

Grain Boundary Incorporation of Interstitial Oxygen in Polycrystalline Si Film by Plasma Oxidation and its Effect on Thin Film Transistors

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Inductively coupled plasma (ICP) oxidation has been used for low-temperature gate oxidation to reduce the trap density at the Si/SiO₂ interface in polycrystalline-Si thin film transistors. Through ICP oxidation, it was found that oxygen atoms were incorporated into the Si film as an interstitial oxygen state and they were located predominantly at grain boundaries. The amount of interstitial oxygen, analyzed by energy dispersive x-ray spectroscopy, increased as the ICP oxidation time increased. With the help of the interstitial oxygen at the grain boundaries, the electron mobility of poly-Si thin film transistors was improved, indicating that ICP oxidation enabled grain-boundary passivation in addition to the previously-known trap reduction at the Si/SiO₂ interface state.

Keywords: interstitial oxygen, plasma oxydation, passivation, polycrystalline silicon thin film transistor

1. INTRODUCTION

The ability to grow silicon dioxide with good quality at low temperatures is necessary to improve the performance of polycrystalline Si (poly-Si) thin film transistors (TFTs). To this end, plasma oxidation methods have been studied to reduce the oxidation temperature of silicon dioxide.^[1-4] It was reported that the electron cyclotron resonance plasma oxidation on a poly-Si substrate reduces the oxidation temperature and minimizes the Si dangling bonds at the Si/SiO₂ interface.^[1,2] On the other hand, Choi *et al.* reported that inductively coupled plasma (ICP) oxidation improved poly-Si TFT performance due to a reduction in the interface trap density at the interface.^[3] Kim *et al.* found the existence of interstitial oxygen by ICP oxidation due to the incorporation of plasma oxygen into Si during ICP oxidation.^[5,6] Nickel *et al.* also reported that the incorporation of hydrogen is the major cause of the defect passivation in poly-Si during a oxygen plasma treatment.^[7,8] However, few efforts have been devoted to clarify this issue in plasma oxidation. To improve the electrical property of a poly-Si TFT in terms of its gate oxide integrity, the effect of the oxygen plasma on the low temperature oxidation of poly-Si film must be fully understood.

In this study, ICP oxidation of a poly-Si film is performed and the incorporation of oxygen into the poly-Si substrate film is examined in detail. A physical evidence of grain

boundary oxidation was found, and its effect on the electron mobility of TFTs is discussed.

2. EXPERIMENTAL

Thermally oxidized Si wafers were used as a substrate. An 84-nm thick layer of amorphous Si was deposited by LPCVD at 550°C with SiH₄ and H₂, and the film was crystallized at 600°C for 48 h. The poly-Si films were cleaned by trichloroethylene, acetone, and methanol for 15 min and boiled in a solution of sulfuric acid and hydrogen peroxide for 20 min. The wafers were then immersed in a 50:1 HF solution until a hydrophobic surface appeared. The ICP oxidation temperature, power, and pressure were 400°C, 2 kW, and 10 mTorr, respectively. The thickness of the oxide was measured using a JEM-3010 JEOL transmission electron microscopy (TEM). Infrared spectra were obtained using a Nicolet MAGNA-IR 560 FTIR spectrometer with a resolution of 4 cm⁻¹ and 32 scans. A sample with no oxidation was utilized as a background reference sample. To investigate the chemical composition of the poly-Si film after ICP oxidation, x-ray photoelectron spectroscopy (XPS) combined with depth profiling measurement (VG Scientific ESCALAB 250) was performed. Energy dispersive x-ray spectroscopy (EDS) was used to study the oxygen content in the poly-Si film.

