Combined Atomic Layer and Chemical Vapor Deposition, and Selective Growth of $Ge_2Sb_2Te_5$ Films on TiN/W Contact Plug

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Received May 15, 2007
Revised Manuscript Received July 2, 2007

Phase change random access memory (PCRAM) has attracted a great deal of interest recently for highly integrated nonvolatile memory devices.[1−5] In PCRAM cells, the high level of reset current ($I_{res} \approx 0.5$ mA), which is required for switching the $Ge_2Sb_2Te_5$ (GST) material from the crystalline to the amorphous state (reset process), has been the major obstacle to the further scaling of PCRAM.[6,7] It has been suggested that confining GST material into the contact plug, which greatly reduces the heat dissipation to the surrounding material, profoundly reduces the value of I_{res}.[8,9] Therefore, it is necessary to deposit the GST film using a process that offers good conformality in terms of its thickness as well as its chemical composition, such as atomic layer deposition (ALD) or chemical vapor deposition (CVD). The authors recently reported that the GST material can be deposited by plasma-enhanced cyclic CVD at temperatures ranging from 180 to 290 °C.[10] It was found that the film deposited at 200 °C showed the best chemical and structural properties (highest density, smooth surface morphology, and lowest carbon impurity concentration).[10] In this study, the selective growth of stoichiometric GST on the TiN plugging material in the contact hole that was formed in the SiO_2 dielectric layer, which has not been previously reported, is reported.

Table 1. Summary of Deposition Conditions

canister temperature (°C) (vapor pressure, Torr)			carrier gas flow rate (sccm)			reduction gas flow rate (sccm)		RF plasma (W)	pressure (Torr)
Ge	Sb	Te	Ge	Sb	Te	Ar	H_2		
25 (2.0)	25 (0.4)	5 (1.2)	200	50	50	200	200	100	1.6−2.1

Changing the deposition conditions was found to alter the selective deposition properties. A model that can explain the selective growth behavior is suggested. For this purpose, an in depth investigation of the growth behavior of the GST film on TiN and SiO_2 surfaces at 200 °C was also reported.

Single component films, such as Ge, Sb, and Te, and GST films were deposited on sputter-deposited TiN/Si and thermally grown SiO_2/Si substrates using a shower-head type 8 in.-scale plasma-enhanced ALD reactor (Quros Co., Plus-200) at a wafer temperature of 200 °C. $Ge(i\text{-}C_4H_9)_4$, $Sb(i\text{-}C_3H_7)_3$, and $Te(i\text{-}C_3H_7)_2$ were used as the Ge, Sb, and Te precursors, respectively. To confirm whether the ALD or CVD reaction took place, we independently varied the precursor purge time ($t_{prec-prg}$) and precursor injection time (t_{inj}). During each precursor purge step, Ar gas at a flow rate of 200 sccm was allowed to flow for 0.5−8 s. Because the incorporation behaviors of each component into the single-component film and the GST film were quite different,[10] the changes in the incorporation behavior of each component were investigated when the other two precursors were also sequentially injected. The sequence of precursor pulses was Sb−Te−Ge−Ge−Te (one supercycle that is composed of 5 elemental cycles, where each elemental cycle is composed of precursor injection and purge steps), as determined in a previous study.[10] The deposition process always began with the Sb pulse step, which offers better nucleation behavior. After each precursor pulse and purge, Ar (200sccm) + H_2 (200 sccm) reduction gas was pulsed for 2 s. During the whole precursor and reduction gas pulse period, a radio frequency (rf) plasma was applied (rf power of 100 W, rf frequency of 13.56 MHz) to the reaction chamber. After the reduction gas pulse period, another purge step using Ar gas (Ar purge) without the plasma power with varying periods (t_{Ar-prg}, 0−6 s) was added to completely remove the residual precursor and reduction gas. Details of the deposition conditions are summarized in Table 1. A contact structure with a top open diameter of 300 nm having TiN/W plugging material in a 500 nm thick SiO_2 layer was fabricated to test the selective growth behavior. A longer pulse time (1.5 s) with double injections of the Ge precursor and Sb and Te pulse time of 0.2 s were used to grow stoichiometric GST film. It has to be noted that none of each precursor purge was performed for the selective growth experiment. The reason for this will be discussed below.

