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TECHNICAL REPORT NO. 50

Halogen Surface Chemistry on Si(100)-(2x1)

by

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Submitted To

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Pittsburgh, PA 15260

29 June-2 July 1992

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4. TITLE (and Subtitle) Halogen Surface Chemistry on Si(100)-(2x1)		5. TYPE OF REPORT & PERIOD COVERED Preprint
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) John T. Yates, Jr., C.C. Cheng, Q. Gao, and W.J. Choyke		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Surface Science Center Department of Chemistry University of Pittsburgh, Pittsburgh, PA 15260		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE 29 June-2 July 1992
		13. NUMBER OF PAGES 19
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) silicon chlorine Eley Rideal Si-Cl bond atomic hydrogen		
20. ABSTRACT (Cont) The surface chemistry of adsorbed halogen atoms on Si(100) has been studied using several surface science methods. It has been found using electron-stimulated desorption ion angular distribution (ESDIAD) that Cl atoms bond to dangling bonds on symmetric Si ₂ dimer sites, and that the Si-Cl bond angle is tilted (25°±4°) from the normal in the vertical plane containing the symmetric Si ₂ dimer bond. The covalently-bonded halogens Cl, Br, and I have been studied on Si(100) using atomic hydrogen bombardment at low substrate temperatures (300 - 630 K). In all cases, facile elimination of the hydrogen halide occurs, and the coverage of halogen may be driven to zero by moderate exposure to atomic hydrogen. The halogen extraction process is almost non-activated, suggesting that the chemical reaction to produce hydrogen halide species is driven by the potential energy carried by the atomic hydrogen species. This is an example of an Eley-Rideal reaction process and provides a potentially useful new approach for controlling atomic layer chemistry on semiconductors.		

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Abstract

The surface chemistry of adsorbed halogen atoms on Si(100) has been studied using several surface science methods. It has been found using electron-stimulated desorption ion angular distribution (ESDIAD) that Cl atoms bond to dangling bonds on symmetric Si₂ dimer sites, and that the Si-Cl bond angle is tilted ($25^{\circ} \pm 4^{\circ}$) from the normal in the vertical plane containing the symmetric Si₂ dimer bond. The covalently-bonded halogens Cl, Br, and I have been studied on Si(100) using atomic hydrogen bombardment at low substrate temperatures (300 - 630 K). In all cases, facile elimination of the hydrogen halide occurs, and the coverage of halogen may be driven to zero by moderate exposure to atomic hydrogen. The halogen extraction process is almost non-activated, suggesting that the chemical reaction to produce hydrogen halide species is driven by the potential energy carried by the atomic hydrogen species. This is an example of an Eley-Rideal reaction process and provides a potentially useful new approach for controlling atomic layer chemistry on semiconductors.

I. Introduction

The development of low temperature surface processes to manipulate adsorbed species on semiconductor surfaces provides the basis for new etching and thin film deposition methods to produce heterostructure semiconductor devices. Our knowledge of the fundamentals governing chemistry on semiconductor surfaces is in its infancy, and mechanistic understanding of elementary semiconductor surface processes is needed[1]. In this paper, the bonding structure of Cl on Si(100) and a new class of surface reaction, involving atomic hydrogen as a reagent, are described.

II. Experimental Details

The ultrahigh vacuum apparatus and methods used for this research have been described previously[2,3]. The methods employed include temperature programmed desorption(TPD), Auger electron spectroscopy(AES), high resolution electron energy loss spectroscopy(HREELS), and digital electron-stimulated desorption ion angular distribution (ESDIAD)[4]. Halogens are adsorbed on the single crystal surface using collimated molecular beam dosers which deliver an absolutely known flux of gas, permitting quantitative exposures and uptake measurements to be made[4].

III. Results and Discussion

A. Structure of Chemisorbed Cl on Si(100)-(2 x 1)

Figure 1 shows a schematic diagram of the digital ESDIAD apparatus employed for this work[3]. An electron beam excites surface species on the Si(100) single crystal, producing beams of positive ions which are spatially detected by the microchannelplate detector system. The pattern of ion emission angles is closely related to the direction of the surface chemical bonds which are ruptured by the electronic excitation process[5]. These ion emission directions are modified by final state image and reneutralization effects[6], as well as by the electrical bias applied to the crystal for pattern compression. Corrections for all three of these effects have been made in the estimation of the Si-Cl bond angle on Si(100)-(2x1)[7,8].

Because the ion emission dynamics are governed by rapid Franck-Condon excitation from the ground state to a repulsive upper state, the statistical summation of millions of ion emission directions from an ensemble of adsorbate species on a single crystal will provide a statistical measurement of the distribution of chemical bond angles caused by thermal disorder at the measurement temperature. This permits digital ESDIAD to be used also

as a powerful tool for the study of the dynamical behavior of adsorbates[5].

