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Observations on Si-based micro-clusters embedded in TaN thin film deposited by co-sputtering with oxygen contamination

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Using scanning electron microscopy (SEM) and high-resolution x-ray photoelectron spectroscopy with the synchrotron radiation we investigated Si-based micro-clusters embedded in TaSiN thin films having oxygen contamination. TaSiN thin films were deposited by co-sputtering on fixed or rotated substrates and with various power conditions of TaN and Si targets. Three types of embedded micro-clusters with the chemical states of pure Si, SiOx-capped Si, and SiO2-capped Si were observed and analyzed using SEM and Si 2p and Ta 4f core-level spectra were derived. Their different resistivities are presumably due to the different chemical states and densities of Si-based micro-clusters. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4928576]

I. INTRODUCTION

Recently, phase-change materials have become highly promising for use in rewritable optical media and non-volatile random access memory devices (PRAM).1–4 These materials manifest extreme changes in both optical reflectivity and electrical resistance during amorphous-to-crystalline phase-changes at 100 ∼ 400°C.4 Samsung Electronics Co. Ltd. (SEC) recently announced a Ge2Sb2Te5-based 8 Gb PRAM device with 20 nm process technology and an operational power requirement of 1.8 V.5 PRAM devices require reasonably high resistivity to employ Joule heating in the PRAM cell for the phase-change from amorphous to crystalline phases. For an electrode material with this resistivity, TaN might be a good choice because it is used in various applications as a diffusion barrier and a stable resistor by virtue of its thermal stability.6,7 To control its resistivity, several groups have studied TaSiN, and it also showed improvement in its resistivity stability.8–12 In our previous study, we found that TaSi2N3 materials with various Si concentrations could improve the power of SET and RESET processes in PRAM devices.8 However, TaSiN material does not fully understand chemical states and intrinsic structure between TaN and Si elements. To control the properties of TaSiN material with different Si concentrations, it is essential to know its intrinsic structure.

In this manuscript, we fabricated TaSiN thin films on SiO2/Si substrates and determined their chemical states and intrinsic structures by scanning electron microscopy (SEM) and high-resolution x-ray photoelectron spectroscopy (HRXPS) with the synchrotron radiation. The resistivities of all samples were also measured. Finally, we found Si-based, micro-scale clusters embedded in TaN thin films. We determined that the resistivities of the thin films and the chemical states of the clusters were correlated.

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II. EXPERIMENTAL DETAILS

TaSiN thin films were deposited with a thickness of 43 – 70 nm in various sputter power ratios at room temperature. Each 6-inch substrate was prepared with SiO$_2$ at a thickness of 100 nm on p-type Si(100). Three different compositions of TaSiN thin films were deposited by co-sputtering Si targets with TaN under high purity (99.9999 %) Ar. The purity of the TaN and Si targets were 99.9 % and 99.999 %, respectively. The base and working pressures of the vacuum chamber were $1 \times 10^{-6}$ and $2 \times 10^{-3}$ Torr, respectively. The flow rate of Ar gas was 30 sccm. To observe the Si content effect, we performed the depositions with different composition ratios by changing the sputtering power of targets and the substrate rotation.

For the rotated substrates with 25 rpm, the sputtering powers of TaN (DC) and Si (RF) targets were A - 80 W : 100 W, B - 80 W : 150 W and C - 80 W : 200 W. For the fixed substrates, we used power ratios of D - 60 W: 50 W and E - 60 W: 150 W.

We used the high-resolution SEM (JEOL JSM 5900LV) to observe morphology. Resistivity and the thickness were measured using a 4-point probe (RT-80; Napson Co.) and an $\alpha$–step profiler (DELTAK).

To determine the chemical states of the formed thin films, we performed high-resolution x-ray photoelectron spectroscopy (HRXPS) using the Pohang Light Source (PLS) synchrotron at beamline 8A1 (U7). The incident photon energy was 630 eV. A PHI 3057 with an Omega lens and a 16-channel detector (Physical Electronic Co.) was used as the electron analyzer. The energy resolution was better than 200 meV. Core-level spectra of the Ta 4$f$, N 1$s$ with Ta 4$d_{5/2}$, Si 2$p$ and O 1$s$ were also obtained. Binding energies were calibrated with reference to the Au 4$f_{7/2}$ level (84.0 eV).

