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Inhibition of Atomic Hydrogen Etching of Si(111) by Boron Doping

by

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Surface Science Center
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20. ABSTRACT

Subsurface boron doping reconstructs the Si(111) surface and alters the electronic character of the surface Si atoms. The interaction of atomic hydrogen with the boron-modified Si(111)-($\sqrt{3}$x$\sqrt{3}$)-R30° surface was studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS) and low energy electron diffraction (LEED). In comparison to the Si(111)-(7x7) surface, we observe a significantly reduced hydrogen saturation coverage, measured by TPD and HREELS, and the absence of silane production. The ordered (1/3 ML) subsurface boron atoms passivate the surface Si atoms and reduce their reactivity with atomic hydrogen. This leads to a surface condition causing suppression of silicon etching by atomic hydrogen, compared to the unmodified Si(111)-(7x7) surface.

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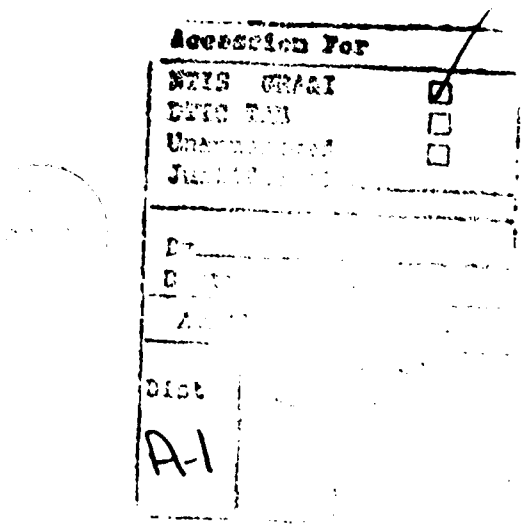

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Abstract

Subsurface boron doping reconstructs the Si(111) surface and alters the electronic character of the surface Si atoms. The interaction of atomic hydrogen with the boron-modified Si(111)-($\sqrt{3}$x$\sqrt{3}$)-R30° surface was studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS) and low energy electron diffraction (LEED). In comparison to the Si(111)-(7x7) surface, we observe a significantly reduced hydrogen saturation coverage, measured by TPD and HREELS, and the absence of silane production. The ordered (1/3 ML) subsurface boron atoms passivate the surface Si atoms and reduce their reactivity with atomic hydrogen. This leads to a surface condition causing suppression of silicon etching by atomic hydrogen, compared to the unmodified Si(111)-(7x7) surface.

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I. Introduction

Understanding of the adsorption and corrosive interaction of atomic hydrogen with silicon surfaces is of fundamental scientific and technological importance. Previous studies have established that the etching of a clean Si(111) surface can take place either in the presence of a continuous atomic hydrogen flux at room temperature [1], or by the thermal activation of SiH_2(a) and SiH_3(a) species at 600 - 700 K, where the etching product, silane, has been detected [2-4]. Recent atomic resolution scanning tunneling microscopy (STM) studies [5,6] have concluded that the etching of the Si(111)-(7x7) surface primarily involves the removal of the Si adatoms, where the breaking of adatom Si-Si backbonds forms silicon di- and trihydride species on the surface. These (adatom) hydrides are believed to be the precursor species for the gas phase etching product, silane. Modification of the surface atomic and electronic structure of silicon by foreign atoms may therefore to be expected to profoundly influence the etching mechanism. Recently, Kao et al. [4] have observed a marked <u>enhancement</u> of silane production on an Al-modified Si(111) surface while Wallace et al. [2] have reported that Ni contamination of the Si(111) surface <u>inhibits</u> silane production. In this paper, we report a study of atomic hydrogen interaction with a boron-modified Si(111) surface. We show that, in comparision to a clean Si(111)-(7x7) surface, a boron-modified Si(111) surface exhibits a substantially lower reactivity with atomic hydrogen.

