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Infrared studies of laser induced oxide on (1 0 0) Si and SiGe layers

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Abstract

Oxide layers have been grown on single crystal (1 0 0) Si and SiGe surfaces with exposure to a pulsed UV laser at 266 nm under various controlled environments. During the growth, sample surfaces were first melted by the laser power. Oxygen related species then diffused into the melt. Oxide was formed after the samples re-solidified. Besides the strong stretching mode absorption at 1080 cm^{-1} (T_2 mode), there was an intense shoulder around 1200 cm^{-1} (the A_1 mode) in the Fourier transform infrared spectrum, compared to thermal oxide. The relative intensity of the shoulder decreased with ambient water vapor concentration. The porosity of this oxide leads to the intense shoulder and more water vapor incorporation can decrease the porosity. The porous oxide could be annealed to some extent with a high-temperature thermal process. Because the adsorption and diffusion of water molecules to and in melted silicon are easier than oxygen molecules, ambient water vapor can fill the voids in the oxide more efficiently and leads to less significant absorption shoulder than oxygen molecules. Also because the diffusion of water molecules in Ge is faster than in Si, less voids are formed and hence the absorption shoulder is less prominent in SiGe samples. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Fourier transform infrared absorption; Laser induced oxide; Porous oxide

1. Introduction

The demand of ultra-thin oxide for modern ultra-large scale integrated (ULSI) circuit applications has driven the technology of rapid thermal oxidation to ramp up the wafer as fast as 100°C s^{-1} , enabling us the growth of thin oxide on the scale of several nm in thickness [1]. The isothermal heating of the rapid thermal process can provide uniform lateral and vertical temperature profiles through the wafer. However, in some ULSI process, local heating in either lateral or vertical direction within an extremely short time duration is needed, such as in the case of the fabrication of extremely shallow junctions. It was reported that a focused laser beam could serve this purpose to heat or even melt Si surface in a small region [2,3]. Recently, the pulsed laser technique has also been used to produce $\text{Si}_{1-x}\text{C}_x$ alloys under non-thermal equilibrium conditions in the fast melting and re-solidification process [4]. In our previous work, we

have used the UV laser induced oxide to fabricate the optical gratings [5], and performed the temperature measurement using such gratings on Si substrate [6]. However, the growth model and oxide properties were not well understood yet.

Infrared absorption spectroscopy is widely used to characterize oxide films. For normal incidence, the transverse optical (TO) mode can be excited [7]. A strong absorption around 1080 cm^{-1} is labeled as the T_2 mode [8]. In the T_2 mode, two oxygen atoms move closer to the Si atom, while the others move away. Besides the intensive absorption, a shoulder appears at 1200 cm^{-1} . It was previously identified as the longitudinal optical (LO) mode, but recently, Sarnthein et al. [8] used the first-principle density function theory to clarify that the shoulder is still TO excitation with the A_1 mode, corresponding to the in-phase motion of all the oxygen atoms towards the Si atom. Chou and Lee also suggested that this shoulder is caused by the porosity of the oxide, which was prepared by liquid phase deposition [15]. In this paper, we propose that the incorporation of water molecules can fill the voids in laser induced oxide, and hence the shoulder in the spectra of laser induced oxide decreases with the increase of water molecule incorporation. The samples were

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melted with the high-power laser. Before re-solidification, molecules containing oxygen diffuse into the melt and the oxide was formed after fast re-solidification. We will show the dependence of the relative intensity of the shoulder on the level of oxygen incorporation, which can be controlled by the ambient conditions. We found that the formation of the absorption shoulder could be attributed to the decrease of porosity in the oxide by the water molecule incorporation.

