State-Specific Enhancement of Cl^+ and Cl^- Desorption for $SiCl_4$ Adsorbed on a Si(100) Surface Following Cl $2p$ and Si $2p$ Core-Level Excitations

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State-specific desorption for $SiCl_4$ adsorbed on a Si(100) surface at ~90 K with variable coverage following the Cl $2p$ and Si $2p$ core-level excitations has been investigated using synchrotron radiation. The Cl^+ yields show a significant enhancement following the Cl $2p \rightarrow 8a_1{}^*$ excitation. The Cl^- yields are notably enhanced at the $8a_1{}^*$ resonance at both Cl $2p$ and Si $2p$ edges. The enhancement of the Cl^- yield occurs through the formation of highly excited states of the adsorbed molecules. These results provide some new dissociation processes from adsorbates on surfaces via core-level excitation.

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The selectivity of photoexcitation and subsequent chemical bond breaking of the molecular adsorbates via inner-shell excitation has been a recent topic of extensive study in surface science. With the advent of a tunable synchrotron light source in the x-ray region, it became feasible to control the specific excitation of a particular atomic site of polyatomic molecules. In addition, the core electrons of a specific element in a molecule can be selectively excited into specific valence orbitals and Rydberg states below the ionization threshold. In the past decade, site-selective fragmentation via core-level excitation was observed in gaseous molecules [1,2], molecular adsorbates on surfaces [3–6], and polymers [7]. However, some molecules, such as $Fe(CO)_2(NO)_2$, showed no site selectivity after excitations of core electrons of different sites [8], and no selectivity was found for $Si_2(CH_3)_6$ after transitions from $Si(2p)$ electrons into various resonances [9]. Accordingly, further investigations to elucidate the mechanism of selective photodissociation of molecular adsorbates following core-level excitation are clearly needed.

It has been shown that there exists some highly excited states near or above the double ionization threshold energies on gas-phase molecules, such as SO_2 and CO [10,11]. However, due to adsorbate-substrate and adsorbate-adsorbate interaction for molecular adsorbates on surfaces, these highly excited states, such as doubly excited Rydberg states, may be quenched or disappeared in the solid phase. Until now, very little research has been conducted to study these highly excited states and their role on ion desorption processes for adsorbates on surfaces. The detection of negative ions has been shown to be a powerful method to expose the highly excited states above the single-ionization threshold energies [10]. In the present study, by combining the photon-stimulated desorption spectra of positive ions and negative ions, resonant photoemission, and x-ray absorption spectra, the mechanisms of selective fragmentation for $SiCl_4$ adsorbed on a Si(100) surface at ~90 K with variable coverage following the Cl $2p$ and Si $2p$ core-level excitations to various unoccupied orbitals is characterized.

The experimental measurements were carried out at the Synchrotron Radiation Research Center (SRRC) in Taiwan, using an ultrahigh-vacuum (UHV) chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr. Before installation into the UHV chamber, the substrate Si(100) crystal was treated with a hydrogen-peroxide-based immersion cleaning procedure. The Si(100) surface was cleaned by repeated resistive heating to ~1100 °C under vacuum. Positive and negative ions were mass selected through a quadrupole mass spectrometer (Balzers model QMA 410). The surface coverage was determined by thermal desorption spectroscopy. 5-L exposure of $SiCl_4$ on Si(100) corresponds to one monolayer ($1\ \mathrm{L} = 1 \times 10^{-6}$ Torr s).

