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Study of Sn and Mg Doping Effects on TiO_2/Ge Stack Structure by Combinatorial Synthesis

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Abstract

The effects of Sn- and Mg-doping to TiO_2 on Ge substrate were investigated to improve the leakage current properties and the Ge diffusion into the TiO_2 layer by combinatorial method. The Sn- and Mg-doping enhanced the crystallization of rutile phase, which is a high dielectric constant phase, and drastically reduced the Ge diffusion into TiO_2. High Sn dopant concentration above 16 at% indicated the improvement of the leakage properties (~10^{-7} A/cm^2 at -0.5V) and the metal-insulator-semiconductor operation.

1. Introduction

Ge is a candidate of the next generation channel material to enhance the MIS (metal-insulator-semiconductor) gate structures in the point of high electron and hole mobility. However, there is an issue of interface states due to the formation of GeO_x. GeO_x is chemically unstable and a low dielectric material. To overcome this issue, we have proposed the direct growth of rutile TiO_2 on Ge (100). Rutile TiO_2 has higher dielectric constant (ε [110]= 86) and lower oxide formation energy than those of Ge, which enable further equivalent oxide thickness scaling and make it possible to suppress the formation of GeO_x. We have demonstrated the thin film growth of (110) rutile TiO_2 on a (100) Ge substrate at a substrate temperature of 450 °C, which is generally the growth temperature of anatase TiO_2, by using pulsed laser deposition [1]. However, due to the semiconducting property of TiO_2, the rutile TiO_2 MIS capacitor showed high leakage current. Furthermore, Ge diffused into the TiO_2 layer, which may degrade the interface properties. To overcome these issues, we have proposed the acceptor doping into TiO_2 films [2]. Doping an acceptor into TiO_2 is expected to improve the insulating property by decreasing the number of electron careers of the semiconductor. Some dopants such as Sn and Mg promote formation of rutile structures in TiO_2 [3]. In this study, to investigate the influence of acceptor doping systematically, we employed the combinatorial sputtering method [4], by which the concentration of metal in the TiO_2 layer can be controlled and the dopant concentration systematically optimized. As the dopant, Sn and Mg were investigated.

2. Experimental procedure

A p-type Ge (100) was used as a substrate. Before the TiO_2 deposition, a naturally oxidized GeO_x layer was removed by annealing at 420°C under an ultra-high vacuum condition (<7×10^{-5} Pa) for 20 min. 20 at% Sn , 20 at% Mg , and un-doped TiO_2 ceramics targets were used for RF-sputtering with sputtering gas pressure of 1 Pa and the substrate temperature of 450 °C. The sputtering gas ratio of O_2 to Ar based gas mixture was set as 2 %. Figure 1 shows sample schematic fabricated by combinatorial sputtering method with the composition spread technique. The film thickness of TiO_2 was set as 30 nm. Hereafter, Sn and Mg doped TiO_2 samples are denoted as Sn- and Mg-TiO_2, respectively. For the electrical measurements, a 150 nm thick- Ru top electrode with diameter of 100 μm was deposited by DC sputtering. Electrical properties were evaluated by current-voltage (I-V), capacitance-voltage (C-V) measurements. Crystal structures were analyzed by x-ray diffraction (XRD) measurement. The chemical bonding states and electronic structure were characterized by x-ray photoelectron spectroscopy (XPS) with Al Kα radiation (hν=1486.6 eV). The total energy resolution was set as 700 meV. Binding energies were calibrated from the Au $4f_{7/2}$ photoelectron peak at 84.0 eV of an Au film deposited on part of the sample.

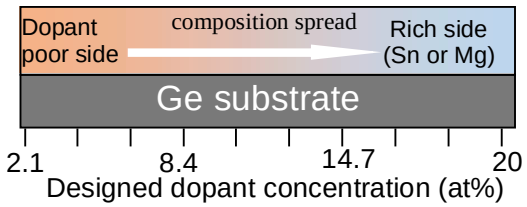

Figure 1 Schematic illustration of composition-spread sample.

3. Results and discussion

Figure 2 shows XRD patterns of Sn- and Mg-TiO_2. With increasing the Sn concentration, (110) reflections from the rutile TiO_2 structure were observed clearly, and amorphous phases were confirmed below the Sn concentration of 8.4

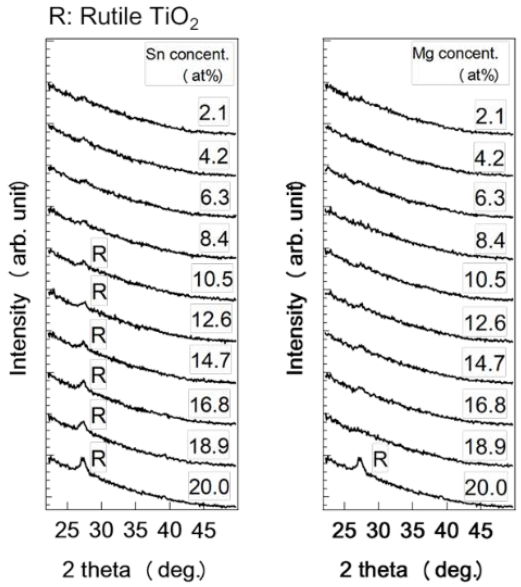

Figure 2 XRD patterns of Sn- (left) and Mg- (right) TiO_2 on Ge stack structures.