II. Experimental

The experiments were performed in a stainless steel UHV system with a typical base pressure of $1x10^{-10}$ torr. The Si crystal used was a 1.3 x 1.3 x 0.15 cm, p-type B-doped (10 ohm cm nominal resistivity) wafer oriented to within

1° of the (111) direction. The crystal mounting and initial cleaning procedures have been described in detail elsewhere [7]. The in situ cleaning of the crystal was achieved by 2.5 keV Ar^+ sputtering at a 60° incidence angle followed by annealing at 1200 K. Atomic hydrogen was produced by dissociating H_2 gas at $5x10^{-7}$ torr with a hot tungsten spiral filament (diam. 1.9 cm, 1800-1900 K) placed ~4 cm in front of the Si(111) crystal. Since the arrival rate of atomic hydrogen at the surface is unknown, all the exposures used here are given as H_2 exposure in the unit of Langmuirs (1 L = 10^{-6} torr sec). H_2 exposures are measured with an uncorrected Bayard-Alpert ionization gauge. During atomic hydrogen exposure, the liquid-N_2 cooled Si(111) sample temperature was stablized at ~310 K.

The preparation of the boron-modified Si(111) surface involves adsorbing decaborane (DB), $B_{10}H_{14}$, at room temperature and subsequent annealing to 1?00 K to facilitate inward boron diffusion and the desorption of excess hydrogen and boranes [9,10]. The details regarding DB thermal behavior on the Si(111) surface will be reported in a separate publication [10]. A well-prepared surface exhibits a sharp ($\sqrt{3}x\sqrt{3}$)-R30° low energy electron diffraction (LEED) pattern. By taking into account the elemental sensitivity of the instrument, Auger electron spectroscopy (AES) measurements show a very reproducible B(KLL) to Si(LVV) intensity ratio (= 0.015 ± 0.002) consistent with 1/3 ML boron concentration. Only those surfaces which met the above LEED and AES criteria were chosen for the experiments described below. There exist a number of publications regarding the characterization of the boron-modified Si(111) surface [8,9]. Briefly, the surface layer consists of Si adatoms in an ordered ($\sqrt{3}x\sqrt{3}$)-R30° arrangement. Each Si adatom has one B atom directly underneath it occupying the substitutional site, yielding a nominal boron concentration of 1/3 ML [8]. The boron-doped surface yields an elastic electron scattering intensity

several times higher than a clean Si(111)-(7x7) surface in high resolution electron energy loss spectroscopy (HREELS) measurements.

III. Result and Discussion

Figures 1 and 2 show temperature programmed desorption (TPD) experiments from the boron-modified Si(111) surface at different atomic hydrogen exposures. Here both H_2 and SiH_4 desorption are monitored. In comparison to the Si(111)-(7x7) surface, three major differences exist for the boron-modified Si(111) surface. (1) H_2 thermal desorption forms only a single desorption state at ~730 K in contrast to the β_1 and β_2-H_2 states usually observed on the Si(111)-(7x7) surface [3,11]; (2) the total H_2 desorption yield on the boron-modified surface is substantially lower (a factor of 3 - 4); (3) no silane production is detected for all atomic hydrogen exposures (up to 500 L H_2). The implications of (1) and (2) will be further discussed in connection with other experimental results. The absence of silane desorption clearly indicates a lack of etching during temperature programming of the H-saturated Si(111)-B surface. It also implies that, on such a surface, the formation of di-and trihydride species is severely hindered since these higher hydrides have been shown to be the precursors for silane production [11]. By contrast, on the Si(111)-(7x7) surface, etching readily occurs when atomic hydrogen is incident. The etching phenomenon is consistent with the detection of a small amount of silane desorbing in the temperature range 400 - 650 K in TPD experiments on unmodified Si(111) on which hydrogen atoms have been adsorbed [2-4].

Under favorable conditions, vibrational spectroscopy is expected to identify different surface hydride species. However, the HREELS measurements on the boron-modified surface are masked by a strong background due to a combination of carrier plasmon excitation and B-Si phonon excitation [10,12].

