# The investigation on the gap fill of ALD GST film and new phase change material for 20nm level PCRAM development

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**ABSTRACT**

We discussed about GST gap fill issue and new phase change material which are going to be very critical for 20nm phase change random access memory (PCRAM). We found that GST deposition should be well controlled especially in a very thin range(<100Å) so that large nuclei are not formed on the substrate. We could successfully fill 20nm sized trench hole with GST film by changing deposition mode during initial ALD growth. New phase change material, S-Cube (SnSbSe) was originally suggested based on the resonance boning theory and actually formed by an ALD deposition process. Thus prepared S-Cube showed very smooth and excellent gap-fill property and also faster crystallization time (40ns) enough to be applied to 20nm technology.

**Key words**: PCRAM, ALD, Gap fill, Crystallization

## 1. INTRODUCTION

There have been a lot of interests in the phase change random access memory (PCRAM) as a candidate for the next generation non-volatile devices coming up to the increasing need for high density, low power consumption, and fast switching speed with CMOS logic process [1,2]. The interest is recently getting much higher especially for the application to storage class memory (SCM) replacing conventional memories, such as DRAM or Flash [3]. It is mainly because PCRAM can be byte-addressable, highly endurable and fast random programmable as well as non-volatility.

However, in order for PCRAM to compete with conventional DRAM or Flash, there are still lots of things to be overcome not only for process integration but also required properties. Firstly, as we go on with scaling-down to 20nm level or beyond, the issue of GST gap filling into very narrow and deep trench hole keeps on getting more and more serious. Therefore, CVD [4] or ALD [5] deposition technology has kept on being tried for good gap fill into very small trench hole less than 20nm. But even still, those depositions have also some problems such as insufficient step coverage or gap fill and difficult reaction control right on the substrate. Because of that, reaction mechanism and resulting gap fill should be well figured out and properly controlled in CVD or ALD process.

Besides, the need for new phase change materials (PCMs) which show lower reset current and fast crystallization is getting more and more important. There have been lots of efforts to reduce reset current by doping [6-14] or modifying GST by another element [15]. Even if the GST has been accepted as the most promising phase change material for a long time, it is also true that the need for new material which has higher resistivity and fast crystallization is getting higher and higher.

In this study, we investigated the general cause of gap fill during ALD GST deposition process and tried to figure it. And furthermore, S-Cube (SnSbTe) was introduced as a new phase change material by showing the detail of ALD deposition process and its properties.

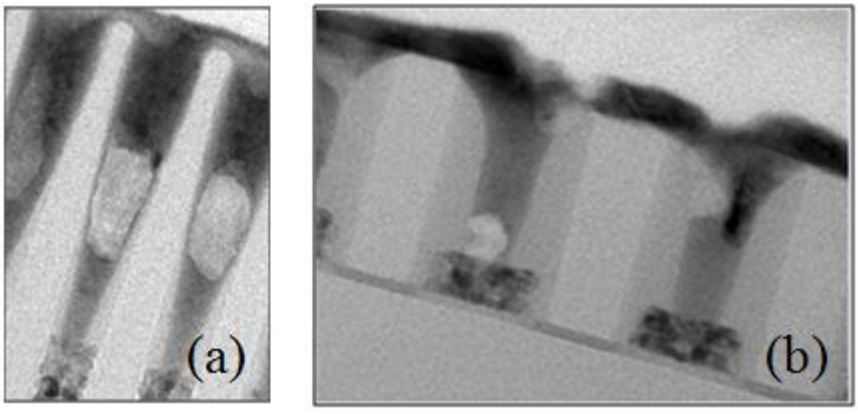
## 2. EXPERIMENTS

GST films were deposited on the bare Si substrate by ALD process in order to investigate the deposition behavior. GST films were formed by changing deposition cycle and then analyzed by such as AFM, SEM, TEM and XRF for surface roughness, morphology, composition and gap-fill property. S-Cube (SnSbSe) thin films were deposited on $Si_3N_4$ (40nm)/Si and bare Si substrate by thermal atomic layer deposition (ALD) using metal-organic precursors. The composition and growth rate were controlled by changing super-cycle concept. One super-cycle for S-Cube consists of binary [SbSe] and single [Sn] sub-cycle. Desired thickness was obtained by repeating the total super-cycle and composition was controlled by changing sub-cycle ratio, [SbS]: [Sn] = (*a*:*b*), where a and b is the number of [SbSe] and [Sn] sub-cycles. The cross section image and surface morphology of the film was observed by a field-emission scanning electron microscopy (FESEM) and film roughness was measured by atomic force microscopy (AFM). The microstructure of the as-deposited film was investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). And also, the crystallization behavior in nano-second scale was tested by using laser static tester. Step-coverage and gap-filling of S-Cube films were evaluated using confined cell structure which has critical dimension of 15nm. (Aspect ratio 5.0:1)

