Chapter 3

Application of Supercritical Fluid Technology on Amorphous Silicon Thin Film Transistors (a-Si:H TFTs)

3.1 Fabrication of SiN_X Film and Experiment Process

In this experiment, a SiN_X film layer was deposited on p-type (100) silicon wafers by Plasma-Enhanced Chemical Vapor Deposition (PECVD) at 300℃. The thickness of as-deposited SiN_X films was 50nm, which was measured by an ellipsometer system. Subsequently, the wafers with 50nm-thick SiN_X film were split into three groups, and processed with different post-treatments to study the properties of low-temperature-deposited SiN_X film. The first group labeled as Baking-only treatment, was designed as the control sample, and was only baked on a hot plate at 150 °C for 2 hrs. The second group labeled as H_2O vapor treatment, was immersed into a pure H_2O vapor ambience at 150 °C for 2 hrs in a pressure-proof stainless steel chamber with a volume of 30cm^3. The third group marked as 3000psi-$SCCO_2$ treatment, was placed in the supercritical fluid system at 150°C for 2 hrs, where was injected with 1500~3000psi of $SCCO_2$ fluids mixed with 5 vol.% of propyl alcohol and 5 vol.% of pure H_2O. The propyl alcohol plays a role of surfactant between nopolar-$SCCO_2$ fluids and polar-H_2O molecules, so that the H_2O molecule uniformly distributes in $SCCO_2$ fluids and be delivered into the SiN_X film.

After these different treatments, the thickness of SiN_X films is almost intact, checked with the ellipsometer measurement. Fourier transformation infrared spectroscopy (FTIR) was also used to investigate the evolution of chemical functional bonding in SiN_X films. Electrical measurements were conducted on metal insulator semiconductor (MIS) capacitors by thermally evaporating Al electrodes on the front surface of the SiN_X films and the backside of the silicon wafer. The current density-electric field (*J*-*E*) characteristics, capacitance-voltage (*C*-*V*) characteristics and breakdown voltage were measured with HP4156C semiconductor parameter analyzer for investigating the transformation of SiN_X film. The experiment processes of thin SiN_X film with various treatments are exhibited in Fig. 3-1.

3.1.1 Fourier Trans-form Infrared Spectroscopy (FTIR) Analysis

Figure 3-2 shows the FTIR spectra of SiN_X films after various post-treatments, including Baking-only, H_2O vapor and 3000 psi-$SCCO_2$ treatment. The absorption peak at 850 cm^{-1} corresponds to the Si-N stretching mode. The remaining absorption peak at around 3340 cm^{-1} corresponds to the N-H stretching mode and at 2180 cm^{-1} to the Si-H stretching mode. The peak intensity of SiN_X films for different treatments is almost the same, meaning that these post-treatments would not make different influence on the thickness and quality of the interfacial SiN_X film.

3.1.2 The current density-electric field (*J*-*E*) characteristics

The leakage current densities of SiN_X films after different treatments are shown as a function of applied negative gate bias voltage in Fig. 3-3. Among various post-treatments, the leakage current is almost the same. The 3000 psi-$SCCO_2$ treatment exhibit the lower leakage current density among all samples. The electrical performance agrees with FTIR analysis.

3.1.3 Breakdown voltage measurement

Figure 3-4 show the breakdown characteristic curves of SiN_X films after various treatments. Among various post-treatments, the breakdown characteristic curves are almost the same. The electrical performance agrees with FTIR analysis.

