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Tungsten nanocrystal memory devices improved by supercritical fluid treatment

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A supercritical CO_2 ($SCCO_2$) fluid technique is proposed to improve electrical characteristics for W nanocrystal nonvolatile memory devices, since the thickness and quality of tunnel oxide are critical issues for the fabrication of nonvolatile memory devices. After $SCCO_2$ treatments, *C-V* curves are restored to normal, as well as the leakage current of W nanocrystal memory devices are reduced significantly. It reveals that W nanocrystal memory devices could be formed with shorter oxidation time, moreover, dangling bonds and trapping states initially created within an incomplete oxidized film will be efficiently repaired after $SCCO_2$ treatment. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2803937]

Recently, nanocrystal-based memory devices have been proposed to replace conventional flash memories.[1,2] By employing distributed nanocrystals as storage media, charges stored in the device would not lose intensity, and the reliability of the devices will be promoted. Among many articles announced for fabricating nanocrystals, one of the approaches is precipitating nanocrystals by thermal oxidation.[3,4] It is beneficial to simplify the procedures for manufacturing memory devices. Utilizing phase change and equilibrium of surface energy with specific materials, the films of specific materials are oxidized and transformed into dielectric matrix. Simultaneously, nanocrystals are precipitated in dielectric matrix. However, some issues are concerned for thermal oxidation precipitating nanocrystals. For instance, thermal oxidation parameters (temperature and time) must be well controlled. During the oxidiation, Si substrate under deposited films transforms into SiO_2 as well and results in a thicker tunnel oxide. An immoderate thickness of tunnel oxide affects not only the electron tunneling of memory devices but also the parameter of the following processes. In contrast, an insufficient oxidation time results in a useless dielectric matrix, which storage charges could not be reserved in nanocrystals.[5] Therefore, the oxidation time is a critical issue for the fabrication of nanocrystal memory devices. In this work, the supercritical CO_2 ($SCCO_2$) fluid technique is proposed to improve the issues described previously. Supercritical fluids, which exist above their critical temperature and pressure, represent liquidlike properties as well as gaslike.[6,7] The repair of the dangling bonds and defects of tunneling oxide is expectable by utilizing $SCCO_2$ as a liquidlike solvent, and permeating into W nanocrystal devices with a gaslike diffusivity.

The flowchart for the fabrication of W nanocrystals memory devices is illustrated in Fig. 1. First, 3-nm-thick SiO_2 was grown on *p*-type wafer by a rapid thermal annealing system. Afterwards, WSi_x (x=2.7 and 4 nm) and amorphous Si layer (*a*-Si, 5 nm) were deposited continuously onto the tunnel oxide by CVD system. To precipitate W

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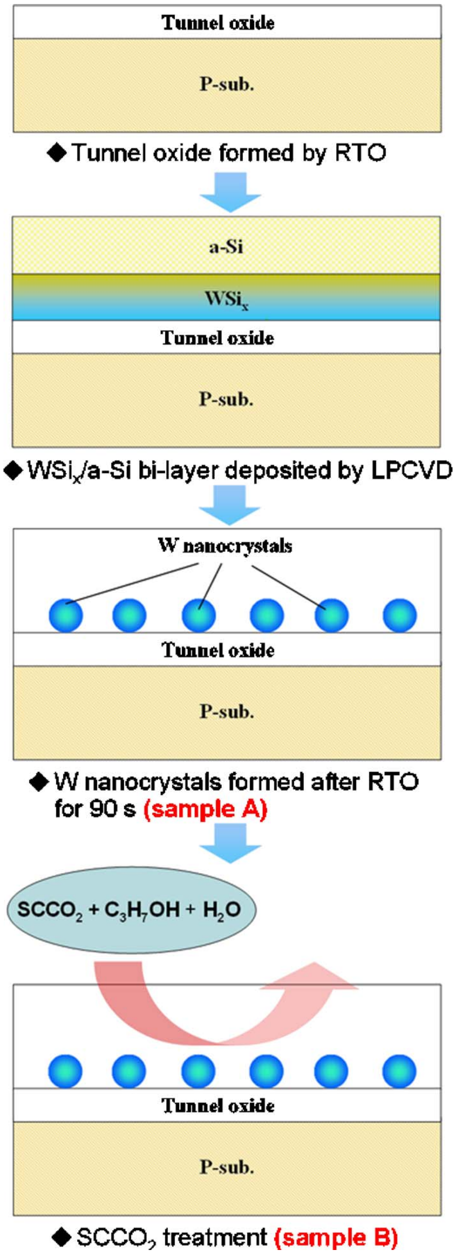

FIG. 1. The flowchart for the fabrication of W nanocrystal memory devices. The samples of a-Si/WSi$_x$/SiO$_2$/Si structure performed only by RTO treatment for 90 s are labeled as "A," while samples achieved by RTO and sequential 3000 psi SCCO$_2$ treatments are labeled as "B."

