Investigation on the improved superresolution effect by nitrogen addition in Ge-doped SbTe

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ABSTRACT

By nitrogen (N) addition in a Ge-doped SbTe (Ge-ST) superresolution (SR) material, improved SR capability and readout cyclability were obtained. These improvements were caused by refinement of the crystalline microstructures of the N-added film, accompanied most likely by a decrease in thermal conductivity. To better understand the role of nitrogen in development of the crystalline microstructures of Sb-rich phase change materials, Sb films of varying nitrogen contents were examined with respect to their phase change characteristics. With increasing nitrogen content, the as-sputtered Sb films were found to have higher thermal stability of the amorphous states and the crystallized films to have smaller crystal grains. In terms of chemical binding states of nitrogen, as-sputtered Sb-N films were characterized by Sb-N bonds alone whereas the crystallized films by N_2 molecules as well due to dissociation of Sb-N bonds during annealing for crystallization. Sb-N bonds and N_2 molecules are believed to impede nucleation and growth of crystals respectively, thereby contributing to the formation of refined crystalline microstructures.

Key words: Ge-doped SbTe, Sb, nitrogen addition effects, superresolution optical data storage, phase-change materials, chalcogenides.

1. INTRODUCTION

Chalcogenide phase-change materials such as $Ge_2Sb_2Te_5$ (GST) and Ge-doped SbTe (Ge-ST) have been employed in functional layers of superresolution (SR) readout for ultrahigh density optical data storage, besides their conventional use in information recording layers [1]. The SR effects of these materials have been proposed to derive from melting [2], ferroelectric transition [3], thermoreflectance [4], and thermally assisted saturable absorption [5], *etc*. Despite difference in physical details, these proposed origins share a common attribute that temperature plays a critical role in the respective SR effect. Laser heating by a readout beam produces a spatial temperature profile that modulates the optical property of the heated material under irradiation. Therefore, a narrower and sharper temperature profile needs to be formed so as to produce more abrupt optical change along the profile hence a better SR capability. This is particularly true for the latter two origins. Such temperature profile may be readily obtained by way of decreasing the thermal conductivity of a phase-change SR material. By a reduced thermal conductivity, laser power for SR readout can be lowered as well. Herein, we show that nitrogen (N) addition in a Ge-ST can significantly improve SR capability and cyclability by means of refined crystalline microstructures with an attribute of decreased thermal conductivity.

With respect to refining microstructures by N-addition in phase change materials, our findings, to be presented below, are ostensibly similar to what has been reported for N-added GST. In early studies, the formation of Ge-N compound or nitrogen segregation along the grain boundaries and the accompanying grain refinement were held responsible for the enhanced performance of phase change optical recording media using N-added GST [6,7]. Recently, more detailed studies have shown that nitrogen exists as Ge_3N_4 or N_2 molecules in the GST [8-10] but no direct evidence of the interactions between nitrogen and other elements, namely, Sb and Te, was obtained. In the case

of Sb-rich phase change materials such as Ge-ST, the underlying cause of grain refinement by N-addition is considered to be somewhat different because Sb is a prevailing constituent while Ge is a minor additive (~5 at. %). It is, therefore, the second objective of the present work to understand the role of nitrogen in development of the crystalline microstructures of Sb-based phase change materials as compared with the case of GST material. For this purpose, we deliberately use Sb as a matrix material and examine the effects of N-addition on its crystallization.

2. EXPERIMENTS

Ge-ST thin films of varying nitrogen content were fabricated via reactive RF magnetron sputtering using a single Ge-ST target and sputter gases that consisted of ($Ar+N_2$) mixtures with various N_2 content, from 0 to 4%. From x-ray fluorescence (XRF) spectroscopic analysis, the Ge-ST sputtered films were found to have almost the same atomic ratios of Ge, Sb and Te (5.5at%Ge-76.3 at%Sb-18.3at%Te) regardless of nitrogen content. Nitrogen contents of N-added Ge-ST films were measured with Rutherford backscattering spectrometry (RBS) at nitrogen resonance mode.

The structural and electrical properties of the Ge-ST films of varying nitrogen content were characterized with x-ray diffractometry (XRD) and Hall measurement, using films of 100nm thick on Si substrates annealed at 250^{o}C for 5 minutes. In order to compare the SR readout capability among the films of varying nitrogen content, ROM disk samples of three-layer stacks comprising Ge-ST films (15 nm) of varying nitrogen content sandwiched with ZnS-SiO_2 layers (86 nm each) were tested using a commercial dynamic tester equipped with a 405 nm laser source and 0.85 NA objective lens. The size of the ROM pit was 75 nm, which was much smaller than the optical resolution, 119 nm, of the pick-up in the tester.