Self-aligned n-channel poly-Si TFTs were fabricated. Si film crystallized at 600°C for 48 h was used for an active layer. The gate oxide was composed of a bottom oxide grown by ICP O₂ oxidation at 400°C and a top oxide grown by LPCVD at 340°C with SiH₄ and O₂. For gate electrodes,

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a 150-nm thick amorphous Si was deposited by PECVD at 400°C with SiH₄ and was crystallized at 600°C for 48 h. The gate and source/drain regions were doped at 450°C using an ion shower method with a dose of $2.2 \times 10^{16} \text{ cm}^{-2}$ by H₂-diluted PH₃ gas at an acceleration voltage of 10 kV. A 300-nm thick interlayer oxide was deposited by LPCVD at 340°C with SiH₄ and O₂, and was annealed at 500°C for 30 min in N₂. After opening contact holes, a 500-nm thick Al layer was deposited by sputtering and the layer was patterned. Finally, the TFT samples were annealed at 450°C for 30 min in a 10% H₂/N₂ gas. Electrical properties of the TFTs were measured using an HP 4145B semiconductor parameter analyzer.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the infrared absorption peaks of a SiO₂/Si film with various oxide thicknesses grown on a poly-Si

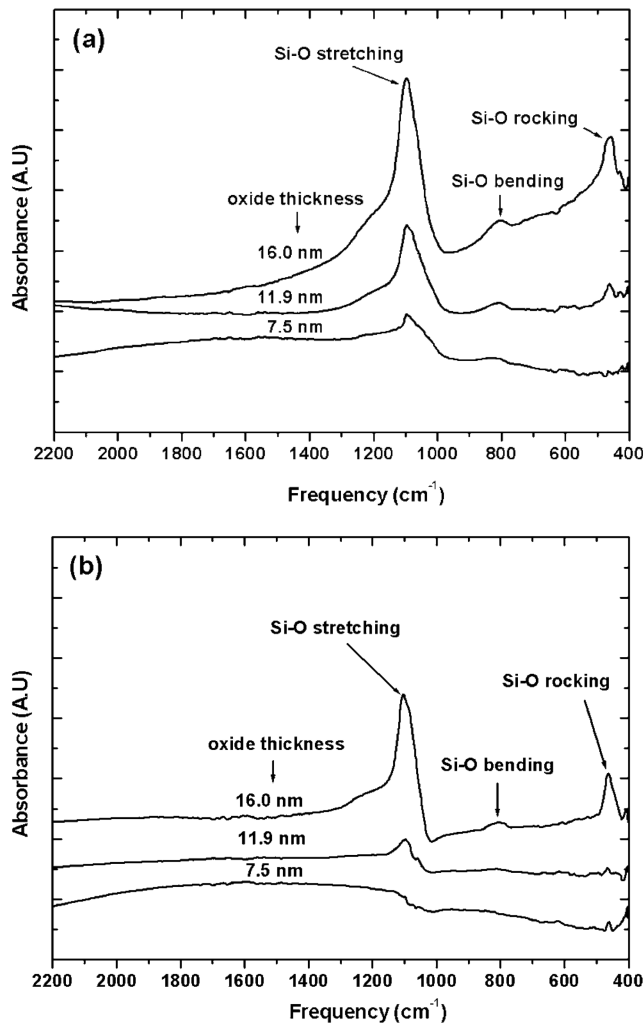


Fig. 1. Infrared absorption spectra of (a) an ICP SiO₂/poly-Si film with various oxide thicknesses and (b) a poly-Si film after removal of the ICP oxide in a 50:1 HF solution.

film by ICP oxidation at 400°C. The oxidation times for 7.5, 11.9 and 16.0-nm thick oxides were 10, 50, and 90 min, respectively. The absorption spectra show the characteristics