## 3. RESULTS & DISCUSSION

3-1. Gap fills of ALD GST film

Fig.1 shows the TEM images of the trench hole (Aspect ratio 10:1 and 5:1 respectively) deposited with GST films by ALD. GST gap-fill is thought to be very important for the process integration of PCRAM less than 20nm or less. It can be seen that holes are not fully filled with GST even though GST film was formed with ALD. Especially, one thing to be noticed is that top region of the hole is mainly blocked similarly to overhang of sputtering when the hole size gets smaller.




Fg. 1. TEM images of trench holes deposited with GST at each hole size. (a) ~20nm, (b) ~40nm

We prepared GST thin films by changing deposition cycle as shown in Fig. 2 so as to figure out the deposition behavior. Fig. 2 shows the change of surface roughness of GST films as a function of ALD cycle, resulting in film thickness. Surface roughness(RMS) increased very drastically until a certain thickness(around 100~150Å) and then reversely decreased. Even though not shown here, this trend was the same regardless of substrate. We particularly noticed the initial thickness range until 100~150Å where RMS increases with the film thickness. That is because that region falls on where we actually have to handle at 20nm level technology. Fig. 3 shows the surface morphology of GST film observed by SEM. It is obvious that GST begins to form by generating large nuclei and then grow in their size. Those nuclei grow in size until 10~15nm (laterally) and 40~50nm (vertically). It was

supposed that the poor gap fill may be due to this island growth during initial deposition period. That is to say, when this kind of islands form within the trench hole especially at the top region, thus formed islands might prevent the precursor molecules from going into the bottom, resulting in making voids within the trench hole just as shown in Fig. 1.

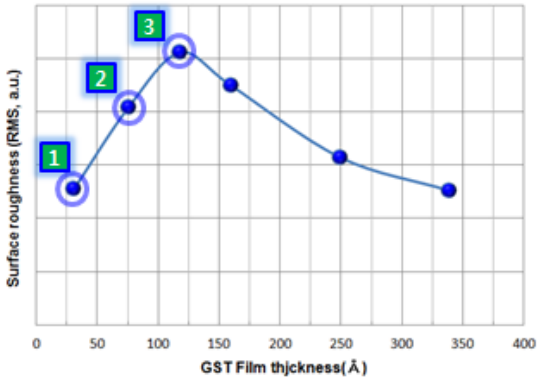



Fig. 2. Surface roughness change of GST films as a function of film thickness.

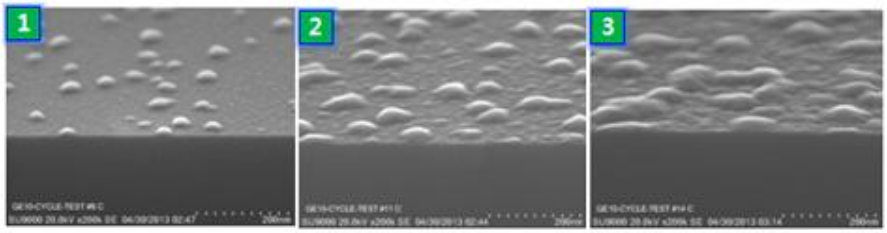



Fig. 3. Surface morphology of GST films with different thickness observed by SEM.

From this result, we could be confident that we can improve the gap fill property if only we can suppress the island growth especially during the initial deposition period. Fig. 4(a) shows the comparison of GST films depending on the process conditions such as deposition temperature or reactant gas ($NH_3$). We found that surface roughness could be effectively improved by lowering deposition temperature and adjusting reactant gas conditions. Moreover, RMS did not show any increase still maintaining very low RMS value. Fig. 4(b) shows the TEM image of trench hole (aspect ratio 10:1) fully filled with new GST film. This result well indicates that smooth film can be formed by suppressing the nucleation and island growth and consequently get to achieve excellent gap fill property which is essential for the process integration in 20nm level PCRAM technology.

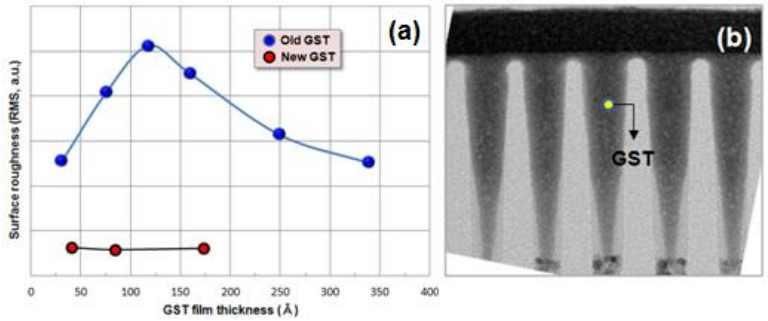



Fig. 4. (a) Change of surface roughness of GST films deposited at different depositions, (b) TEM image of trench hole with new GST.

