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Contract N00014-82-K-0280

Task No. NR413E001

TECHNICAL REPORT NO. 42

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APR 7 1992
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**Interaction Of Atomic Hydrogen With The Surface Methyl Group On Si(100) -
Removal Of Surface Carbon**

by

C.C. Cheng, S.R. Lucas, H. Gutleben, W.J. Choyke, and J.T. Yates, Jr.

Submitted to

Surface Science Letters

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March 6, 1992

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92-08860

Submitted to: Surface Science Letters

Date: 18 February 1992

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Abstract

The interaction of atomic hydrogen with an overlayer derived from methyl iodide on the Si(100) surface has been studied using Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) mass spectroscopy. Efficient removal of surface iodine by reaction with atomic hydrogen is observed. However, experiments with large exposures of atomic hydrogen also show the depletion of surface carbon. In contrast to the almost non-activated behavior observed for the extraction of halogen by an Eley-Rideal process producing the hydrogen halides, the carbon removal rate decreases with increasing temperatures ($T \geq 450$ K). The depletion of surface carbon by atomic hydrogen correlates well with H-etching on the Si(100) surface in which $\text{SiH}_4(\text{g})$ is evolved, and is shown to be due to $\text{CH}_3\text{SiH}_3(\text{g})$ production during H-etching. In addition, isotopic exchange of the deuterium from $\text{CD}_3(\text{a})$ with hydrogen atoms supplied from the gas phase is also observed; this is found to be the most rapid kinetic process for the interaction of atomic hydrogen with the surface methyl group on Si(100). Finally, the selectivity of the H-induced reaction for two types of adsorbates, the methyl group and the halogen, is discussed.

I. INTRODUCTION

Studies of chemical reactions between gas phase species and semiconductor surfaces can provide molecular level understanding of the initial stages of chemical vapor deposition (CVD), of epitaxial thin film growth, as well as for the surface etching process. Among the different gas phase species which have been studied on semiconductor surfaces, atomic hydrogen is one of the most thoroughly investigated species due to its widespread presence in semiconductor processes.

Atomic hydrogen is a common reactant used both in the growth and etching processes of silicon. The interaction of atomic hydrogen with the clean Si(100) surface has been studied extensively using various surface science techniques [1-4]. It is well established now that etching of the Si(100) surface by atomic hydrogen proceeds via the breaking of the Si-Si bonds and the formation of higher surface hydrides, $\text{SiH}_2(\text{a})$ and $\text{SiH}_3(\text{a})$; these species are precursors for the formation of the etching product, $\text{SiH}_4(\text{g})$ [2-4].

The importance of atomic hydrogen in diamond film deposition using CVD techniques has also been addressed [5]. Recently, efforts have been focused on the measurement of gaseous species in the growth chamber [6]. For a filament-assisted reactor containing a mixture of H_2 , Ar, and CH_4 , direct detection of gas phase radical species, $\text{H}\cdot$ and $\cdot\text{CH}_3$, has been reported using molecular beam mass spectrometry [6]. Predictions of the gaseous composition by numerical modeling have been reported by several groups [7-10]. Postulated surface reactions were included in the calculations [7]. However, all the computational results have failed to explain the mass spectroscopic measurements [6], and heterogeneous reactions on the substrate surfaces were suggested to be one of the causes for the discrepancy between the experimental measurement and

the numerical modeling [6]. Knowledge of key surface reactions occurring during the growth process is apparently required for the advanced understanding of the diamond film deposition.

The goal of this work is to study the surface reactions which may be initiated by gas phase atomic hydrogen on a Si(100) surface containing both CH₃(a) and I(a). Investigations of surface reactions using gas phase hydrogen atoms as one of the reactants have been carried out on Si(100) recently. We have shown, in a previous paper [11], that abstraction of halogen adsorbates from the Si(100) surface can be efficiently induced by the use of incident atomic hydrogen from the gas phase producing the hydrogen halides by an Eley-Rideal process. The experiments showed that thermal activation of the solid surface is of minor importance for the removal of halogen by atomic hydrogen. This suggests that atomic hydrogen, with its excess potential energy (52 kcal/mol compared to the zero energy of 1/2 mole of H₂(g)), can be a promising driver of surface reactions. This class of reaction is thought to involve atomic hydrogen which is not thermally accommodated with the surface.

In this work, we report the interaction of atomic hydrogen with a surface layer derived from methyl iodide (CH₃I) and its deuterated counterpart (CD₃I) on the Si(100) surface. Methyl iodide dissociates to produce CH₃(a) and I(a) upon adsorption on the Si(100) surface at 100 K [12,13]. This enables one to study the interaction of atomic hydrogen with the surface methyl group. A further understanding of the H-induced surface reaction is revealed by two new observations. First, evidence is presented that the surface reaction induced by atomic hydrogen can remove surface iodine with high selectivity. Secondly, surface carbon present as CH₃(a) can be removed by atomic hydrogen at a much slower rate than that for adsorbed iodine. Studies of the temperature dependence for this reaction show that the carbon removal rate decreases with

increasing temperatures in the range of 450-650 K. Combining the Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD) studies, we conclude that the interaction of atomic hydrogen with the adsorbed methyl group involves the removal of surface carbon via an H-etching process which produces methylsilane, CH_3SiH_3 .