nanocrystals, a rapid thermal oxidation (RTO) process was performed at 900–1100 °C. Meanwhile, control oxide layer and SiO$_2$ matrix surrounding W nanocrystals were formed as well. After the formation of W nanocrystals, the samples were placed in a supercritical fluid system for SCCO$_2$ treatment. The samples were immersed into a 3000 psi SCCO$_2$ fluid mixed with 5 vol % propyl alcohol and 5 vol % deionized H$_2$O at 150 °C for 2 h. The propyl alcohol acts as a surfactant which links the nonpolar-SCCO$_2$ fluid and polar-H$_2$O molecules, prompting H$_2$O molecules distributed in SCCO$_2$ fluid and delivered to the samples uniformly. Samples with a-Si/WSi$_x$/SiO$_2$/Si structure performed only by RTO treatment for 90 s are labeled as "A," while samples achieved by RTO and sequential 3000 psi SCCO$_2$ treatment are labeled as "B." Finally, Al electrodes were patterned by thermal evaporation for producing capacitor structure. The structure was observed by transmission electron microscopy

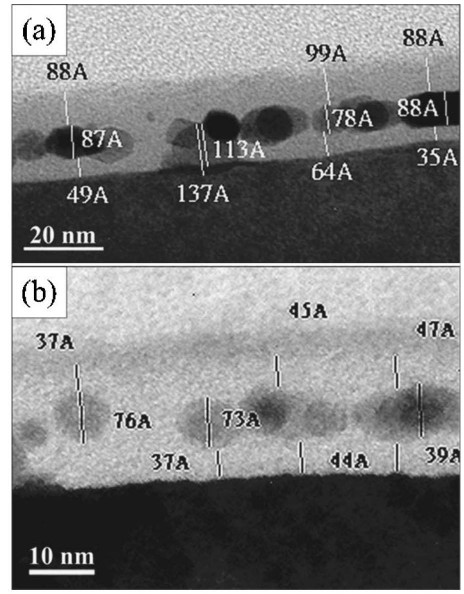

FIG. 2. The cross-sectional TEM images of (a) A and (b) B, indicating that isolated W nanocrystals are embedded in the SiO$_2$ and no obvious differences in thickness are observed.

(TEM). The electrical characteristics of the samples were performed by a precision *LCR* meter (HP4284A) to observe capacitance-voltage (C-V) and current-voltage (I-V) characteristics.

Figures 2(a) and 2(b) show the cross-sectional TEM images of samples A and B, respectively. Both figures display that W nanocrystals are embedded in SiO$_2$ matrix. No obvious variations in the morphology and density of W nanocrystals are found expectably after the SCCO$_2$ treatment. The density and mean size of W nanocrystals in both samples are $\sim$10.3 nm and $\sim 1.55 \times 10^{11}$ cm^{-2}, respectively. Besides, the tunneling oxide of these two samples displays equally in thickness, i.e., SCCO$_2$ treatment would not induce the oxidation reaction of Si substrate critically. For this reason, the comparisons of electrical characteristics are based on the identical thickness of tunneling oxide.

The (C-V) curves of sample A (RTO for 90 s) are shown in Fig. 3(a). The sweeping C-V curves exhibit asymmetry hysteresis phenomena, which imply that the holes are the preferable store centers for W nanocrystal memory devices. Furthermore, the capacitance switched from accumulation to inversion always arises at initial operation bias, while the gate voltage operates from negative to positive. The appearance of unstable capacitance is regarded that the SiO$_2$ matrix surrounding W nanocrystals is oxidized incompletely. Followed by the SCCO$_2$ treatment, surprisingly, the outstanding improvements of electrical characteristics are observed. As shown in Fig. 3(b), regular C-V curves of sample B are displayed, which are consistent with the well oxidized sample. In addition, the abrupt slopes of C-V curves indicate that the dangling bonds and interfacial trapping states in W nanocrystal memory devices are passivated after SCCO$_2$ treatment.[8] The evaluation of flatband voltage shift attains to $\sim$0.67 V, while the gate voltage sweeps from 1 to -5 V and back to 1 V. The significant threshold voltage shift is sufficient to be defined as "1" and "0" by a typical sensing amplifier for a memory device under low voltage operation. Also, the exhibition of counterclockwise C-V hysteresis for p-type Si substrate suggests that both injection and exclusion of storage