3-2. Development of ALD S-Cube (SnSbSe) as a new phase change materials

As mentioned at introduction, the request for new phase change material which can show fast crystallization as well as higher resistivity is now growing higher and higher than any other previous time. When we develop new material, one thing to note is that CVD (or if possible ALD) should be possible along with material property itself such as crystallization time or resistivity. Even though certain material can be possible in terms of required properties, it will be of no use unless we can apply to the real cell structure such as confined or dashed with high aspect ratio.

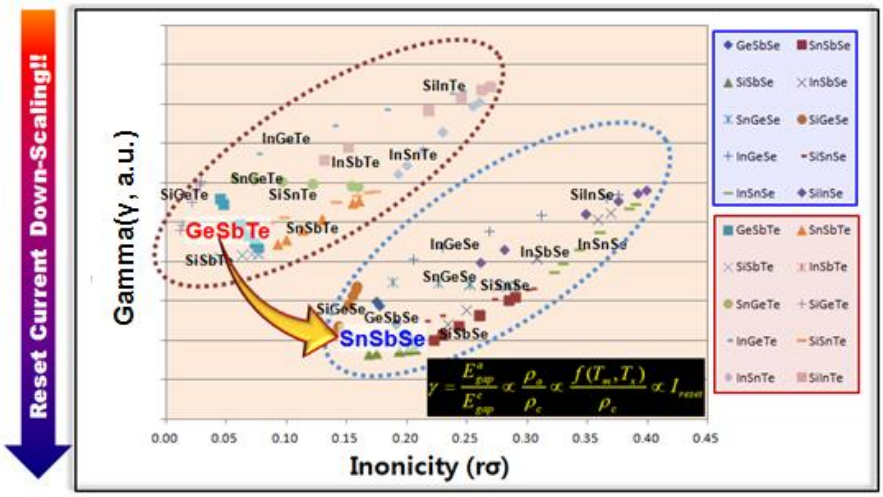



Fig. 5. Resonance bond strength with phase change materials

And so, we tried to develop new phase change material that is suitable for 20nm tech or beyond. Firstly, we newly designed material system based on the resonance bond strength theory [16] as shown in Fig. 5. SnSbSe(after here we call it S–Cube) was predicted to have lower reset current than conventional GST due to lower gamma(γ) value. Fig. 6 shows the growth behavior of single Sn phase film. As can be seen in Fig. 6(a), single Sn layer is formed as a shape of *island*. This phenomenon might be because Sn-Sn adatom cohesive force is stronger than surface adhesive force between Sn and $Si_3N_4$ substrate. However, this behavior could be changed by in-situ gas treatment as shown in Fig. 6(b). We could suppose that effective site for Sn precursor adsorption on substrate could be activated by in-situ gas treatment before Sn precursor feeding.

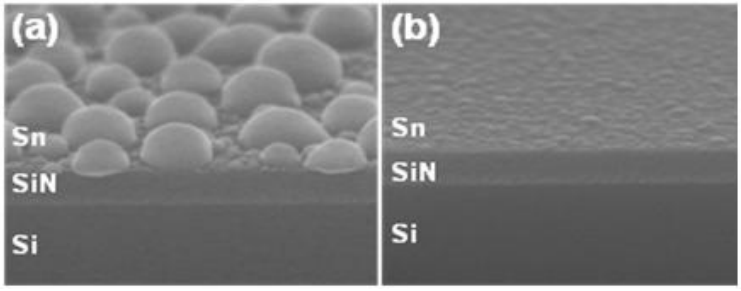



Fig. 6. Growth behavior of ALD single Sn by SEM (a) without in-situ treatment, (b) with in-situ treatment

And it was also found that we could control the stoichiometry of ternary S-Cube films by changing the exposure ratio of Sb and Se precursor at a given SbSe and Sn sub-cycle ratio as shown in Fig. 7.

