MASTER

INVESTIGATION OF HYDROGEN AND CHLORINE AT THE SiO_2/Si INTERFACE

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ABSTRACT

Silicon oxides thermally grown in H_2O, O_2, HCl/O_2 and Cl_2/O_2 ambients were analyzed, via $^1H(^{19}F,\alpha\gamma)^{16}O$ nuclear reaction and SIMS, for the presence of hydrogen. In addition, those oxides grown in HCl/O_2 and Cl_2/O_2 ambients were analyzed with SIMS for the presence of chlorine. The SIMS data show that the hydrogen levels in these oxides were below the limit of detection for nuclear reaction experiments. The $^{35}Cl^-$ depth-profiles show that chlorine is enriched at the SiO_2 interface for the HCl/O_2 grown oxides while it is more evenly distributed in oxide bulk in the Cl_2/O_2 grown samples.

INTRODUCTION

It has long been speculated that hydrogen (or water) is incorporated into thermally grown SiO_2 films on silicon during the oxidation process and this hydrogen contaminant plays an important role in the interface properties [1-3]. However, apart from the measurements by Beckmann and Harrick [4] using infrared internal reflection spectroscopy, direct evidence of the existence of hydrogen has been lacking. Recent development of nuclear reaction techniques such as $^1H(^{19}F,\alpha\gamma)^{16}O$ and $^1H(^{15}N,\alpha\gamma)^{12}C$ [5,6] show great promise for absolute determination of hydrogen in solids, but search for hydrogen at the SiO_2/Si interface has produced negative results [7]. One problem associated with nuclear reaction experiments is beam-induced hydrogen mobility [7,8,9] which could conceivably drive the hydrogen away from the interface. Since this beam-induced migration is thought to be a thermal effect, we have, in the present work, undertaken to perform ^{19}F nuclear reaction experiments on samples cooled to $-40°C$ to determine the hydrogen concentration and distribution in thermally grown SiO_2. In addition, we have also used the secondary ion mass spectrometry (SIMS) technique to obtain hydrogen depth profiles on the same samples.

It is well known that the presence of chlorine during the oxidation of silicon produces several beneficial effects in the electrical characteristics of MOS devices. As a result, numerous studies have been carried out on the role of chlorine incorporation in SiO_2 films and the results have been extensively reviewed recently by Monkowski [10]. In the present study, we have determined the depth-profiles of chlorine using SIMS in several SiO_2 films grown in HCl/O_2 and Cl_2/O_2 ambients under a variety of conditions. These results are compared with data from previous work and their significance are discussed.

EXPERIMENTAL

The $^1H(^{19}F,\alpha\gamma)^{16}O$ resonant nuclear reaction experiments were carried out at the Oak Ridge National Laboratory Tandem Van der Graaff accelerator. The experimental set-up was similar to that described previously [9,11]. The sample holder was in contact with a liquid nitrogen reservoir via a copper shroud such that the samples could be cooled by conduction. After several hours of cooling, a final temperature of -40°C was reached. Depth profiling was accomplished by raising the beam energy (in the lab frame) from 16.4 MeV to 17.4 MeV, equivalent to a depth of about 0.4 μm in SiO_2. A second strong resonance at 17.56 MeV lab energy limits the useful range to this particular depth.

The SIMS depth profiles were measured using a newly developed SIPS-SIMS scanning ion probe. The sputtered-induced photon spectrometry (SIPS) part of the apparatus was not used in this series of experiments. To perform hydrogen analysis using SIMS, special care was made to keep the hydrogen partial pressure low during analysis and the Ar^+ ion beam was mass analysed so that no proton component was allowed to reach the target. Typical pressure in the target chamber during analysis was 5×10^{-9} torr. The 7 keV Ar^+ beam was focussed to 100 μm in diameter with a current density of 6 mA cm^{-2}. Raster-gating technique [12] was used to achieve maximum depth resolution. To overcome charging of the SiO_2 surface, a 2 keV electron beam focussed to a 3 mm diameter spot was directed on to the target surface. Neutralization was complete with an electron beam current of about 40 μA. These neutralization conditions were very similar to those described by Magee and Harrington [13].