Figure 2 shows a sequence of Cl^+ ESDIAD patterns from chlorine adsorption on $\text{Si}(100)-(2 \times 1)$ [7,8]. At an adsorption temperature of 120 K, a normal Cl^+ beam is observed to overlap an underlying Cl^+ pattern exhibiting two-fold symmetry. Upon annealing the chlorine-covered surface to temperatures above 120 K, the central Cl^+ beam is seen to disappear, revealing the inclined beams which become more pronounced. This process culminates at about 673 K. The normal Cl^+ beam is caused by a minority of adsorbed Cl atoms which bridge the symmetric Si dimer sites. These species have a high cross section for ESD production of Cl^+ , and the normal emission from these bridged-Cl species therefore dominates the low temperature ESDIAD pattern. As the system is heated, the bridged-Cl species convert to terminal-Cl species, with the inclined Si-Cl bonds oriented in the vertical plane which includes the [011] crystallographic axis. This azimuthal plane corresponds to the Si-Si bond directions in the Si_2 surface dimers on a $\text{Si}(100)$ terrace. The orthogonal Si-Cl beam directions correspond to inclined Si-Cl bonds on the mixture of two types of crystal terraces present on the slightly misaligned $\text{Si}(100)$ crystal. The Si-Cl bonds are inclined $25^\circ \pm 4^\circ$ from the normal [7,8].

Figure 3 shows the vibrational behavior of the surface as a chlorine layer is heated over the same

temperature range as used in the ESDIAD experiments[8]. At 100 K, two Cl-related vibrational modes are observed at 600 cm^{-1} and at about 300 cm^{-1} . The 600 cm^{-1} mode is due to the Si-Cl stretching mode of the inclined Si-Cl bonds. Its frequency and intensity remains almost constant as the heating process occurs. The weak mode at about 300 cm^{-1} is assigned to a bridging-Cl species, linked between two Si atoms in a dimer pair on the Si(100)-(2 x 1) surface. The good analogy to the vibrational frequency of bridging-Cl in compounds such as Al_2Cl_6 was employed to make this assignment[8,9]. The vibrational behavior suggests that the bridging-Cl species is a minority species, since the intensity of the 600 cm^{-1} mode does not vary significantly during the heating process as the 300 cm^{-1} mode decreases in intensity. The bridging-Cl species is metastable with respect to the inclined Si-Cl species, which is the most stable species on Si(100). Similar behavior was observed in the theoretical calculations of Wu and Carter[10] for F on Si(100), except that an energy barrier for the bridge-to-inclined Si-F structure was predicted to be negligible theoretically. The large change observed in the Cl^+ ESDIAD pattern for the heating range 100 K - 673 K is related to the high ESD cross section for Cl^+ production from the small surface coverage of bridged-Cl which exists below 673 K.

B. Facile Extraction of Chemisorbed Halogen Atoms by Atomic Hydrogen

The silicon-halogen bond may be broken easily by bombarding the surface with atomic hydrogen, produced on a hot tungsten filament in the ultrahigh vacuum system containing a low pressure of molecular hydrogen[11]. Figure 4 shows the behavior of the Cl surface coverage at a surface temperature of 300 K, along with similar measurements made for adsorbed Br and adsorbed I on Si(100). These measurements have been made in a way in which the small effect of the Auger electron beam on the halogen coverage has no effect on the interpretation. The fitted curves are best fits to first-order kinetics in halogen surface coverage. It is seen that the relative rate of halogen extraction is $I > Br > Cl$. A similar trend has been observed in gas phase studies for the reaction of atomic hydrogen with the methyl halides to produce hydrogen halide species[12].

The bromine extraction rate was studied as a function of the pressure of H_2 used in the chamber, as seen in Figure 5. The flux of atomic hydrogen is known to be proportional to the H_2 pressure under these conditions[13]. As the hydrogen pressure is increased, the rate of Br extraction increases at a surface temperature of 430 K; the inset shows that the Br extraction rate is linearly proportional to the atomic H

flux employed. This provides direct evidence for the first-order dependence of the extraction rate on the atomic H flux.

The temperature dependence of the atomic-H induced extraction of bromine was measured as shown in Figure 6. An activation energy for this process of only 1.6 ± 0.2 kcal/mol was measured over the range 300 K - 630 K, as shown in the inset to Figure 6. Similar studies of the kinetics of extraction of adsorbed Cl gave an activation energy of 2.1 ± 0.2 kcal/mol for Cl/Si(100). These low activation energies are indicative that the thermal excitation of the surface species is of little importance in governing the rate of the halogen extraction process.

