Verification of GeSbTe composition in the high aspect hole filled by Chemical Vapor Deposition

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Large scale integrated memory devices require filling small holes with GST material, so chemical vapor deposition (CVD) technology has been studied as a way to overcome this problem[1]. Recently, we succeeded in obtain stoichiometric $Ge_2Sb_2Te_5$ thin films on flat SiO_2 and TiN substrates[2] (Fig. 1.). However, a basic experiment of filling is not performed enough, such as composition control in the holes. We are verifying of GeSbTe Composition and interaction of precursors in the high aspect hole by CVD method.

In this paper, we report on GST film deposition involving the use of appropriate precursors. The precursors have moderate vapor pressure and are in liquid state, thereby enabling easy control of film composition. They also have low decomposition temperature to avoid carbon incorporation in the film.

Tert-butylgermanium [t-$C_4H_9GeH_3$, Fig. 2(A)] was selected as the Ge precursor. A conventional Ge precursor such as $(CH_3)_4Ge$ has a strong Ge-C bond; thus, its decomposition temperature may be high, and many carbon impurities may be incorporated in its films.[3)] Low deposition temperature and low carbon impurity should be observed after using t-$C_4H_9GeH_3$ with one hydrogen atom of dangerous GeH_4 substituted for a bulky t-C_4H_9- group, which however can easily be removed. Triisopropylantimony [$(i\text{-}C_3H_7)_3Sb$, Fig. 2(B)] and diisopropyltellurium [$(i\text{-}C_3H_7)_2Te$, Fig. 2(C)] were selected as the Sb and Te precursors.

A schematic diagram of the low-pressure CVD system used is shown in Fig. 3. The precursor vapors were precisely controlled by adjusting H_2 carrier gas flow rate, bottle temperature, and pressure. After the SiO_2 and TiN substrates were heated at the deposition temperature, vapors of the three precursors were injected into the chamber. The typical experimental conditions are as follows. Deposition temperature and total pressure varied from200 to 350 °C and from 1 to 50 torr, respectively. The atomic concentrations of Ge, Sb, Te, and C in the films were estimated using X-ray photoemission spectro-

scopy calibrated using Rutherford backscattering spectrometry (RBS) measurement. The film structures were observed using scanning electron microscopy (SEM).

GST films of various compositions were deposited by controlling CVD conditions such as pressure, temperature, and the precursor supply ratio. The obtained films comparatively had a smooth surface structure at 275 °C, 30 torr (Fig. 4). SEM image of the deposited GST film on patterned substrate by CVD was shown in Fig. 5. High aspect hole was filled with GeSbTe materials. As a result, GST-CVD can have a considerable expectation in the next generation's large capacitance PCRAM manufacturing.

The control in a high aspect hole is important. However, it is difficult to analyze the compositional change in the microscopical region as in the hole. Thus, we deposited GST films in a macro cavity with 700 mm gap and more than 20 mm length for the purpose of achieving the composition control in the minute holes. Fig 6 shows some results of the composition in macro cavity with different depth from the entrance. The Ge composition increases toward the direction of depth of the hole and Sb decrease. We therefore inferred from this result that there is some strong relationship between precursors in such a narrow space at deposition temperature. To fill the high aspect ratio hole with desired GeSbTe composition, it is necessary to make detailed CVD experiments in two precursor systems (Ge-Sb, Ge-Te, Sb-Te) and to control the fine CVD conditions based on this experimental results.

The control of surface roughness is also important. Fig.7 shows that surface roughness increases by the increase of Te concentration of the film. So we tried two-step deposition for small hole filling. As for 1st step low Te smooth film was deposited. Te dope by diisopropyltellurium vapor flow followed as the 2nd step to achieve the desired Ge/Sb/Te ratio. We successfully filled under 150nm diameter hole by this 2step method. (Fig.8)