The photon stimulation ion desorption (PSID) spectra of $SiCl^+$, $SiCl_2{}^+$, $SiCl_3{}^+$, Si^+, and Cl^+ for solid $SiCl_4$ (~100-L exposure) are reproduced in Fig. 1. The Cl L_{23}-edge x-ray absorption spectrum for condensed $SiCl_4$ measured by the total electron yield (TEY) mode is also included in Fig. 1 for comparison. The features labeled as 1 and 1′ are assigned to the transition, Cl $2p \rightarrow 8a_1{}^*$ [12]. The features labels as 2 and 2′ correspond to Cl $2p \rightarrow 9t_2{}^*$ excitations. The transitions to the Rydberg orbitals are responsible for the features labels as 3 and 4. A broadband at ~216 eV labeled as 5 is ascribed to the shape resonance. As noted from Fig. 1, the PSID spectra of $SiCl^+$, $SiCl_2{}^+$, $SiCl_3{}^+$, and Si^+ show a close resemblance with the Cl L_{23}-edge x-ray absorption spectrum of condensed $SiCl_4$. In contrast, the Cl^+ PSID spectrum exhibits a clear dissimilarity with the Cl L_{23}-edge x-ray absorption spectrum. The transition, Cl $2p \rightarrow 8a_1{}^*$, leads to a significant enhancement in the Cl^+ desorption yield when compared to the transitions, Cl $2p \rightarrow 9t_2{}^*$ and Cl $2p \rightarrow$ Rydberg states. This indicates that the character of unoccupied orbitals plays a vital role in the ion desorption processes.

The photoemission spectra of condensed $SiCl_4$ excited with various photon energies through the Cl L-edge absorption profile are shown in Fig. 2. In general, the core-excited states with an excited electron in the empty orbital decay primarily to two-hole one-electron ($2h1e$)

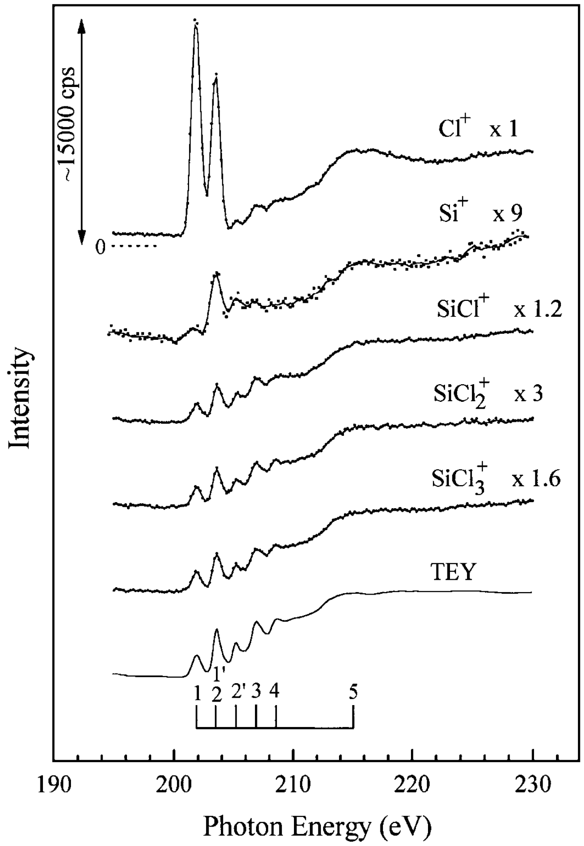

FIG. 1. A comparison of the Cl L-edge TEY spectrum and PSID spectra of Cl^+, Si^+, $SiCl^+$, $SiCl_2{}^+$, and $SiCl_3{}^+$ for solid $SiCl_4$ (~100-L exposure). The dashed line represents the zero of signal intensity for the desorbed ion.

