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Oxygen plasma and high pressure H_2O vapor heat treatments used to fabricate polycrystalline silicon thin film transistors

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ABSTRACT Oxygen plasma and high pressure H_2O vapor heat treatment were applied to fabrication of n-channel polycrystalline silicon thin film transistors (poly-Si TFTs). 13.56 MHz-oxygen-plasma treatment at 250 °C, 100 W for 5 min effectively reduced defect states of 25-nm-thick silicon films crystallized by 30 ns-pulsed XeCl excimer laser irradiation. 1.3×10^6-Pa-H_2O vapor heat treatment at 260 °C for 3 h was carried out in order to improve electrical properties of SiO_x gate insulators and SiO_x/Si interfaces. A carrier mobility of 470 cm^2/V s and a low threshold voltage of 1.8 V were achieved for TFTs fabricated with crystallization at 285 mJ/cm^2.

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Low-temperature fabrication of polycrystalline silicon films formed by pulsed laser crystallization is suitable for electron-device fabrication, such as thin-film transistors (TFTs), because crystallization occurs rapidly and no thermal damage is induced in a cheap substrate such as glass [1–4]. However, rapid laser annealing causes a high density of defect states. Defect-reduction technologies at low temperature are therefore very important. Many investigations, such as plasma hydrogenation, have been reported for defect reduction [5–10]. We have also recently reported application of high-pressure H_2O vapor to reduce defect states in silicon films and SiO_2/Si interfaces [11–14]. We recently reported that application of high-pressure H_2O vapor to laser-crystallized silicon films resulted in high-performance characteristics of polycrystalline silicon thin film transistors (poly-Si TFTs) because of defect reduction of the silicon films [15]. However, H_2O vapor heat treatment has a problem of a low reaction ratio to reduce defects in silicon. Especially, it takes a few hours and a temperature above 300 °C to reduce dangling bonds in polycrystalline silicon to lower than 10^{17} cm^{-3} [14].

In order to solve the problem of the low reaction ratio, in this paper we apply oxygen treatment to silicon films for TFT fabrication. The story of TFTs with high performance at low temperature is as follows. Oxygen-plasma treatment is applied to polycrystalline silicon films. It rapidly reduces defect states with a deep energy level associated with oxidation of dangling bonds for silicon films [16]. High-pressure H_2O vapor heat treatment is applied after TFT fabrication. It reduces defect states in SiO_x gate insulators and SiO_x/Si interfaces. We show that the present defect-reduction processing results in a low threshold voltage and a high drain current with a high carrier mobility.

Figure 1 shows schematic fabrication steps of poly-Si TFTs. Hydrogenated amorphous silicon (a-Si:H) films doped with 7×10^{20} cm^{-3} phosphorus and with a thickness of 30 nm were first formed on glass substrates at 330 °C using plasma-enhanced chemical vapor deposition (PECVD). The doped films were removed at a channel region with a length of 25 μm by etching and they were used as dopant sources for forming source and drain regions. 25 nm-thick undoped a-Si:H films were then deposited using PECVD over the whole area. The silicon layers were crystallized at 250 °C in vacuum at 3×10^{-4} Pa by a 30 ns-pulsed XeCl excimer laser with 50 shots. Undoped crystallized regions were used as the channel region. Source and drain regions were simultaneously formed through diffusion of phosphorus atoms into the overlaying silicon layer during the laser crystallization. The melt duration of silicon during the laser crystallization was shorter than 100 ns, so that the diffusion distance of the dopant atom was at most 60 nm in liquid silicon [17] and the channel length hardly changed. After laser crystallization, the silicon films were treated with oxygen plasma at 250 °C for 5 min at a 13.56 MHz RF power of 100 W and at a gas pressure of 130 Pa. The oxygen-plasma condition was determined by our investigation of the electrical conductivity, with 7.4×10^{17} cm^{-3}-phosphorus-doped laser-crystallized silicon with oxygen-plasma treatment giving the highest electrical conductivity of 10 S/cm [16]. The molecular beam deposition method was used for formation of the gate insulator. A 115–135 nm-thick SiO_x layer was deposited at room temperature as the gate insulator by thermal evaporation of SiO powders using a Knudsen cell in oxygen radical atoms with excited states at 1×10^{-2} Pa, which was generated by 300 W induction-coupled remote plasma equipment [18]. Contact holes were then opened in the SiO_x layer on the source and drain regions. Gate, drain and source electrodes were formed with Al metal. After TFT fabrication, some