III. RESULTS AND DISCUSSION

We prepared samples with various TaN:Si ratio on sputter target power of A (80:100), B (80:150), C (80:200), C (60:50), and D (60:150). And we measured the resistivity of all samples with the reference sample of TaN film (Fig. 1 and Table I). The resistivities of A (80:100) and D (60:50) with 315.3 and 346.7 $\mu\Omega\cdot$cm are similar with TaN reference sample. As increasing Si target power ratio, we observed the improvement of resistivity. It means that we can control a resistivity of TaN thin film by Si concentration. These results are very consistent with the previous results.$^8$–$^{12}$

To see the intrinsic structure of these films with various resistivities, we performed SEM in all samples (Fig. 2(a)-2(e)). We clearly observed the embedded clusters with different densities and sizes except the B (80:150) and D (60:50) samples (Table II) and we actually observed small particles in the B sample. However, it is difficult to calculate the size and density because their...
TABLE I. The sheet resistance and resistivity of various thicknesses with the different TaN:Si ratio.

| Sample (TaN:Si) | Thickness (nm) | Sheet Resistance (Ω/sq) | Resistivity (µΩ·cm) |
|----------------|----------------|-------------------------|---------------------|
| A - 80:100     | 52             | 60.8                    | 315.3              |
| B - 80:150     | 56             | 93.6                    | 559.0              |
| C - 80:200     | 70             | 108.4                   | 770.0              |
| D - 60:50      | 43             | 79.4                    | 346.7              |
| E - 60:150     | 45.5           | 136.1                   | 624.3              |

FIG. 2. SEM images of each sample. The power ratio of TaN:Si targets with (a) A - 80:100, (b) B - 80:150, (c) C - 80:200, (d) D - 60:50 and (e) E - 60:150. The (d) and (e) samples were created with rotation of the substrate.

TABLE II. The size and density of observed clusters in the different TaN:Si ratio organized by SEM.

| Sample (TaN:Si) | Average size (µm) | Average density (#/cm²) |
|----------------|-------------------|-------------------------|
| A - 80:100     | 0.8               | 1.8 ×10⁷                |
| B - 80:150     | Not clear         | Not clear               |
| C - 80:200     | 1                 | 2.0 ×10⁷                |
| D - 60:50      | Not clear         | Not clear               |
| E - 60:150     | 1.6               | 1.8 ×10⁷                |

shapes are not clear. Moreover, the D sample has a cluster with a large diameter (∼ 2 µm). However, the density of micro-clusters in the D sample was very poor because the sample ratio of the TaN:Si target was only 60:50. In these results, we can assume the thin films are possible to have different chemical states between micro-cluster and base material.

To turn out the chemical element of micro-cluster, we performed HRXPS with synchrotron radiation. (Fig. 3) In Ta 4f core-level spectra at various deposition ratios of TaN and Si targets, we observe big shoulders at the high binding energy (Fig. 3(a)). It means that the chemical state of Ta is variable. To understand this variability, we also obtained N 1s, Si 2p and O 1s core-level spectra (Fig. 3(b)-3(d)). We could observe O 1s core-levels from all samples (Fig. 3(d)), indicating that all thin films had oxygen contamination. However, in all samples this oxygen contamination
had the same binding energy and similar peak width implying that it originated from the fabrication environment. N 1s core-level spectra likewise exhibited the same binding energy and similar peak width in all samples (Fig. 3(b)). These characteristics were unrelated to the ratios of TaN and Si and also to substrate rotation.

In Si 2p core-level spectra of all samples, on the other hand, we observed two significant features (Fig. 3(c)). The 80:150 (fixed substrate) and 60:150 (rotated substrate) ratios of TaN/Si targets exhibited like the chemical states of SiO$_2$ and SiO$_x$, respectively. In other samples primarily the chemical state of pure Si (Si-Si bonding) was observed. Also, Si peak intensity depended on the deposition power of the Si target. We can assume that Ta chemical states with wide FWHM are impregnated with SiO$_2$ and SiO$_x$. These results suggest that SiO$_2$ and SiO$_x$ in TaN thin films are probably structurally isolated because both N and O 1s chemical states have fixed binding energies and similar peak widths in all samples.