For a detailed study according to the present work's second objective, Sb films of varying nitrogen content were also prepared (100 nm-thick on a Si substrate except for TEM) and characterized similarly. Structural analyses were carried out by use of XRD as well as TEM; each TEM sample was made to consist of a 20nm-thick film sandwiched with 10 nm-thick ZnS-SiO_2 protective layers on a C-coated Cu grid. To compare crystallization characteristics among films of varying nitrogen content, resistance vs. temperature curves were measured at a fixed scanning rate of 10°C/min using as-deposited films on a hot-stage electrical-probe under Ar gas flow. The chemical binding states of the as-deposited and annealed at 200 ^{o}C for 5 minutes Sb films with and without nitrogen were examined using X-ray photoelectron spectroscopy (XPS) and near-edge x-ray-absorption fine structure (NEXAFS) technique..

3. RESULTS & DISCUSSION

Figure 1 shows the XRD spectra taken from the annealed Ge-ST films of varying nitrogen content. Nearly all the x-ray peaks may be indexed according to a hexagonal crystal structure. In fact, the 2 theta positions of some detectable peaks are essentially the same among films of different nitrogen contents, indicating that nitrogen incorporation into the films may take place nearly without homogenous deformation of the crystal lattice. As for the strongest peaks, FWHM values representing the degrees of line-broadening are found to become larger with increased nitrogen addition as shown in the inset. In view of the possible sources of line-broadening, it follows that N-added films are likely to have smaller crystal grains, more non-uniform strain and perhaps more planar faults. This conclusion was confirmed from our TEM observation of the annealed films of varying nitrogen contents [11].

Figure 2 shows carrier concentration and Hall mobility of the annealed films as a function of nitrogen content. It should be noted that Hall mobility decreases monotonously with increasing nitrogen content. Considering that variation in carrier concentration is relatively negligible, the decrease in mobility may be accounted for by the growing carrier scattering at structural defects such as grain boundaries, complying with the preceding conclusion. It is obvious that increased density of structural defects can reduce electron and photon mean free paths, leading to the reduction in electrical conductivity also in thermal conductivity.

Figure 3 (a) and 3 (b) display respectively CNR vs. readout power and CNR vs. readout cycles of the ROM disks with Ge-ST films of varying nitrogen content, measured at the linear velocity of 5 m/s under the tracking-off condition. Above all, it should be noted that readout power decreases significantly with increasing nitrogen content. From XRF results and also from XPS results not shown here, we tend to believe that such decrease may not be related to difference in Ge, Sb and Te ratios nor in melting temperatures but most likely to the reduced thermal conductivity in N-added films. In light of our recent work on the origin of the SR effects in chalcogenide materials [5], significant

increase of CNR value with nitrogen content may be ascribed to more abrupt thermo-optic changes along sharper temperature profiles due to the reduced thermal conductivities.

Since all the data shown in Fig. 1 to Fig. 3 may be comprehended on the basis of changes in crystalline microstructures with N-addition, and the studied material is of a very high Sb fraction, it is reasonable to expect that better understanding of the role of nitrogen may be gained from a study employing Sb as a base material. Major results of the study are summarized in Fig. 4 to Fig. 8. Figure 4 represents XRD spectra of the as-deposited Sb films of varying nitrogen contents. Interestingly, Sb without nitrogen is crystalline but N-added Sb films are evidently amorphous. Figure 5 shows variation of film resistance with temperature for Sb films of varying nitrogen contents. It should be noted that each of the N-added Sb films, amorphous in the as-deposited state, undergoes a transition to its low-resistance crystalline state with increasing temperature. The crystallization temperature as well as amorphous /crystalline film resistance is found to increase with increasing nitrogen content. As can be seen from TEM bright field images as well as selected area diffraction patterns of Fig. 6 taken from the films annealed at 200 ^{o}C for 5 minutes, N-added (14.5 at.%) Sb film has remarkably fine-grained microstructures as compared with those of N-free Sb film. These apparent trends displayed in Fig. 5 and Fig. 6 are no different from what has been reported for N-added GST and N-added Ge-ST as well [6, 11]

