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Tungsten oxide/tungsten nanocrystals for nonvolatile memory devices

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In this work, the fabrication of WO3/W nanocrystals for nonvolatile memory devices has been achieved via rapid thermal oxidation of tungsten silicide. Amorphous Si and WSi1-x-y layers were deposited onto the tunneling oxide and sequentially oxidized to form well-shaped WO3/W nanocrystals. The mean size of WO3/W nanocrystals is ~8.4 nm, while density is ~1.57 × 1011 cm−2. Moreover, the nonvolatile memory device for WO3/W nanocrystals exhibits ~0.53 V threshold voltage shift under 1 V/−5 V operation. The sample without capping a-Si layer was also fabricated for comparison. By material analyses, reasonable formation mechanisms are proposed in this letter. © 2008 American Institute of Physics. [DOI: 10.1063/1.2822401]

In recent years, extensive articles have been published relating with nanocrystal application on nonvolatile memory devices. The memory devices employing distributed nanocrystals as storage elements have exhibited outstanding performance in high speed and low power consumption so that it has been regarded as a candidate to replace conventional dynamic random array memories and/or flash memories.1–3 Theoretically, metal nanocrystals possess more advantages than other materials for nonvolatile memory devices, such as a wide range of available work functions, higher density of states, and smaller energy perturbation due to carrier confinement.4–6 However, few metal materials could be employed in manufacture of current semiconductor industry because of incompatibilities with various processes. Among the practicable metals for semiconductor industry, tungsten provides excellent physical as well as electrical properties for satisfaction of both requirements. For example, high melting point prevents deformation at high temperature, high work function provides high density of states for electrons trapping, chemical stability with Si atom, and so on.7,8

In this letter, the fabrication of well-shaped WO3/W nanocrystals embedded in SiO2 for nonvolatile memory device application has been demonstrated. Additionally, the failure mechanism of imperfect WO3/W nanocrystal-based nonvolatile memory without capping a-Si layer is discussed as well.

8 in. (100) oriented p-type silicon wafers were chemically cleaned by a standard RCA procedure, followed a 3 nm tunnel oxide was grown in a rapid thermal anneal system. Subsequently, a 4-nm-thick WSi1-x-y layer was deposited onto the tunneling oxide using chemical vapor deposition system. An amorphous Si layer (a-Si, 5 nm) was capped onto the tungsten silicide layer to provide sufficient Si atoms for forming the control oxide layer. Afterward, a dry oxidation was utilized for the formation of the control oxide at 900–1100 °C and WO3/W nanocrystals were precipitated in the matrix of SiO2 as well. In addition, the sample without capping a-Si layer was also oxidized in the same conditions. Chemical compositions of samples were investigated by x-ray photoelectron spectrometry (XPS) (Physical Electronics PHI 1600) with Mg Kα (energy=1253.6 eV) radiation. Finally, Al gate electrode was patterned and sintered. The structural analyses were performed by transmission electron microscopy (TEM). The capacitance-voltage (C-V) measurements were performed by a precision LCR meter (HP4284A) to observe the memory characteristics of WO3/W nanocrystal-based devices.

Figure 1(a) shows the cross-sectional TEM image of WSi1-x-y/SiO2/Si structure for RTO process. An about 150 nm cluster was observed on the tunneling oxide. The clusters...
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appear repeatedly on the sample every several micrometers. Besides, the dark contrast in TEM suggests that it was composed of tungsten and/or tungsten compounds. The square shows a highlighted high-resolution TEM (HRTEM) image from the Fig. 1(a). WO₃/W nanocrystals are conspicuously observed embedded in SiO₂ matrix, while the nanocrystals are segregated imperfectly in shape.