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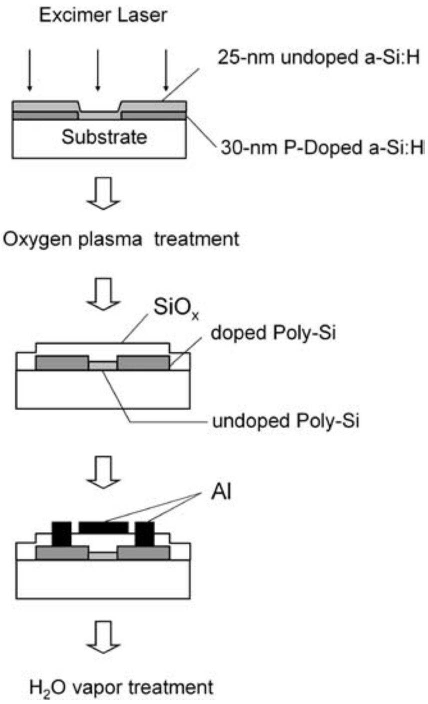

FIGURE 1 Schematic fabrication steps of poly-Si TFTs

samples were also heated at 260 °C with 1.3×10^6-Pa-H_2O vapor for 3 h for defect reduction in SiO_x as well as SiO_x/Si interfaces. From measurements of the capacitance response with a frequency of 1 MHz as a function of gate-bias voltage for Al-gate metal–oxide–semiconductor (MOS) capacitors with n-type silicon, the specific dielectric constant, the densities of SiO_x/Si interface traps and fixed oxide charges were estimated to be 8.7, $3.9 \times 10^{11}\ cm^{-2}\ eV^{-1}$ and $4.5 \times 10^{11}\ cm^{-2}$, respectively, for as-fabricated SiO_x films. The high specific dielectric constant of 8.7 results from a high dielectric-dispersion characteristic at the low-frequency regime compared with that of thermally grown SiO_2, 3.9, while the specific dielectric constant was 2.16 in the visible-wavelength range, which is almost the same of that of thermally grown SiO_2. The high dielectric-dispersion characteristic was probably caused by bonding distortion of Si−O associated with lack of oxygen atoms in the SiO_x films [13]. H_2O vapor heat treatment oxidized the SiO_x films well and improved the specific dielectric constant, the densities of interface traps and fixed oxide charges. They were estimated to be 4.9, $2 \times 10^{10}\ cm^{-2}\ eV^{-1}$ and $1.7 \times 10^{11}\ cm^{-2}$, respectively.

Figure 2a shows transfer characteristics of TFTs fabricated at 280 mJ/cm^2 laser crystallization with no defect-reduction treatment (A) and oxygen-plasma treatment (B). The gate insulator is an as-fabricated SiO_x film. No H_2O vapor heat treatment was carried out in the case of Fig. 2a. The gate width and length are 80 μm and 25 μm, respectively. A very low drain current with a high threshold voltage were measured for TFTs with no defect-reduction treatment, as shown by curve (A) in Fig. 2a. This means that highly dense defect states in the channel region trapped most of electron charges under the gate voltage ranging from 0 to 5 V. On the other hand, a sharp increase in the drain current was observed for TFTs with oxygen-plasma treatment applied to the silicon films, as shown by curve (B) in Fig. 2a. The threshold voltage and the peak effective carrier mobility were obtained from a linear model of the transfer characteristics and the gate capacitance determined by C–V measurements. They were 3.2 V and 251 cm^2/V s. The oxygen-plasma treatment effectively changed the defect states to be electrically inactive and made the channel region conductive under the low gate voltage application. It is important that a 5 min oxygen-plasma treatment improved the TFT characteristics.

High-pressure H_2O vapor heat treatment was applied after TFT fabrication. Characteristics of a TFT with no treatment after crystallization were markedly improved with a steep increase of the drain current, as shown by curve (C) in Fig. 2b. The threshold voltage and the peak carrier mobility were 2.2 V and 175 cm^2/V s, respectively. This result shows that high-pressure H_2O vapor heat treatment reduced defect states at SiO_2/Si interfaces as well as in silicon films via Al-metal and SiO_2 layers. Better characteristics were obtained for the case of oxygen plasma applied after laser crystallization as shown by curve (D). The threshold voltage decreased to 1.8 V and the peak carrier mobility increased to 470 cm^2/V s.