Considered together, the kinetic behavior of the halogen extraction process induced by atomic hydrogen corresponds to the well known, but infrequently observed, Eley-Rideal kinetic process[11]. The process involves the use of the potential energy carried by the atomic H to produce the active complex involved in the removal of surface halogen. An active complex, Si...X...H is produced when atomic H collides with the covalently-bonded halogen atom, X. Accomodation of the incoming H atom by the silicon surface is not required in this mechanism. The potential energy of the atomic hydrogen is 52 kcal/mol compared to $1/2 H_2(g)$, and this energy is the primary driver for the halogen extraction process observed. Such a process, occuring at low surface temperatures, could be

of significance in a variety of semiconductor technologies.

The Eley-Rideal process observed for atomic hydrogen as a reagent is potentially important for a wide range of surface chemistry. Other gas phase free radical species may be expected to be active in similar extraction processes on surfaces, and we will have to await future experiments before knowing the full implications of these first observations involving the most simple free radical species, atomic hydrogen. In particular, the use of atomic hydrogen extraction procedures for removal of surface halogen ligands (present in atomic layer epitaxy processes involving monolayers of group IV halide species) is expected to be of importance.

IV. Summary

This is a brief review of the bonding structure of chlorine on Si(100)-(2x1) and use of atomic hydrogen as a reagent for inducing halogen extraction reactions on silicon.

1. The Si-Cl bonds are inclined $25^{\circ} \pm 4^{\circ}$ from the normal in a perpendicular plane parallel to the Si-Si bonds in the (2x1) reconstruction of Si(100).

2. It has been shown that covalently-bonded halogen atoms may be efficiently removed from Si(100) by atomic hydrogen via an Eley-Rideal process yielding volatile hydrogen halide species. The rate of the Eley-Rideal process is almost temperature independent, indicating that thermal activation from the substrate is of little importance compared to the activation induced by the potential energy of the incident atomic hydrogen itself.

V. Acknowledgement

We thank the Office of Naval Research for full support of this work.

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Figure Captions

Figure 1. Digital ESDIAD apparatus for imaging chemical bond directions in adsorbed species.

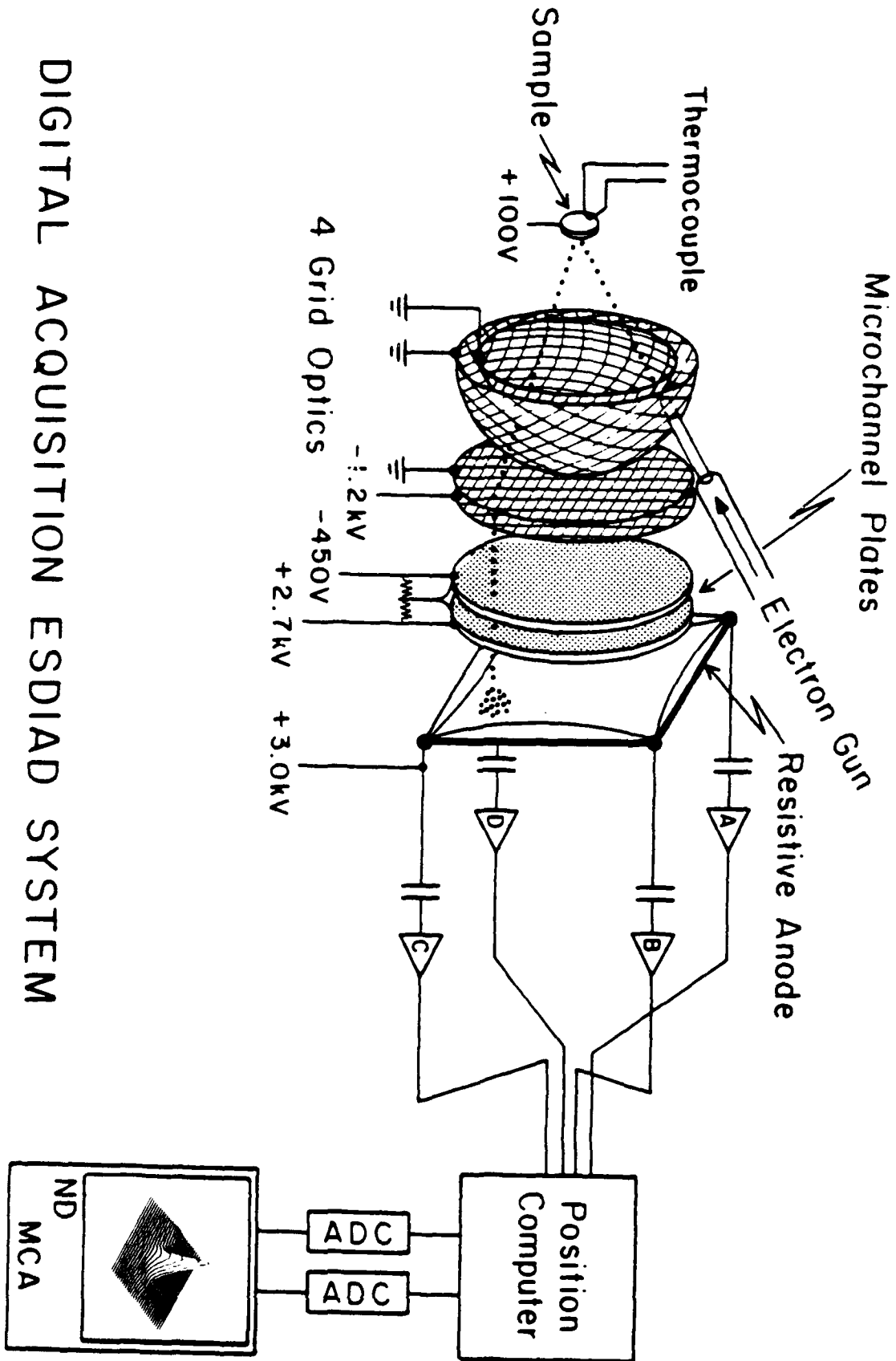
Figure 2. ESDIAD patterns of Cl^+ from $\text{Si}(100)$ as a function of annealing temperature. The initial Cl coverage is near 1 monolayer.