The growth behavior, chemical composition, and area layer density of the film were investigated by an X-ray fluores-

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10.1021/cm071313x CCC: $37.00 © 2007 American Chemical Society
Published on Web 08/14/2007

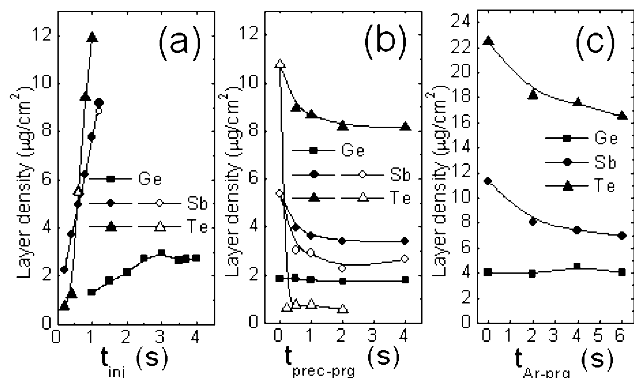

Figure 1. Variations in the area density of each component as a function of the (a) precursor injection time (closed symbol, $t_{prec-prg}$ of Ge = 1 s, $t_{prec-prg}$ of Sb = 2 s, $t_{prec-prg}$ of Te = 1 s; open symbol, $t_{prec-prg}$ of Sb and Te = 8 s), (b) precursor purge time (closed symbol, area density of each component with varying $t_{prec-prg}$ of Ge while no precursor purge for Sb and Te; open symbol, area density of Sb and Te with varying $t_{prec-prg}$ of Sb and Te, respectively), and (c) Ar purge time.

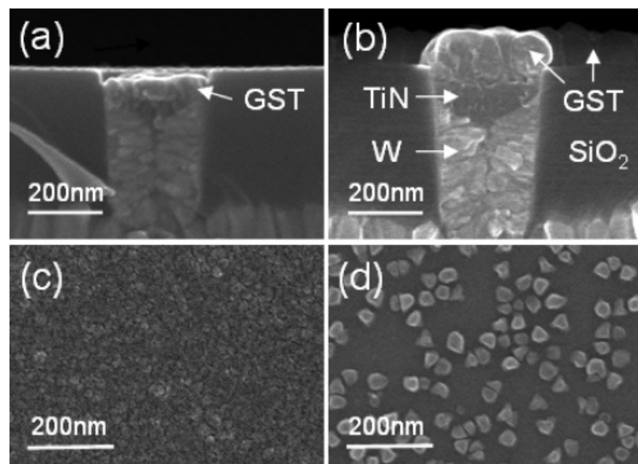

Figure 2. Cross-section SEM images of the GST film deposited on the TiN/W contact plug formed in the SiO_2 layer grown with t_{Ar-prg} values of (a) 0 and (b) 4 s. The plan-view SEM pictures show the surface morphologies of the 30 nm thick GST film (40 cycles) on planar (c) TiN and (d) SiO_2 substrates.

cence analyzer (XRF), for which the atomic concentration and density measurements were calibrated by proton induced X-ray emission (PIXE). The cross-section of the film was investigated by field-emission scanning electron microscopy (FESEM).

First, the t_{inj} and $t_{prec-prg}$ values of each precursor were changed to confirm whether the ALD or CVD reaction occurs. Panels a and b in Figure 1 show the variations in the layer density of each component of the GST films on TiN substrate as a function of the t_{inj} and $t_{prec-prg}$ values, respectively. Here, the number of supercycles and t_{Ar-prg} were 40 and 4 s, respectively. The layer density of Ge increases with increasing t_{inj} up to 2.5 s and then saturates, as shown in Figure 1a ($t_{prec-prg}$ = 1 s), and shows a constant value with respect to $t_{prec-prg}$ when t_{inj} = 1.5 s, as shown in Figure 1b. While varying the values of t_{inj} and $t_{prec-prg}$ for Ge, the corresponding values for Sb and Te were kept constant at 0.2 and 0 s, respectively. This clearly shows that the incorporation of Ge into the GST film occurs via an ALD type reaction. Figure 1b also shows the variation of the layer densities of Sb and Te with increasing $t_{prec-prg}$ of Ge (closed circle and triangle symbols). Interestingly, they also decrease with increasing $t_{prec-prg}$ of Ge up to ~2 s and then saturate. This is due to the removal of the residual Sb and Te precursor gas from the reaction chamber.