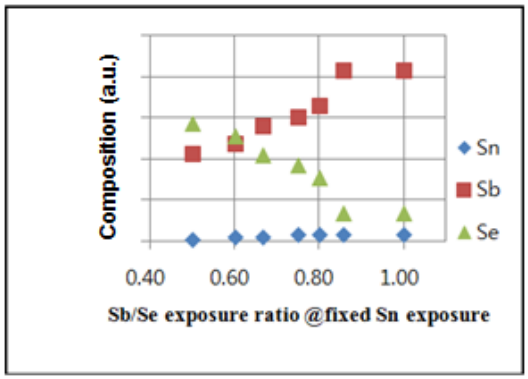



Fig. 7. ALD S-Cube composition with Sb/Se exposure ratio at fixed Sn exposure (Feeding time and sub-cycle)

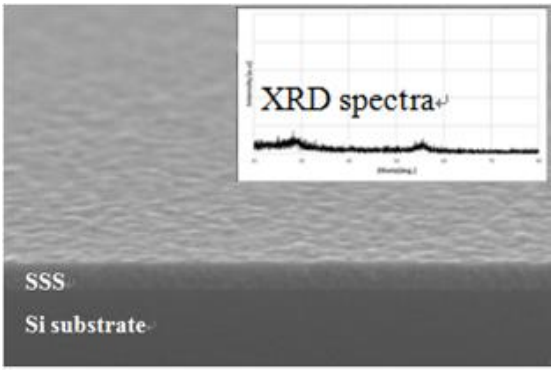



Fig. 8. Surface morphology of as-deposited ALD SSS film (SEM)

Thus prepared S-Cube showed very smooth and turned to be amorphous phase as shown in Fig 8. ALD S-Cube film showed good gap fill property at confined cell structure which has dimension of aspect ratio 5.0, 15nm bottom hole size as shown in Fig. 9.

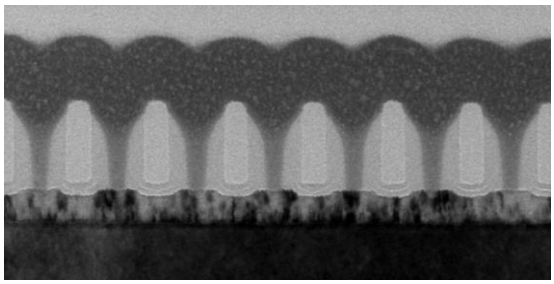


Fig. 9. Gap-filling of ALD S-Cube film using confined cell structure. (Aspect ratio 5.0, Cell dimension of 15nm)

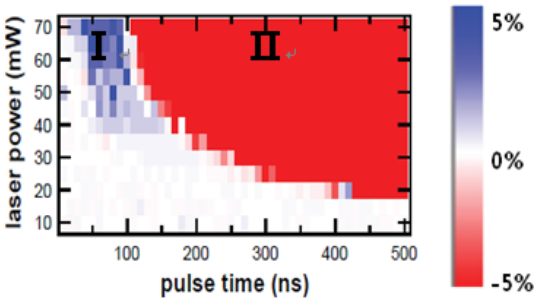



Fig. 10. Contour map of reflectivity variation of as-deposited ALD S-Cube film as a function of laser power and pulse duration.

We did the laser static test in order to investigate the laser induced phase transition behavior of as-deposited S-Cube film. Fig. 10 shows the contour map of reflectivity variation with laser power and laser pulse duration. It can be seen that there are two regions which show crystallized region (I) and ablated region (II) respectively. However, crystallization was only possible above laser power of 40mW and below 150ns pulse duration. The crystallization speed of ALD S-Cube film is 40ns at 70mW laser power. This value is thought to be relatively faster than the one of conventional GST film.

## 4. CONCLUSION

We investigated the cause of poor gap fill property of ALD GST films in a very narrow and deep trench hole. It was found that GST growth mode during the initial deposition period plays a key role in

good gap fill. We also demonstrated that deep trench hole could be well filled with ALD GST just by suppressing nucleation during initial deposition period. And also we demonstrated new phase change material, S-Cube (SnSbSe) just by ALD deposition. It was originally designed based on the resonance bond strength theory so that it can show lower reset current. We successfully developed ALD deposition process which shows amorphous, smooth surface morphology and also good gap fill performance. In terms of the property, S-Cube showed fast crystallization of about 40ns at 70mW laser power.

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### Biographies

D. S. Kil studied material science and engineering at POSTECH (Pohang University of Science and Technology) and received Ph.D. degree in material science and engineering from Seoul National University, Seoul, Korea in 1999. Since he joined SK Hynix in 1999, he has worked for the development of high-k dielectrics such as $HfO_2$, $ZrO_2$ and electrode materials like Ru mainly by ALD process for the application of DRAM and ReRAM. He has also served as an ITRS member for the DRAM chapter of FEP working group from 2008 to 2010. He is currently in charge of the development for phase change material.