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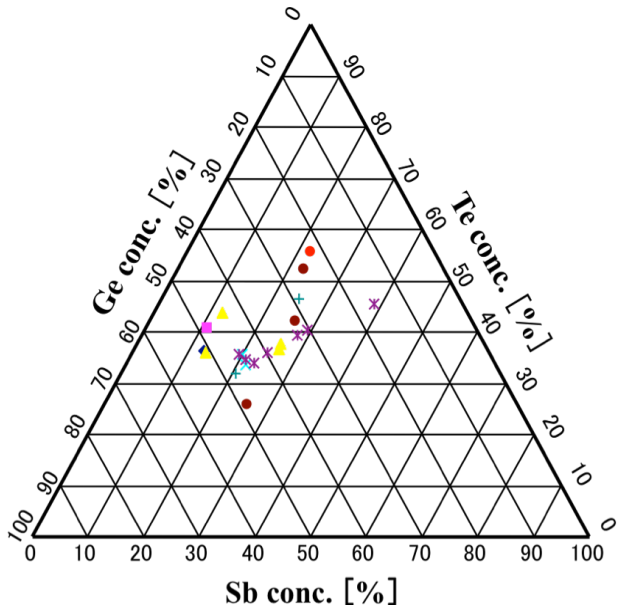


Fig. 1. Composition diagram of obtained films. The red circle key is $Ge_2Sb_2Te_5$. Other keys denote various film compositions under different deposition conditions (pressure: 1-50 torr; temperature: 200-350 °C).

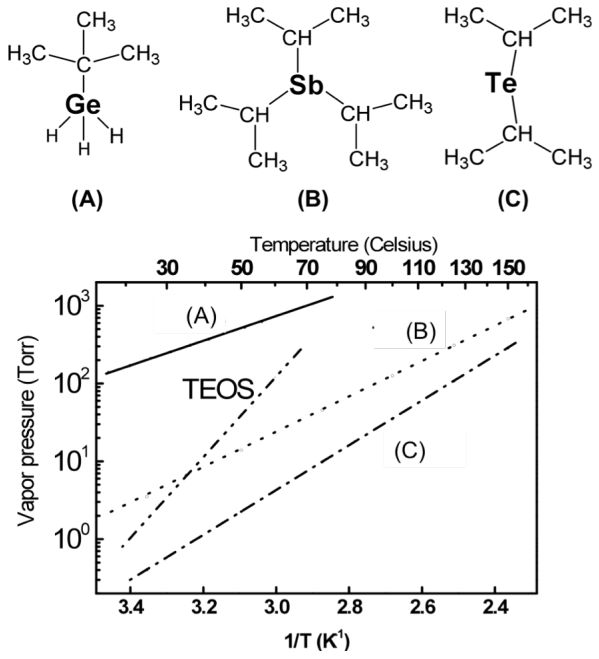


Fig. 2. Structural formulae and vapor pressures of three precursors:

(A)= t-$C_4H_9GeH_3$, (B)= (i-$C_3H_7)_3Sb$, (C)= (i-$C_3H_7)_2Te$

[TEOS= $Si(OC_2H_5)_4$ for comparison].

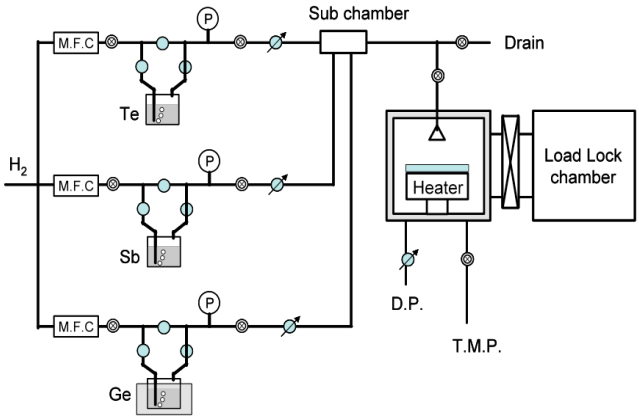


Fig. 3. Schematic diagram of CVD equipment.

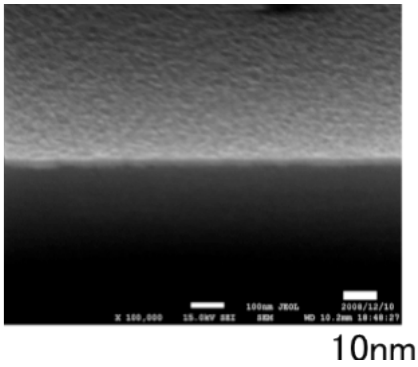


Fig. 4. SEM image of obtained film surface.

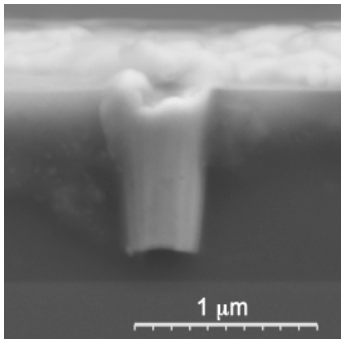


Fig. 5. SEM image of the GST in the hole.