Figure 3. HREELS study of the spectral changes as a function of annealing temperature for $\text{Cl}/\text{Si}(100)$.

Figure 4. Atomic hydrogen extraction for halogen adsorbates from $\text{Si}(100)$.

Figure 5. Hydrogen pressure dependence of Br extraction rate from $\text{Si}(100)$.

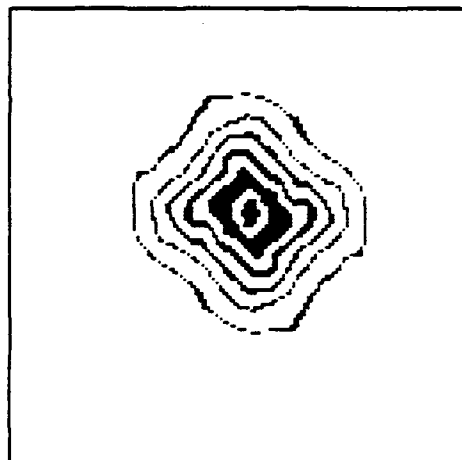
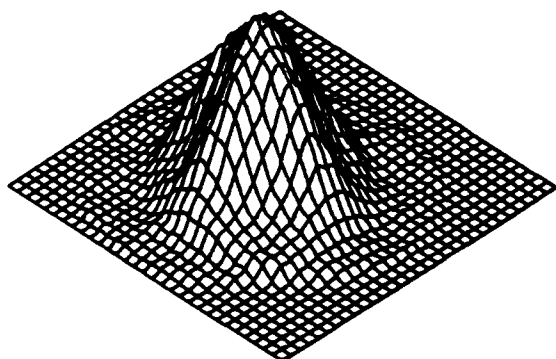
Figure 6. Temperature dependence of Br extraction rate from $\text{Si}(100)$.



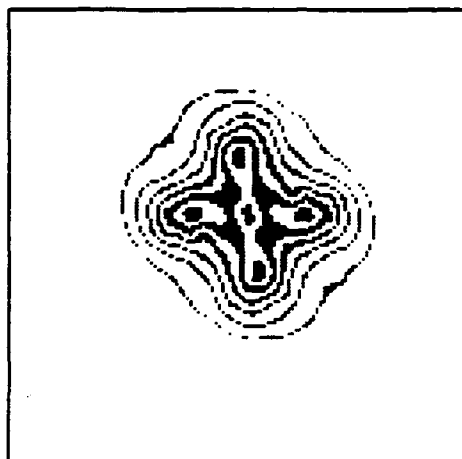
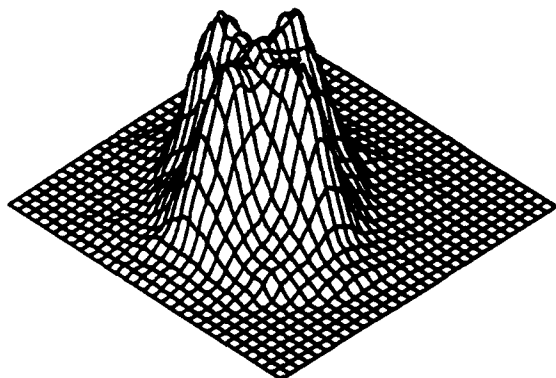
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Figure 1