II. EXPERIMENTAL

The ultrahigh vacuum system (with a base pressure of 1×10^{-10} Torr) and the Si(100) crystal preparation have been described previously [12,14-16]; selected aspects will be summarized here. The system is equipped with an Auger electron spectrometer, an argon ion sputtering gun, a calibrated microcapillary array doser producing a collimated beam [14], and a multiplexed quadrupole mass spectrometer (QMS) with capabilities for both random flux and line-of-sight detection. Programmed heating of the Si(100) crystal (15x15x1.5 mm; p-type; B-doped; 10 Ω -cm) is carried out with a Honeywell programmable temperature controller which is used to drive a feedback circuit to control the power to the crystal [17].

For the adsorption of methyl iodide, a calibrated multicapillary array doser was used to deliver the gas molecules onto the Si(100) surface giving carefully controlled absolute adsorbate exposures [14]. Dosing of methyl iodide in this study was performed at a silicon temperature of 300 K. For dosing of H atoms onto the prepared surface, a tungsten-spiral filament (wire diameter = 0.25 mm; spiral radius = 1 cm; $T=1800$ K) with line-of-sight exposure to the crystal surface at a distance of ~ 4 cm was used to produce atomic hydrogen during H_2 exposure. The characteristics of molecular hydrogen dissociation by a hot tungsten filament have been examined previously [18,19]. The rate of atomization of molecular hydrogen on a hot tungsten filament ($T \geq 1800$ K) is

linearly dependent on the H₂ pressure at P(H₂) < 1x10⁻⁶ Torr [18,19]. However, owing to the uncertainties in determining the absolute flux of atomic hydrogen, the exposures of atomic hydrogen are given by the H₂ exposures in Langmuir (L) [1 L = 1 x 10⁻⁶ Torr.s], uncorrected for ion gauge sensitivity.

Surface cleanliness and the relative surface coverages of adsorbed carbon and iodine were verified by AES. All the AES data reported here were obtained by averaging at four or more positions on the prepared surface and the measurements of iodine coverage were made in a manner eliminating electron stimulated desorption effects [11]. TPD measurements were made with a line-of-sight detection geometry, using the shielded, differentially-pumped QMS.

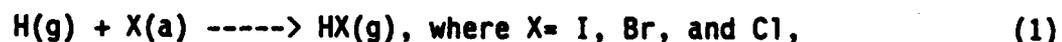
III. RESULTS

Dissociative adsorption of methyl iodide on the Si(100)-(2x1) surface has been investigated previously [12,13]. The CH₃I molecule dissociates upon adsorption at 300 K into a covalently-bonded methyl group and a chemisorbed iodine atom. A saturation coverage of ~ 2.9 x 10¹⁴ CH₃I/cm² was determined [12] which suggests that the surface species resulting from the dissociative adsorption of CH₃I are the methyl group and the iodine atom, each bound to one dangling bond on the surface (a perfect Si(100)-(2x1) surface nominally contains 6.8 x 10¹⁴ Si atoms/cm² or 3.4 x 10¹⁴ Si₂ dimers/cm²; 1 monolayer (ML) therefore nominally involves 6.8 x 10¹⁴ dangling bonds/cm²). In addition, studies of the thermal behavior of the methyl group on the Si(100) surface showed that the methyl group is stable up to ~ 630 K; above 630 K adsorbed CH₃(a) decomposes into lower CH_x species, which leads to Si-H species formation followed by the liberation of molecular hydrogen, beginning near 700 K [13]. Therefore, all the following experiments were performed at Si(100) substrate temperatures ≤ 630 K to avoid the chemical complexity which would be introduced at high temperatures.

A. Preferential removal of surface halogen by atomic H

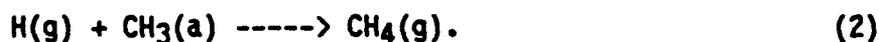
Figure 1 shows the AES results after exposing an $[\text{CH}_3(\text{a}) + \text{I}(\text{a})]$ overlayer on Si(100) to atomic hydrogen. The experiments were performed at a silicon temperature of 300 K and using the same H flux (the same H_2 pressure and W-filament temperature during atomic hydrogen dosing), so that the relative reaction rate constant, k , for the different adsorbates ($\text{CH}_3(\text{a})$ and $\text{I}(\text{a})$) can be obtained. The AES spectra were taken after each H exposure. The characteristic AES signals used for data analysis are C(KLL) at 272 eV and I(MNN) at 511 eV. The intensities of all AES signals are normalized to the intensity at reaction time zero, and therefore, each data point represents the relative surface coverage at reaction time t . In the case of chemisorbed iodine, the data were obtained at a constant electron fluence for each point, avoiding the effect of electron stimulated desorption in determining the relative surface coverages as described previously [11].