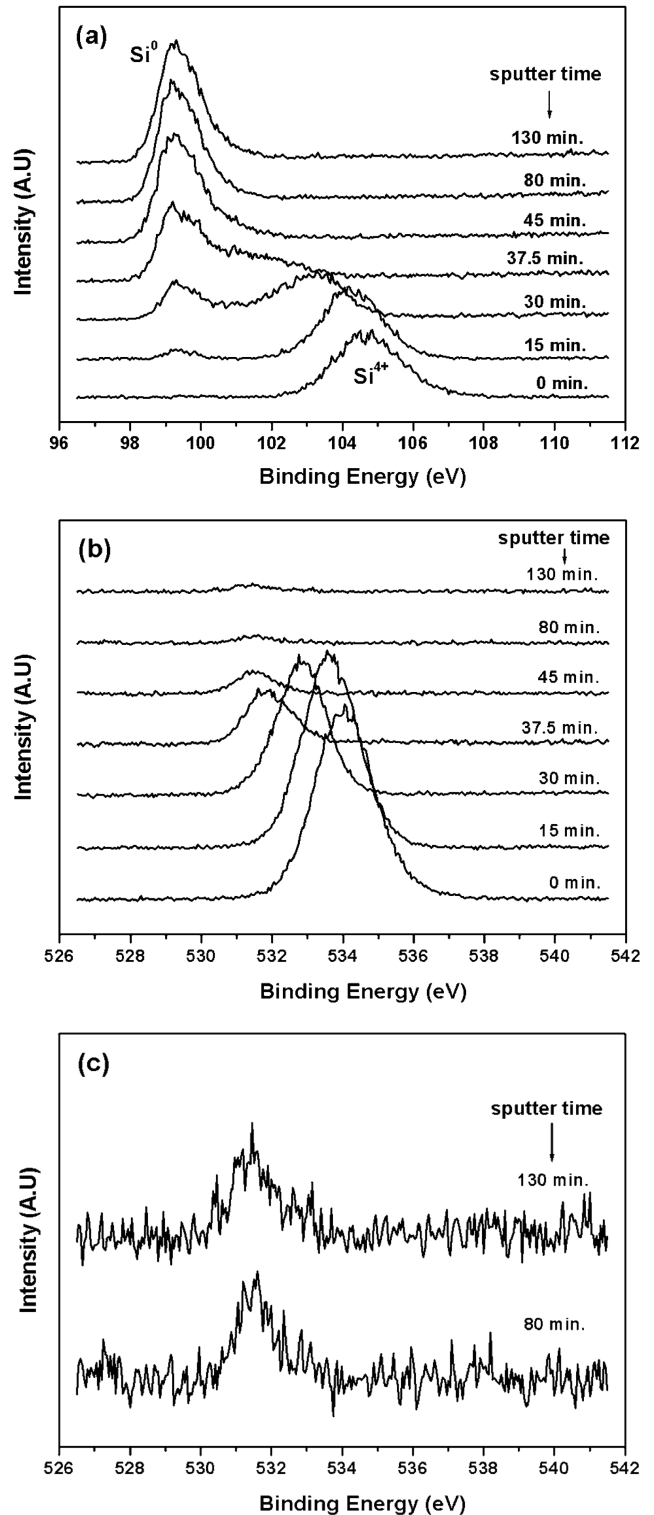


Fig. 2. XPS depth profile of the (a) Si 2*p* and (b) O 1*s* peaks of a poly-Si film with a 16.0-nm thick ICP oxide, and (c) the enlarged O 1*s* peak from (b) after sputtering of 80 and 130 min.

of SiO₂ with stretching, bending, and rocking bands located at 1100, 800, and 455 cm⁻¹, respectively.^[9] Figure 1(b) shows the infrared absorption peaks of the poly-Si film after etching away the ICP oxide in a 50:1 HF solution until hydrophobia appears. The absorption peaks do not exist on the poly-Si film on which a 7.5-nm thick oxide was grown and etched away. However, the Si-O absorption peak appears on the poly-Si film where 11.9-nm thick oxide was grown and removed. The poly-Si film on which 16.0-nm thick oxide was grown and removed shows clear Si-O bonding characteristics, including Si-O stretching, bending, and rocking bands. The results indicate that oxygen exists in the poly-Si film and the amount of oxygen within the film increases as the oxidation time increases.

