Electrical and structural properties of TaSiN electrode for phase change random access memory

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Characteristics of tantalum silicon nitride (TaSiN) thin films have been investigated as an electrode material for Ge2Sb2Te5 chalcogenide phase change material. The films were deposited by co-sputtering system in which the ratio of tantalum nitride to silicon was controlled by the plasma power on each target. The TaSiN films showed tunable resistivity from 260 to 560 μΩ cm with increasing Si content. From the evaluation of PRAM cell structures consisting of the TaSiN and the Ge2Sb2Te5, we found that the SET voltages are nicely correlated with the resistivity of the TaSiN. Moreover, the sensing margin (resistance ratio: $R_{SET}/R_{RESET}$) turned out to be good for practical application.

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1. Introduction

In recent years, DRAM, NOR, and NAND flash memory are widely used in electric devices. However, following the rapid development of electric device industries, new non-volatile memory of faster processing data and random access is required. Among them, PRAM (phase change random access memory) which is competitive in speed and power consumption has been studied for a promising next generation non-volatile memory device [1–4]. In PRAM, requirements for the electrode include the reasonably high resistivity which can induce the phase transition of chalcogenide and low degradation after repetitive operation of SET (crystallization) and RESET (amorphization). For now, study on the electrode is mostly focused on TiN and TiAlN which are one of the binary and ternary systems based on Ti because nitride has low reactivity with chalcogenide [5]. However, as the commercialization of PRAM becomes fastly preceded, problems related to electrode such as RESET current and reliability are rising. Now, the point is to search phenomenon, develop property enhancement technology and optimize the characteristics [6].

TaSiN is a good substitute for an electrode material in PRAM application. TaN is a well-known material for many applications such as diffusion barrier and stable resistor [7]. It has been found that the resistance value of the resistor fabricated from tantalum nitride changes only 1.3% in a 2500 h reliability test (100 mA dc, 125 °C) [8]. This implies that tantalum nitride has excellent electrical resistance and thermal stability. Based on these attractive properties, we investigated TaSiN thin film in depth. In this study, we focused on the evaluation of electrical and structural properties of TaSiN thin films with different Si compositions in order to test the feasibility as an electrode.

2. Experimental

We deposited two kinds of TaSiN thin films with a thickness of 50 nm and 100 nm at room temperature on a 100 nm thick SiO2 grown p-type <100> silicon wafers by magnetron sputtering system. Three different compositions of TaSiN thin films were co-sputtered using a tantalum nitride (TaN) target and a silicon (Si) target under an Ar ambient of 6 N purity. A TaN and a Si target have 99.9% and 99.999% purity, respectively. Before the deposition of films, the sputtering chamber was maintained at $1 \times 10^{-6}$ Torr. The flow rate of argon gas was 30 sccm and working pressure was 3 mTorr. In order to study the effect of the Si contents in the TaSiN on the structural and electrical properties, we controlled the compositions by changing the sputtering power on the target. DC power of a TaN target was fixed to 60 W, while 3 different RF powers of 50 W, 100 W, and 150 W at a Si target were chosen. As a reference, pure TaN was also prepared. The compositions of thin films were determined by Rutherford backscattering spectroscopy (RBS) with He2+ ions at 2 MeV. X-ray diffractometry (XRD) was used to identify the phases in the films. The resistivity and the thickness of the films were measured by 4-point probe and α-step profilometer, respectively. X-ray photoelectron spectroscopy (XPS) was used for the chemical states analysis. To correct the Fermi level of the XPS peaks, peaks were calibrated by C 1s peak of a hydrocarbon that has a binding energy of 284.6 eV. Because the melting point of Ge2Sb2Te5 (GST) is approximately 630 °C, the films for above analysis were annealed at 700 °C in a nitrogen atmosphere for 2 min by rapid thermal annealing process (RTA). After fabricating PRAM cell structure consisting of the various TaSiN electrodes and the GST
chalcogenide, the electrical properties such as SET voltage and RESET voltage were measured. In order to transform the cell from the amorphous state to crystalline state (SET state), we applied voltage using voltage sweep mode in semiconductor parameter analyzer. On the other hand, voltage pulse with a few hundreds nanoseconds pulse width was introduced to transform from crystalline state to amorphous state (RESET state). In the case of RESET operation, the temperature of GST has to exceed the melting point (around 630 °C) and to be cooled down to the room temperature within several nanoseconds. Therefore, we set the cooling rate at 5 ns.

3. Results and discussion

Fig. 1 shows the RBS spectra of TaN and TaSiN films deposited at three different sputtering powers for determining the relative concentration ratio of Ta/Si. The Si content in the electrode increases from 13 to 41 at.% as the RF sputtering power at the Si target increases from 50 W to 150 W, as expected. The composition variation will be correlated with the structural and electrical properties such as resistivity and SET voltage of the films later.

XRD analysis was performed to investigate the phase change before and after annealing. Fig. 2 shows the XRD peaks from the TaSiN films deposited on a SiO₂-passivated Si substrate with different conditions (a) as-deposited and (b) annealed at 700 °C in N₂ ambient. The XRD results of the as-deposited TaSiN film reveal only peak from the hexagonal TaN (110) at 2θ = 33° indifferent from the compositions and an additional peak from the cubic TaN (111) at 2θ = 37° in case of pure TaN film. Annealing at 700 °C, however, induces the formation of minor phases like Ta₅Si₃, Ta₄N, and Ta₂O₅ as well. The Ta₄N and Ta₂O₅ phases were found in the Ta-rich film of pure TaN sample A (RF power of Si target: 0 W), while the formation of Ta₅Si₃ phase was observed in the Si-rich film of D (150 W) composition [9–11]. It seems that the Ta₂O₅ phase was formed due to the reaction between Ta in the film and oxygen impurity incorporated in the ambient gas. However, new phases were almost not found in B (50 W) or C (100 W) composition.

