Nuclear Instruments and Methods in Physics Research B 276 (2012) 56–61

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Detection of H^+ recoiled from Si(1 1 1)–1 × 1-H by medium energy Ne^+ impact

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ARTICLE INFO

Article history:
Received 8 August 2011
Received in revised form 19 January 2012
Available online 3 February 2012

Keywords:
Elastic recoil detection of H
Si(1 1 1)–1 × 1-H
Medium energy Ne^+ impact
H^+ fraction
Zero-point energy
Doppler broadening

ABSTRACT

We detected the H^+ ions recoiled from Si(1 1 1)–1 × 1-H by medium energy 80–150 keV Ne^+ impacts. The H^+ fraction is dependent on emerging angle and emerging energy. With decreasing the emerging angle scaled from the surface normal the H^+ fraction increases and reaches a saturation below ~70° and almost 100% for emerging energy above 13 keV. In contrast, the charge state is not equilibrated even at ~85°. Such strong dependence on emerging angle is due to the location of H bound by Si atoms on top of the surface. The sensitivity to H on the surfaces is estimated to be better than 5×10^{12} atoms/cm^2 at a small emerging angle ($\theta_{out} < \sim 75°$), where the H^+ fraction reaches ~100%. The unexpectedly large energy spread for the recoiled H^+ spectra is attributed to the Doppler broadening caused by the zero-point energy of the vibrating H–Si system and additionally to small energy transfers among the three bodies of Ne^+ and H–Si, although the assumption of binary collision between Ne^+ and H is approximately valid. This H detection technique can be widely applied to analysis of chemical reactions including adsorption and desorption mediated by water and hydroxyl on various kinds of metal-oxide surfaces.

1. Introduction

The role of H in materials science expands over many fields, including stabilization of dangling bonds in amorphous Si and Si_x-Ge_y films applied to solar cells and thin film transistors giving a positive effect, while H embrittlement of metals and deterioration of large scale integrated circuits (LSI) by inclusion of H result in a negative effect. It was also reported that H passivates the Si(1 1 1) and (0 0 1) surfaces by terminating the dangling bonds and keeps clean surfaces [1,2]. In catalysis, hydroxyl group (OH) plays an important role to enhance catalytic activities of metal clusters on metal oxides surfaces [3,4].

Variety of methods to detect H have been reported so far, induction coupled plasma, secondary ion mass spectrometry [5], elastic recoil detection analysis (ERDA) [6,7], nuclear resonant reactions [8,9] and electron stimulated emission [10]. Temperature programmed desorption combined with a quadrupole mass filter and infrared absorption analysis have been also employed to detect adsorbates containing H and vibrational modes of H bonds on surfaces, respectively. In traditional ion beam analysis, ERDA using MeV He^+ and heavy ions has been utilized to probe H in depth down to several hundred nm. In this case, an absorber foil is necessary to eliminate elastically scattered ions. Alternative ERDA techniques with time-of-flight detection [11–13] and combination of magnetic and electrostatic fields [14] have been also proposed.

Previously, we reported direct detection of H for Si(1 1 1)–1 × 1-H and hydroxylated TiO_2(1 1 0) surfaces using medium energy He^+ and Ne^+ ions [15]. This method was applied to the analysis of a gas phase CO oxidation on rutile TiO_2(1 1 0) surfaces [16], where the density of oxygen vacancies were determined by ERDA for the surface exposed to H_2O leading to paired OH formation. In this work, we first show strong dependence of a H^+ fraction on emerging angle and emerging energy for recoiled H from Si(1 1 1)–1 × 1-H surfaces. Detailed discussion is also made on the broadening of recoiled H^+ spectra considering the Doppler effect caused by the zero-point energy of the vibrating H–Si bond and other probable factors.

2. Experiment

We prepared carefully uniform Si(1 1 1)–1 × 1-H surfaces according to the methods recently proposed by Kato et al. [17] to obtain high quality surfaces and confirmed a clear 1 × 1 pattern by reflection high energy electron diffraction (RHEED). This method using a 40% w/w NH_4F buffered solution including $(NH_4)_2SO_3$ (1.0% w/w) instead of an HF solution led to stronger water-repellency and more sharp 1 × 1 RHEED patterns than the usual treatment reported by Higashi et al. [18]. The key issue is to eliminate oxygen in the etching solution [17]. Therefore, we regard the surface as terminated completely by one monolayer (ML) of H (1 ML: 0.783×10^{15} atoms/cm^2).