To understand the correlation between micro-cluster and chemical states in the thin films, we fitted Ta 4f and Si 2p core-level spectra using Doniach-Sunjic curves convoluted with a Gaussian distribution of 0.5 eV full-width at half maximum (Fig. 4). Background due to inelastic scattering was subtracted by the Shirley (integral) method. In the Ta 4f$_{7/2}$ curve fittings, we found three chemical states of Ta$_1$, Ta$_2$, and Ta$_3$ with the binding energy of 22.6, 22.8, and 23.4 eV in all samples, respectively. Basically, the binding energy of Ta oxide such as Ta$_2$O$_5$ is appeared from 26.2 to 26.7 eV. And also the Ta-Si bonding peaks such as TaSi$_2$ and Ta$_5$Si$_3$ are located at 26.8 and 26.5 eV, respectively. It means that Ta1-3 chemical states do not related directly with O and Si elements. Normally, the Ta 4f$_{7/2}$ binding energies of Ta metal and TaN appear around 21.8 and 23.0 eV. To know the exact chemical states of Ta 4f core-levels, we also performed the curve fitting of Si 2p core-level spectra. And we found clearly Si$^{4+}$ and Si$^{2+}$ components with Si$^{0+}$ (Si-Si bonding) in 80:150 and 60:50 samples, respectively. The binding energies of Si$^{2+}$ and Si$^{4+}$ are similar with the previous Si oxide report. It means that Si element has the chemical bonding with only oxygen element. The other samples have only Si$^{0+}$ component. This is the evidence that Si has no chemical bonding with Ta and N elements. In these results, we can confirm the chemical states of Ta 4f are not correlated with Si element and the chemical states of Ta1, Ta2, and Ta3 are originated from Ta-N bonding such as Ta$_x$N$_{1-x}$ with 0 < x < 1. It means that the micro-cluster in the thin films consists with only Si, SiO$_x$ and SiO$_2$. And also we can confirm the resistivity improvement is correlated by these micro-clusters with different chemical states. In the case of 60:50 sample with the low density of pure Si micro-clusters, the resistivity was 346.7 $\mu \Omega \cdot$cm, which is similar to the reference sample of TaN. However, 60:150 sample shows 624.3 $\mu \Omega \cdot$cm. This originated from pure Si capped
FIG. 4. (a) and (b) Curve-fitting data of Ta 4f core-level spectra. We can find three chemical states of Ta 4f core-level. (Ta1 = 22.6 eV, Ta2 = 22.8 eV, and Ta3 = 23.4 eV) (c) Curve-fitting data of Si 2p core-level spectra. We found Si^{2+} and Si^{4+} with Si^{0} chemical states in the ratio of 60:50 and 80:150 samples, respectively.

with SiO\textsubscript{x} insulator. In the case of 80:100, 80:150, and 80:200 samples, we observed resistivities of 315.3, 559.0, and 770.0 \(\mu\Omega\cdot\text{cm}\), respectively. With increasing Si target power ratios from 100 to 200 W, the resistivity of films increased dramatically. The resistivity of the 80:150 sample is similar to that of 60:150 sample because of the capped materials (SiO\textsubscript{x} and SiO\textsubscript{2}). In the case of 80:200 sample, we can assume the high resistivity which is due to the high density and large diameter of Si-based micro-cluster. Finally, the resistivity of these films is strongly dependent on the diameter and density of Si-based micro-cluster.

IV. CONCLUSION

In conclusion, TaSiN thin films were deposited by co-sputtering on fixed or rotated substrates and with various power conditions of TaN and Si targets. We observed three types of Si-based micro-clusters (pure Si, SiO\textsubscript{x} capped Si, and SiO\textsubscript{2} capped Si) embedded in TaN thin films having oxygen contamination. Their different resistivities are presumably due to the different chemical states and densities of Si-based micro-clusters. We suggest that the resistivity of these films depends strongly on the chemical state and density of Si-based micro-clusters that were formed by oxygen contamination.

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