ESDIAD Patterns of Cl on Si(100)

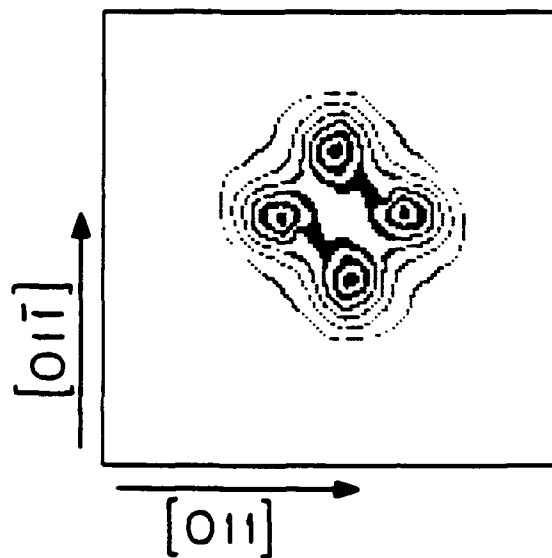
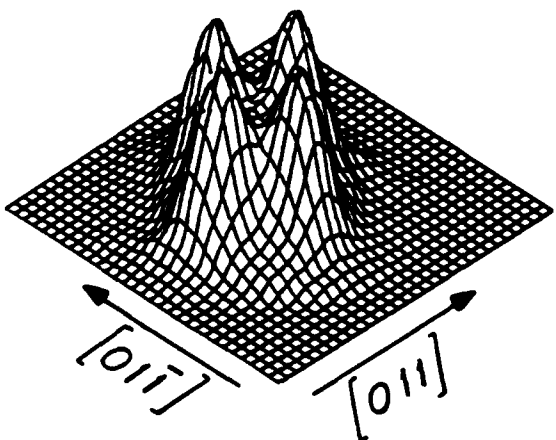
(a) $T = 120\text{K}$