In order to estimate the density of defect states in polycrystalline silicon films as well as in SiO_2/Si interfaces, transfer characteristics were analyzed using a numerical calculation program constructed with the finite-element method combined with statistical thermodynamic conditions with defect states localized at SiO_2/Si interfaces as well as silicon films [15, 19, 20]. We introduced the deep-level defect states localized at the mid-gap, which

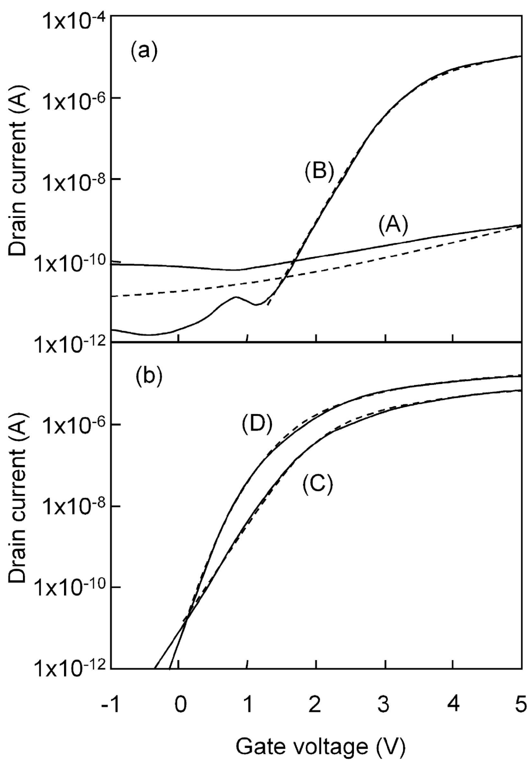

FIGURE 2 **a** Transfer characteristics of TFTs fabricated at 285 mJ/cm^2 laser crystallization with a width of 80 μm and a length of 25 μm for the case of no oxygen-plasma treatment (A) and oxygen-plasma treatment at 250 °C, 100 W for 5 min after crystallization (B). **b** The cases of heat treatment with 1.3×10^6-Pa H_2O vapor at 260 °C for 3 h after TFT fabrication with no oxygen-plasma treatment (C) and oxygen-plasma treatment after laser crystallization (D). The drain voltage was 0.1 V. *Dashed curves* show calculated drain currents obtained by numerical calculation program

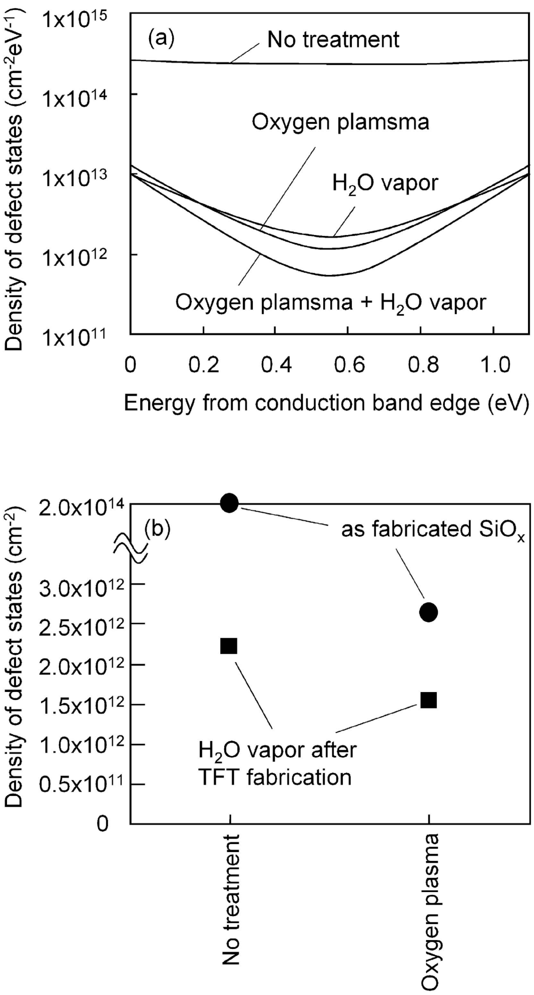

FIGURE 3 **a** Calculated density of acceptor-type defect states of silicon films as a function of energy level in the silicon band gap, **b** calculated total density of the unoccupied acceptor-type defect states in the flat-band condition including SiO_x/Si interfaces and silicon films for as-fabricated TFTs and TFTs treated with high-pressure H_2O vapor after their fabrication in the case of no oxygen-plasma treatment and oxygen-plasma treatment after crystallization

had an assumed Gaussian-type energy distribution. Tail-state-type defect states were also introduced. The density exponentially decreased from the conduction band as well as the valence- band edges to a deep energy level symmetrically in the band gap. The defect states were placed spatially uniformly in the silicon films. We assumed a symmetrical energy distribution of gap states in the silicon band gap. For the interface defect density of SiO_x/poly-Si, we used the density of interface traps obtained by C–V measurements of MOS capacitors. The best agreement of calculated transfer characteristics to experimental ones, as shown in Fig. 2, resulted in the density of defect states.