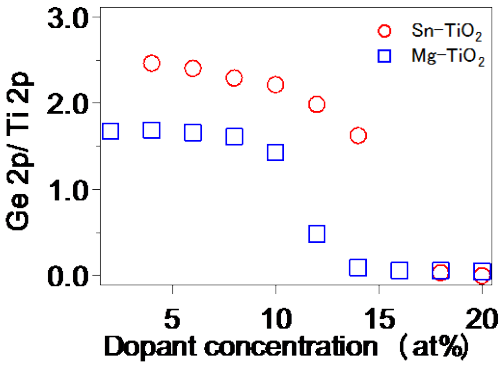

Figure 3 Sn and Mg concentration dependence of intensity ratio of core-level spectra of Ge $2p_{2/3}$ to Ti $2p_{3/2}$.

at%. In contrast, Mg-TiO_2 indicated the crystallization at the dopant concentration of 20 at%. These results are consistent with the previous reports [3], indicating that Sn and Mg dopants promote the rutile phase crystallization.

To investigate the Ge diffusion, the chemical bonding states were investigated by XPS. For the low dopant concentration region, Ge $2p_{3/2}$ spectra corresponding to the GeO_2 bonding state at 1220.5 eV were observed (not shown). Note that the inelastic mean free path (IMFP) of a photoelectron from the Ge $2p_{3/2}$ core level in XPS calculated using the Tanuma–Powell–Penn (TPP-2M [5]) equation is 0.9 nm, meaning that the information depth of Ge 2p is about 2.7 nm (3×IMFP). Therefore, the GeO_2 bonding state originated from the Ge atoms diffusing into the TiO_2 film, which nearly reached the surface. Figure 3 shows the area intensity ratio of Ge $2p_{3/2}$ to Ti $2p_{3/2}$ as a function of the dopant concentration. With increasing the dopant concentration, the ratio decreased. Above the concentration of 16 at%, the Ge $2p_{3/2}$ peaks were almost below the detection limit.

The I-V properties indicated that improvements of electrical properties with increasing the Sn concentration, as shown in Fig.4. In contrast, Mg-TiO_2 showed poor leakage current at the high Mg concentration region. Furthermore, the C-V properties of 16 at% Sn-TiO_2 indicated the MIS capacitor operation with the effective dielectric constant of 42. These results suggested that the Sn doping into TiO_2 improved the leakage current and C-V properties of TiO_2/Ge MIS structure.

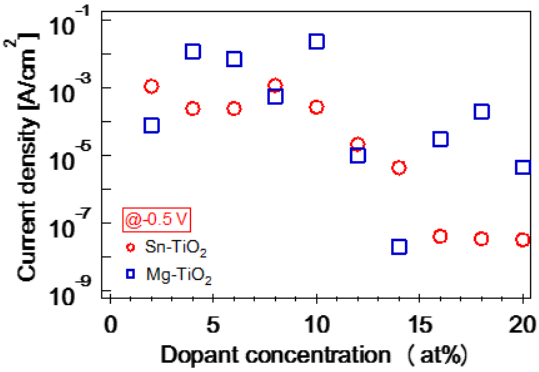

Figure 4 Sn and Mg concentration dependence of current density at a bias voltage of -0.5V.

3. Conclusions

The effects of Sn and Mg doping to TiO_2 on Ge substrate were investigated by combinatorial method. The Sn- and Mg-doping enhanced the rutile phase crystallization, and eliminated the Ge diffusion into the TiO_2 layer. The Sn doping also indicated the improvement of electric properties with increasing the dopant concentration. These results suggest that the Sn doped rutile TiO_2 has potential for use in high-k dielectric material.

Acknowledgements

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References

[1] T. Nagata *et al.*, *Thin Solid Films*. 591, 105 (2015).
[2] Y. Suzuki *et al.*, *Jpn. J. Appl. Phys*. 56, 06GF11 (2017).
[3] D.A. H. Hanaor and C.C. Sorrell, *J. Mater. Sci.* 46, 855 (2011).
[4] H. Koinuma and I. Takeuchi, *Nat. Mater*. 3, 429 (2003).
[5] S. Tanuma, *et al.*, *Surf. Interface Anal.* 11, 577 (1988).