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C. H. Chen  
Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

T. C. Chang  
Department of Physics and Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Republic of China and Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Republic of China

I. H. Liao  
ProMOS Technologies, No. 19 Li Hsin Rd., Science-Based Industrial Park, Hsinchu, Taiwan 300, Republic of China

P. B. Xi  
Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Republic of China

C. T. Tsai  
Institute of Electronics Engineering, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

P. Y. Yang  
Department of Photonics and Display Institute, National Chiao Tung University, Hsinchu, Taiwan 300, Republic of China

Joe Hsieh and Jason Chen  
ProMOS Technologies, No. 19 Li Hsin Rd., Science-Based Industrial Park, Hsinchu, Taiwan 300, Republic of China

U. S. Chen and J. R. Chen  
Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

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A supercritical CO2 (SCCO2) 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 SCCO2 treatments, C-V curves are restored to normal, as well as 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 SCCO2 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 oxidation, Si substrate under deposited films transforms into SiO2 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 CO2 (SCCO2) 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 SCCO2 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 SiO2 was grown on p-type wafer by a rapid thermal annealing system. Afterwards, WSi1 (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
achieved by RTO and sequential 3000 psi SCCO2 treatment for 90 s are labeled as “A,” while samples achieved by RTO treatment for 90 s are labeled as “A,” while samples achieved by RTO and sequential 3000 psi SCCO2 treatments are labeled as “B.” Finally, Al electrodes were patterned by thermal evaporation for producing capacitor structure. The samples were immersed into a 3000 psi SCCO2 surfactant which links the nonpolar-SCCO2 fluid and polar-H2O molecules, prompting H2O molecules distributed in SCCO2 fluid and delivered to the samples uniformly. W nanocrystals, a rapid thermal oxidation (RTO) process was performed at 900–1100 °C. Meanwhile, control oxide layer and SiO2 matrix surrounding W nanocrystals were formed as well. After the formation of W nanocrystals, the samples were placed in a supercritical fluid system for SCCO2 treatment. The samples were immersed into a 3000 psi SCCO2 fluid mixed with 5 vol % propyl alcohol and 5 vol % deionized H2O at 150 °C for 2 h. The propyl alcohol acts as a surfactant which links the nonpolar-SCCO2 fluid and polar-H2O molecules, prompting H2O molecules distributed in SCCO2 fluid and delivered to the samples uniformly. Samples with a-Si/WSi/SiO2/Si structure performed only by RTO treatment for 90 s are labeled as “A,” while samples achieved by RTO and sequential 3000 psi SCCO2 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 (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 SiO2 matrix. No obvious variations in the morphology and density of W nanocrystals are found expectably after the SCCO2 treatment. The density and mean size of W nanocrystals in both samples are ~10.3 nm and ~1.55 × 1011 cm−2, respectively. Besides, the tunneling oxide of these two samples displays equally in thickness, i.e., SCCO2 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 SiO2 matrix surrounding W nanocrystals is oxidized incompletely. Followed by the SCCO2 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 SCCO2 treatment. The evaluation of flatband voltage shift attains to −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
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.

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