Figure 2 shows the XPS depth profile of the (a) Si 2*p* and (b) O 1*s* peaks from the SiO₂/poly-Si film with 16.0-nm thick ICP oxide. In Fig. 2(a), two Si 2*p* peaks are clearly seen: Si⁴⁺ in the oxide layer and Si⁰ in the poly-Si film.^[10] In the beginning, only the Si⁴⁺ peak (104.4 eV) was evident. The Si⁰ peak (99.3 eV) then appeared after 15-min of sputtering. The Si⁴⁺ peak completely disappeared after 45-min of sputtering and only the Si⁰ peak remained. This indicates that a sputtering time of 45 min completely removes the ICP oxide from the SiO₂/poly-Si film. In Fig. 2(b), initially, the O

1*s* peak (534.0 eV) from SiO₂ is shown and then the peak gradually shifts to an interstitial O 1*s* peak (531.5 eV). The SiO₂ O 1*s* peak completely disappears after 45-min of sputtering. Figure 2(c) shows the enlarged O 1*s* peak with 80- and 130-min sputtering from Fig. 1. Here, the O 1*s* peak can still be detected after 130-min of sputtering, whereas the SiO₂ layer on the poly-Si film is completely removed after 45-min of sputtering, as shown in Figs. 2(a) and 2(b). This clearly demonstrates that interstitial O atoms exist deep in the poly-Si film as well as on the surface of the film. The oxygen content in the poly-Si film after 130-min of sputtering was approximately 5.2 at% from the XPS analysis.

To investigate the oxygen distribution within the poly-Si film, TEM and EDS were utilized. Figure 3 shows a cross-sectional TEM micrograph of the poly-Si film on which (a) 7.5-, (b) 11.9-, and (c) 16.0-nm thick ICP oxide were grown and removed. The areas with arrows are the sites where the EDS measurements were performed.

Figure 4 shows the oxygen atomic contents inside the grains and at the grain boundaries in the poly-Si film where the ICP oxides with various thicknesses were grown and removed. The oxygen atomic contents in the poly-Si film, on which 16.0-nm thick ICP oxide was grown and removed, were 15.0 at% inside the grains and 33.7 at% at the grain boundaries. The oxygen content measured by EDS is larger than that measured by XPS (5.2 at%). As the beam size used in the EDS measurement was approximately 5 nm, the precise content at a specific point cannot be determined. The thermal SiO₂ below the poly-Si and the ICP oxide above the poly-Si may have had a background effect on the oxygen atomic content in the poly-Si. However, a trend in the compositional difference between the grains and grain boundaries is clearly seen. Given that no oxygen within the grains is expected during thermal oxidation, the oxygen detected by

