

Direct Recoil Time-of-Flight Technique: In Situ Analysis of H, C, N, and O on Si(100) and Polyimide Surface

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Surface light species H, C, N, and O are simultaneously detected by direct recoil time-of-flight technique to study cleaning, oxidation annealing processes of Si(100) and polyimide surfaces. The presenting technique has been found to be applicable to analyze both conductors and insulators. Difference of hydrogen amounts between pure H₂O and O₂ oxidation is confirmed in the low pressure region of 10⁻⁵ - 10⁻⁸Pa.

1. Introduction

There are various kinds of surface chemical reactions in which hydrogen takes part as a reactant in semiconductor device processing. However, little information has been available on surface hydrogen since hydrogen is the most difficult element to detect by conventional electron spectroscopic techniques. Thus new techniques and concepts are necessary as pointed out by many researchers(1, 2). From this viewpoint, this paper describes the potential usefulness of direct recoil time-of-flight (DR) technique. It is shown here that in situ rapid DR measurements of surface light species H, C, N, and O on Si(100) substrates and polyimide (PIQ®:Hitachi Chem. Company) films can be made to clarify their cleaning, annealing and oxidation processes.

2. Experimental

The equipment requirements(3) and experimental details(4) have been presented elsewhere. The apparatus used is shown in Fig. 1. In short, a pulsed keV ion beam directed at a grazing incidence onto a sample surface induced the direct recoil of surface atoms and of adsorbed species at the surface. The recoiled atoms were largely neutral sputtered atoms with single collisions between the surface atoms and primary ions. The energy E_r of a surface atom of mass M₂ recoiling

from a primary ion of energy E₀ and mass M₁ is given by the binary collision formula expressed by,

$$E_r = E_0 \left[\frac{4A}{(1+A)^2} \right] \cos^2 \phi, \quad (1)$$

where $A = M_2/M_1$ and $\cos \phi$ is the recoil angle (angle between direction of incidence of the primary ion and the recoiling surface atom). These recoiled atoms passed through a flight tube and were detected by a particle multiplier (channeltron). Spectra are collected as a histogram of the distribution of particle flight time using a

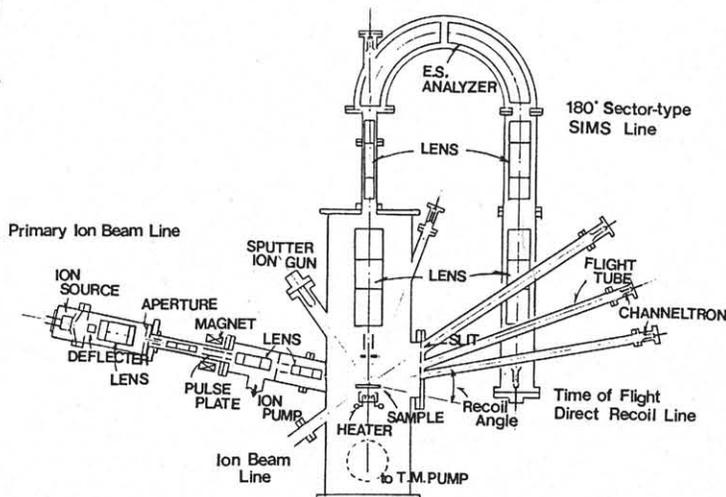


Fig. 1 Experimental apparatus for direct recoil time-of-flight measurements.

time-to-amplitude converter. By careful selection of the energy and mass of the primary ion, time-of-flight spectra for the direct recoils were obtained in which the carbon, nitrogen, and oxygen peaks were resolved in addition to that of hydrogen. The experimental parameters used were K^+ ions with 4 keV, a 15 nanosecond pulse width, 10 kHz pulse repetition, a 100 pA average current, and a 1 mm spot in diameter. The length of the flight tube was 100 cm and the recoiling angle was set at 21 degrees. The chamber pressure was kept at 10^{-8} Pa during measurements.

Samples used were n-type and p-type Si (100) wafers and PIQ films coated on Si wafers.