3.1.4 The capacitance-voltage (*C*-*V*) characteristics

The capacitance-voltage (*C-V*) characteristics are also generally used to judge the quality of dielectric films. Figure 3-5 shows capacitance-voltage characteristics of SiN_X films after different treatment, measuring at 1M Hz with gate bias swing from negative voltage to positive voltage (forward) and from positive voltage to negative voltage (reverse). The slope of C-V curve in transient region, i.e. from C_{max} to C_{min}, is relative to the interface states, for example, the sharp slope indicates fewer defects exist in the interface between SiN_X and Si wafer. In Fig. 3-5, the shift of C-V curve under forward and reverse swing is also appears in baking-treated and H_2O vapor-treated SiN_X films. It is resulted from the trapped electron in defects of SiN_X films, and that is not expected for gate insulator of transistors. Under negative gate bias, the electric inject from Al gate into SiN_X films and trapped by defects, leading to the larger gate bias is required for inducing electron-inversion layer. For describing clear, we define the flat-band voltage is the gate bias as $C/C_{max} = 0.8$, and the shift of the flat-band voltages under forward and reverse swing is observed. It is evidently observed that the baking-treated SiN_X film hold numerous defects because of the extensive shift of flat-band voltage, and the defects decrease a little after 3000 psi-$SCCO_2$ treatment.

These results conform to the tendency in current-voltage characteristics and again verify that the $SCCO_2$ technology could not effectively deactivate defects in SiN_X films.Another interesting detection, in Fig. 3-5, is the change of flat-band voltage of different-treated SiN_X films under forward swing. For baking- treated SiN_X film, the flat-band voltage is away from ideal gate bias voltage (about 0~0.3 volt.), and that of 3000 psi-$SCCO_2$ treated SiN_X is shifted to zero a little. The main reason could be referred to the fixed positive charges are removed by $SCCO_2$ fluids. The mechanism of extracting of fixed charge is shown in Fig. 2-15, including positive and negative fixed charge [44]. The polarized-H_2O molecule is taken as a dipole which would attract the fixed charge in SiN_X films. Afterward, the H_2O molecule and fixed charge are carried away by $SCCO_2$ fluids mixed with propyl alcohol. For H_2O vapor-treated SiN_X film, the un-zeroed flat-band voltage could be attributed to the poorer capability for H_2O vapor to remove fixed charge. Hence, it is necessary for H_2O molecule to be driven into SiN_X films and carried away by $SCCO_2$ fluids.

In 3.2, we applied the SiN_X films on a-Si:H TFTs to analysis and discuss of Electric Characteristics.

3.2 Fabrication of a-Si:H TFTs and Experiment Process

Conventional back channel etching (BCE) a-Si:H TFTs on glass substrate were investigated with supercritical CO_2 fluids ($SCCO_2$) technology in this study. The tri-layer, a-SiNx/ a-Si:H/ n^+-a-Si:H with thickness of 300 nm/ 150 nm/ 50 nm, respectively, were formed over patterned chromium gates at a plasma enhancement chemical vapor deposition (PECVD) system at 300 °C. Afterward, the source/drain metal film was deposited, and patterned by microlithography and etch processes. The structure of a-Si:H TFT is shown in Fig. 3-6. For improving electric characteristics, one group of a-Si:H TFTs was placed in the supercritical fluid system at 150°C for120 min, where was injected with a 3000 psi of $SCCO_2$ fluids mixed with 5 vol.% of propyl alcohol and 5 vol.% of pure H_2O.

The propyl alcohol plays a role of surfactant between nopolar-$SCCO_2$ fluids and polar-H_2O molecules, so that the H_2O molecule uniformly distributes in $SCCO_2$ fluids and be delivered into the a-Si:H film by $SCCO_2$ fluids. In addition, another group of a-Si:H TFTs with no $SCCO_2$ treatment was taken as the control sample, and which were only baked on a hot plate at 150 °C for 120 min. The experiment processes of a-Si:H TFTs with various treatments are shown in Fig. 3-7

The transfer and output characteristics of a-Si:H TFTs were measured by HP 4156-A semiconductor analyzer at 30 °C. For extracting activation energy, the transfer characteristics of TFT devices were also measured at different temperatures (from 30 °C to 75 °C), and density of states of TFTs were obtained from the resultant analysis of activation energy.