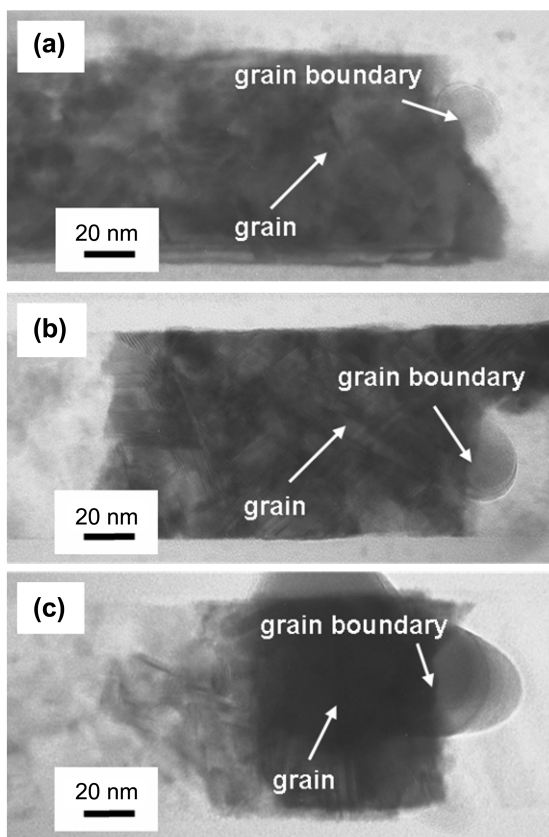


Fig. 3. Cross-sectional TEM micrograph of a poly-Si on which (a) 7.5-, (b) 11.9-, and (c) 16.0-nm thick ICP oxide was grown.

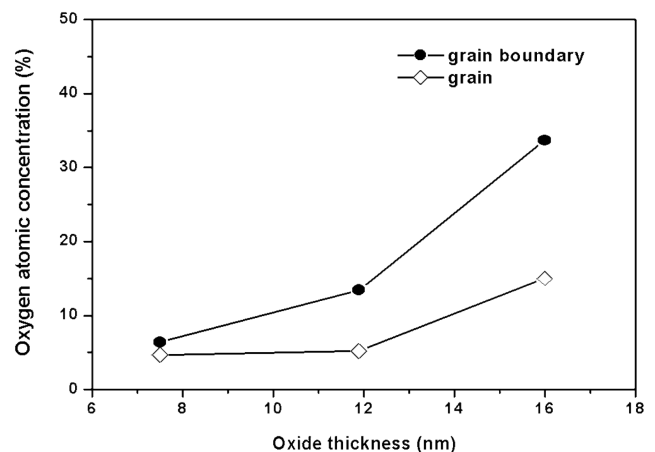


Fig. 4. EDS analysis of the interstitial oxygen content inside the grains and at the grain boundaries in the poly-Si film where the ICP oxide was grown and removed as a function of the ICP oxide thickness.

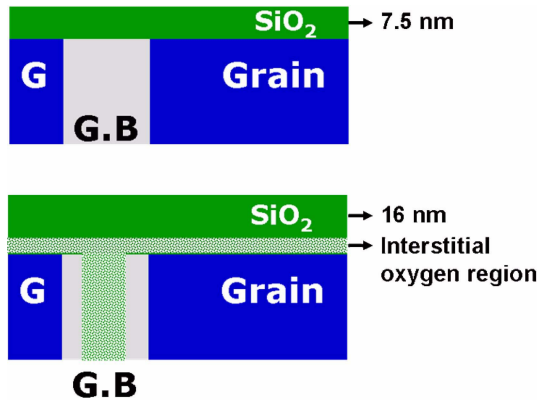


Fig. 5. Schematic diagram of interstitial oxygen distribution in polycrystalline Si film by plasma oxidation: The interstitial oxygen content is high at the grain boundaries.

XPS must have originated from the oxygen at the grain boundaries. The amount of oxygen at the grain boundaries increases as the oxidation time increases. This result indicates that the main route of oxygen incorporation in the poly-Si film is the grain boundaries.

Figure 5 shows a schematic diagram of oxygen incorporation by ICP oxidation. When the ICP oxidation time is long, the concentration of interstitial oxygen is high at the grain boundaries, whereas it is low when the oxidation time is short. The incorporation of oxygen at the grain boundaries is an important finding in this paper.

Figure 6 shows the drain current and electron mobility versus the gate voltage of the poly-Si TFTs with two different gate oxides. One gate oxide was prepared by growing a 7.5-nm ICP oxide and a 72-nm LPCVD oxide (total 79.5 nm), and the second gate oxide was prepared by growing a 16.0-nm ICP oxide and a 68-nm LPCVD oxide (total 84 nm). The ICP oxide was grown at 400°C. The width and length of the transistor are 10 and 10 μm, respectively, and the drain-source voltage, V_{DS} , is 3 V. The field effect mobility, μ_{FE} , was calculated from the transconductance. The maximum μ_{FE} value of a TFT with a 7.5-nm thick ICP oxide is 11.4 cm^2/Vs , while that of a TFT with a 16.0-nm thick ICP oxide is 13.0 cm^2/Vs . A TFT with a thicker ICP oxide and more oxygen in the active layer shows a higher value of μ_{FE} .