Figure 7(a) and 7(b) show XPS core level spectra of Sb 3d and N 1s respectively, taken from the amorphous and the crystalline Sb films of two different nitrogen contents; N-free and N-14.5 at.%. From the Sb 3d spectra, there is found no detectable difference in both peak position and shape between N-free and N-14.5 at.% films. From the N 1s spectra, however, noticeable differences are found. With N-addition of 14.5 at.%, the as-deposited film is found to develop a nitrogen binding state with a characteristic peak at around 396~397eV. By annealing for crystallization, another binding state appears at around 403eV with a decay of the binding state preferred at the as-deposited state. The former binding state represents Sb-N bonds in view of the fact that XPS peaks at around 397eV were observed commonly for many metal nitrides including Sb nitride [13]. The latter binding state corresponds to N_2 molecules [12]. This clearly suggests that an amorphous phase is favored with N-addition in Sb through the formation of Sb-N bonds and crystallization of an amorphous Sb-N film may not be activated and progressed without dissociation of Sb-N bonds to form a mixture of Sb and N_2 molecules. The same interpretation was also obtained from analysis of the NEXAFS spectra (not shown here).

Consequently, the following conclusion may be reached regarding the role of nitrogen in development of the crystalline microstructures of Sb-rich phase change materials. As long as Sb atoms are bound to Sb-N bonds, nucleation of Sb clusters may not be possible. With dissociation of Sb-N bonds, crystalline Sb clusters may form, but their growth may be hindered by drifting N_2 molecules. Because of these difficulties, the resulting crystalline microstructures would be fine-grained.

4. SUMMARY

We demonstrated that N-addition in a Ge-ST SR material could significantly improve SR capability and cyclability as well. These improvements are closely related to the refinement of crystalline microstructures by N-addition that would lead most likely to decreased thermal conductivity of the SR material. In order to better understand the role of nitrogen in development of the crystalline microstructures of Sb-rich phase-change materials, crystallization of Sb films of varying nitrogen contents was examined. As we found out, N-addition in Sb resulted in the formation of Sb-N bonds and an amorphous phase in the as-sputtered state. These Sb-N bonds were found unstable with respect to dissociation into a mixture of crystalline Sb and N_2 molecules by thermal annealing. Sb-N bonds and N_2 molecules are considered to play vital roles in impeding nucleation and growth of Sb crystals respectively, leading to the refined crystalline microstructures of the N-added Sb-rich phase change materials.

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Biographies

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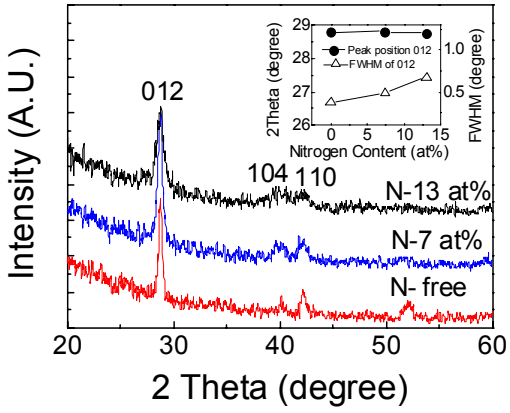


Figure 1. XRD spectra and FWHM values of the crystalline Ge-ST films of varying nitrogen contents.

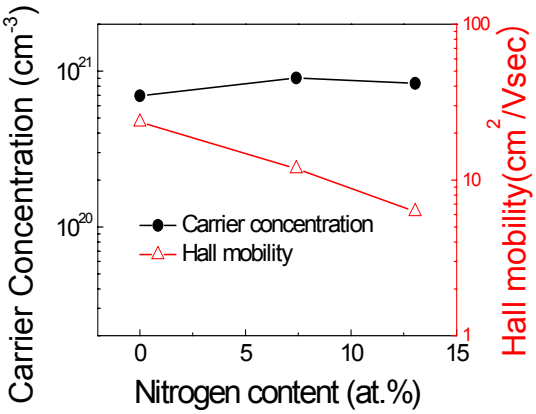
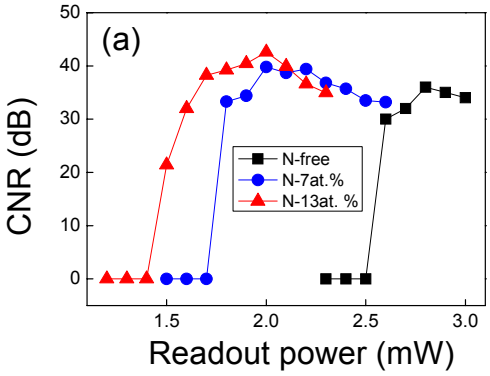


Figure 2. Carrier concentration and Hall mobility of Ge-ST films of varying nitrogen contents annealed at 250 ^{o}C for 5 minutes.