2. Experiments

The laser induced oxide was grown in a leak-tight chamber with a quartz window, allowing the passage of the UV laser beam. The chamber could be purged with nitrogen and oxygen under various ambient conditions, including the variations of moisture and temperature. A water container was placed inside the chamber to provide water vapor. Moisture inside the chamber was controlled either by temperature variation and nitrogen flow rate. The chamber was kept at the atmospheric pressure. The fourth harmonic of a Q-switched Nd:YAG laser with the wavelength at 266 nm was used to provide 5 ns pulses with 25 Hz pulse repetition rate. Before laser exposure, the samples were cleaned with HF dip. The Si surface can maintain oxide-free within 10 min in our experimental environments as measured by ellipsometer. The infrared absorption spectra were recorded with a Perkin-Elmer spectrum 2000 machine. The 100 nm thick $\text{Si}_{1-x}\text{Ge}_x$ samples used in this study were prepared with ultra-high vacuum chemical vapor deposition (UHV-CVD) [9].

3. Results and discussions

The relative intensities of the absorption shoulder at 1200 cm^{-1} in the FTIR spectra of laser induced silicon oxide at three relative humidity levels, M (controlled by the nitrogen flow rate), are shown in Fig. 1. The chamber temperature

Fig. 1. FTIR spectra of laser induced oxide at different relative humidity levels at the ambient temperature of 20°C , compared with that of thermal oxide. The samples were exposed to laser pulses with the fluence 40 mJ cm^{-2} and the repetition rate 25 Hz for 200 s.

Fig. 2. FTIR spectra of laser induced oxide at two different ambient temperatures in the water vapor environments as well as in the oxygen molecule environment. The laser pulse has the fluence of 40 mJ cm^{-2} with the repetition rate of 25 Hz. The laser exposure times are 90 s and 10 min for water vapor treatment and dry oxygen treatment, respectively.

was fixed at 20°C . The laser fluence was 40 mJ cm^{-2} and the exposure time was 200 s. The much smaller fluence used in this study, compared to those previously reported [2–4], means prevent the ablation of Si surface [10]. We can see that the shoulder level decreases with humidity. For comparison, the FTIR spectrum of thermal silicon oxide is also shown. The relative strength of shoulder increases with the decrease of moisture, and is much more prominent than that of thermal oxide. Meanwhile, the amount of oxygen content, indicated by the equivalent oxide thickness (the numbers in the parentheses in Fig. 1), also increases with the moisture level. The equivalent oxide thickness was estimated through the intensity integration of FTIR signal, as compared to the thermal oxide. Note that the equivalent oxide thickness is only a measure of oxygen content in the oxide because of the gradient distribution of oxygen concentration along the depth. Since oxygen incorporation is determined by the water vapor concentration on the silicon surface and the diffusion coefficient of oxygen carrier in the Si melt, large moisture level can increase the amount of water vapor incorporated into the Si. This results to the increase of oxygen content at high moisture level. The increase of oxygen in the laser induced oxide can fill the voids of the Si melt during the oxidation process, and decreases the shoulder intensity in the FTIR spectra.

Fig. 2 compares the shoulder levels of three cases: (1) without water vapor, the chamber was purged with oxygen molecules; (2) saturated vapor pressure at 30°C in nitrogen; and (3) saturated vapor pressure at 100°C in nitrogen. The laser fluence was fixed at 40 mJ cm^{-2} . For cases (2) and (3), the exposure time was 90 s.; however, for case (1) of the pure O_2 ambient condition, the exposure time was as long as 10 min. The relatively higher shoulder of case (1) indicates the weak incorporation of O_2 into the Si melt, compared with water molecules. The relatively stronger incorporation of H_2O with melted silicon, compared with O_2 , can be

Fig. 3. FTIR spectra of as-grown laser induced oxide and thermally annealed oxide. The annealing time is 30 min. The samples were exposed to laser pulses with the fluence 40 mJ cm^{-2} and the repetition rate 25 Hz for 200 s.

attributed to the polarized nature of a H_2O molecule. This nature makes the adsorption of H_2O to silicon surface much stronger [11]. The other possibility is that H_2O diffusion in melted silicon is faster than O_2 . The O_2 diffusion coefficient in Si melt was estimated as 1.5×10^{-4} – $3.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, which was obtained from the molecular dynamics and solidification experiments [12,13]. Although that of water molecules is still unknown, it is believed that a water molecule diffuses faster than an oxygen molecule in Si melt, similar to solid silicon. The comparison between cases (2) and (3) in Fig. 3 shows that a higher temperature leads to a higher vapor concentration, a higher oxygen incorporation and hence a lower shoulder level.