3. Results and discussion

-- Surface cleaning of Si (100) --

The DR spectrum of a Si(100) surface without any treatment in the reaction chamber is shown in Fig. 2 as a solid curve. The peaks assigned were derived from the flight time calculation using Eq. (1). It is obvious that the surface was

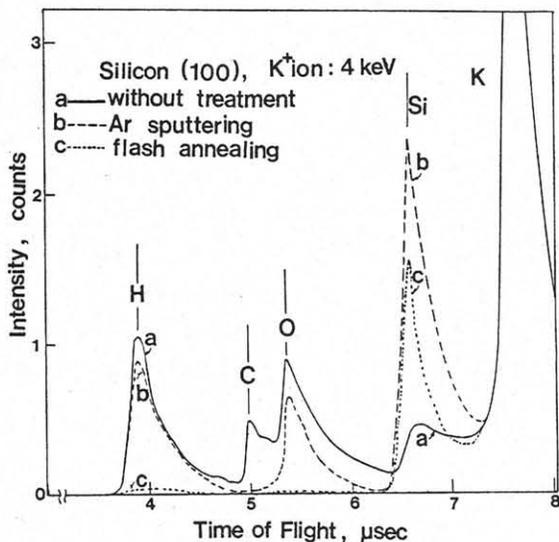


Fig. 2 Direct recoil time-of-flight spectra for Si(100) surfaces (a) without any treatments, (b) sputtered by Ar^+ ions, and (c) cleaned by subsequent flash annealing.

covered with water and hydrocarbon contaminants. For Si (100) cleaning, Ar^+ ion sputtering and flash annealing have been used in MBE and surface studies. Both treatments were examined to clarify the cleaning process. The Ar^+ ion sputtering with 500 - 3000 eV was found effective for sputtering out the surface carbon but not for the hydrogen and oxygen. These elements were dis-

appeared after flash annealing at 1000 °C for 2 minutes. The spectra of the Si (100) surface were measured as a function of time after cleaning to study the residual gas effects on the clean reconstructed surface. The result is shown in Fig. 3. This shows that the cleaned Si surface was quickly covered with H and O. The spectra indicate that 1 Langmuir H_2O exposure is sufficient to fully cover the surface, which agrees with the gas exposure experiments. Hence the control of the H_2O partial pressure is quite important to obtain reproducible results in MBE, SOI and surface experiments. Only 2 or 3 minutes are allowed to keep the Si(100) surface clean before processing in 10^{-7} Pa.

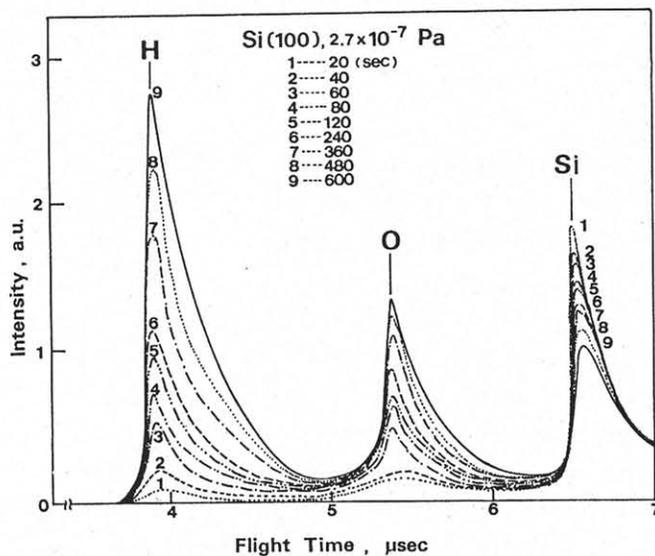


Fig. 3 DR spectra for Si(100) surface as a function of time after cleaning.

-- Oxidation of Si (100) --

Oxidation of Si (100) was carried out with pure O_2 gas and H_2O gas in a low pressure region of 1.5×10^{-5} - 3.0×10^{-3} Pa at 600 - 1100 °C, and with O^+ ion implantation with 3 keV. Then, the DR spectra of these obtained surfaces were measured to find the differences in the peak height of the surface hydrogen. Oxygen and silicon recoils from SiO_2 were obtained in the dry oxidation case. The DR spectrum obtained after 800°C oxidation with O_2 pressure of 2.7×10^{-4} Pa for 1 minute is shown in Fig. 4. The oxides grown at 700 - 800 °C and the higher pressure range of 7×10^{-5} - 3×10^{-3} Pa were found to have the same DR spectra as that obtained for those grown in

the conventional furnace. For the H_2O oxidation, hydrogen was found on the surface in addition to O and Si, as shown by the broken line in Fig. 5. Here, the H peak became low with subsequent heat treatments ($600^\circ C$) for 20 minutes but did not disappear. These results indicate that the vapor pressure of SiOH is higher than that of SiO, so that the oxide does not cover the whole Si surface in the very low pressure H_2O oxidation. After O^+ ion implantation, a small amount of hydrogen was detected as a surface contaminant as shown in Fig. 6. However, the H peak disappeared after $800^\circ C$ annealing. Of particular note is that the peak ratio of Si to O was slightly lower than that measured for thermally grown SiO_2 .

