

Study on nitrogen doped Ge₂Sb₂Te₅ films for phase change memory

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The demand for non-volatile memories has increased as the market for mobile instruments, such as Personal Digital Assistants (PDAs), cellular phones, electronic digital cameras, and others has expanded. With its many advantages over other existing memories, Phase Change Memory (PCM) is one of the candidates for unified memory technology [1].

PCM is a technology that uses fast and reversible phase transition of materials between crystalline and amorphous. Compositions of the GeSbTe system are used for the phase change material. The phase of GeSbTe can be changed by the electrical currents. When using a lower electrical current, high resistance in the crystalline state is necessary to change the material from a crystalline state to an amorphous state. Thus, the nitrogen-doping method has been employed in an attempt to solve this problem by increasing the electrical resistance of the phase change material [2]. In the present study, we have investigated the crystalline structure and sheet resistance of nitrogen-doped Ge₂Sb₂Te₅ films.

Ge₂Sb₂Te₅ films and nitrogen-doped GeSbTe films were deposited on *p*-type (100) Si (MEMC-Korea, KOREA) and SiO₂ substrates by DC magnetron sputtering using a composite target, Ge₂Sb₂Te₅, at room temperature. The Si wafers were cleaned in trichloroethylene (TCE), acetone, and methyl alcohol and rinsed in deionized water at room temperature for 3 min, respectively. Then, to remove the native oxide, the wafers were treated with a 10% hydrofluoric (HF) solution. The SiO₂ substrates were cleaned in the same way as Si except for HF dipping.

The background pressure was 4.0×10^{-6} torr, and the process pressure was 7.0×10^{-3} torr. A system power of 14 W was used for sputtering, and the deposition rate was 50 Å/min. Nitrogen was doped in the Ge₂Sb₂Te₅ films during sputtering by the introduction of N₂/Ar mixed gases. The gas flow rate was 10 sccm for N₂ and 30 sccm for Ar. The deposited films were annealed in a vacuum, $\sim 10^{-5}$ torr, for 20 min. The heat treatments were carried out at specific temperatures between 150 and 380.

We used X-ray diffraction (D/MAX-2500H, Rigaku, Japan) to examine the structure of the crystallized films. Atomic force microscopy (AFM) and scan-

ning electron microscopy (SEM) were used to observe the morphology of crystallized films. The sheet resistance (R_s) was measured by a four-point probe (FPP-5000).

It is known that the Ge₂Sb₂Te₅ films change into NaCl-type structure at around 150 [3]. To investigate the crystallization phenomena of nitrogen-doped GeSbTe films annealed in the region of this transition temperature, the nitrogen-doped films were annealed at 150 and 200.

The morphology of annealed films and as-deposited film were measured by AFM. The RMS-roughness increased from 15.2 for as-deposited films to 25.5 for annealed films at 150. However, the films annealed at 200 had very rough surfaces compared to the other samples; hence, AFM was unsuitable for measuring the morphology. Therefore, we also used SEM to observe the surface morphology changes at different annealing temperatures (Fig. 1). The as-deposited film and the film annealed at 150 had relatively uniform surfaces, but many crystallites had grown on the surface of the film annealed at 200.

In this preliminary study, two kinds of films, nitrogen-doped and un-doped, were deposited on Si and SiO₂ substrate. We showed through SEM measurement that the crystal grains appeared at 200. Thus, nitrogen-doped films were annealed at higher temperatures than 200 to investigate the characteristics of crystallized films. These films were annealed at 280 and 380 for 20 min in vacuum.

The XRD patterns of these films are shown in Figs 2 and 3. Fig. 2 shows that the structure of un-doped films annealed at 280 were identified as a NaCl-type crystal structure, as has previously been reported [4]. The structure of nitrogen-doped films differed from un-doped ones in that the XRD peaks of the former were broader and of lower peak height.