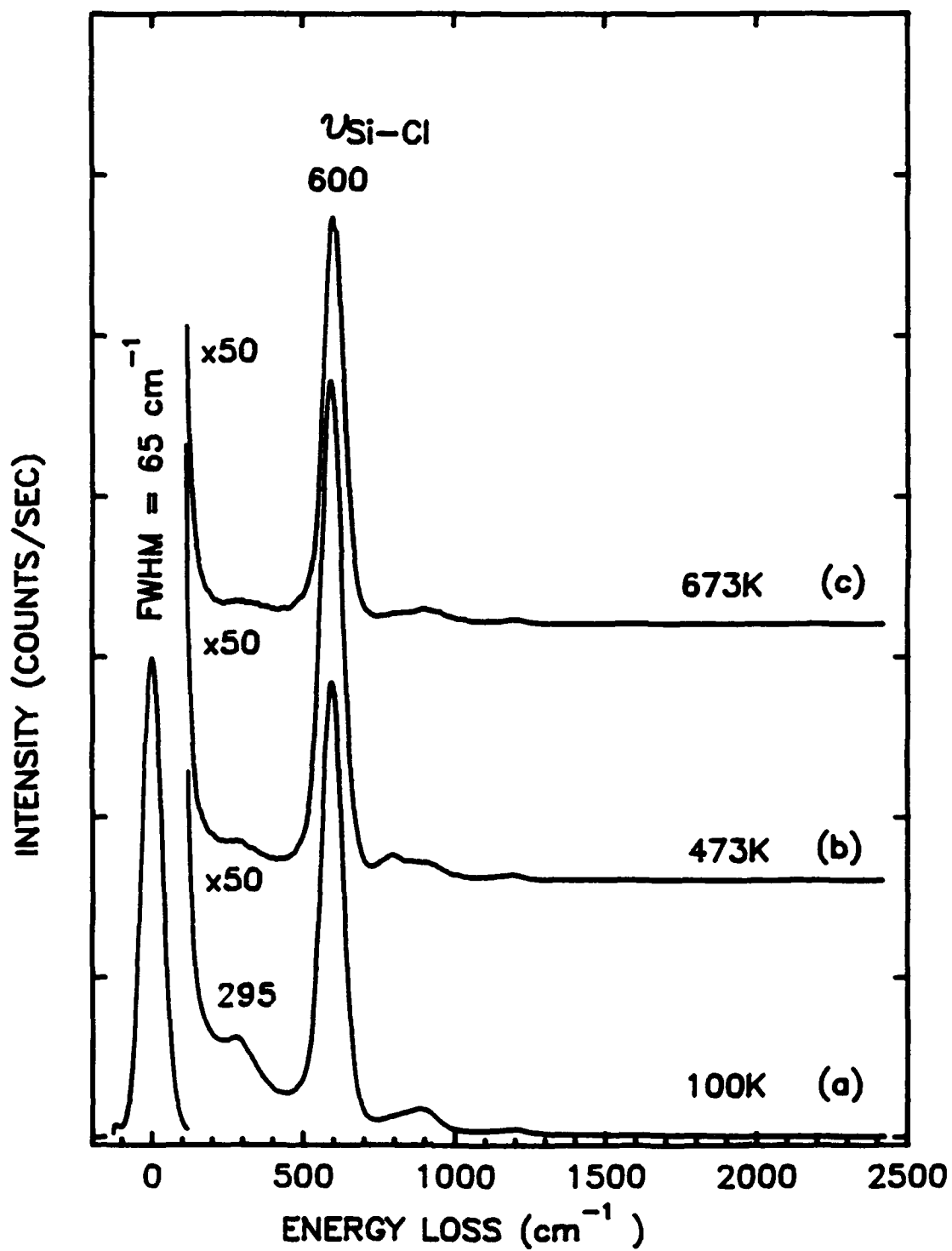
(b) $T_{\text{anneal}} = 423\text{K}$



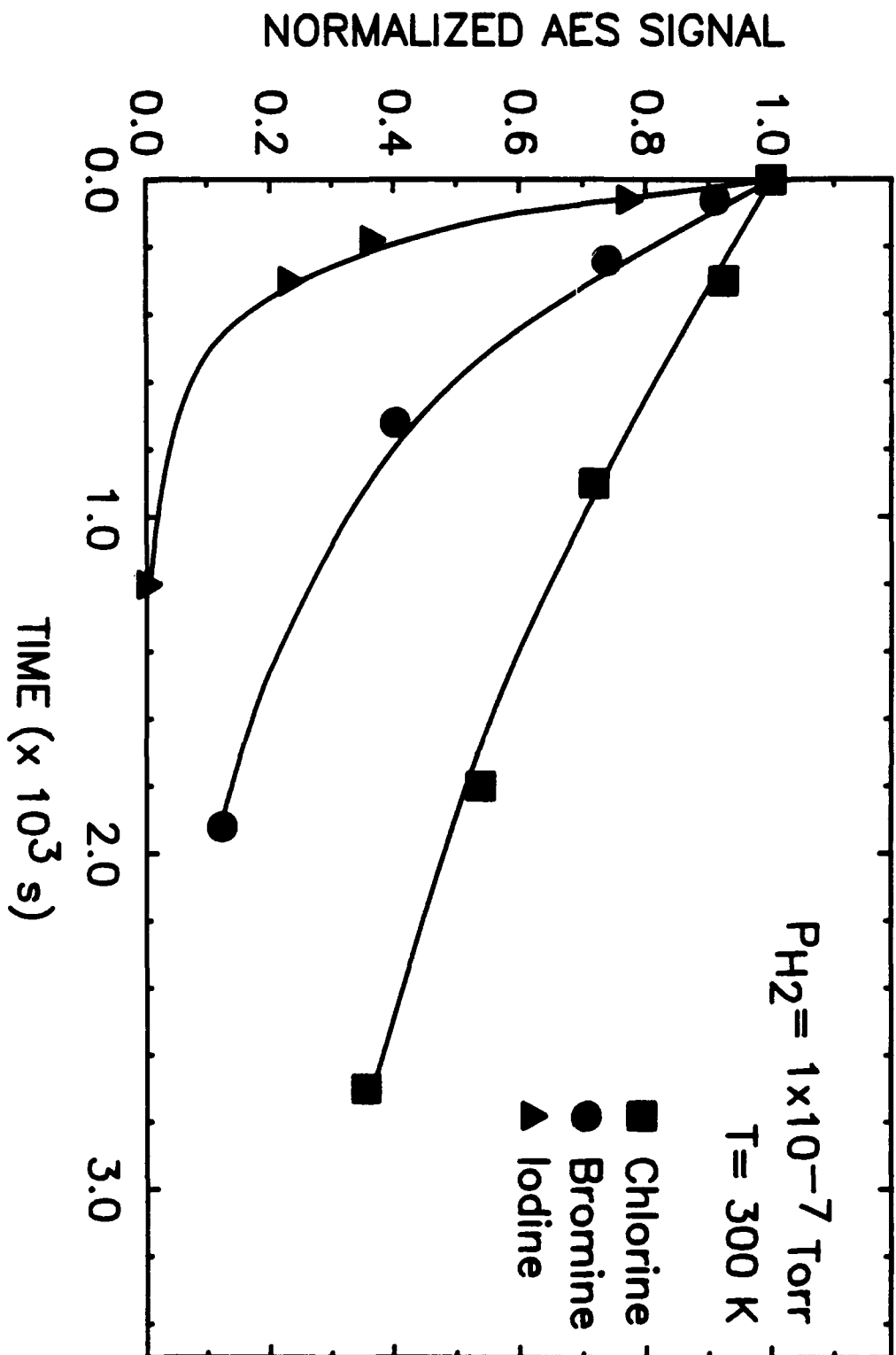