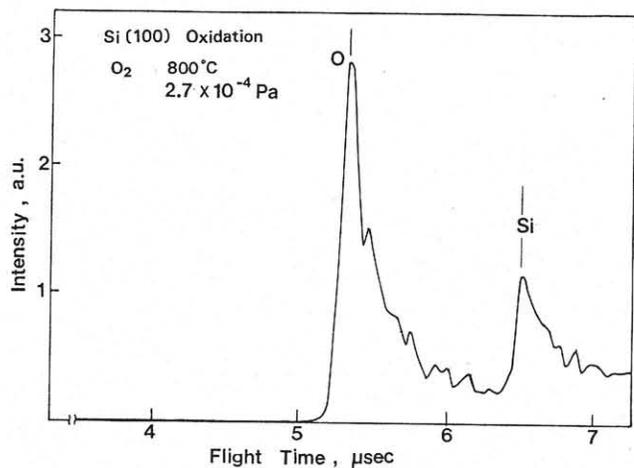


Fig. 4 DR spectrum for Si(100) surface oxidized by pure O_2 gas with $2.7 \times 10^{-4} Pa$ at $800^\circ C$ for 2 min.

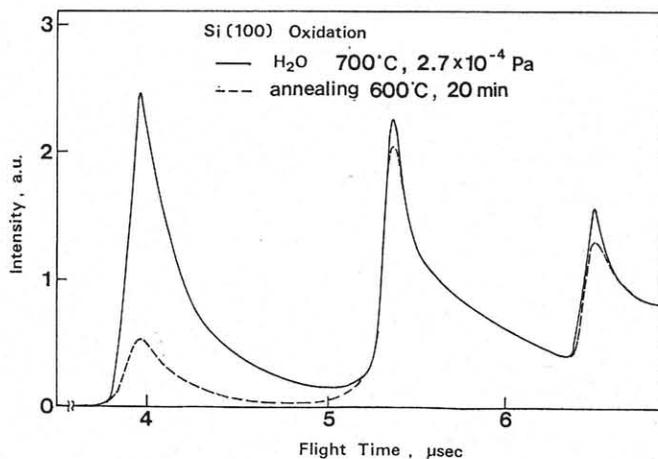


Fig. 5 DP spectra of Si(100) surface oxidized by H_2O at $700^\circ C$, $2.7 \times 10^{-4} Pa$ for 2 min (solid line) and annealed at $600^\circ C$ for 20 min (broken line).

Concerning the oxidation of Si (100), the stoichiometric ratio of the Si to O of the outermost surface layer can be obtained by dry oxidation under low gas pressure. These results clearly show that the DR measurements are applicable to analyze thin insulator surfaces without a charge-up effect due to the use of a very short ion pulse.

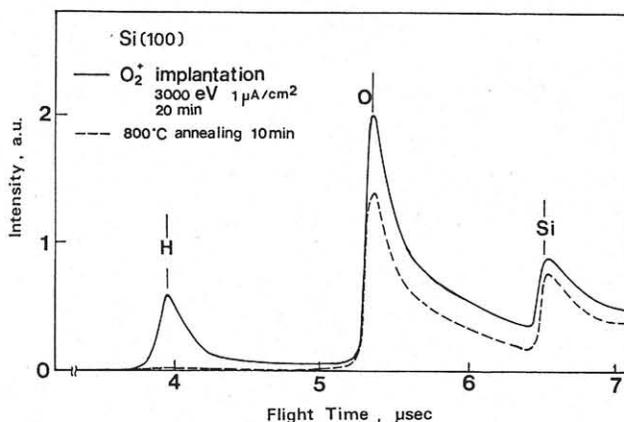


Fig. 6 DR spectra of O_2^+ ion implanted Si surface with 3 keV, $1 \mu A/cm^2$ for 20 min (solid line) and annealed at $800^\circ C$ for 10 min (broken line).

-- PIQ surface --

The DR spectra of PIQ ($1 \mu m$ thick) were measured to reveal the resolution of the DR analysis and its applicability to monitoring thick insulating film surfaces. The resulting DR spectra shown in Fig. 7 indicate the C, N, and O peaks in addition to the H peak. Further analysis of the recoiled line shape provided information about the atomic ratio of the PIQ surface. The derived ratio agrees within 1% with that estimated from the chemical formula of PIQ. The DR spectra of PIQ surfaces bombarded by Ar^+ , O_2^+ , and N_2^+ ions with 3 keV, $20 \mu A/cm^2$ for 20 minutes are shown in Fig. 8. The Ar^+ and N_2^+ irradiation induced a low O peak and a high N peak. The films were electrically conductive. A deficit of oxygen from the surface seems to lead to redistribution of the polymer bonding. The same occurred with 500 eV ions. For O_2^+ ions, Oxygen ratio of the surface atoms became high. It was then obvious that PIQ surfaces were easily modified by low energy ion bombardment. Since analysis of the surface structure and atomic bonding are needed to clarify the effect of ion