RESULTS

^{19}F Nuclear Reaction

Four SiO_2 films grown in (a) H_2O at 900°C for 40 mins., (b) dry O_2 at 1100°C for 50 mins., (c) HCl(6%)/O_2 at 1150°C for 20 mins., and (d) Cl_2(0.7%)/O_2 at 1150°C for 20 mins. were depth-profiled. Throughout the 0.4 μm depth being probed, the γ-ray counts never rose above background which was determined with the beam on and no target. Our calculation indicated that the level of hydrogen throughout the bulk must be less than $\sim 10^{20}$ atoms cm^{-3} and if the hydrogen was concentrated at the interface, then its density must be below 2×10^{14} atoms cm^{-2} since the depth resolution of the ^{19}F beam was ~ 200 Å.

SIMS

In addition to the above four SiO_2 films, four other films were examined by SIMS. Samples (e), (f) and (g) were grown in HCl(6%)/O_2 ambient at 1100°C for 10 min., 35 min. and 55 min. respectively, and sample (h) in Cl_2(5%)/O_2 at 1100°C for 10 min.

Fig. 1 shows the $^{16}O^+$ and $^{30}Si^+$ depth profiles of the HCl(6%)/O_2 (1150°C) oxide, i.e., sample c, under conditions of complete and incomplete neutralization. It is clear that if the surface is not completely neutralized by the electron beam, the $^{16}O^+$ and $^{30}Si^+$ profiles become distorted. Before profiling $^1H^+$ or $^{35}Cl^+$ for each sample, an $^{16}O^+$ profile was always taken to see if complete neutralization was in effect.