As shown in Fig. 3, the structure of un-doped films annealed at 380 changed from NaCl-type to hexagonal. However, the peak of the (200) plane in NaCl-type crystal structure partially remained in the films annealed at 380. It was deduced that there was no effect on type of substrate. We observed that the peaks of nitrogen-doped films appeared between the peak for the (200) plane of cubic and the (103) plane of hexagonal structure. We

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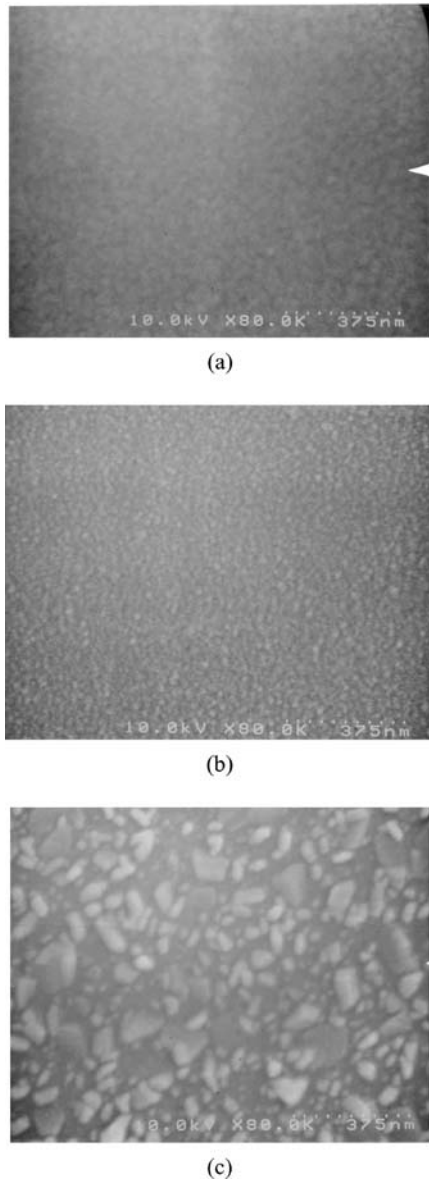


Figure 1 SEM images of nitrogen-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films: (a) as-dep, (b) annealed at 150, and (c) 200.

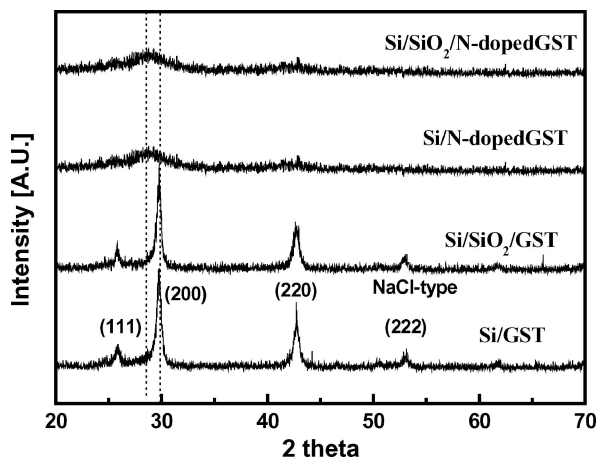


Figure 2 XRD patterns of nitrogen-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films and un-doped films annealed at 280 for 20 min.

surmised that there was an intermediate crystal structure between the hexagonal and cubic structures due to nitrogen doping. The resulting nitrogen effect is similar to the previous report [5].

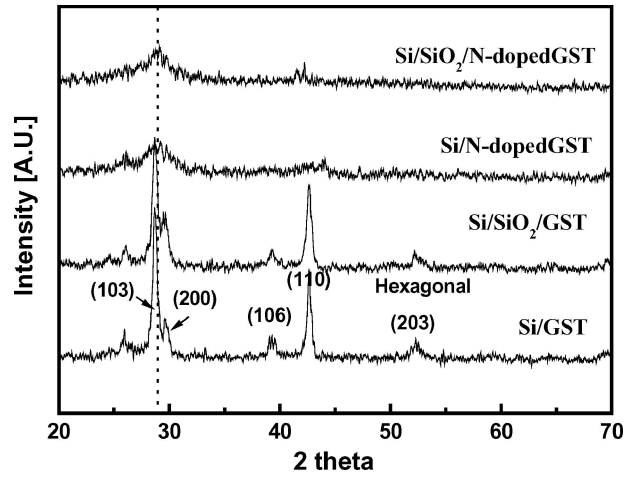


Figure 3 XRD patterns of nitrogen-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films and un-doped films annealed at 380°C for 20 min.