Fig. 3 shows the annealing effect in the resistivity of TaN and 3 different TaSiN electrodes: (A) Ta₀.₆₁N₀.₃₉, (B) Ta₀.₅₃Si₀.₁₃N₀.₃₄, (C) Ta₀.₃₄Si₀.₃₈N₀.₃₈, and (D) Ta₀.₂₆Si₀.₄₁N₀.₃₃.
indicating that B or C composition is thermally more stable than A or D up to 700 °C. The thermal stability at 700 °C is meaningful because the film temperature increases up to 630 °C during the operation of SET and RESET.

Dependency of the resistivity of TaSiN films on various compositions before and after annealing is shown in Fig. 3. It reveals that the resistivity of as-deposited films increases steadily from 260 to 560 μΩ cm as the content of Si increases. It confirms the tunability in resistivity that can be easily controlled by the co-sputtering power. After annealing, the resistivity of films A, B, and C increased slightly and ranged from 290 to 510 μΩ cm. However, the Si-richest TaSiN film exhibited a considerable decrease in the resistivity from 560 to 380 μΩ cm.

In order to understand the structural and electrical behavior of TaSiN films of C (Ta0.34Si0.30N0.36) and D (Ta0.26Si0.41N0.33) in detail, XPS analysis was performed under Mg Kα X-ray source, referenced to C 1s at 284.6 eV [12]. Fig. 4 shows the Ta 4f XPS spectra of TaSiN films with C and D compositions, as-deposited and annealed at 700 °C. Fig. 4 (a) illustrates the Ta 4f photoelectron spectra of as-deposited TaSiN film of C composition. The Ta 4f spectra can be fitted to three sets of Ta 4f doublet with an S.O.S (spin-orbit splitting) of 1.9 eV [13], which are located at 22.3 eV (area ratio 51%), 23.6 eV (29%), and 26.4 eV (20%).

Fig. 4. Ta 4f XPS spectra of TaSiN films with C composition, (a) as-deposited and (c) annealed at 700 °C, TaSiN films with D compositions, (b) as-deposited and (d) annealed at 700 °C.

Fig. 5. Current–voltage characteristics of PRAM cell consisting of different electrode materials: (a) Ta0.61N0.39, (b) Ta0.53Si0.13N0.34, (c) Ta0.34Si0.30N0.36, and (d) Ta0.26Si0.41N0.33.
After annealing, the doublets are located at 22.7 eV (38%), 23.9 eV (44%), and 26.4 eV (18%) as shown in Fig. 4(c). These binding energies represent the bonds from Ta–Si, Ta–N, and Ta–O in order [14–17]. According to the spectra, the binding energy of Ta–Si bond increased by 0.4 eV, whereas the area of Ta–Si peak decreased by 13% after annealing [18]. This variation implies that the number of Ta–Si bonds decreased although the bonding strength became stronger. By the same token, the increase in the peak area by 15% suggests that the number of Ta–N bonds increased during the annealing.

The Ta 4f doublets of TaSiN film with D composition are located at 22.2 eV (area ratio 59%), 23.3 eV (27%), and 26.3 eV (14%) as shown in Fig. 4(b). The film has the doublets at 22.9 eV (66%), 23.8 eV (19%), and 26.6 eV (15%) after annealing as shown in Fig. 4(d). There are 7% increase in the area of Ta–Si bond and 8% decrease in the peak area of Ta–N bond after annealing in sample D. Regardless of the peak area variation, the binding energy shift of Ta–Si in sample C and D is associated with the crystallization of tantalum silicide, which was identified by the XRD analysis of Ta5Si3 phase shown in Fig. 2. Furthermore, the significant decrease in the resistivity after annealing in sample D (Fig. 3) can also be interpreted in terms of the increase in the number of Ta–Si bonds and the decrease in the number of Ta–N bonds because tantalum silicide has a lower resistivity than tantalum nitride [19–20].

The electrical properties of SET and RESET as a function of electrode composition were evaluated. As the resistivity of electrode increases, the threshold voltage for SET process tends to decrease from 2.4 V to 1.7 V as shown in Fig. 5. Because the electrode with higher resistivity can induce more joule heating, it is more probable to transform the phase of chalcogenide at lower SET voltage. The sensing margin, which is a resistance ratio between SET state and RESET state was observed to be 3 orders of magnitude (from 10³ Ω to 10⁶ Ω). It is a sufficiently high margin for the practical application [5,21]. In addition, RESET current can be roughly extracted from Fig. 5 (current at 5 V). It seems that the RESET current also reduces due to the resistivity increase of electrode.

4. Conclusion

We evaluated TaSiN films as an electrode and a heater in PRAM. Depending on the Si content in the film that can be easily adjusted by the deposition condition, the highly tunable resistivity was obtained. The resistivity of as-deposited sample (A, B, C, and D) increased monotonically as the Si content increased. The resistivity of films increased slightly after annealing at 700 °C, while that of TaSiN film with high concentration of Si decreased drastically. Such a decrease in the resistivity can be explained by the formation of low resistivity phase, tantalum silicide. The results of XRD and XPS analysis agree well with the experimental observations. In PRAM cells fabricated using TaSiN electrode and Ge2Sb2Te5, the SET voltages were found to be nicely correlated with the resistivity of annealed samples. In this study, the TaSiN electrode with C composition (Ta0.25Si0.30N0.36) resulted in the best composition in view of thermal stability, proper resistivity, and low SET voltage.

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References