Figure 3 compares the HREEL spectra obtained from a Si(111)-(7x7) and the boron-modified Si(111) surfaces following atomic hydrogen adsorption. On a Si(111)-(7x7) surface (Figure 3 A), a 30 L H_2 exposure yields fully developed mono- and dihydride loss features (560, 2075 and 860 cm^{-1}, respectively), in excellent agreement with a number of earlier HREELS studies [13-15]. In contrast, following more extensive atomic hydrogen exposure on the boron-modified Si(111) surface (Figure 3 B), only a weak Si-H stretching mode is seen at ~2075 cm^{-1}. Although it is difficult to quantify the Si-H intensities on the different surfaces, we notice that a lower Si-H stretching intensity on the boron-modified surface is consistent with the observed low H_2 desorption yield on the same surface. Simple dangling bond counting yields a relative dangling bond density of 0.33 (=1/3) on the Si(111)-B surface, rather close to 0.39 (=19/49) on the Si(111)-(7x7) surface. Given the fact that there are appreciable amounts of di- and trihydride on the latter surface at saturation [11], the observation of a factor of 3 to 4 lower H_2 desorption yield on the boron-modified Si(111) surface can only be accounted for by assuming that very few or no higher hydride species are present on this surface, since all the surface Si dangling bonds which are modified by B are equivalent. In fact, the hydrogen adsorption on Si(111)-B surface may be attributed to the presence of a small fraction of unmodified surface Si sites which are known to be generally more reactive than the boron-modified Si sites [9]. In an independent experiment [16], we have determined that typically there are about 12% of such unmodified Si adatoms present on a boron-modified surface compared to Si(111)-(7x7). These more reactive Si atoms are postulated to adsorb atomic hydrogen, and are probably responsible for the weak Si-H stretching mode observed in HREELS in Figure 3 B. On this basis we conclude that the perfect boron-modified Si(111) surface is unreactive toward atomic H, which is the

fundamental reason for the lack of atomic H etching of this surface as observed by TPD. Through STM and photoemission investigations, Avouris et al. [9] have demonstrated that, due to the subsurface B acceptor atom altering the Si adatom dangling bond electronic character, the Si(111)-B surface has a significantly reduced reactivity toward NH_3. Similarly, we observe a loss of reactivity toward atomic H, since it is the surface Si dangling bond that determines the chemical reactivity of the surface.

A second aspect concerning the etching of the boron-modified Si(111) surface is whether it is occurring slowly during the exposure to the atomic hydrogen flux at a Si temperature of ~310 K. Although we can not directly monitor SiH_4 species, if any, coming off the surface during atomic hydrogen exposure, we have monitored the Si and B Auger signal levels before and after the termination of each atomic hydrogen exposure. LEED measurements were made to monitor any structural change on the surface during atomic hydrogen exposure. The largest atomic hydrogen exposure received by the boron-modified Si(111) surface is about an order of magnitude higher than that required to saturate a clean Si(111)-(7x7) surface, as determined from TPD and HREELS measurements. Such a high exposure would certainly cause substantial SiH_4 formation (etching) to occur on a clean Si(111)-(7x7) surface [1,2,5,6]. The AES measurements (Figure 4) show a constant B(KLL) to Si(LVV) intensity ratio characteristic of 1/3 ML subsurface boron during high atomic hydrogen exposures. This result suggests that massive removal of surface Si atoms is not occurring during the atomic hydrogen exposure. In addition, there is no B-H vibrational mode observed near 2550 cm^{-1} by HREELS after atomic H treatment, as might be expected if Si etching should cause the exposure of B atoms to atomic H. LEED showed very little change in the $\sqrt{3}$ beams for hydrogen exposures below 200 L, consistent with the picture of no etching. Nevertheless, at higher exposures