In order to improve the formation of imperfect-shaped nanocrystals aforementioned, a 5 nm a-Si layer was capped on WSiₓ layer and followed oxidizing in the same conditions. The inset of Fig. 2(a) represents the HRTEM image of oxidized a-Si/WSiₓ/SiO₂/Si structure. It displays that the WO₃/W nanocrystals were formed into distributed- and well-shaped ellipsoids. The confirmation of mean size of WO₃/W nanocrystals is approximately 8.4 nm in diameter. Figure 2(a) shows the density of WO₃/W nanocrystals versus rapid thermal oxidation (RTO) time. At initially 30 s, WO₃/W nanocrystals nucleated rapidly and sequentially coarsened. As RTO performed at 60 s, the density of WO₃/W nanocrystals decreases to 1.57×10¹¹ cm⁻², and there is no obvious variation from 60 to 120 s. The C-V characteristics of WO₃/W nanocrystals embedded in oxide are shown in Fig. 2(b). While the voltage swept from 1 to −5 V and back to 1 V, a threshold-voltage shift of 0.53 V was observed, which is sufficient to be defined as “1” or “0” for the logic-circuit design.

XPS was used to determine the chemical nature of the a-Si/WSiₓ/SiO₂/Si sample which was oxidized for 120 s RTO process. Ar sputtering for 100 sec is utilized for cleaning. Figure 3 presents the XPS spectra of W 4f. The peaks centered at 3.14 and 33.4 eV were identified as W 4f⁷/₂ and W 4f⁵/₂, respectively. Slight WO₃ chemical states were observed at 35.8 and 37.8 eV as well. Nevertheless, Si atoms in the sample are mostly oxidized, which the evidence is SiO₂ signal identified from Si 2p XPS spectra. Because of extremely little solid solubility of O atoms within W material, O atoms could not exist in W nanocrystals except absolutely oxidation of tungsten. Therefore, it is a reasonable speculation that the position of WO₃ should be on the surface of W nanocrystals. Namely, W nanocrystals are encapsulated by a very thin WO₃ layer.

To elucidate the appearance of samples with and without a-Si layer, a schematic diagram is shown in Fig. 4. Initially, tungsten silicide is oxidized and decomposes to W and Si. Two elements transform to oxygen compounds simultaneously. Comparing with the oxides of W and Si, the heats of formation per oxygen atom are −67.1 kcal/mole for WO₃ and −73.0 kcal/mole for SiO₂, respectively. It is reasonable to believe that the primitive oxidation mostly arises with Si atoms, and only slight W atoms are transformed into W oxides. At the same time, tungsten also aggregates to diminish free energy of surface. However, WO₃ is not stable at high temperature. Some WO₃ vaporized during the nucle-
ation, thus the imperfect shape of WO₃/W nanocrystals formed, as shown from Fig. 4(a) to Fig. 4(c). It is confirmed in Fig. 1(b). Furthermore, difference thermal expansion coefficients are induced between the tunneling oxide and W silicide (0.5 ppm/°C for SiO₂ and 12.5 ppm/°C for WSi₂). W silicide film is compressed by thermal stress during thermal oxidation process. The stress attributes to enhance the aggregation of the WO₃/W and results in clustered, as shown in Fig. 1(a).

Because the cluster formation is due to raising a violent thermal stress in a W silicide film during oxidation, WO₃/W nanocrystals must be precipitated before the W silicide film reacts with oxygen to alleviate the cluster formation. Capping an a-Si layer on W silicide film, as shown in Fig. 4(d), is a significant way to retard oxygen diffusing into the W silicide film. First, an upper a-Si layer is beneficial to reduce the formation of stress at high temperature. Moreover, great parts of SiO₂ are transformed from a-Si capping layer during oxidation. Oxide layer also moderates the diffusion of oxygen into W silicide. The delay time of the W oxidation makes the decomposed W atoms to aggregate completely, as shown in Fig. 4(e). Even if tungsten is slightly oxidized, the thin SiO₂ layer also plays a significant role in keeping WO₃ from evaporation. Capping a-Si layer onto W silicide before oxidation indeed results in perfect shape of WO₃/W nanocrystals.

In summary, the fabrication of WO₃/W nanocrystals as memory devices by oxidizing a-Si/WSi₂/SiO₂/Si structure has been achieved. The nonvolatile memory device with WO₃/W nanocrystals exhibits ~0.53 V threshold voltage shift under 1 V/(-5 V) operation. Meanwhile, the mechanisms of formation of WO₃/W nanocrystals also are proposed. Volatile WO₃ and excessive stress lead to the production of imperfect nanocrystals without capping an a-Si layer. The implementation of the present structure is compatible as well as practicable for nonvolatile memory technology.

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