(c) $T_{\text{anneal}} = 673\text{K}$



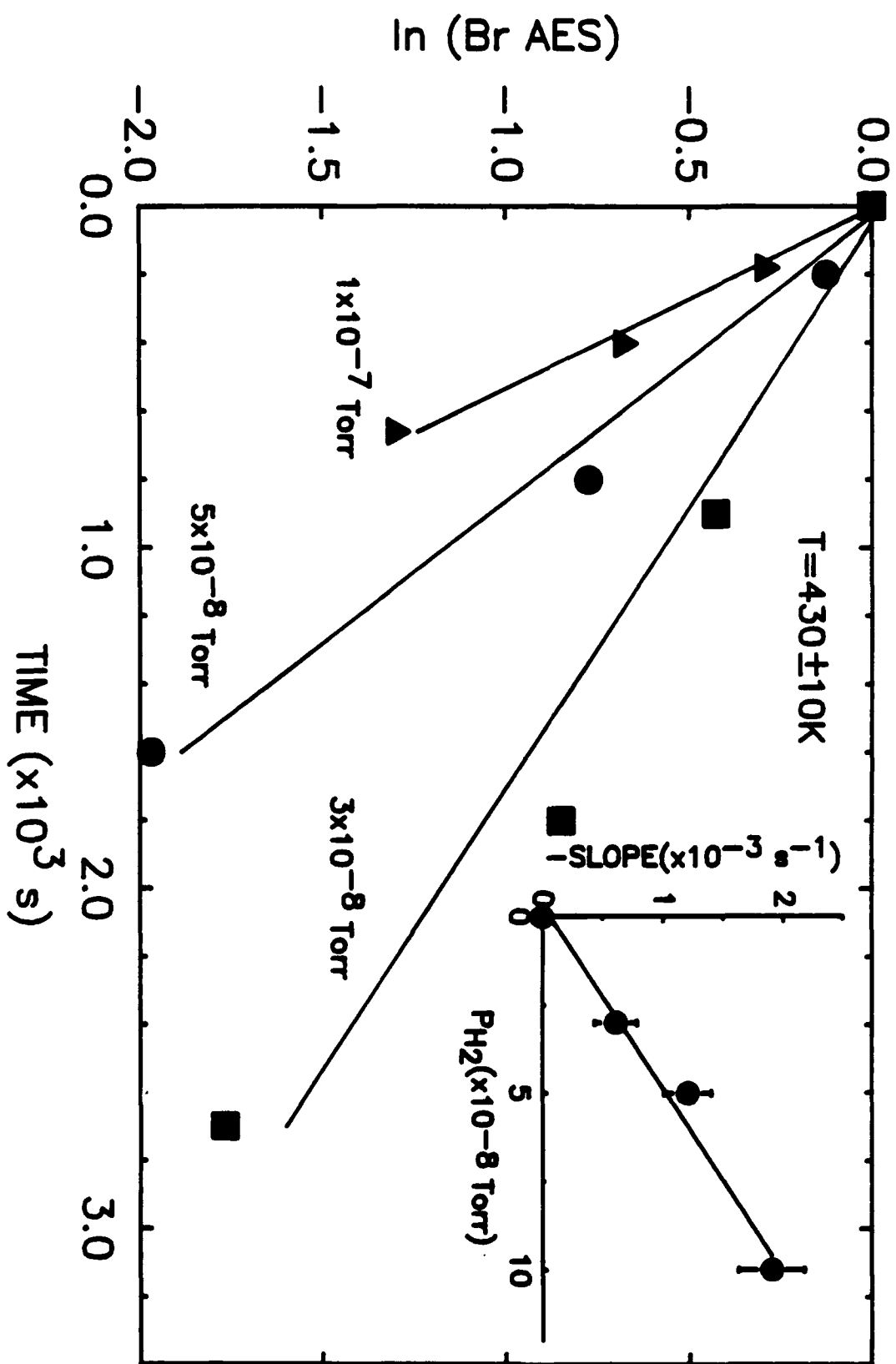
HREELS Study of Spectral Changes
During Annealing-Cl/Si(100)-(2x1)