the $\sqrt{3}$ beams were weakened along with the formation of increased background intensity and weak (1x1) beams as shown schematically in Figure 4. After the highest hydrogen exposure, LEED showed a (1x1) pattern and an increased background intensity, indicating disruption of the $\sqrt{3}$ registry on the surface. In view of the AES, TPD and HREELS data, it is unlikely that effects at high hydrogen exposures are due to massive removal of the $\sqrt{3}$-Si adatoms (etching). A possible rationale for the ($\sqrt{3}$x$\sqrt{3}$)-R30° to (1x1) conversion, with disordering on the Si(111)-B surface due to large hydrogen exposures, may involve H adsorption at Si sites which are not passivated by B. Adsorption at these "defect" sites on the ($\sqrt{3}$x$\sqrt{3}$)-R30° Si(111)-B surface may alter the stability of B-modified Si atoms which are neighbors to the "defect" sites. In a recent STM study on clean Si(111)-(7x7), Boland [5] observed that at high atomic H exposures, Si adatoms diffuse and form island structures, producing disorder on the surface. Upon the desorption of H_2 (~800 K), the Si adatoms redistribute themselves to reform the adatom deficient (7x7) surface. Our LEED measurements, made on the Si(111)-B surface treated with high atomic hydrogen exposure, show that a (1x1) to ($\sqrt{3}$x$\sqrt{3}$)-R30° conversion indeed occurs after H_2 desorption (~825 K), indicating that the disorder is induced by hydrogen adsorption.

The important role played by foreign atoms on the reactivity of the Si(111) surface toward atomic H is demonstrated by three observations made to date: (1) As-terminated Si(111) exhibits inhibited etching by atomic H [17]; (2) Ni impurity atoms (< 5 atomic % in the near surface region inhibit etching by atomic H [2]; (3) Al impurity atoms (another group III element) causes a pronounced (sixfold) enhancement of SiH_4 production compared to the unmodified surface [4].

In summary, we have studied the interaction of atomic hydrogen with the boron-modified Si(111)-($\sqrt{3}$x$\sqrt{3}$)-R30° surface. In comparison to the

Si(111)-(7x7) surface, a reduced saturation hydrogen coverage and the absence of silane production have been observed. The ordered subsurface boron atoms reduce the reactivity of surface Si atoms with atomic hydrogen. This leads to a surface condition where the saturation coverage of hydrogen is reduced far below that of unmodified Si(111) and hence to the suppression of SiH_4 formation [18]. LEED studies indicating ($\sqrt{3}$x$\sqrt{3}$)-R30° to (1x1) structural changes accompanied by surface disorder at high atomic hydrogen exposures are not well understood at present. This work suggests that the use of implanted B in silicon surfaces may provide a new method for the spatial control of atomic hydrogen etching processes.

IV. Acknowledgement

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Figure Captions

Figure 1: Temperature programmed desorption spectra of H_2 (m/e = 2) from H/Si(111)-(7x7) and H/Si(111)-B for various hydrogen exposures. Inset shows the integrated $H_2(g)$ desorption yields as a function of H exposure. The heating rate is 1 K/sec.

Figure 2: Temperature programmed desorption spectra of SiH_4 (fragment SiH_2^+, m/e = 30) from H/Si(111)-B for various hydrogen exposures. SiH_2^+ is the major cracking product from SiH_4 [3] and is not observed in these experiments. The heating rate is 1 K/sec.

Figure 3: HREELS spectra at 110 K from A) Si(111)-(7x7) surface after 30 L H_2; B) clean and H-exposed Si(111)-B surface. Hydrogen exposures are 60 L and 300 L H_2. The elastic electron beam intensity is 4.5×10^4 s^{-1} with a resolution (FWHM) of 90 cm^{-1}.

Figure 4: B(KLL) and Si(LVV) Auger intensity ratio as a function of hydrogen exposure. The spectra were taken in the dN(E)/dE mode at 110 K and each data point represents a 3- or 4-point average across the Si(111) crystal. Error bars show typical scatter in the measurements. The corresponding LEED observations as a function of atomic hydrogen exposure are also indicated. The initial increase in the B(KLL)/Si(LVV) ratio, above that for the clean surface (open circle), is due to atomic H adsorption on unmodified Si sites, where a significant change in the Si(LVV) Auger line shape occurs [19].

