Chapter 4

Application of Supercritical Fluid Technology on Nanocrystal Non-volatile Memories

4.1 Fabrication of Non-volatile Memories and Experiment Process

4-in (100) oriented p-type silicon wafers were cleaned with standard RCA process, followed by a dry oxidation in an rapid thermal anneal(RTA) to form a 6-nm-thick tunnel oxide. Subsequently, an 8-nm-thick tungsten-silicide layer was deposited onto the tunnel oxide by low pressure chemical vapor deposition (LPCVD) furnace. The tungsten-silicide layer was capped by a 12-nm-thick amorphous Si layer deposited also by low pressure chemical vapor deposition furnace. A schematic diagram of the structure is shown in Fig. 4.1. The stacked structure was, afterwards, dry oxidized by rapid thermal anneal to form a layer with control oxide on the top. Nanocrystals were found to precipitate and embed between tunnel oxide and control oxide, as depicted in Fig. 4.1 . Subsequently, the wafers with tungsten-silicide film were split into two groups, and processed with different post-treatments to study the properties of tungsten-silicide 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 3000psi-$SCCO_2$ treatment, was placed in the supercritical fluid system at 150°C for 2 hrs, where was injected with 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 film for passivating defects. Finally, Al gate electrode was patterned and sintered, as illustrated in Fig. 4.1. The structural examinations were carried out in a transmission electron microscope (TEM). The current density-electric field (*J-E*) characteristics was measured with HP4156C semiconductor parameter analyzer for investigating the transformation of tungsten-silicide film. The capacitance-voltage (C-V) measurements were performed by a precision LCR meter HP 4284A to study the electron charging and discharging effects of the nanocrystals.

4.2 Analysis of Characteristics and Discussion

4.2.1 Transmission Electron Microscopy (TEM) Analysis

Figure 4-2 (a), (b) show the influence of various post-treatments on Non-volatile Memory samples in TEM material analysis. 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 marked as 3000psi-$SCCO_2$ treatment, was placed in the supercritical fluid system at 150°C for 2 hrs, where was injected with 3000psi of $SCCO_2$ fluids mixed with 5 vol.% of propyl alcohol and 5 vol.% of pure H_2O. The tunnel oxide for different treatments is almost the same.

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

The leakage current densities of Non-volatile Memory after different treatments are shown as a function of applied negative gate bias voltage in Fig. 4-3. Among various post-treatments, the baking-treated Non-volatile Memory film exhibits the most serious leakage current, inferentially due to its poor dielectric characteristics with numerous traps inside the Non-volatile Memory film and the interface between parasitical tunnel oxide and tungsten-silicide. After Baking-only treatment, effective improvement of electrical characteristic is obtained by the 3000 psi-$SCCO_2$ treatment, exhibiting the lowest leakage current density among all samples. Low leakage current density (~3×10^{-8} A/cm^2) is kept constantly, even biased at a larger electric field.

Fig. 4.3 show the tungsten-silicide nanocrystals were split into two groups, and processed with different post-treatments to study the properties of tungsten-silicide 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 3000psi-$SCCO_2$ treatment, was placed in the supercritical fluid system at 150°C for 2 hrs, where was injected with 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 film for passivating defects. The spherical tungsten-silicide nanocrystals are observed.

4.2.3 The capacitance-voltage (*C-V*) hysteresis and retention characteristics

Fig. 4.4 (a) and (b) shows the forward and reverse sweep C-V characteristics, indicating the electron charging and discharging effects of tungsten-silicide nanocrystals with Baking-only treatment and 3000psi-$SCCO_2$ treatment, respectively. The bidirectional C-V sweeps were performed from deep inversion to deep accumulation and in reverse, which exhibit electron charging effect. As shown in Fig. 4.4, with the voltage swept from -1 to -3 V and back to -1 V, outstanding threshold voltage shifts are observed for Baking-only treatment and 3000psi-$SCCO_2$ treatment, respectively. As the whisked voltage is increased from 1 to -5 V, more obvious C-V shifts are seen for Baking-only treatment and 3000psi-$SCCO_2$ treatment, respectively. At larger voltage, the memory window of the sample with Baking-only treatment is larger than the sample with 3000psi-$SCCO_2$ treatment is due to the defects with the same physical thickness.

Figure 4.5 shows the retention characteristics for the tungsten-silicide nanocrystals with Baking-only treatment and 3000psi-$SCCO_2$ treatment. The degraded retention characteristics can be seen in Fig. 4.5. The capacitance was degraded 20% for 3000psi-$SCCO_2$ treatment after 9.32E+04 sec. The retention characteristic was rather poor for the samples with Baking-only treatment, as shown in Fig. 4.5 (a). It is ascribed to the defects of Si dangling bonds and interface states. 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 tungsten-silicide and tunnel oxide. Furthermore, the best improvement is achieved by 3000 psi-$SCCO_2$ treatment. This exhibits that the $SCCO_2$ treatment possesses excellent ability to passivate the defects, including Si dangling bonds and interface states.

Summary of electrical Characteristics for Non-volatile Memory after various post-treatments are shown in Table 4-1.

4.3 Summary

In this study, the $SCCO_2$ fluid technology is successfully used to carry H_2O molecule into tungsten-silicide film at 150 °C and passivates the trap defects effectively. From theses experimental results, the interface states between tungsten-silicide and tunnel oxide are obviously reduced, and some Si dangling bonds are depressed via this proposed $SCCO_2$ processing. Hence, better program / erase, retention time and ideal capacitance-voltage curve are gained after $SCCO_2$ fluids treatment. This proposed technology, therefore, is applicable to improve effectively the electrical characteristics of non-volatile memories, and consistent with the low-temperature manufacture processes.