However, the layer densities of Sb and Te increase almost linearly with increasing t_{inj} in Figure 1a ($t_{prec-prg}$ = 2 s (Sb) and 1 s (Te), closed symbol). Here, the t_{inj} ($t_{prec-prg}$) value of Ge was 1.5 (0) s and the t_{inj} ($t_{prec-prg}$) values of Te and Sb for the various values of t_{inj} for Sb and Te were commonly 0.2 (0) s. Increasing $t_{prec-prg}$ up to 8 s does not decrease the layer density of Sb and Te (open symbols in Figure 1a). Figure 1b shows that increasing the $t_{prec-prg}$ values of Sb and Te up to only 0.5 s substantially decreases the layer densities of Sb and Te (open symbols). Here, the t_{inj} values of Ge, Sb, and Te were 1.5, 0.2, and 0.2 s, respectively. No precursor purge was performed for the other two precursors. The large decrease in the layer density of Sb and Te caused by adding such a short purge step is believed to be due to the removal of the residual precursors from the chamber volume. Therefore, it can be understood that the incorporation of Sb and Te proceeds via a CVD-type reaction under these conditions. Therefore, it was concluded that no precursor purge steps are required for t_{inj} values of 1.5, 0.2, and 0.2 s for Ge, Sb, and Te, respectively, under which conditions stoichiometric GST was obtained, because Ge is incorporated under the subsaturated ALD condition, and Sb and Te are incorporated under the CVD conditions. The higher thermal decomposition temperature of the Ge precursor (~300 °C) compared to those of the Sb− (~250 °C) and Te− (~200 °C) precursors under Ar atmosphere may cause the ALD- and CVD-type reactions, respectively, for Ge and Sb/Te incorporation.

Figure 1c shows the variations in the layer densities of Ge, Sb, and Te as a function of t_{Ar-prg}, where the supercycle number was 60. Here, no precursor purge was performed. As discussed previously, the Ge layer density was constant, because it is incorporated under the subsaturated ALD condition, whereas the layer densities of Sb and Te decrease because of the purge out of the residual precursor gases during the Ar purge step. The film composition saturated to the stoichiometric value (22.5:22.5:55.0) after a t_{Ar-prg} of 4 s. The film thickness also saturated after a t_{Ar-prg} of 4 s. The saturated growth rate was 0.79 nm/supercycle (average 0.16 nm/elemental cycle). Therefore, the selective growth experiments were performed without including any precursor purge steps.

Images a and b in Figure 2 show the cross-section SEM images of the GST film deposited on the TiN/W contact plug formed in the SiO_2 layer grown with t_{Ar-prg} values of 0 and 4 s, respectively. Here, the TiN contact layer was recessed from the surface by ~40 nm by wet-etching after the chemical−mechanical polishing of the TiN layer to check the selective growth property. It was confirmed that the recessed area was successfully filled with the GST material under both conditions. Here, the t_{inj} of the Sb and Ge precursors are slightly increased in Figure 2a, in order to make the film stoichiometric. One interesting finding is that the GST film was selectively grown on the TiN contact plug in the case of Figure 2a, whereas it grew on both the TiN and SiO_2 in the case of Figure 2b. The plan-view SEM

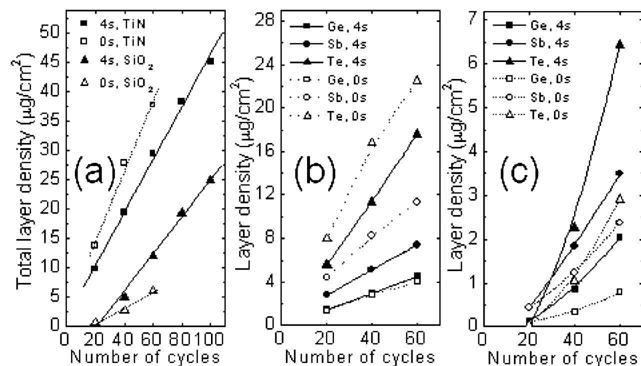

Figure 3. (a) Variations in total area density of the GST film on TiN and SiO_2 deposited with t_{Ar-prg} values of 0 and 4 s. Variations in the area density of each component for t_{Ar-prg} values of 0 and 4 s on the (b) TiN and (c) SiO_2 substrates.

pictures of images c and d in Figure 2 show the surface morphologies of the 30 nm thick GST film (40 cycles) on the planar TiN and SiO_2 substrates, respectively. Although the cross-section view of the GST film on the SiO_2 layer shown in Figure 2b appears to be rather uniform, it was actually quite nonuniform and has an islandlike growth behavior, as shown by Figure 2d. The GST film on the TiN surface shows a high nucleation density and very smooth surface (Figure 2c). It was also found that the thickness of the film grown on the TiN contact plug was higher in the case of Figure 2b. The X-ray diffraction showed that the GST films on the TiN and SiO_2 substrates have fcc (200) and fcc (111) preferred growth directions, respectively (data not shown). To understand the reason for the selective growth behavior, we performed the following experiments.