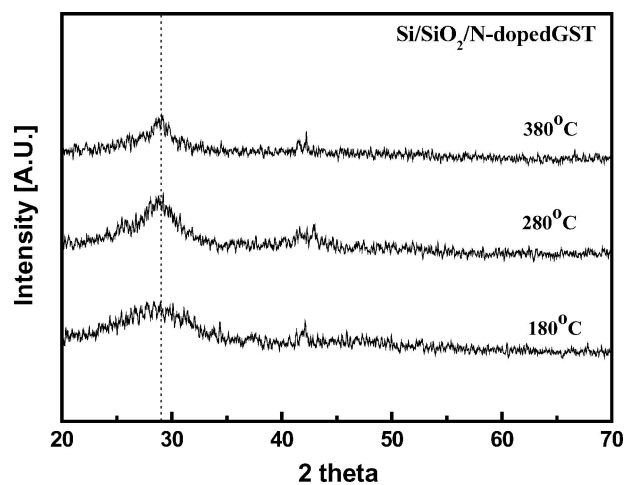


Figure 4 XRD patterns of nitrogen-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films annealed at 180, 280, and 380°C for 20 min.

Fig. 4 shows XRD analysis of the nitrogen-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films as a function of annealing temperature. As the annealing temperature increased from 180 to 380, the peaks became sharper. This means crystalline grain size increased as the annealing temperature increased. However, it was surmised that there was no phase change because there were no shifts of peak positions comparing each samples. This result is opposite the result obtained for un-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films.

We measured the sheet resistance of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films on SiO_2 substrate in order to investigate the electrical characteristics resulting from nitrogen doping. The samples were annealed at 280 and 380°C .

In the case of un-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films, the R_s of films which were annealed at 280 was $0.80 \text{ k}\Omega_{\text{sq}}$. The R_s value decreased to $0.36 \text{ k}\Omega_{\text{sq}}$ as the annealing temperature increased to 380. These results are similar to the previous report [3]. In the case of nitrogen doped films, the R_s was $24.6 \text{ M}\Omega_{\text{sq}}$ for 280 annealed films and $41.2 \text{ M}\Omega_{\text{sq}}$ for 380. The sheet resistances of nitrogen-doped films were 10^4 – 10^5 times higher than un-doped ones.

The NaCl-type structure of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ has some vacancies [6] and some nitrogen atoms can occupy the vacant sites. The nitrogen atoms probably exist as Ge–N,

Sb—N, and Te—N in Ge₂Sb₂Te₅ film [7]. As the nitrogen concentration increases, excess nitrogen atoms may precipitate at the grain boundaries as nitrides. These nitrides have been known to inhibit crystal growth and hence maintain a large number of grain boundaries [5]. As a result, the sheet resistance of nitrogen-doped films is larger than that of un-doped films.

Generally, if the grain size increases, the resistance of films decreases. However, the sheet resistances of nitrogen-doped films slightly increased as annealing temperature increased. This means there are some other factors, such as film stress, lattice strain, local nitridation, and so on, playing a role. More detailed research will be needed on this phenomenon.

In summary, the nitrogen-doped films were deposited by a DC magnetron sputter system flowing N₂/Ar mixed gas during sputtering. As the annealing temperature increased, the roughness of films increased and crystal grains appeared on the film surface at 200. There was only one crystalline phase in nitrogen-doped film and grain growth occurred as a result of heat treatment. The sheet resistance of nitrogen doped films annealed at 280 and 380 increased approximately 10⁴–10⁵ times than that of un-doped crystallized films.

Acknowledgement

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