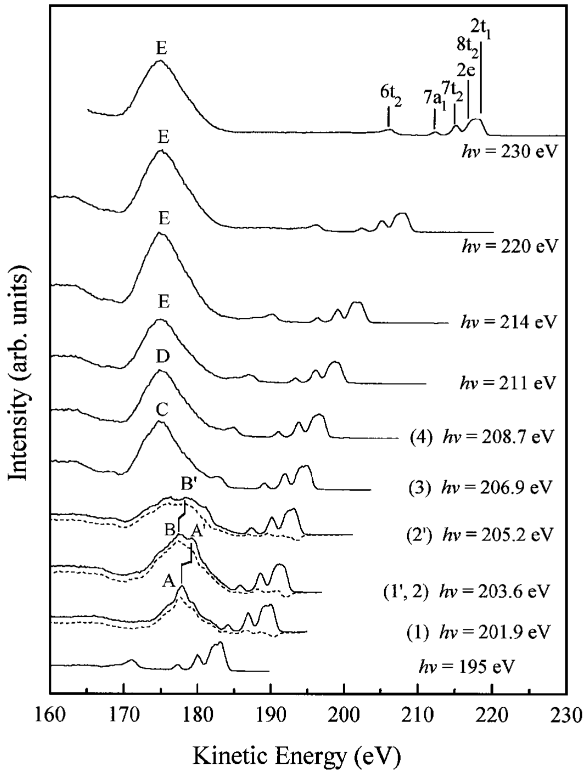

FIG. 2. Photoemission spectra of $SiCl_4$ (40-L exposure) on Si(100) at ~90 K. The number indicated in each spectrum corresponds to absorption peaks marked in the TEY spectrum in Fig. 1. The dashed lines show the difference spectra between the resonance photoemission spectra and the normal photoemission spectrum excited at 195 eV (shifted by the photon energy difference).

final states via spectator Auger transition or one-hole ($1h$) final states via participant Auger transition. $2h$ and $1e$ represent two holes in the valance orbitals and one excited electron in the unoccupied orbitals, respectively. The peaks A and B' are attributed to the superposition of predominant spectator Auger peaks and the minor inner-valence orbital, $6t_2$. The peak E with kinetic energy of ~175 eV corresponds to a normal Auger peak.

The most striking feature in the photoemission spectra of Fig. 2 is the pronounced spectator Auger structures labeled A and B', as the photon energy varies through valence resonances. This result reveals that the spectator Auger transition prevails predominantly following core-to-valence excitation. The spectator Auger peaks marked as A and A' correspond to the spectator Auger transitions following the Cl $2p \rightarrow 8a_1{}^*$ excitation, and the peaks marked as B and B' originate from those via the Cl $2p \rightarrow 9t_2{}^*$ excitation. This finding suggests that the spectator electron is localized at the respective valence orbital during the Auger decay. In contrast, shape-resonance excitation was followed by the normal Auger decay, because at even larger photon energies the normal Auger peak labeled E remains the constant kinetic energy of ~175 eV. In addition, for Rydberg excitation, peaks C and D exhibit the same kinetic energy of ~175 eV as the normal Auger peak. This implies that the excited electron in the Rydberg orbitals is delocalized during the Auger decay.

As deduced from Fig. 2, the spectator Auger and normal Auger transitions were the dominant decay channels for the excited Cl($2p$) core hole of condensed $SiCl_4$, leading to the excited states with multiple holes in the valence orbitals. Accordingly, a close similarity of the Cl L-edge TEY spectrum and PSID spectra of Si^+, $SiCl^+$, $SiCl_2{}^+$, and $SiCl_3{}^+$ for condensed $SiCl_4$ is attributed to the Auger decay of core-excited states and subsequent Coulomb repulsion of multivalence-hole final states, which confirms the Auger-initiated desorption (AID) mechanism [13]. However, the state-specific enhancement of Cl^+ yield via the Cl $2p \rightarrow 8a_1{}^*$ excitation implies that there exists an additional process for Cl^+ desorption from condensed $SiCl_4$.

An enhanced H^+ desorption yield was reported for condensed H_2O [14], NH_3 [15], and benzene [6] via resonant excitations of core electrons to strong antibonding orbitals. This enhancement was proposed to be via an ultrafast dissociation channel. For $SiCl_4$, after excitations of Cl $2p$ core electrons into the unoccupied antibonding orbitals, the core equivalent molecule is Cl_3Si-Ar in its fundamental state. This core-excited state is expected to present a strongly repulsive potential curve, consequently leading to a fast dissociation of the system. Our experimental results reveal that the fast ion desorption occurs even for desorption of a heavy ion such as Cl^+ through a repulsive potential surface.