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Figure 1

HYDROGEN DESORPTION FROM Si(111) AND Si(111)–B SURFACE

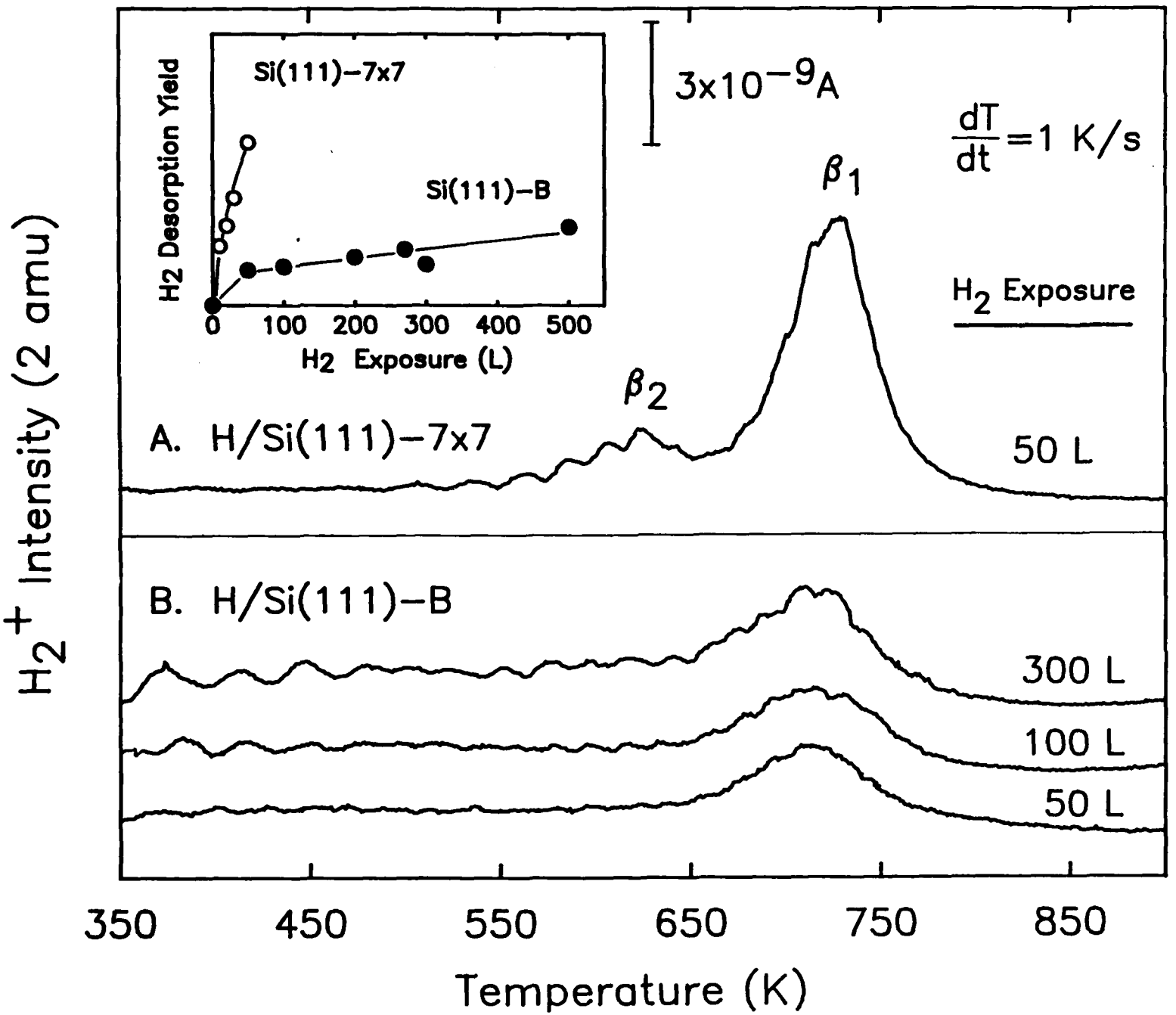

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