Figure 3a shows the calculated density of acceptor-type defect states of silicon films as a function of energy level in the band gap for TFTs with an as-fabricated SiO_x gate insulator. It does not include the density of SiO_x/Si interface traps. Although silicon had a high density of gap states of 2×10^{14} $cm^{-2}\,eV^{-1}$ in the case of no defect-reduction treatment, oxygen-plasma treatment at 250 °C, 100 W for 5 min after crystallization effectively reduced the density of mid-gap states to $1.2 \times 10^{12}\,cm^{-2}\,eV^{-1}$. The peak density of tail states was $1.3 \times 10^{13}\,cm^{-2}\,eV^{-1}$ and the width was 0.18 eV. The high-pressure H_2O vapor heat treatment after TFT fabrication further reduced the density of defect states in the silicon films. The density of mid-gap states, the peak density of tail states and the width of the states were reduced to $1.7 \times 10^{12}\,cm^{-2}\,eV^{-1}$, 1×10^{13} $cm^{-2}\,eV^{-1}$ and 0.22 eV for the case of a TFT fabricated with no oxygen-plasma treatment after laser crystallization. They were also reduced to $5.4 \times 10^{11}\,cm^{-2}\,eV^{-1}$, 1.0×10^{13} $cm^{-2}\,eV^{-1}$ and 0.15 eV for the case of a TFT fabricated with oxygen-plasma treatment after laser crystallization. Those results show that H_2O molecules were effectively incorporated into the silicon films through Al-gate metal and SiO_2 gate insulator, and that they reduced defect states remaining in the silicon films. They also reduced the defects in SiO_x gate insulators and SiO_x/Si interfaces, as rev ealed with C–V measurements.

Figure 3b shows the calculated total density of the unoccupied acceptor-type defect states in the flat-band condition including SiO_x/Si interfaces and silicon films for TFTs with as-fabricated SiO_x gate insulators and TFTs treated with high-pressure H_2O vapor after TFT fabrication. Although TFTs fabricated with no defect treatment had a high density of defect states of $2 \times 10^{14}\,cm^{-2}$, 5 min oxygen-plasma treatment reduced the density of defect states to $2.6 \times 10^{12}\,cm^{-2}$. H_2O vapor heat treatment after TFT fabrication reduced the total density of defect states to 2.2×10^{12} cm^{-2} for TFTs fabricated with no oxygen plasma and to $1.5 \times 10^{12}\,cm^{-2}$ for TFTs fabricated with oxygen plasma. The combination of H_2O vapor heat treatment with oxygen plasma is effective to reduce defects in TFTs. The low threshold voltage of 1.8 V and the high carrier mobility of 470 cm^2/V s were consequently obtained.

The fabrication process with oxygen plasma applied to polycrystalline silicon films and high-pressure H_2O vapor heat treatment after TFT fabrication is attractive. TFTs can be fabricated using dry processing including oxygen-plasma treatment. The wet process of H_2O vapor heat treatment is carried out at the final stage after TFT fabrication. The present defect-reduction process can therefore be applied to conventional fabrication process.

In summary, a combination of high-pressure H_2O vapor heat treatment with oxygen plasma treatment was investigated in order to reduce defect states of silicon films and SiO_x films in the fabrication of n-channel polycrystalline silicon thin film transistors using XeCl excimer laser crystallization. 13.56 MHz oxygen-plasma treatment at 100 W for 5 min at 250 °C reduced defect states of 25 nm-thick laser-crystallized silicon films to $2.6 \times 10^{12}\,cm^{-2}$. A carrier mobility of 251 cm^2/V s and a low threshold voltage of 3.2 V were achieved for TFTs fabricated with laser crystallization at 280 mJ/cm^2. Heat treatment at 260 °C with 1.3×10^6-Pa-H_2O vapor for 3 h was applied after TFT fabrication in order to improve the SiO_x gate insulator and reduce the density of defect states at SiO_x/Si interfaces. The density of defect states of TFTs was reduced to $1.5 \times 10^{12}\,cm^{-2}$. A carrier mobility of $470\,cm^2/V\,s$ and a low threshold voltage of 1.8 V were achieved.

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