Moreover, the Cl $2p \rightarrow 8a_1{}^*$ excitation leads to a Cl^+ desorption yield much greater than the Cl $2p \rightarrow 9t_2{}^*$ excitation, although both excitations decay primarily by the spectator Auger transitions. This significant difference may be due to the disparate steepness of repulsive potentials between the $8a_1{}^*$ and $9t_2{}^*$ resonances. The relationship between the steepness of the potential surface and the width of the spectrum is well known in the absorption spectroscopy of molecules [16]. In other words, the steeper the slope in the Franck-Condon region, the broader the absorption spectrum. The feature 1 in the x-ray absorption spectrum (Fig. 1) is considerably broader than the feature $2'$ (full width at half maximum of 0.83 eV for peak 1, and that of 0.61 eV for peak $2'$). Thus, the potential curve at the $8a_1{}^*$ resonance is expected to be much steeper than that at the $9t_2{}^*$ resonance. Accordingly, within the lifetime of $2h1e$, Cl^+ can gain more kinetic energy from the $8a_1{}^*$ resonance, leading to lower ion reneutralization rates and thus higher Cl^+ desorption yield.

Unlike the positive-ion desorption, the Cl^- was the only ion predominantly observed in the negative-ion desorption of $SiCl_4$/Si(100) following the Cl $2p$ core-level excitation. In order to get more insight into the mechanism of negative-ion desorption, the Cl^- yield was measured as a function of $SiCl_4$ exposure on Si(100) at ~90 K, as presented in Fig. 3(a). As noted, the Cl^- yield spectra in Fig. 3(a) exhibit several interesting features. There is a significant enhancement in Cl^- yield at the $8a_1{}^*$ resonance and an increase in Cl^- yield at shape resonance with $SiCl_4$ exposures. In addition, the Cl^- yield at the $8a_1{}^*$ resonance was increased up to 12-L exposure and then was decreased slowly after 12-L exposure of $SiCl_4$ on Si(100).

To quantify the results, the Cl^- yields at shape resonance (~216 eV) and Rydberg states (~207 eV) excitations are plotted against the $SiCl_4$ exposure on Si(100) in Fig. 3(b). As noted from Fig. 3(b), the Cl^- yield was increased drastically up to 5-L exposure of $SiCl_4$ on Si(100). After 12-L exposure, the Cl^- yield was increased slowly with $SiCl_4$ exposures. To corroborate the Cl^- yield, the corresponding total electron yield is plotted against the Cl^- yield at shape resonance and Rydberg excitations for the respective $SiCl_4$ exposure (for 12-L exposure and more) in Fig. 3(c). As shown, the Cl^- yields at both shape resonance and Rydberg excitations show linear behavior with electron yield. This implies that the possible desorption process of atomic fragment Cl^- from $SiCl_4$/Si(100) was likely due to dissociative attachment on molecules of secondary electrons created by photoabsorption of molecular adsorbates. This desorption mechanism was called dissociative electron attachment (DEA). At low coverage, the rapid increase of Cl^- yields at shape resonance or at Rydberg excitation of $SiCl_4$/Si(100) can be understood in terms of the lowering of the potential energy surface of intermediate anions due to polarization induced by the substrate [17].