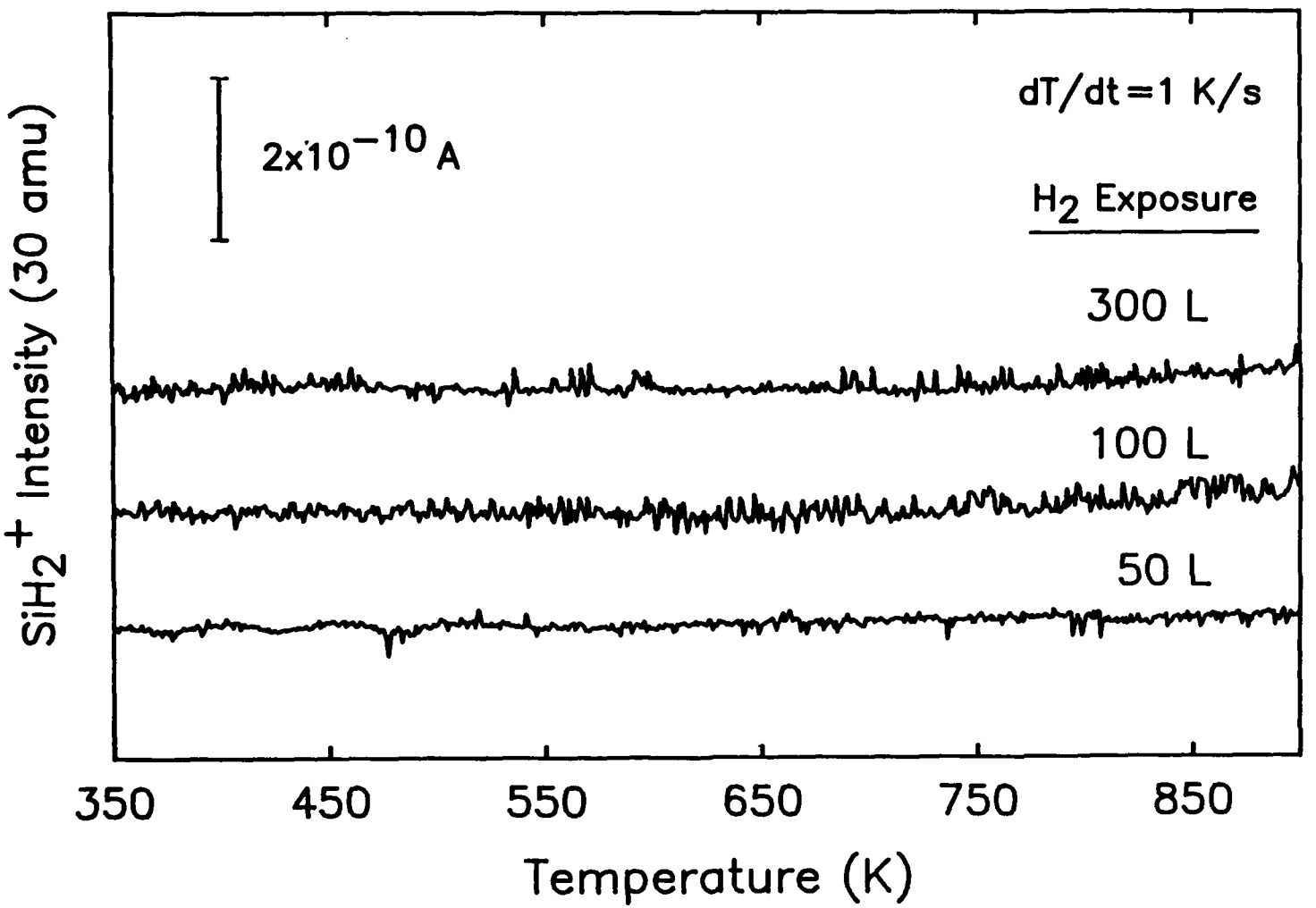
Figure 2

SiH_4 DESORPTION EXPERIMENT FROM H/Si(111)–B



HREELS Studies of Hydrogen Adsorption on Clean and B–Modified Si(111)