The $^1H^+$ depth profiles for the eight samples are shown in Figs. 2(a) and 2(b). The hydrogen concentration was calibrated by a single-crystalline Si wafer implanted with a known dose of protons. This would serve as an approximate
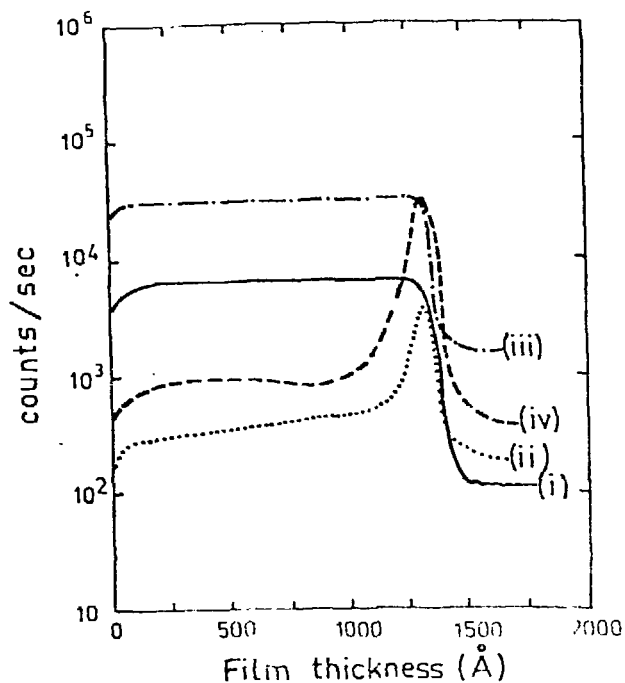
Fig. 1 SIMS depth profiles of $^{16}O^+$ in SiO_2 under (i) complete charge neutralization and (ii) incomplete charge neutralization. Depth profiles of $^{30}Si^+$ in SiO_2 under (iii) complete and (iv) incomplete charge neutralization.
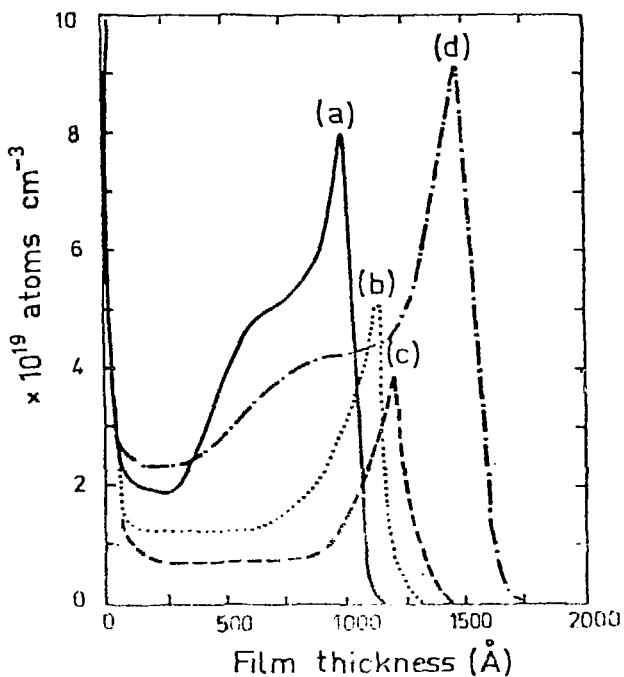
Fig. 2(a) SIMS $^1H^+$ depth profiles of SiO_2 films grown in (a) H_2O at 900°C, (b) dry O_2 at 1100°C, (c) HCl(6%)/O_2 at 1150°C and (d) Cl_2 (0.7%)/O_2 at 1150°C.
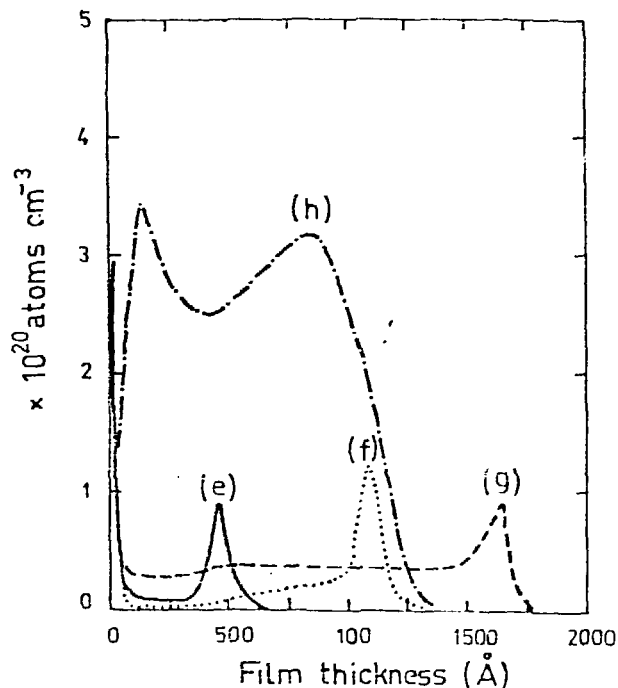
Fig. 2(b) SIMS $^1H^+$ depth profiles of SiO_2 films grown in HCl(6%)/O_2 at 1100°C for (e) 10 mins., (f) 35 mins., and (g) 55 mins., and film (h) grown in Cl_2(5%)/O_2 at 1100°C.
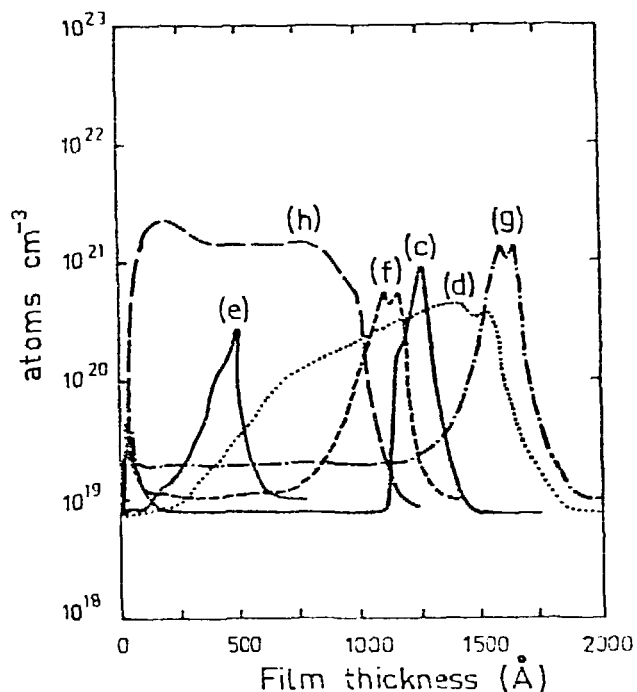
Fig. 3 SIMS $^{35}Cl^+$ depth profiles of SiO_2 films grown in HCl(6%)/O_2 (c) 1150°C, 20 mins., (e) 1100°C, 10 mins., (f) 1100°C, 35 mins., (g) 1100°C, 55 mins., and films grown in (d) Cl_2 (0.7%)/O_2, 1150°C, 20 mins., and (h) Cl_2(5%)/O_2, 1100°C, 10 mins.