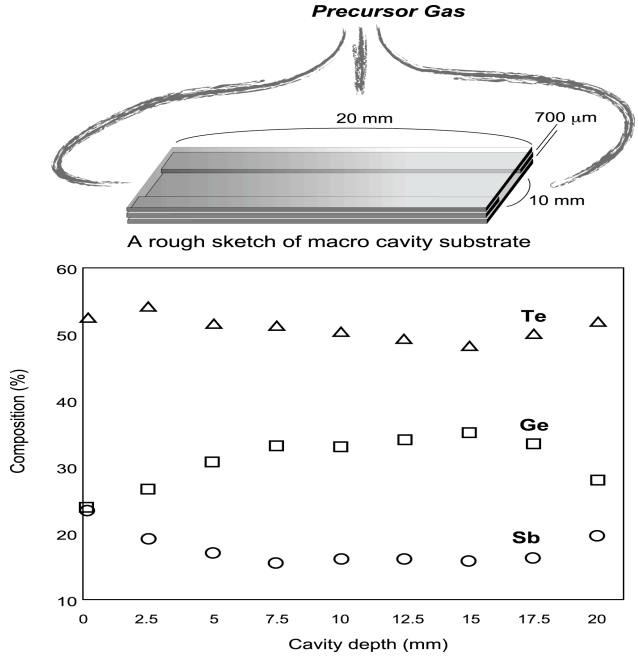


Fig. 6. Diagram of micro cavity and film compositions in the cavity.

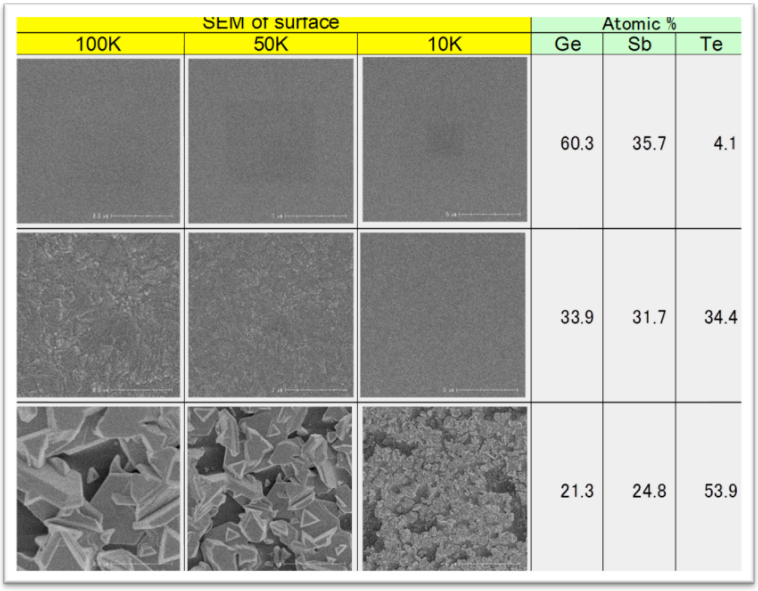
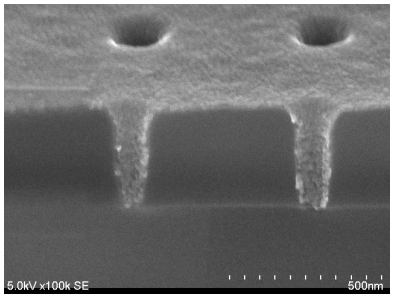
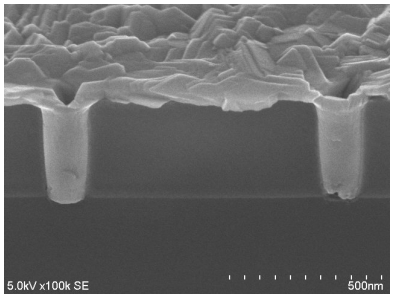


Fig. 7. Surface of various Ge/Sb/Te ratio films.



(a) 1st srep: Smooth Low Te film deposition (Ge/Sb/Te=57/41/2 at%)



(b) 2nd step: composition control by Te dope (Ge/Sb/Te=19/27/54 at%)

Fig. 8. Filling of small hole under 200nm diameter by two-step deposition.