The mobility of a poly-Si TFT is affected by surface scattering within the grains and by grain boundary scattering. According to the thermionic emission model^[11], the drain current, I_D , is expressed by

$$I_D = (W/L) \mu C_{ox}(V_G - V_{FB})V_{DS} = (W/L) \mu_0 \exp(-qE_B/kT) C_{ox}(V_G - V_{FB})V_{DS}, \quad (1)$$

where W is the channel width, L is the channel length, μ_0 is the carrier mobility within each grain and C_{ox} is the gate oxide capacitance, respectively. The electron mobility term, μ , is divided into μ_0 and $\exp(-qE_B/kT)$. The second term is

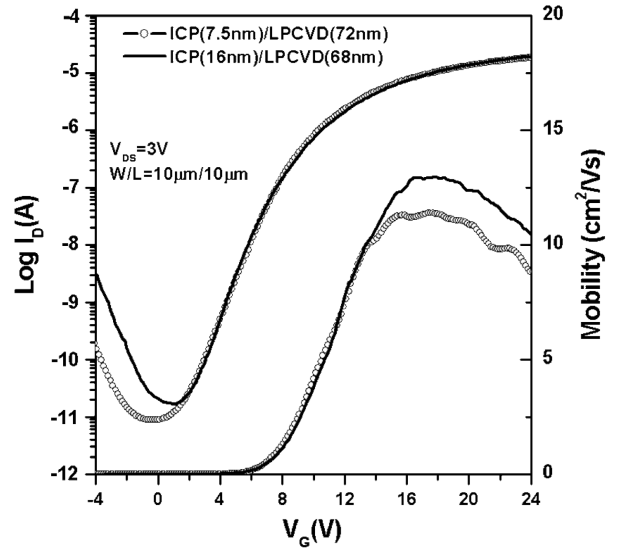


Fig. 6. Log I_D versus V_G and electron mobility versus the V_G characteristics of poly-Si TFTs with two different double-layer gate oxides: one with ICP oxide (7.5 nm)/ LPCVD oxide (72 nm) and the other with ICP oxide (16.0 nm)/ LPCVD oxide(68 nm).

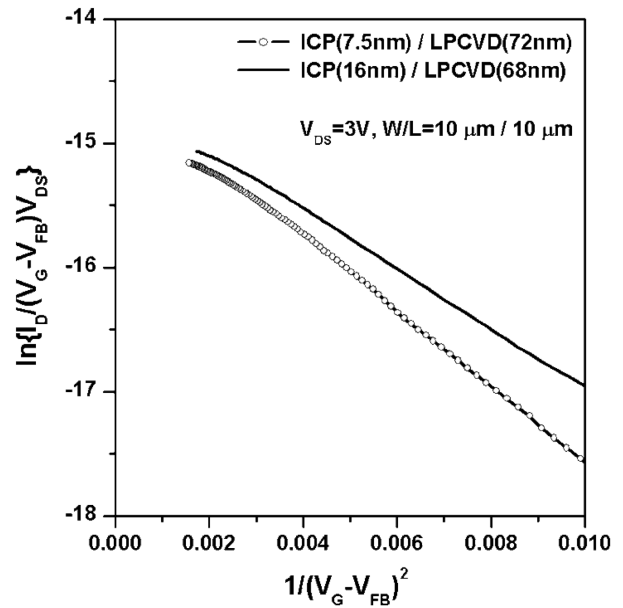


Fig. 7. Plot of $\ln\{I_D/(V_G - V_{FB})V_{DS}\}$ versus $1/(V_G - V_{FB})^2$ of poly-Si TFTs with two different double-layer gate oxides: one with ICP oxide (7.5 nm)/ LPCVD (72 nm) and the other with ICP oxide (16.0 nm) / LPCVD (68 nm).