Next, we studied the effects of thermal annealing after the laser treatment. Si samples were first exposed to laser with the fluence 40 mJ cm^{-2} for 200 s. in the ambient saturated vapor pressure at 40°C . No N_2 or O_2 flow was applied in this case. The samples were then annealed in a nitrogen purged furnace for 30 min at 800 and 1000°C . From Fig. 3, we can see that the thermal annealing process has reduced the shoulder level. This result indicates that the laser induced oxide decreases the porosity of SiO_2 during the annealing process. A similar phenomenon was observed in liquid-phase-deposition samples [15].

Then, we compare the laser induced oxidation on Si and SiGe surfaces. One Si and two SiGe (with 0.1 and 0.2 Ge fractions, respectively) samples were first exposed to 40 mJ cm^{-2} fluence for 200 s. The ambient condition was 45% moisture at 20°C controlled by nitrogen purge. The 100 nm thick $\text{Si}_{1-x}\text{Ge}_x$ samples were prepared with ultra-high vacuum chemical vapor deposition (UHV-CVD) [9]. Since oxygen diffuses faster in solid Ge than in solid Si, the addition of Ge into Si is expected to increase water vapor diffusion and hence enhance the oxygen incorporation in the melt. As a result, the oxygen content in the laser induced oxide increases with the Ge content and hence the

Fig. 4. FTIR spectra of laser induced oxide on Si and SiGe surfaces. The laser pulse has the fluence of 40 mJ cm^{-2} and the repetition rate of 25 Hz. The oxide was grown with ambient 45% humidity level at 20°C .

porosity decreases with Ge content. Meanwhile, the relative intensity of the shoulder drops as the Ge concentration increases. Note that the peak from the 800 – 900 cm^{-1} is the bending mode absorption.

The similar absorption shoulder has been reported earlier. The physical origin of the shoulder has been attributed to several mechanisms. Pai et al. [14] suggested that the shoulder was due to out-phase movement of Si–O–Si bond, different from the in-phase movement for the absorption at 1080 cm^{-1} . Also, Chou and Lee [15] suggested that the porosity in oxide might be responsible for the shoulder. We, therefore, conclude that the oxygen incorporation in the Si melt can fill the voids in the Si melt, and less porosity in the oxide yields the relatively weaker shoulder in the FTIR spectra. Note that Fogarassy et al. [16] also reported that monoxide (SiO) has a peak around 980 cm^{-1} . Our samples also show this peak (Figs. 1–4), indicating possible monoxide components in our films.

Theoretical analysis for the laser induced oxidation is difficult. A simple one-dimensional model of the melting process can be found in literatures [17,18]. However, during the laser induced oxidation process, oxide exists on sample surfaces after the first laser pulse exposure. Therefore, accurate modeling is difficult because the thermal properties of laser induced oxide are not known. Besides, because of the short duration of laser pulse and melted period (at the order of 100 ns), the non-equilibrium growth of oxide makes it different from the Deal–Grove type of growth [19]. The melted Si surface with oxygen may be quenched during the cooling process, producing a porous oxide layer.

4. Summary

In summary, we have demonstrated laser induced oxidation of Si and $\text{Si}_{1-x}\text{Ge}_x$ with a high-power UV laser.

The non-equilibrium incorporation of oxygen into the samples during the melted period causes porosity in the oxidation process. The porosity reflected the prominent shoulder at 1200 cm^{-1} in the infrared absorption spectra. The water molecule incorporation could be enhanced with higher moisture, higher ambient temperature and Ge addition to Si. Less voids are formed in the oxidation process with more oxygen incorporation. It was shown that the enhancement of oxygen incorporation decreased the shoulder level due to less porosity.

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