Two important features are noticed from Figure 1. First, the exponential behavior of iodine removal, as shown by the fitted experimental solid line in Figure 1, indicates that the extraction process is first order in the surface coverage of iodine. It has also been shown that the extraction reaction is first order in atomic hydrogen flux, and that it is almost a non-activated process [11]. The H-extraction process follows an Eley-Rideal type reaction mechanism where the surface reaction,



is driven mainly by the high potential energy of the incident atomic hydrogen. Details of the abstraction of different halogen adsorbates from the Si(100) surface have been presented elsewhere [11]. Secondly, the carbon surface

coverage remains almost constant throughout the H exposures indicated in Figure 1, in sharp contrast to the behavior of adsorbed iodine. The initial reaction rate constant for the removal of surface iodine is 170 ± 20 times higher than that for surface carbon at 300 K. This estimate is based on the assumption that the removal process for $\text{CH}_3(\text{a})$ follows first order kinetics as was experimentally verified for iodine [11]. The preferential removal of surface iodine demonstrates the selectivity of the H-induced reaction for the different surface species, $\text{CH}_3(\text{a})$ and $\text{I}(\text{a})$. The results also indicate a low reaction cross section for the removal of the methyl group by atomic hydrogen via a similar extraction type reaction, which might be postulated to occur,



The difference in reactivity for two types of adsorbed species, the methyl group and the halogens, will be discussed later.

B. Depletion of surface carbon (present as $\text{CH}_3(\text{a})$) by atomic H

A decrease of surface carbon concentration is observable following long atomic H exposures. Under the same experimental conditions as employed in Figure 1 (a silicon temperature of 300 K and a H_2 pressure of 1×10^{-7} Torr), a much slower rate of decrease of the C(KLL) intensity occurs, as shown in Figure 2(a). The error bar shown at reaction time zero indicates the reproducibility of preparing a 1 ML CH_3I overlayer. Also shown in Figure 2 is the effect of substrate temperature on the depletion rate of surface carbon by atomic hydrogen. A plot of the relative reaction rates versus substrate temperatures is shown in Figure 2(b). The relative first order reaction rates and hence the error bars shown in Figure 2(b) have been obtained by least square fitting of the logarithm of the C(KLL) signal at H_2 exposures ≥ 200 L. This is the region

were all iodine has been extracted, and Auger screening effects by surface iodine (which will influence the Si Auger intensity) are not present. The reaction rates at 300 K and 450 K are nearly the same for the exposures investigated here; the difference is within the experimental error. At higher temperatures ($T \geq 500$ K), a significant decrease of the carbon removal rate is observed. While the temperature-independent reaction rate observed at $T \leq 450$ K could suggest an Eley-Rideal type reaction, the decrease of reaction rate at $T \geq 500$ K indicates that the Eley-Rideal process is not involved in the adsorbed methyl extraction phenomenon.

C. Temperature-programmed desorption studies

Figure 3 shows typical TPD spectra obtained after exposing the prepared $\text{CH}_3/\text{Si}(100)$ surface to moderate exposures of atomic hydrogen at 300 K. Different H_2 desorption states (β_1 , β_2 , and β_3) and silane (SiH_4) desorption are observed. These desorption products are known to be the main products from the hydrogenated $\text{Si}(100)$ surface [2], and their production is confirmed as shown in Figures 3(a) and 3(b), respectively. In addition to the desorption of H_2 and SiH_4 , the desorption of CH_3SiH_3 is also observed and shown in Figure 3(c) by its major mass fragment ($m/e = 44$) [20]. From a saturated CH_3I layer, untreated with atomic hydrogen, neither the β_2 and $\beta_3\text{-H}_2$ states nor the CH_3SiH_3 and SiH_4 products are detected [12].

D. Interaction of atomic hydrogen with $\text{CD}_3(\text{a})$

Figure 4 shows the thermal desorption yield of H_2 , HD and D_2 obtained after a saturated $[\text{CD}_3(\text{a}) + \text{I}(\text{a})]$ adlayer, produced from the dissociative adsorption of CD_3I , has been exposed to different doses of atomic hydrogen at 300 K. The amount of desorbing H_2 and D_2 was calibrated by the desorption yield of the

saturated monohydride (monodeuteride) phase whose coverage corresponds to 1 ML on the Si(100) surface [2,12]. The amount of molecular hydrogen desorbing as HD was estimated from the relative sensitivities of the QMS for different hydrogen species as reported in the literature [21,22]. The initial uptake of H (see Figure 4), as shown by the increase of H₂ and HD desorption yield, occurs during the efficient removal of surface iodine (see Figure 1); the created dangling bond sites are occupied by the incoming atomic hydrogen. The initial decrease of the D₂ desorption yield is due to the exchange effect between CD₃(a) and H(g), to be discussed below.

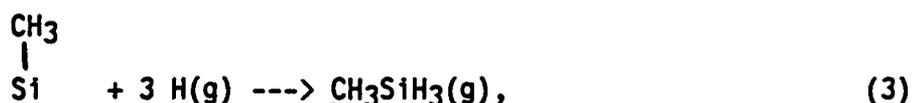
IV. DISCUSSION

In the following discussion, we will first focus on the interaction of atomic hydrogen with the adsorbed methyl group, which is further divided into two subsections: (1) the depletion of surface carbon by atomic H; and (2) the isotopic exchange interaction of atomic H with CD₃(a). Then, the selectivity for the H-induced surface reaction is discussed based on the results obtained for two types of adsorbates, the methyl group and the halogen.