calibration since a proton implanted SiO_2 standard was not available. Allowing for oxygen enhancement effect in the SiO_2 in which the $^{30}Si^+$ signal is 20 times higher than in Si, we obtain a calibration factor of 1×10^4 counts s^{-1} for 1×10^{21} H atoms cm^{-3} in SiO_2. The neutralizing action of the electron beam also caused electron-stimulated desorbed (esd) $^1H^+$ to form a background $^1H^+$ signal. The $^1H^+$ profiles shown in Fig. 2 all have this esd background subtracted. The esd background was measured periodically during the depth-profiling process by simply blocking off the ion beam momentarily.

The $^{35}Cl^+$ profiles are shown in Fig. 3. The chlorine concentration was calibrated by Rutherford backscattering performed on samples e, f and g, at Brookhaven National Laboratory. The consistency between the RBS and the SIMS data is extremely good, with all three samples yielding a calibration factor of $(8.4 \pm 0.1) \times 10^{17}$ atoms cm^{-3} per c/s at a sputtering rate of 3.1 ± 0.1 Å s^{-1}.

DISCUSSION

Hydrogen

The fact that hydrogen was not detected in the ^{19}F nuclear reaction experiments is consistent with previous observations by Benenson et al. [7] using the ^{15}N reaction. However, from the SIMS data, it is clear that the reason for the lack of hydrogen is due to the low levels of hydrogen concentration in samples a, b, c and d, all $\sim 10^{19}$ atoms cm^{-3}, thus falling below the limit of detection for nuclear reaction.

SIMS measurements show an enrichment of hydrogen at the SiO_2/Si interface in all the samples. The highest level of hydrogen concentration occurs in sample h, thermally grown in 5% Cl_2/O_2 ambient. The hydrogen is distributed throughout the bulk in this sample, with an average concentration of $\sim 3 \times 10^{20}$ atoms cm^{-3}.

Chlorine

The SIMS $^{35}Cl^+$ depth profiles of the oxides grown in HCl/O_2 ambients (samples c, e, f and g) agree very well with previous SIMS data obtained by Deal et al. [14]. The chlorine shows enrichment at the SiO_2/Si interface as well as on the immediate surface of SiO_2.

The $^{35}Cl^+$ depth profiles in the Cl_2/O_2 oxides (samples d and h) show that the chlorine is more evenly distributed in the oxide rather than simply piling up at the interface. This finding closely resembles that of van der Meulen et al. [15] who used Rutherford backscattering to show that under similar growth conditions the additive species Cl_2 results in higher, more evenly distributed chlorine levels in the oxide as opposed to the occurrence of highest chlorine concentration at the SiO_2/Si interface for the HCl oxides.

A feature quite apparent in the $^{35}Cl^+$ profiles is the presence of a sharp peak at the SiO_2/Si interface as well as a diffuse buildup within the bulk oxide extending from a maximum near the interface. The development with increasing oxidation time of these two aspects of the profile can be followed in the series (e), (f), (g). At 10 min., the diffuse buildup is present only as a slight shoulder, while at 35 and 55 min. it appears as a prominent peak. The effect of increased chlorine partial pressure can be seen in (d) and (h) as the chlorine extends further away from the interface into the oxide, while the interface peak becomes only a shoulder in the profile of the $Cl_2(5\%)/O_2$ film.

These developments can be explained as due to the incorporation of chlorine into the SiO_2 network within the bulk, and into a separate phase at the SiO_2/Si interface. Observations of such an interfacial phase have been described by Monkowski et al. [16]. Support for this hypothesis is found in the $^1H^+$ profiles (Figs. 2a and b) which appear to coincide more with the network chlorine than with the interfacial phase.

The total amount of chlorine in the film (determined by integrating the area under the $^{35}Cl^+$ profiles) in the HCL(6%)/O_2 series is quite linear with oxidation time. This trend, despite the existence of chlorine in two disparate phases, indicates that chlorine incorporation is limited by a reaction with silicon at the interface as suggested by earlier work [17]. This implies that the shape of the network chlorine profile is likely due to the relative increase in Cl_2 partial pressure at the growth interface as the transport of O_2 becomes diffusion limited.

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