Figure 3a shows the variations in the total area density on the TiN and SiO_2 surfaces as a function of the number of supercycles (n_{cy}) for t_{Ar-prg} values of 0 and 4 s, respectively. The calculated growth rates (from the slopes) on the TiN and SiO_2 surfaces are 0.601 and 0.137 μg cm^{-2} cycle^{-1} (selectivity ratio ~4.39) for a t_{Ar-prg} value of 0 s and 0.449 and 0.316 μg cm^{-2} cycle^{-1} (selectivity ratio ~1.42) for a t_{Ar-prg} value of 4 s, respectively. The higher growth rate on TiN is explained by the higher nucleation density, as shown by Figure 2c. The lower nucleation density on SiO_2 suggests that the growth of GST on the SiO_2 surface is much less favorable than that on TiN and GST itself. The less favorable growth of GST on SiO_2 results in a rather long incubation period ($n_{cy} \approx 20$), as shown in Figure 3a. Taking the incubation cycles into consideration, the selectivity ratio increases to ~24 (at $n_{cy} = 20$) and 11 (at $n_{cy} = 40$) for a t_{Ar-prg} value of 0 s.

Figure 3b shows the variations in the area density of each component on the TiN substrate for t_{Ar-prg} values of 0 and 4 s. It can be understood that the growth rate of each component was higher for a t_{Ar-prg} value of 0. The linear fitting and extrapolation shows that there was a negligible incubation period for all three elements for both t_{Ar-prg} values. For the t_{Ar-prg} of 0 s, the film was slightly Ge deficient and contained excess Sb, whereas for the t_{Ar-prg} of 4 s, the film was stoichiometric. Figure 3c shows the variations in the area density of each component on the SiO_2 substrate for t_{Ar-prg} values of 0 and 4 s. Initially, the film is almost entirely Sb ($n_{cy} \approx 20$), and it then becomes stoichiometric GST after $n_{cy} \sim 60$. This suggests that the nucleation of Sb on SiO_2 is much better than that of Ge and Te. This can also be understood from the fact that the number of incubation cycles for Ge and Te was ~20, whereas that for Sb was much smaller. Therefore, Sb nucleates first on SiO_2 and then Ge and Te adsorb on the predeposited Sb nuclei and react to form GST after the larger n_{cy}. A more notable finding is that the growth rate of GST on SiO_2 is higher for a longer t_{Ar-prg}. This result in the loss of the selective growth behavior combined with the reduced growth rate on TiN for a t_{Ar-prg} of 4 s.

The decrease in the growth rate of the GST film on SiO_2, which resulted in selective growth, when $t_{Ar-prg} = 0$ s, is believed to result from the adverse interference of the residual gas with the chemical adsorption of Sb on the SiO_2 surface, which should have functioned as the nucleation site for further GST growth. When a sufficient t_{Ar-prg} (4 s) is used, the residual gas is removed and the active adsorption of Sb on SiO_2 occurs and GST grows effectively, which in turn reduces the selectivity. When Te precursor input was increased by increasing the Te canister temperature or its carrier gas flow rate, selectivity ratio increased up to ~25 (at $n_{cy} = 60$) because of the further inhibited growth on SiO_2 and increased growth on TiN. Excessive Te adsorption on SiO_2 inhibited the film growth. However, when excessive Te precursor was injected, film had a rough surface morphology and nonstoichiometric composition, and the contact hole was not filled uniformly with the material.

In summary, GST thin films were deposited by combined plasma-enhanced ALD (for Ge) and CVD (for Sb and Te) at a temperature of 200 °C. The selective growth behavior of GST on the contact hole having a TiN/W plug formed in the SiO_2 layer was observed, especially when t_{Ar-prg} was 0 s. When the t_{Ar-prg} value was increased to 4 s, this selective growth behavior was not observed because of the reduced and increased growth rates on the TiN and SiO_2 surfaces, respectively. This was explained by the preferential nucleation property of Sb and subsequent adsorption of Te and Ge on the Sb nuclei, allowing for further GST growth on SiO_2.

Acknowledgment. This work was supported by the 0.1 Tbit NVM project of the Korean government.

CM071313X