A. Depletion of adsorbed CH₃ by atomic H

The temperature dependence of the carbon removal, as shown in Figure 2, is similar to that of H-etching on the Si(100) surface. Etching of the Si(100) surface by atomic hydrogen is known to be more efficient at low temperatures ($T \leq 400$ K) and high hydrogen coverages [2-4,23,24]. This is due to the need to achieve high hydrogen coverages to cause the breaking of the Si-Si bonds and to cause the formation of higher surface hydrides, SiH₂(a) and SiH₃(a), which serve as precursors for the formation of the etching product, SiH₄(g) [2-4]. Therefore, the observations of both the decrease of surface carbon coverage at

high atomic hydrogen exposures and the inefficient rate of removal of carbon at higher temperatures strongly suggests the following mechanism: the depletion of surface carbon on Si(100) by atomic hydrogen occurs via the etching of the C-incorporated Si(100) surface by the formation of volatile methyl silane compound(s), e.g., CH₃SiH₃(g). Further support for carbon removal by the etching mechanism is obtained from the TPD studies shown in Figure 3. The high surface coverage of chemisorbed hydrogen (as indicated by the β₂ and β₃ states) and the SiH₄ desorption indicate that etching occurs on the C-incorporated Si(100) surface at the exposures of atomic hydrogen used here [2]. Moreover, the observation of the etching product, CH₃SiH₃ (see Figure 3(c)) also strongly supports the etching mechanism for carbon removal by a process like,



where the surface methyl group is schematically shown attached to a surface silicon atom which is bonded to the bulk through three Si-Si bonds. The configuration shown in Reaction 3 does not imply a specific bonding structure of the Si atom on the Si(100) surface.

B. Interaction of atomic H with CD₃(a)

The fact that the removal of surface carbon proceeds via the H-etching process indicates that the interaction of atomic hydrogen with the surface methyl group can not be described by the Eley-Rideal process (Reaction 2) which would produce methane. As a matter of fact, based on the study where the deuterated methyl group (CD₃(a)) is used (Section III. D), it is evident that in addition to the etching reaction channel, additional surface reactions occur between the gas phase atomic H and the surface methyl group.

As shown in Figure 4, a significant decrease of D₂ yield is observed at an exposure for 3000 s, where ~ 0.1 ML of carbon (a saturation overlayer of CH₃I on Si(100) corresponds to ~ 0.5 ML of carbon) is expected to be removed at this exposure (as judged from Figure 2), but ~ 0.6 ML of D has been removed. This indicates the existence of an additional reaction channel between the incoming atomic hydrogen and the adsorbed methyl group, in addition to the H-etching process (Reaction 3).

A likely process for this additional reaction is the direct abstraction of D from the adsorbed methyl group, CD₃(a), by the incident atomic hydrogen,



and



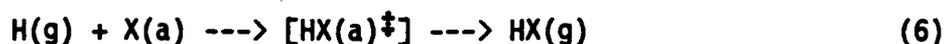
A similar reaction with low activation energy has also been proposed for the exchange of surface deuterium with incoming atomic hydrogen on the Si(100) surface, i.e., SiD(a) + H(g) ---> HD(g) + Si(a) [25]. Therefore, combining the AES and TPD results, we conclude that the interaction of atomic hydrogen with the surface methyl group on Si(100) surface involves multiple reaction channels, including Reactions 4 and 5, and the etching process (Reaction 3) to produce CH₃SiH₃(g). These results also indicate that the rate of the exchange reactions 4 and 5 exceed the rate of extraction of the methyl group by atomic hydrogen.

C. Selectivity of H-induced surface reaction

An unanswered question is: "Why is the reaction cross section so low for the elementary step, H(g) + CH₃(a) → CH₄(g), if the driving force mainly resides in the high potential energy of atomic hydrogen?", or "What is the key

factor controlling the selectivity of the H-induced surface reactions?".

As proposed previously [11], the extraction of halogens on Si(100) by atomic hydrogen follows the Eley-Rideal reaction mechanism where the gas phase reactant (in this case, atomic hydrogen) enters the transition state directly without equilibrating at the surface prior to reaction. The Eley-Rideal reaction can be expressed as,



where the first step, the formation of the transition complex $[\text{HX(a)}^\ddagger]$, is the rate determining step.

The comparable reaction for the surface methyl group,



does not occur or is inefficient compared to Reaction 6. This may be understood since the transition state in Reaction 7 is expected to be highly energetic compared to that in Reaction 6. The transition complex produced in Reaction 7 from the surface methyl group is expected to be highly energetic because of the perturbation of the $\text{C(sp}^3\text{)}$ electronic structure, producing pentavalent carbon. In contrast, for adsorbed halogen atoms, the transition complex with a divalent halogen atom, $[\text{HX(a)}^\ddagger]$, should exist in a lower-energy state compared to that for $[\text{CH}_4\text{(a)}^\ddagger]$ due to the halogen capability to form multiple-coordinated compounds [27]. From adsorption experiments, it is known that the reaction between $\text{CH}_4\text{(g)}$ and the Si(100) surface is very unfavorable [26], again suggesting a high energy transition complex in Reaction 7. Finally, screening of the carbon atom in $\text{CH}_3\text{(a)}$ by the methyl hydrogens may also be an effective factor in decreasing the reactivity with atomic hydrogen. As a result, Reaction

7 is less likely to occur compared to the etching mechanism (Reaction 3) and the H-exchange process (Reaction 4).