Immediately after the surface treatment, the samples were introduced into an analysis chamber evacuated to an ultra high vacuum (~2×10^{-10} Torr). Ne^+ ions created in a duoplasma ion

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doi:10.1016/j.nimb.2012.01.035

source were accelerated to 80–150 keV and collimated to a size of 0.18 mm in horizontal and of 2.0 mm in vertical planes before impinging on the samples mounted on a 6-axis goniometer. We measured precisely the beam current of ions incident on the samples which were positively biased by 90 V to suppress secondary electrons emission. The same bias voltage of +90 V was also applied to a final aperture placed 50 mm in front of the sample holder to absorb secondary electrons emitted from it. It is crucial to avoid the ion irradiation effect leading to decrease in areal H density on the Si(1 1 1) surface. Therefore, we utilized a low beam current of 1–2 nA and shifted slightly the beam position on the surface after a dose of 0.1 μC. The H ejection rate from the surface was evaluated quantitatively and the correction for the areal density of H on the surface was made to determine the H^+ fractions. A toroidal electrostatic analyzer (ESA) detected recoiled H^+ ions with an energy resolution (FWHM: full width at half maximum) of $\Delta E/E = 1–3 \times 10^{-3}$. Indeed, we estimated the energy resolution for 10–120 keV He^+ ions incident at 45° on Au(0.6 ML)/Ni(1 1 1) and scattered to 45° with respect to surface normal. The detailed discussion on the energy resolution will be made later in terms of the energy spread of recoiled H^+ profiles. The detection efficiency of the three-stage micro-channel plate coupled with a position sensitive detector attached to the toroidal ESA was measured in advance using 150 keV H^+ beams. From the scattering yield from Au of Ni(10.1 Å)/Au(4.0 Å)/Si(1 1 1) which was analyzed by Rutherford backscattering with 2.0 MeV He^+ ions, the detection efficiency was derived to be 0.44 ± 0.02.

3. Results and discussion

First we calculated numerically the cross sections for H recoiled by medium energy He^+, N^+ and Ne^+ incidence using the Ziegler–Biersack–Littmark (ZBL) potentials [19]. The calculated recoil cross sections for 100 keV He^+, N^+ and Ne^+ impact are shown in Fig. 1. The recoil cross sections for N^+ and Ne^+ impacts are more than two orders of magnitude larger than for He^+ impact. It must be also noted that the above cross sections are five orders of magnitude larger than for MeV He^+ incidence [7]. Thus an excellent sensitivity to surface H is expected, if one uses medium energy Ne^+ ions. However, such high recoil cross sections may eject H significantly from the surface at a relatively small Ne^+ dose. We roughly estimate the total recoil cross section for medium energy Ne^+ impact on H at an impact parameter less than 1 Å. Note that the bond length of H–Si for Si(1 1 1)–1 × 1-H was derived to be 1.49 and 1.54 Å, respectively, by the tight binding method [20] and first principles calculations [21]. If one assumes an unscreened Coulomb potential and an impact parameter (s) less than 1 Å, which result in ejection of H, the total recoil cross section (πs^2) is deduced to be 3.14×10^{-16} cm^2. This leads to H ejection of ~5% after a Ne^+ dose of 0.1 μC. Actually we checked the H loss from the surface by Ne^+ impact by measuring the H^+ yields as a function of Ne^+ dose. Fig. 2 shows the H^+ yield for 143.9 keV Ne^+ impact on Si(1 1 1)–1 × 1-H at incident and emerging angles of 54.7° and 85.0°, respectively, without shifting the irradiation area. The H^+ yield indicated at a dose of 0.1 μC, for example, means the data acquisition during Ne^+ irradiation from 0 to 0.1 μC. Unexpectedly, a strong H reduction takes place exponentially. The observed H^+ yield, $Y_H(I)$ is well reproduced by