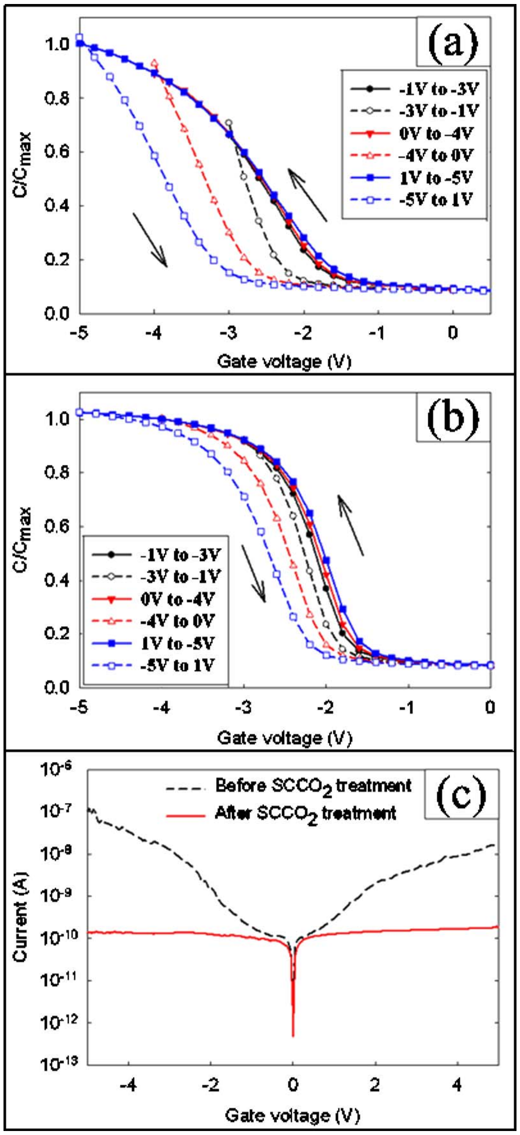

FIG. 3. The *C-V* hysteresis characteristics of W nanocrystal memory devices: (a) sample A and (b) sample B. (c) The *I-V* characteristics of W nanocrystal memory devices before/after (sample A/sample B) 3000 psi $SCCO_2$ treatment.

charges are achieved from Si substrate. Figure 3(c) shows the *I-V* curves of samples A and B. It is noticed that three orders of leakage current was suppressed at −5 V gate voltage after the $SCCO_2$ treatment. Unnecessary power loss is reduced as well.

The improvement of W nanocrystal memory devices by $SCCO_2$ treatment is illustrated in Fig. 4. Although sample A is treated by RTO process for 90 s, as shown in Fig. 4(a), the tungsten silicide film is not completely oxidized. Amounts of dangling bonds and nanocrystal-oxide interfacial trapping states are generated, thus unstable capacitance and inferior leakage current are found. Figure 4(b) illustrates the mechanism of $SCCO_2$ treatment. Owing to the characteristic of $SCCO_2$, H_2O linked $SCCO_2$ penetrated into the film. The electrical characteristics of W nanocrystal memory devices are improved due to the dangling bonds repaired by H_2O molecules.[9]

In summary, the supercritical fluid treatment is successfully applied on the electrical characteristics improvement of memory devices. Supercritical fluid-CO_2 and cosolvent treatment damage neither W nanocrystals nor change the thickness of tunnel oxide. Also, dangling bonds and interfacial trapping states initially created within the incomplete oxidized film are efficiently repaired. In other words, $SCCO_2$ treatment exhibits a passivated effect on dangling bonds and interfacial trapping states. It is a promising technique to apply to a lower temperature manufacturing technology of semiconductor industry in the field of nonvolatile memory in the future.

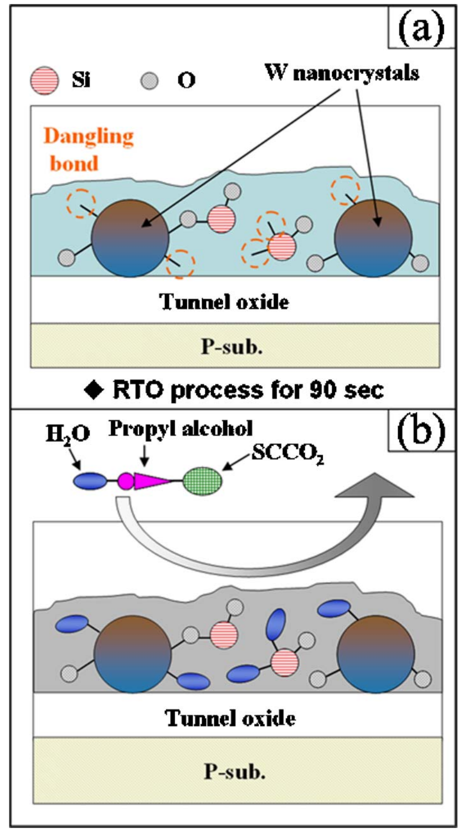

FIG. 4. Schematic diagrams of W nanocrystal memory devices. (a) The sample of a-Si/WSi_x/SiO_2/Si structure is performed by RTO for 90 s. Dangling bonds and nanocrystal-oxide interfacial trapping states are left in the oxide matrix. (b) During $SCCO_2$ treatment, supercritical fluid which linked with H_2O molecules by propyl alcohol penetrated into W nanocrystal devices. Dangling bonds and nanocrystal-oxide interfacial trapping states are passivated by H_2O molecules.

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