V. CONCLUSIONS

The interaction of atomic hydrogen with an overlayer of $[CH_3(a) + I(a)]$ on the Si(100) surface has been studied. The following results have been obtained:

- (1) Efficient removal of surface iodine by reaction with atomic hydrogen is observed. The initial removal rate of surface iodine is 170 times higher than that of surface carbon at 300 K.
- (2) The removal of $CH_3(a)$ by atomic hydrogen occurs slowly through an etching process in which silanes such as $CH_3SiH_3(g)$ are evolved. This reaction is favored at silicon temperatures below 450 K, where the coverage of surface H may be increased to levels sufficient for silane production.
- (3) An efficient isotope exchange reaction between $CD_3(a)$ and $H(g)$ has also been observed; this is the most rapid process for the interaction of atomic hydrogen with the surface methyl group on Si(100) at 300 K.
- (4) It is argued that H-induced extraction of $CH_3(a)$ to form $CH_4(g)$, based on the assumption of a transition state complex, $[Si-CH_4^\ddagger]$, is not favored compared to the hydrogen exchange reaction and the etching process to produce silane.
- (5) The chemical activity of atomic hydrogen is observed, even on silicon surfaces covered to saturation coverage by covalent-bound species such as $CH_3(a)$ or $I(a)$. This indicates that coordinative unsaturation of the surface is unnecessary for H-induced surface chemistry to occur. Technological surface processes, such as CVD, epitaxial film growth,

and etching may be governed by the chemistry induced by atomic hydrogen interaction with fully-covered surfaces.

V. ACKNOWLEDGEMENT

We acknowledge with thanks the support of this work by the Office of Naval Research.

Figure Captions

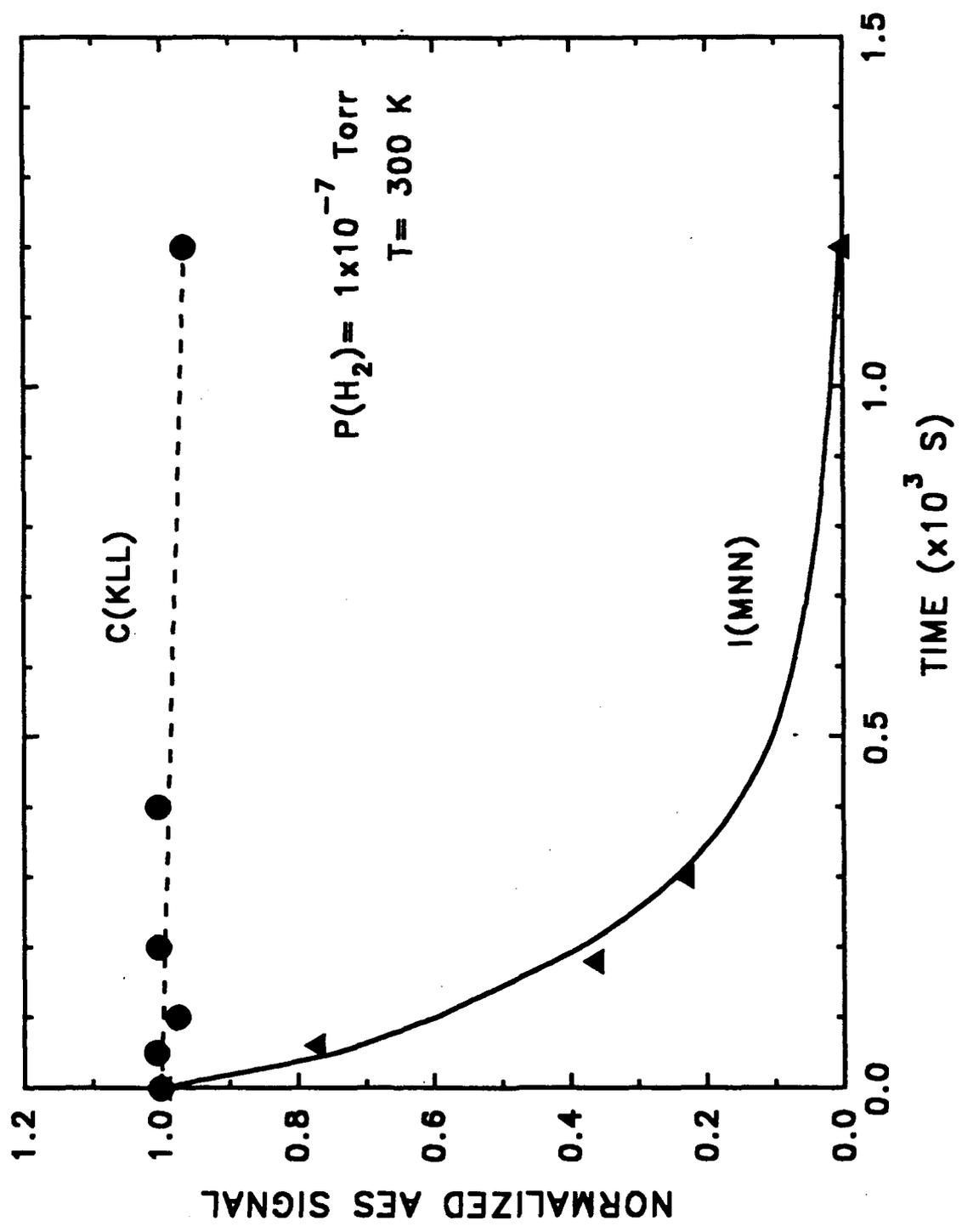
- Figure 1. The selectivity of the H-induced reaction on a overlayer of $\text{CH}_3\text{I}/\text{Si}(100)$ at 300 K. The solid line through the data points of the I(MNN) Auger intensity is calculated based on the first order rate law.
- Figure 2. Temperature dependence of carbon removal from $\text{CH}_3/\text{Si}(100)$ by atomic hydrogen. (a) shows the depletion of surface carbon at different Si(100) substrate temperatures; (b) shows the relative reaction rate versus substrate temperature where the relative reaction rate at each temperature is obtained based on the results of (a). The lines have been added as a guide for the eyes.
- Figure 3. Typical TPD spectra for different desorbing species after exposing $\text{CH}_3/\text{Si}(100)$ to atomic hydrogen at 300 K.
- Figure 4. Thermal desorption yield of different hydrogen species after exposing a $[\text{CD}_3(\text{a}) + \text{I}(\text{a})]$ overlayer on Si(100) to atomic hydrogen. The lines going through the data points are to guide the eyes.