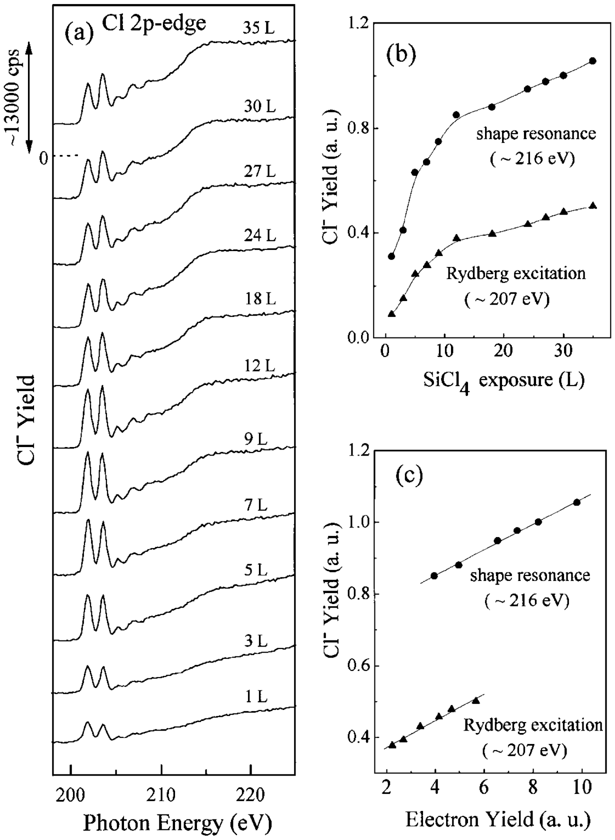

FIG. 3. (a) Cl^- yield spectra for $SiCl_4$ on Si(100) at ~90 K with variable exposures in the vicinity of the Cl $2p$ edge. (b) The Cl^- yields at shape resonance and Rydberg excitations as a function of $SiCl_4$ exposure. (c) The Cl^- yields at shape resonance and Rydberg excitations versus the corresponding total electron yields for the respective $SiCl_4$ exposures (12-L exposure and more).

In contrast, the enhancement of Cl^- yield at the $8a_1{}^*$ resonance is not due to DEA processes, but it originates from unimolecular processes. This is due to the fact that the observed 1 and $1'$ resonances have the same energies and widths among Cl^- yield, positive-ion yield, and TEY spectra. One of the possible processes for negative-ion formation by photoexcitation of a molecule is due to ion-pair formation, in which core-excited AB^* molecules are predissociated by ion-pair states, leading to the fragmentation into A^+ and B^- [18]. In this case, one would encounter a $(Cl^*SiCl_2)^+Cl^-$ or $(SiCl_3)^+Cl^{-*}$ ion-pair for $SiCl_4$ following the Cl $2p$ core-level excitation. We assumed that the core-hole relaxation by the ion pair formation occurs before the excited molecules decay by Auger relaxation processes. Thus, the core-excited $(Cl^*SiCl_2)^+$ ion would yield a doubly charged entity after Auger decay. However, this doubly charged ion has not been observed in the PSID spectra, possibly due to neutralization. In addition, the decay spectra of core-excited $(Cl^*SiCl_2)^+$ or Cl^{-*} should differ from those of core-excited $SiCl_4$ molecules, as discussed in Ref. [19]. However, decay features of

