggest an interesting scenario of a stepwise $SiCl_4$ elimination triggered by removal of a Cl atom from Si1. A delicate electronic balance in the molecule induces further conformational twisting as well as Fe−Si1 double-bond formation and Fe−Si2 bond dissociation in a synergetic process which eventually yields an unstable $SiCl_4$ adduct of the silylene complex $Fe(CO)_4{=}SiCl_2{\leftarrow}SiCl_4$. This adduct spontaneously dissociates into the products. The silylene complex $[Fe(CO)_4{=}SiCl_2]$ is a highly reactive species, which is thought to decompose and nucleate further finally to FeSi via CO and Cl_2 elimination. A stable HMPA adduct, $Fe(CO)_4{=}SiCl_2{\cdot}HMPA$, has been reported (HMPA = hexamethylphosphoric triamide).[21]

It has to be pointed out that the reaction sequence occurs at the surface of the substrate/FeSi product. Knowledge about the volatile elimination products of the reaction allows only indirect evidence for a possible decomposition mechanism of the precursor.

A complete mechanistic scheme presumably involves two cascades of either CO or $SiCl_4$ elimination reactions (Scheme 1), which both are in accordance with our experimental data. Furthermore, also Cl migration from Si to Fe (after loss of CO) appears as a possibility but is energetically less favored. A direct observation of highly reactive surface species such as $[Fe(CO)_4{=}SiCl_2]_{surf}$, $[Fe(CO)_3{=}SiCl_2]_{surf}$, and $[FeCl(CO)_3{=}SiCl_2]_{surf}$ is the subject of current research efforts.

In light of a surface reaction, an activation barrier of 47 kcal mol^{-1} (**C**), estimated for the gas-phase elimination of $SiCl_4$ from *cis*-$Fe(CO)_4(SiCl_3)_2$, can be viewed as an upper value of the activation energy of the first step of the decomposition reaction on the surface. Adsorption of the involved species may lead to a drastic lowering of this barrier.

Due to the large number of electrons involved, pseudopotentials had to be employed for Cl and Si, which precluded the introduction of a frequency analysis of the transition state.[22] However, product and starting material were calculated both with full electron configuration and with pseudopotentials for Si and Cl. The energy difference in reaction enthalpy for both calculations was less than 1%.

On the basis of experimental PE spectra, $SiCl_4$ elimination from surface-bound *cis*-$Fe(SiCl_3)_2(CO)_4$ seems to be probable at an early stage of the decomposition reaction. $SiCl_4$ elimination is energetically competitive with CO elimination. This allows us to formulate cascades of different combinations of $SiCl_4$-/CO-elimination steps from the starting material which all involve surface-bound, highly reactive $[X_xFe{=}SiCl_2]$ species.[23] These intermediates are assumed to nucleate and condense further finally to FeSi by loss of chlorine.[24]

The observation of adsorbates or even short-lived reactive intermediates such as $[Fe(CO)_4{=}SiCl_2]$ on a hot surface is still at the limits of experimental techniques.

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[19] For the two isomers *ax*- and *eq*-$Fe(CO)_4{=}SiCl_2$, a frequency analysis has been done.

[20] Two further minima were found on the potential energy surface: The cationic Cl-bridged bis-silylene complex $[(CO)_4Fe({=}SiCl_2)_2(\mu\text{-}Cl)]^+Cl^-$ and the anionic complex $[SiCl_3]^+[Fe(SiCl_3)(CO)_4]^-$, which are of higher total energy and are not assumed to participate in a CVD reaction. A complete study of the potential energy surface will be published elsewhere.