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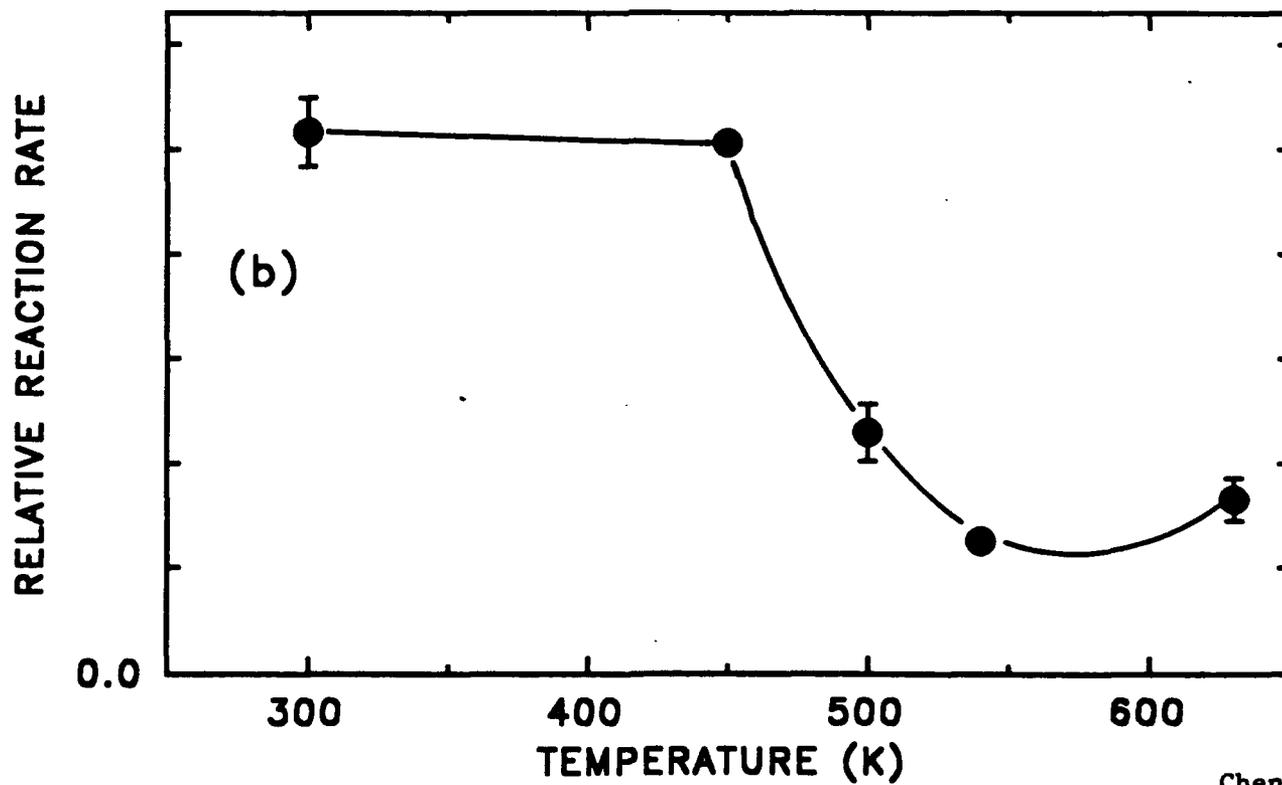
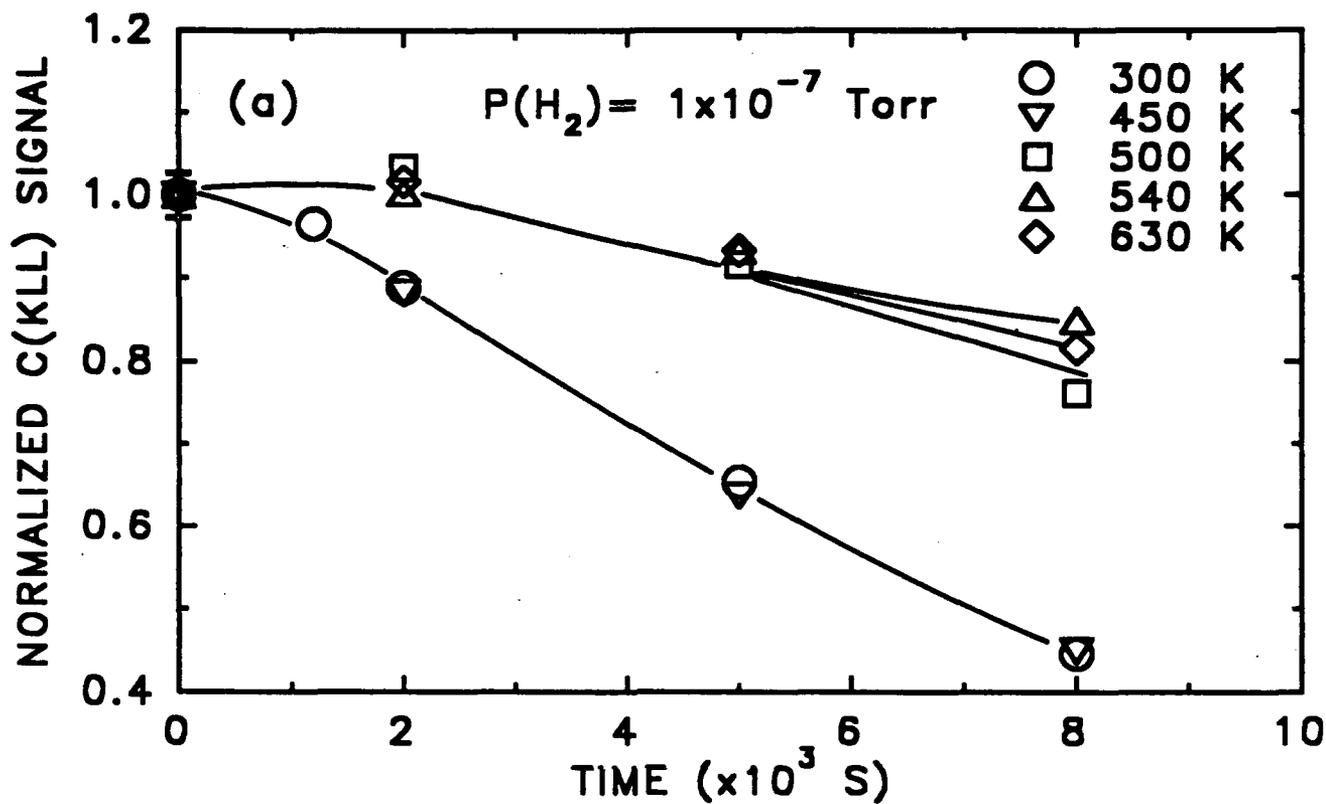