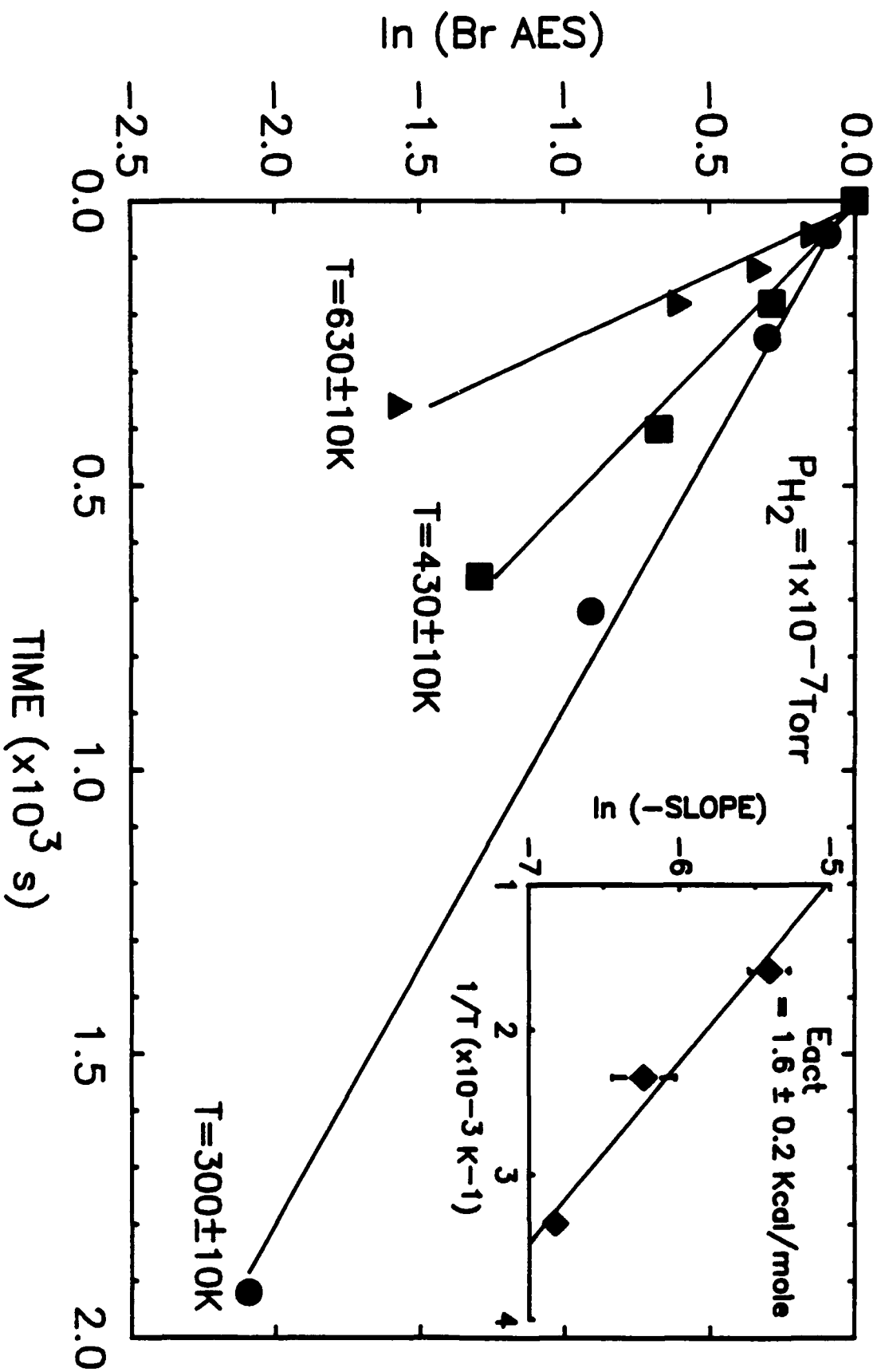
ATOMIC HYDROGEN EXTRACTION OF HALOGEN ADSORBATES ON Si(100)



HYDROGEN PRESSURE DEPENDENCE OF Br EXTRACTION RATE



TEMPERATURE DEPENDENCE OF BROMINE EXTRACTION FROM Si(100)



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Figure 6

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