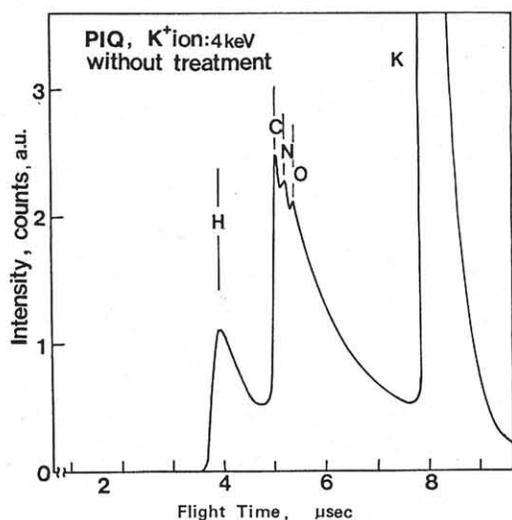


Fig. 7 Direct recoil time-of-flight spectrum for PIQ surface without any treatment.

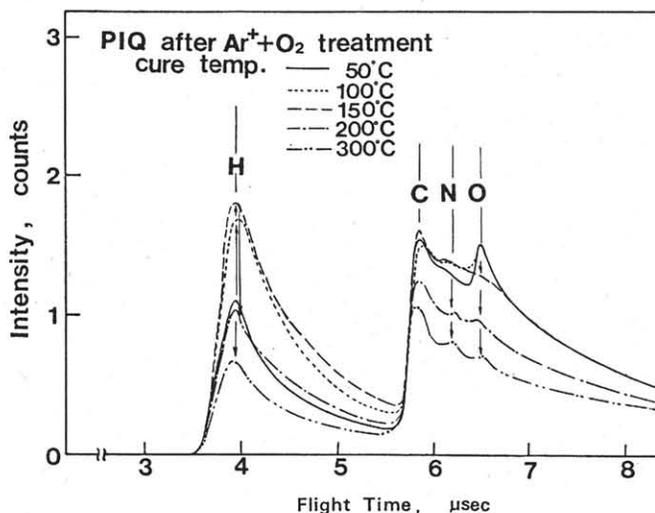


Fig. 9 DR spectra for O_2^+ implanted PIQ surface as a function of cure temperature.

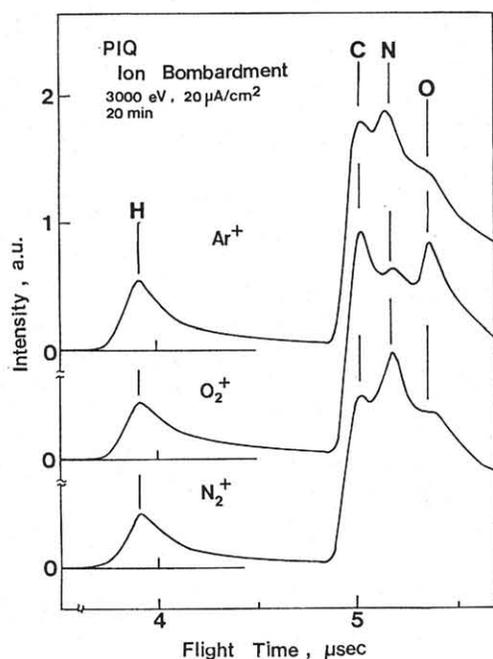


Fig. 8 DR spectra of PIQ surfaces bombarded by Ar^+ , O_2^+ , and N_2^+ ions with 3 keV, $20 \mu A/cm^2$ for 20 min.

bombardment on PIQ, more studies are required. The PIQ films hit by O_2^+ were then cured to understand the behavior of films. PIQ is known to withstand temperature up to 450 °C. Figure 9 shows the in situ DR spectra of PIQ annealed at 50 – 300 °C. The modified PIQ surface was found to change dramatically in its surface atomic ratio as a function of the cure temperature. The 300 °C cure was enough to renew the altered surface to the previous one.

4. Conclusion

In conclusion, DR analysis was found to be applicable to simultaneous detection of any kind of surface atom, including hydrogen, on both conductors and insulators. It should be noted that the measurement time for one spectrum was typically 2 minutes and was even reduced to 20 seconds for the experimental apparatus employed here. Furthermore, since energetic neutrals were detected with a time-of-flight technique, it was possible to make measurements in pressures up to 10^{-4} Pa.

Acknowledgement

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