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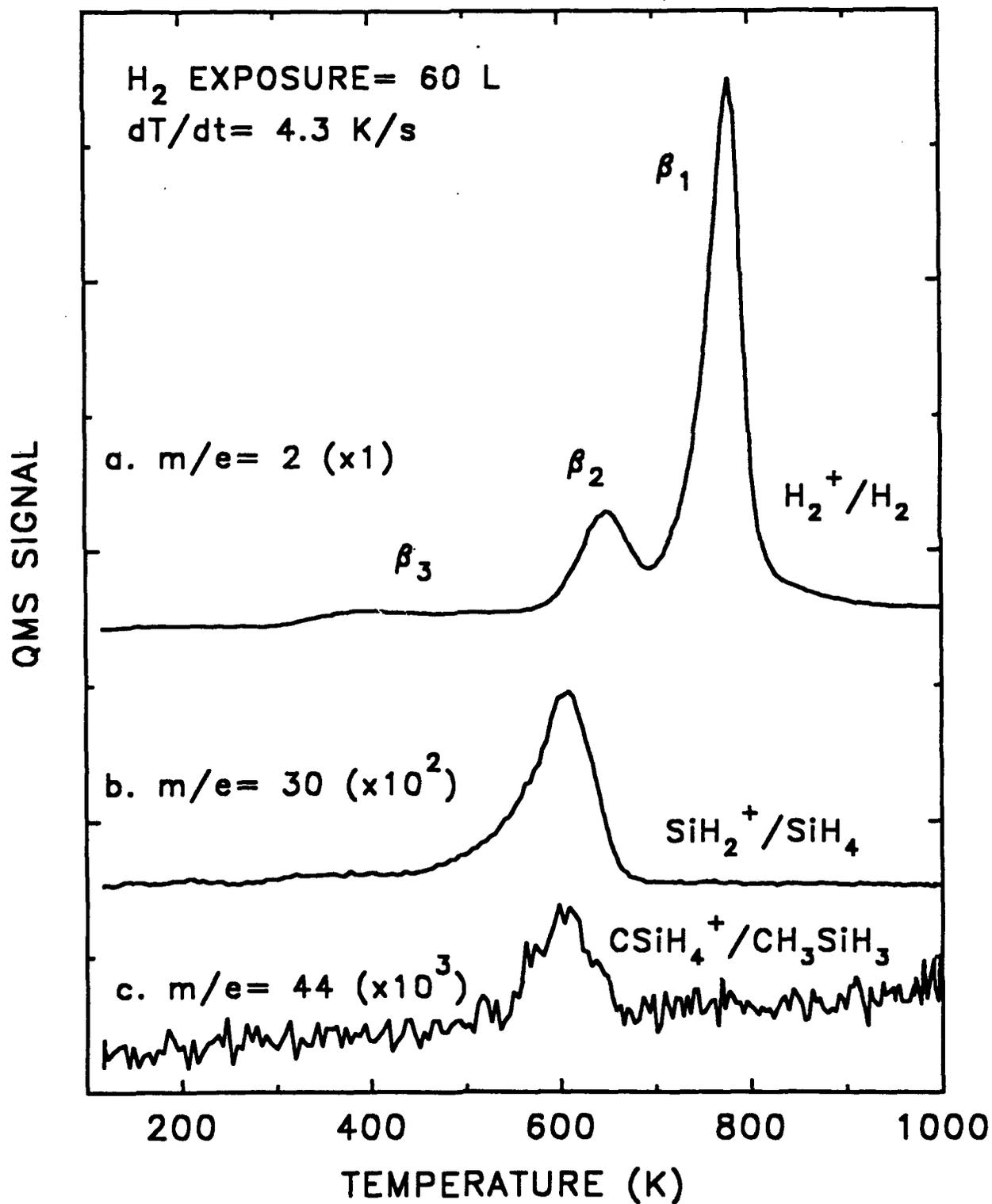
SELECTIVITY OF H-INDUCED EXTRACTION ON AN OVERLAYER OF CH₃I/Si(100)