the energy barrier term at the grain boundaries. The energy barrier, E_B , and the thickness of the channel, t_{ch} , are expressed, respectively, as

$$E_B = q^2 N_T^2 t_{ch} / 8 \epsilon_{Si} C_{ox} (V_G - V_{FB}) \quad (2)$$

$$t_{ch} = [8kT t_{ox} (\epsilon_{Si} / \epsilon_{SiO_2})^{0.5}] / [q(V_G - V_{FB})], \quad (3)$$

where ϵ_{Si} and ϵ_{SiO_2} are the permittivities of Si and SiO_2 ,

respectively, and N_T is the grain boundary trap density. μ_0 and N_T can be calculated from a plot of $\ln\{I_D/(V_G-V_{FB})V_{DS}\}$ vs $1/(V_G-V_{FB})^2$, which is deduced from equations (1), (2) and (3).

Figure 7 shows a plot of $\ln\{I_D/(V_G-V_{FB})V_{DS}\}$ vs. $1/(V_G-V_{FB})^2$ of poly-Si TFTs with two different gate oxides: one with 7.5-nm ICP oxide/72-nm LPCVD oxide and the second with 16.0-nm ICP oxide/68-nm LPCVD oxide. The μ_0 values for the TFTs with the 7.5-nm thick oxide and the 16.0-nm thick ICP oxide are $12.8 \text{ cm}^2/\text{Vs}$ and $11.1 \text{ cm}^2/\text{Vs}$, respectively. The N_T values for the TFTs with the 7.5-nm thick oxide and the 16.0-nm thick ICP oxide are $2.1 \times 10^{12}/\text{cm}^2$ and $1.7 \times 10^{12}/\text{cm}^2$, respectively. Thus, the larger field effect mobility, μ_{FE} , in the TFT with a gate consisting of 16.0-nm ICP oxide/68-nm LPCVD oxide is attributed to the decrease of the value of N_T . This reduction might result from the passivation of grain boundary traps by interstitial oxygen incorporated by ICP oxidation. From the infrared measurement, neither $\text{SiH}_2(2090 \text{ cm}^{-1})$ nor $\text{SiH}(2000 \text{ cm}^{-1})$ stretching bands by plasma oxidation was detected (Fig. 1).^[12] Thus, the hydrogen passivation effect can be excluded.

The primary purpose of plasma oxidation is to reduce interface states such as a fixed oxide charge and a fast oxide charge.^[3] In addition to the reduction of the interface states, it was found that ICP oxidation reduced the grain boundary trap density by the formation of interstitial oxygen at the grain boundary. This result is highly significant, as no such finding has been clearly reported despite the fact that ICP oxidation is known to enhance TFT performance.

4. CONCLUSIONS

From the analysis of a poly-Si film that is oxidized by inductively coupled plasma in O_2 , the following results were discovered. Atomic oxygen was incorporated into Si film as an interstitial oxygen state according to IR absorption spectra and XPS analysis. It was found that the oxygen content at grain boundaries is much higher than that inside grain by EDS analysis. This is most likely due to fast diffusion of atomic oxygen along the grain boundaries. The amount of interstitial oxygen in the Si film increased as the oxidation

time increased. In particular, the interstitial oxygen at grain boundaries significantly increased as the oxidation time increased. The electron mobility of n-channel TFT increased as the ICP oxidation time increased, indicating that interstitial oxygen at grain boundaries reduces the density of trap centers at the grain boundaries. Detecting an interstitial oxygen state at grain boundaries and reducing the grain boundary trap density by the interstitial oxygen are highly significant despite the fact that ICP oxidation is known to enhance TFT performance.

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