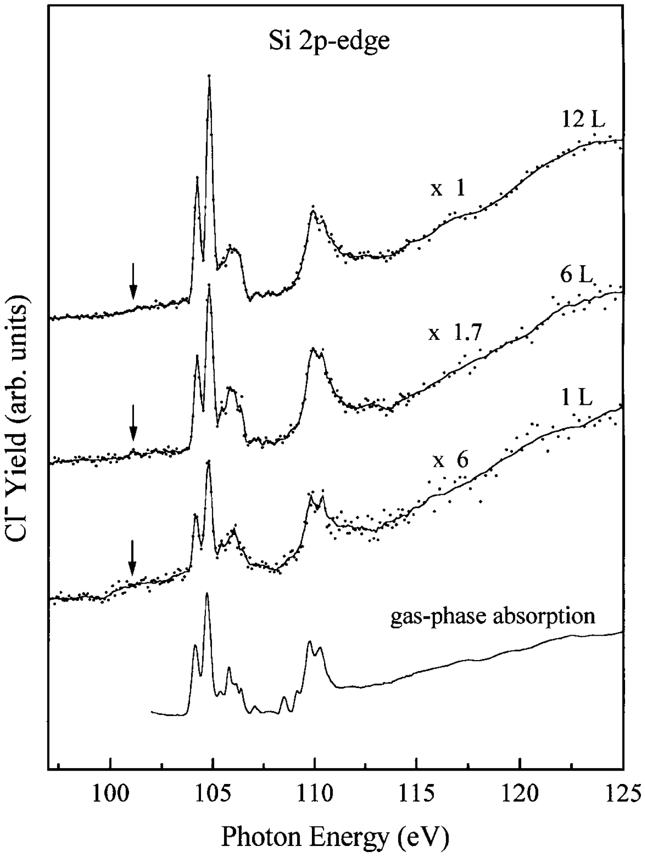

FIG. 4. Cl^- yield spectra from $SiCl_4/Si(100)$ at ~90 K with variable exposures near the Si $2p$ edge. Si L-edge x-ray absorption spectrum of gaseous $SiCl_4$ is shown at the bottom of this figure for comparison (Ref. [20]).

$(Cl^*SiCl_2)^+$ or Cl^{-*}, particularly for Cl^{-*}, are not shown in the decay spectra of Fig. 2. We therefore rule out the direct dissociation of core-excited states via the ion-pair formation. It is thus speculated that negative-ion formation might originate from some highly excited states of the parent ion that are predissociated by ion pair or directly dissociate, as proposed previously by Dujardin *et al.* [10]. Here, we consider that the resonances of $SiCl_4$ molecules via the Cl $2p$ core-level excitation can decay by Auger transition to these highly excited states. Based on this model, it has been demonstrated that the intensities of the resonances in the negative-ion spectrum are strongly correlated to the probability of spectator electrons to be attached to the electronegative atom during the fragmentation of the molecules [10]. From the multiple-scattering X_α calculations in $SiCl_4$, the spectator electron in the $8a_1{}^*$ orbital is more localized at the Cl side, while the $9t_2{}^*$ orbital is delocalized between Cl and Si atoms [12]. It is thus expected that the Cl $2p \rightarrow 8a_1{}^*$ excitation leads to an enhancement in Cl^- yield, as compared to the Cl $2p \rightarrow 9t_2{}^*$ and Cl $2p \rightarrow$ Rydberg excitations. This is indeed observed in Fig. 3(a).

If the highly excited states exist, it is reasonably expected that these states can also be populated by Auger decay of Si($2p$) core-excited states of $SiCl_4$. Figure 4 shows the Cl^- yield spectra form $SiCl_4/Si(100)$ at ~90 K with variable exposures following the Si $2p$ core-level excitation, along with the gas-phase x-ray absorption spectrum. As shown, the relative Cl^- yield at the Si $2p_{1/2} \rightarrow 8a_1{}^*$ excitation (~104.8 eV) and the Si $2p_{1/2} \rightarrow 9t_2{}^*$ excitation (~106.1 eV) shows a continuous increase up to 12-L exposure of $SiCl_4$ on Si(100). The enhancement of Cl^- yield at the $8a_1{}^*$ resonance is clearly observed (particularly for 12-L exposure). This gives evidence in support of the existence of some highly excited states. A similar phenomenon has been found for $OPCl_3$ (P $2p$ and Cl $2p$ edges), $Si(CH_3)_{4-n}Cl_n$ ($n = 1$–3) (Si $2p$ and Cl $2p$ edges), SO_2Cl_2, (S $2p$ and Cl $2p$ edges), etc. [21]. The negative-ion formation through the highly excited states is thus not specific to $SiCl_4$ molecules, but of a general nature. In addition, the Cl^- yield at ~101 eV, as indicated by arrows, is induced by the secondary electrons produced by the Si $2p$ core-level excitation of substrate. This also reveals the existence of DEA processes.

In conclusion, the Cl^- desorption yields are notably enhanced at the $8a_1{}^*$ resonance at both Cl $2p$ and Si $2p$ edges. The resonance enhancement of Cl^- yield occurs through the formation of highly excited states of the adsorbed molecules. These highly excited states, which have always been ignored, indeed play a notable role on ion desorption of adsorbed molecules via core-level excitation. The present results demonstrate some new dissociation channels for adsorbates on surfaces via inner-shell excitation.

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