3.3 Analysis of Electric Characteristics and Discussion

Figure 3-8 shows the transfer characteristics of identical a-Si:H TFT, before and after $SCCO_2$-treatment. The a-Si:H TFT with a ratio of channel length to width 10μm/20μm was operated in linear region at V_{DS} = 0.1 V. The threshold voltage of a-Si:H TFTs was defined as normalized drain current (NI_{DS}) reaching 10^{-9} A. The sub-threshold swing was calculated from $NI_D=10^{-12}$ A to 10^{-10} A, which is forward sub-threshold region. In Fig. 3-8, it is observed after $SCCO_2$ treatment the a-Si:H TFT device exhibits a lower threshold voltage, lower subthreshold swing (from 1.05 volt./dec. to 0.82 volt./dec.), and a slightly enhanced mobility from 0.30 $cm^2V^{-1}s^{-1}$ to0.32 $cm^2V^{-1}s^{-1}$. For a-Si:H TFTs, it has been reported the subthreshold and mobility are dependent on the deep level of states and tail-states in the mobility gap of a-Si:H film, respectively [47, 48]. This indicates, in this study, that the defect states in a-Si:H film can be passivated by H_2O molecule during $SCCO_2$ fluids processing, especially effective for deep trap states. Additionally, the lower threshold voltage can be attributed to the relaxing of trapped-charge from SiNx and the decrease of deep trap states in a-Si:H film [48]. Also, the improvement of leakage current in the reverse sub-threshold regime, as shown in region 3 of Fig. 3-8, can support the proposed contention again, due to the repairing of density of states at the back channel interface [49].

The output characteristics of a-Si:H TFTs were shown in Fig. 3-9, and the higher saturation current is achieved after the $SCCO_2$ treatment. The improvement of saturation current is mainly caused by the lowering of threshold voltage, due to insignificant variation in mobility. Besides, after $SCCO_2$ treatment, a fine contact between a-Si:H and source/drain metal is retained because of no current crowding in the output characteristics.

For further study, the activation energy thereby was extracted from transfer characteristics at different measured temperatures [50], as shown in Fig. 3-9, in linear operation region with V_{DS} = 0.1V. The activation energy is defined as $E_{act.} = E_C - E_F$, where E_C and E_F is conduction band and Fermi-level energy of a-Si:H film respectively. In generally, the activation is greatly relative to the drain current of transistors, and could be obtained by the following simply equation, in linear operation region:

$$ln(I_{DS}) = C_0 - E_{act.}/k_BT \quad ; C_0 = ln(\frac{W \times d}{L} \times V_{DS} \times \sigma_0)$$

where σ_0, W, L, d are the channel intrinsic conductivity, width , length and thickness sequentially. The k_B and T expresses Boltzmann constant and Kevin temperature. The inset of Fig. 3-10 shows the plot of $ln(I_{DS})$ versus reciprocal of temperature (1/T), and the slopes are used to calculate the activation energy at different gate bias.

Figure 3-11 shows the plot of activation energy versus gate bias. In the transient region, i.e. from off-state to on-state, the sharper variation of activation energy exhibits the higher capability for gate to control transistor, lower density of states and better subthreshold swing [48, 50]. After $SCCO_2$ treatment, the variation rate of activation energy in the transient region increases obviously, so that the improvement of sub-threshold swing is expected, exactly as shown in Fig. 3-8. Besides, the lower activation energy at on-state and higher at off-state are achieved which corresponding to the higher mobility in above-threshold region and lower leakage in reverse sub-threshold region, respectively.