$$Y_H(I) = Y_H(0)\exp[-I/\lambda], \tag{1}$$

where I is integrated beam current (μC), $Y_H(0) = 874.8$ and $\lambda = 0.372$ μC. This result indicates that ~25% of H is lost from the surface after Ne^+ dose of 0.1 μC. Note that the data acquisition from 0 to 1 μC in this case corresponds to the recoil yield from the surface with an average H amount of 88% of the initial value. The λ value is, of course, dependent on incident angle and Ne^+ energy. The data shown hereafter are after the correction of the H loss from the surface. As an additional contribution to H loss from the surface, we consider the sputtering effect and/or ion beam stimulated desorption like the electron stimulated desorption [10]. According to Matsunami et al. [22], the sputtering yield for 143.9 keV Ne^+ impact on Si is ~0.3, which leads to an H loss of ~6% after a dose of 0.1 μC, if one assumes the same ejection rate for H as the sputter etching rate for Si. Therefore, the high ejection rate for H from the surface is probably due to the processes of recoil as well as sputtering and/or ion beam stimulated desorption.

Now, we show a typical ERDA spectrum observed for 143.9 keV Ne^+ ions incident on the Si(1 1 1)–1 × 1-H at an angle of 58.0° (see Fig. 3). The H^+ ions recoiled to 72.5° with respect to surface normal were detected (recoil angle: $\varphi = 49.5°$). The recoiled H^+ spectrum was best-fitted by a symmetric Gaussian shape with FWHM of 213 eV, indicating no significant multiple scattering by underlying Si atoms. If we assume the amount of H on the Si(1 1 1) to be just one monolayer, the H^+ fraction is deduced to be 79.0 ± 7%. As mentioned before, the H^+ fractions are dependent strongly on emerging angle and also significantly on emerging energy (the energy of H when emerging from the surface). The former is attributed to the location of H terminating the dangling bonds of the top layer Si

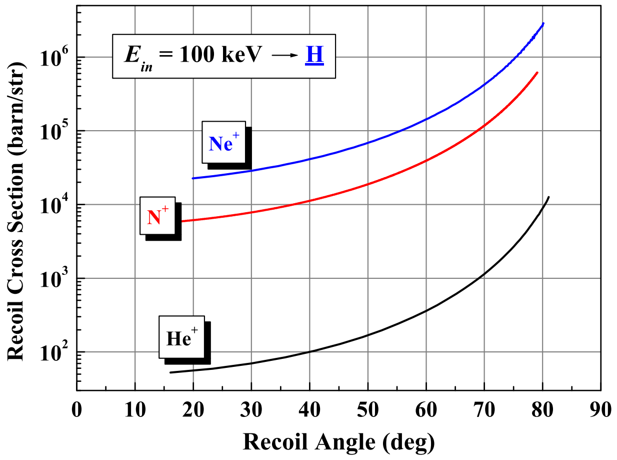

Fig. 1. Recoil cross sections calculated for 100 keV He^+, N^+ and Ne^+ impacts on H as a function of recoil angle using the ZBL potentials.

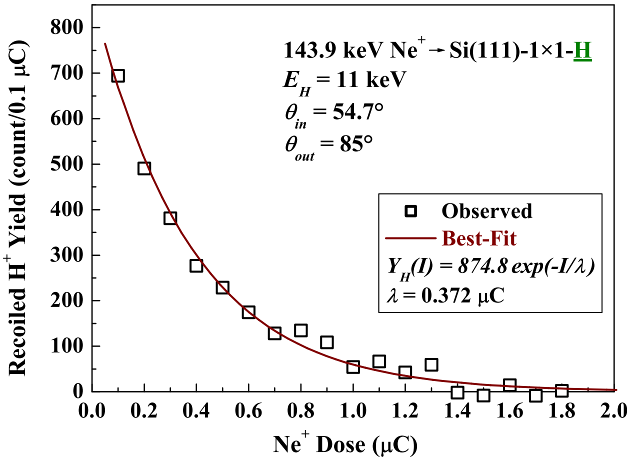

Fig. 2. H^+ yield (count per 0.1 μC) observed for 143.9 keV Ne^+ impact on Si(1 1 1)–1 × 1-H, as a function of Ne^+ dose (μC). The Ne^+ ions impinged on the same area of the surface during the measurement.