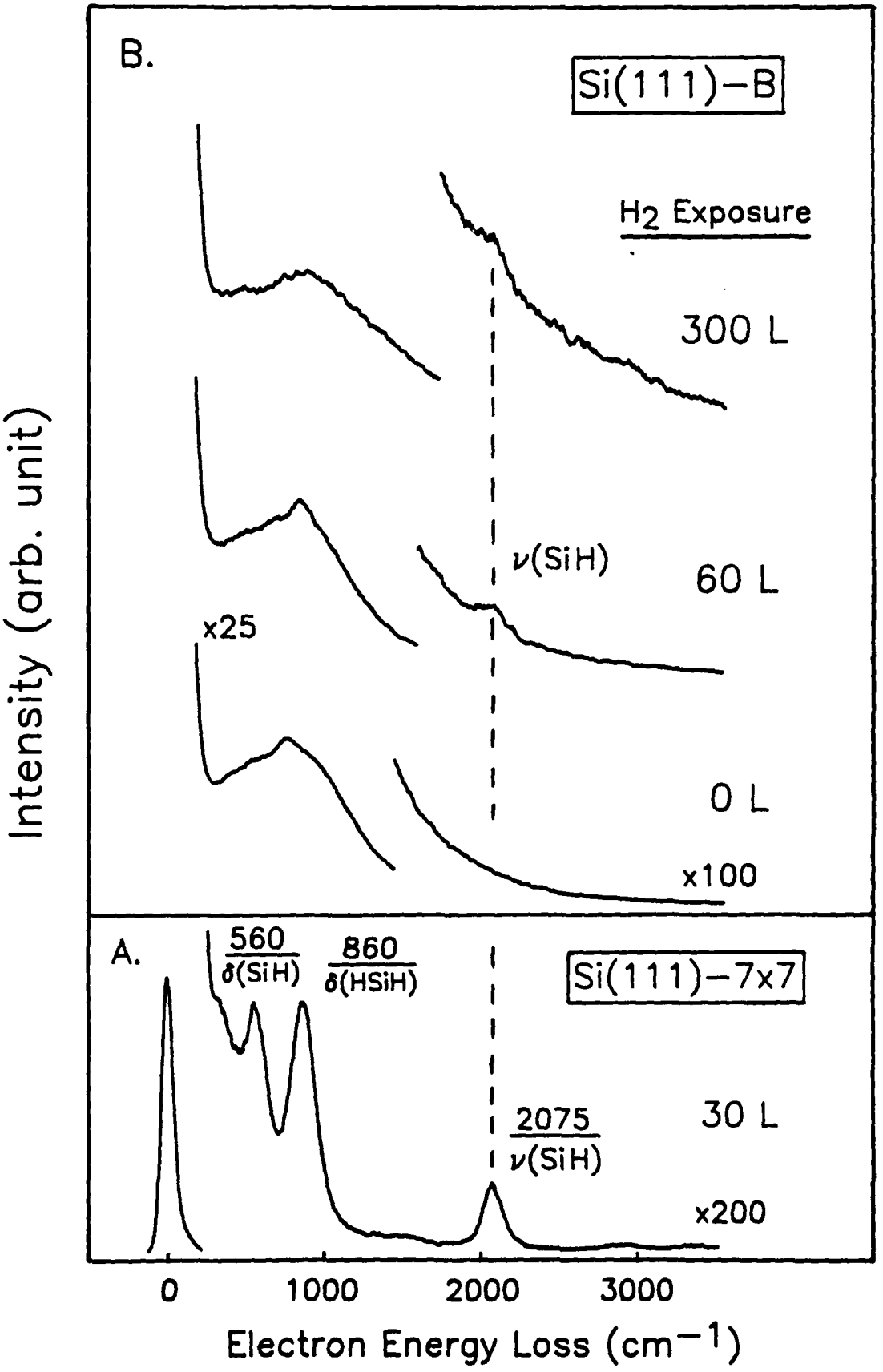


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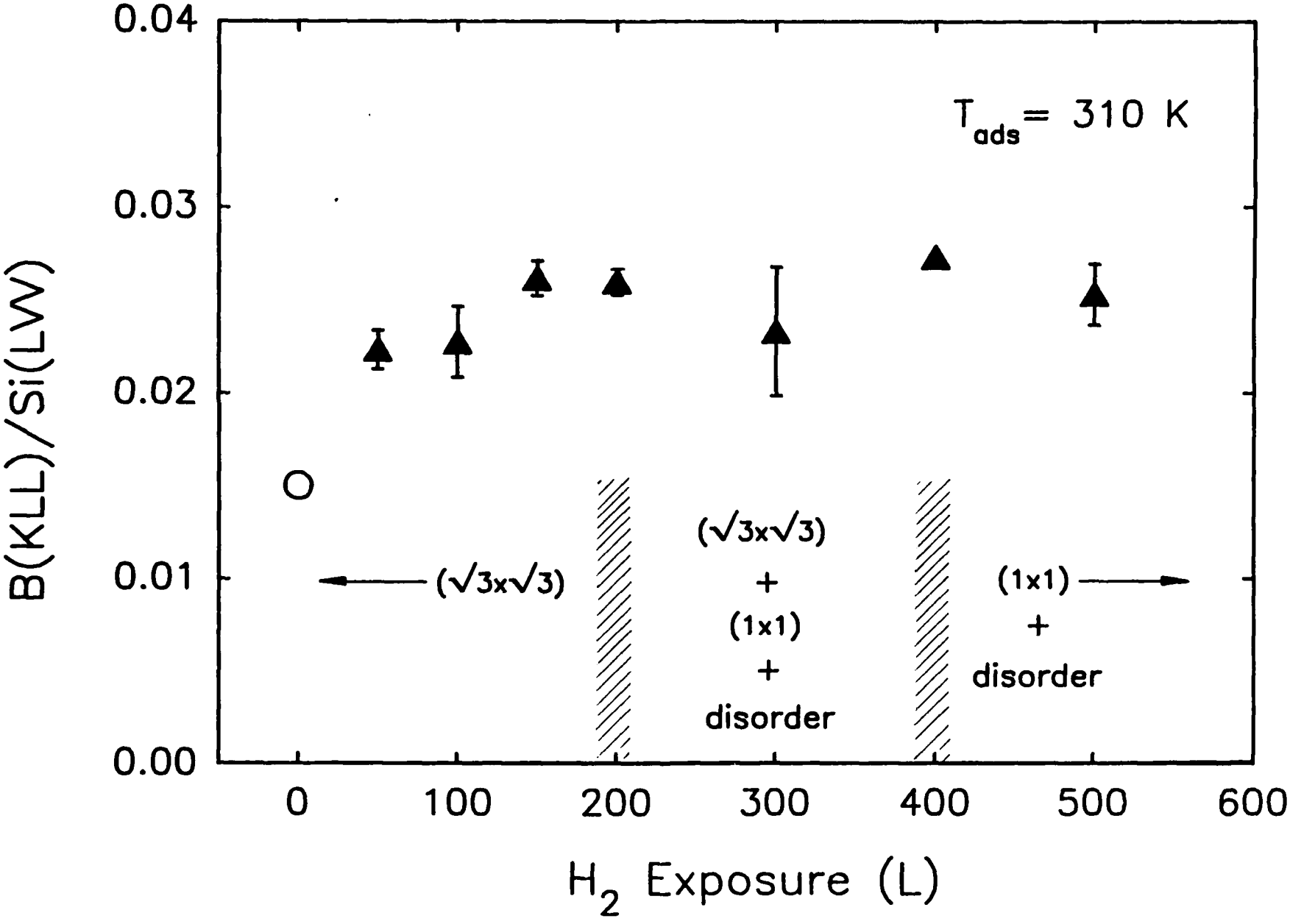
Figure 3

Effects of Atomic H on Si(111)–B
Auger and LEED Measurements



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