The distribution of density of states is very important to understand the physical mechanisms of transistors and judge the device behavior, because it correlates with the threshold voltage, subthreshold swing, and carrier mobility of transistor. In 1994, Globus et al. [50] proposed a method with electrical measurement to evaluate the density of states in a-Si:H TFTs, from the dependence of activation energy and gate bias. If it is assumed that the density of states does not suffer sharp changes for energy interval about k_BT, the charge of acceptor-like states Q_t filled by the gate bias is given by

$$Q_t = q\int_{E_C - E_{F0}}^{E_C - E_{F0} + qV_s} g(E)\, dE$$

where q is the electron charge, Vs is the surface potential, E_{F0} is the equilibrium Fermi level in the a-Si:H film, and g(E) is the density of states. The charge Q_t could also be expressed as

$$Q_t = \frac{qn_t}{d_t} = \frac{\varepsilon_i}{d_i d_t}(V_{GS} - V_{FB})$$

where qn_t is the surface charge, V_{FB} is the flat-band voltage, ε_i and d_i are the gate dielectric permittivity and gate dielectric thickness, respectively, and d_t is the thickness of the space-charge region in a-Si:H film. Differentiating previous two equations with gate bias (V_{GS}), we would gain

$$\frac{d}{dV_{GS}}\left(\frac{n_t}{d_t}\right) = g(E_{act.})\frac{dqV_s}{dV_{GS}} = -g(E_{act.})\frac{dE_{act.}}{dV_{GS}}$$

where $E_F = E_{F0} - qV_s$ is quasi-Fermi level. The density of states thereby could be related to derivative of the activation energy with respect to gate bias, as following equation:

$$g(E_{act.}) = \frac{-\frac{d}{dV_{GS}}\left(\frac{n_t}{d_t}\right)}{\frac{dE_{act.}}{dV_{GS}}}$$

If we assume that the band bending in a-Si:H film is small compared to the characteristic energy of the density of states variation, then $d_t \sim t$ where t is the a-Si:H film thickness, and previous equation could be reduced to

$$g(E_a) = -\frac{\varepsilon_i}{q \times di \times t} \times \frac{1}{\frac{dE_a}{dV_{GS}}}$$

This technology only accounts for the acceptor-like states in the mobility gap of a-Si:H film. Advantage of the method is its simplicity, and only transfer characteristics at different temperature are required.

Figure 3-12 shows the density of states in mobility gap of a-Si:H film, and the distribution is calculated by previous equation. From Fig. 3-12 (a), the density of states for baking-only treated transistor which is taken as the control sample , it indicates the electrical characteristics of a-Si:H TFTs would not be improved under the heating at 150 °C alone, as result of no obvious modification in density of states observed after a baking treatment. In Fig. 3-12 (b), the density of states for $SCCO_2$-treated transistor, the deep trap states which caused mainly by the existence of dangling bonds, are evidently decreased from a value of 10^{17} $cm^{-3}ev^{-1}$ to 10^{16} $cm^{-3}ev^{-1}$ after $SCCO_2$- treatment, and also partial tail states lowered. Consequently, it is believed that the H_2O molecule is effectively transferred into a-Si:H film by $SCCO_2$ fluids, and effectively passivates the dangling bonds with H_2O molecule at 150 °C [31-34]. Because primary variation occurs in deeps trap states, the enhancement is conspicuous in sub-threshold swing and not shown in the mobility for $SCCO_2$-treated a-Si:H TFT, as shown in Fig. 3-8.

3.4 Summary

In this study, the $SCCO_2$ fluid technology is successfully used to carry H_2O molecule into a-Si:H film at 150 °C and passivates the trap defects effectively. From theses experimental results, the deep states are obviously reduced from 10^{17} $cm^{-3}ev^{-1}$ to 10^{16} $cm^{-3}ev^{-1}$, and some tail states are depressed via this proposed $SCCO_2$ processing. Hence, better sub-threshold swing and lower threshold voltage are gained after $SCCO_2$ fluids treatment. Also, a superior output characteristic is kept during $SCCO_2$ processing. This proposed technology, therefore, is applicable to improve effectively the electrical characteristics of a-Si:H TFTs, and consistent with the low-temperature manufacture processes.