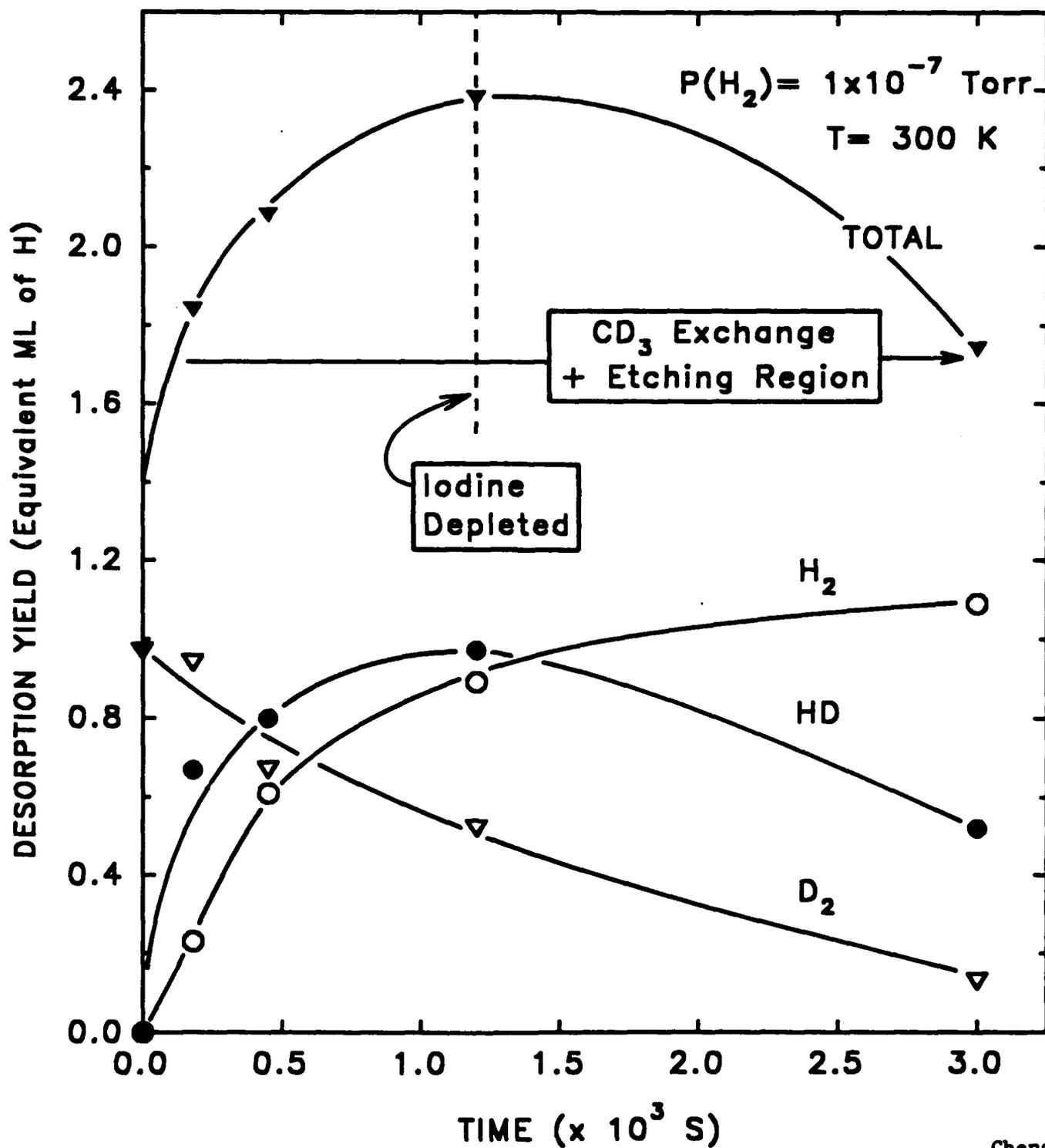
TEMPERATURE DEPENDENCE OF CARBON REMOVAL FROM CH₃/Si(100) BY ATOMIC HYDROGEN



TYPICAL TPD SPECTRA AFTER EXPOSING $\text{CH}_3/\text{Si}(100)$
TO ATOMIC HYDROGEN AT 300 K



DESORPTION YIELD OF DIFFERENT HYDROGEN SPECIES AFTER EXPOSING A CD_3I OVERLAYER ON $Si(100)$ TO ATOMIC HYDROGEN



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