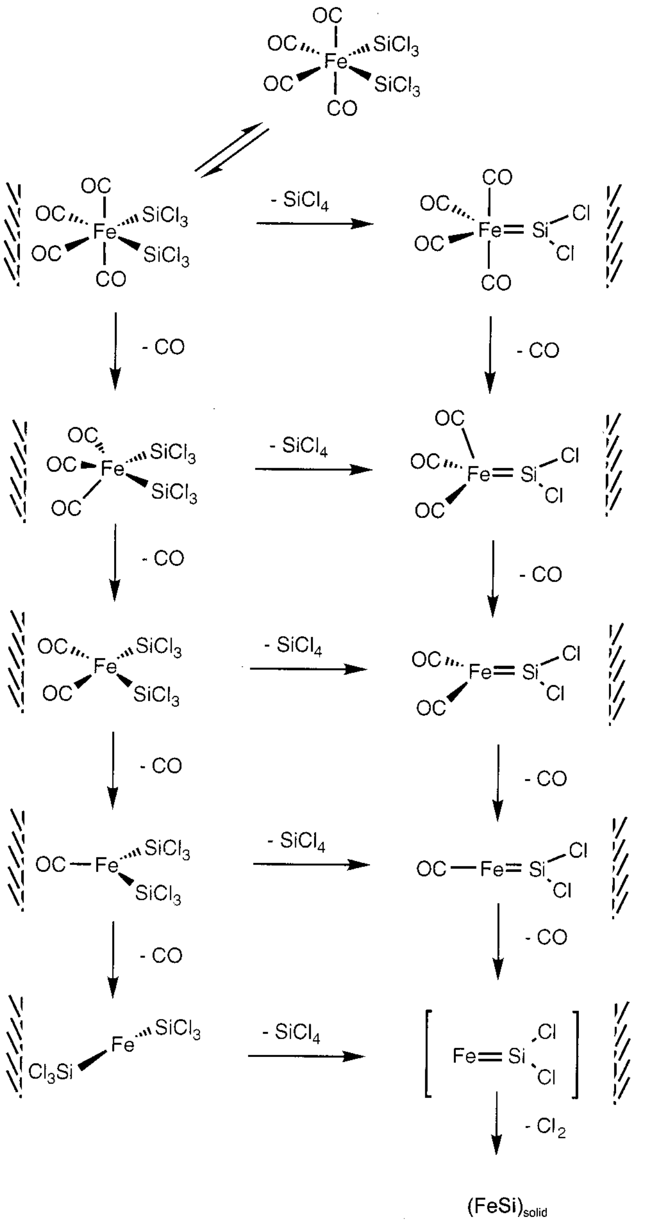
[21] Leis, C.; Wilkinson, D. L.; Handwerker, H.; Zybill, C.; Müller, G. *Organometallics* **1992**, *11*, 514.

[22] A correction of about 5−10 kcal mol^{-1} to lower energies was obtained by comparing data of all electron calculations with ones using ECP's.

[23] A dimeric silylene complex could also be formed, but it would be much less reactive.

[24] Samples which have been pyrolyzed under vacuum contain some chlorine (as $FeCl_2$). Virtually Cl-free FeSi films are obtained in the presence of H_2 as reactive carrier gas.

Scheme 1



In this situation, PE spectroscopy in combination with the calculation of a simplified gas-phase reaction serves to provide a better mechanistic understanding for a complex reaction sequence which otherwise is very difficult to assess. The data are sufficient for a fine-tuning of the deposition reaction toward higher product selectivity.

Experimental Section

He I photoloelectron spectra were measured on a Leybold-Heraeus UPG-200 spectrometer with a specially designed inlet system using Ar$^+$ $^2P_{3/2}$ (15.759 eV) and CH$_3$I $^2E_{1/2}$ (9.54 eV) as calibration lines. The same lines were used to check the linearity of the energy scale. The resolution of the spectrometer was 18−25 meV (fwhm) as measured on a $^2P_{3/2}$ Ar$^+$ line. The assignment of the spectra was based on Slater TS calculations and literature references. DFT calculations were performed on a Cray YMP computer using the DGauss 3.0 program package.[25] Our calculations used a nonlocal density approximation, DZVP basis set, and BP/LDA correction.[26] All molecular ground state geometries were fully optimized, and the geometries were established to be genuine minima on the potential energy surfaces, as indicated by the absence of imaginary vibrational frequencies. For the calculations along the reaction coordinate, pseudopotentials had to be introduced for Si and Cl because of limitations in CPU time. The Cl···Si2 distance was constrained to fixed values, and the rest of the molecule was subjected to geometry optimization.

The decomposition was done in a hot tube quartz reactor connected to the inlet of the PE spectrometer. The temperature was measured inside the reactor with a Cr/Ni thermocouple, and the heating element was regulated with a Eurotherm temperature controller/thermocouple. The surface-to-volume ratio of the reactor was 0.75 (1.5 cm diameter); the ratio of sample surface to reactor volume amounted to 0.02.

Acknowledgment. We thank Professor F. Koch, Physics Department E16, Technical University of Munich, for support.

Supporting Information Available: Figures giving selected calculated structures of **A**−**E** along the reaction coordinate and tables giving calculated parameters for **A**−**E** (9 pages). Ordering information is given on any current masthead page.

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