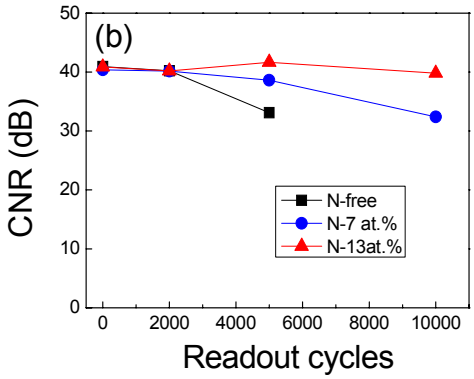


Figure 3. (a) CNR vs. readout power and (b) CNR vs. readout cycles of ROM disks with Ge-ST superresolution layers of varying nitrogen contents; readouts were made for ROM pits of 75nm long at the linear velocity of 5m/s.

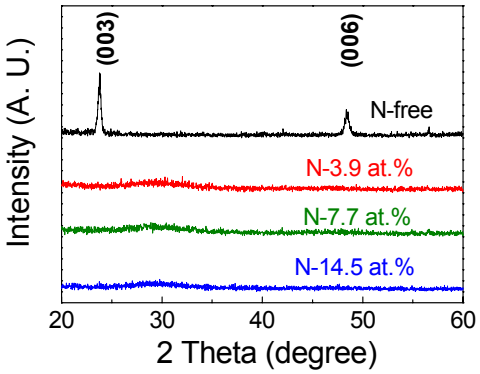


Figure 4. XRD spectra of the as-deposited Sb films of varying nitrogen contents.

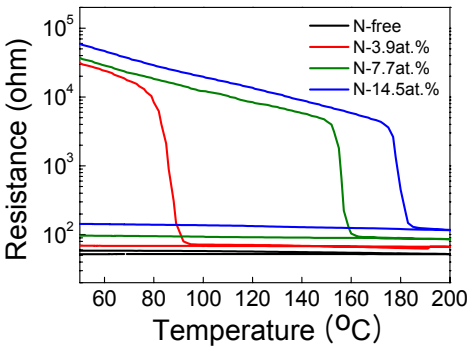
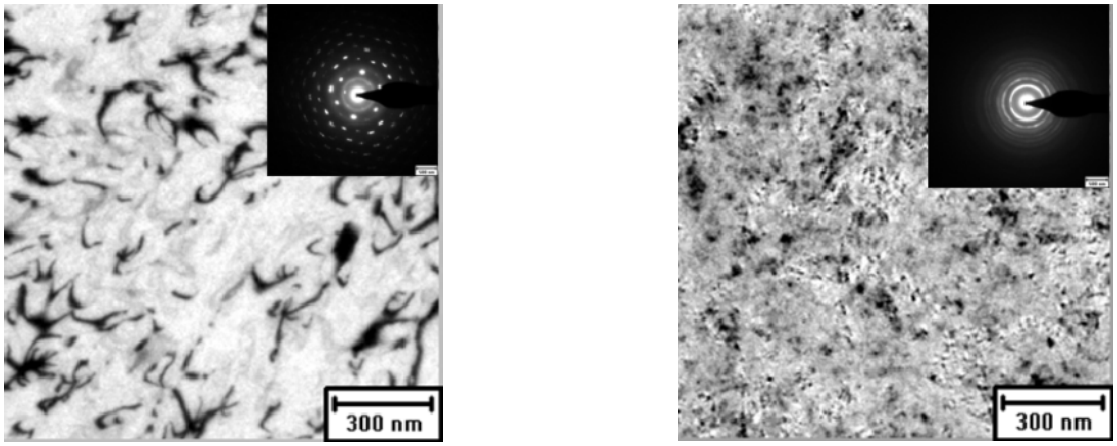


Figure 5. Amorphous to crystalline phase change characteristics of Sb films of varying nitrogen contents as measured by temperature dependence of film resistance.



(a) (b)

Figure 6. TEM images and the associated diffraction patterns of (a) N-free and (b) N-added (14.5 at.%) Sb films annealed at 200 ^{o}C for 5 minutes.

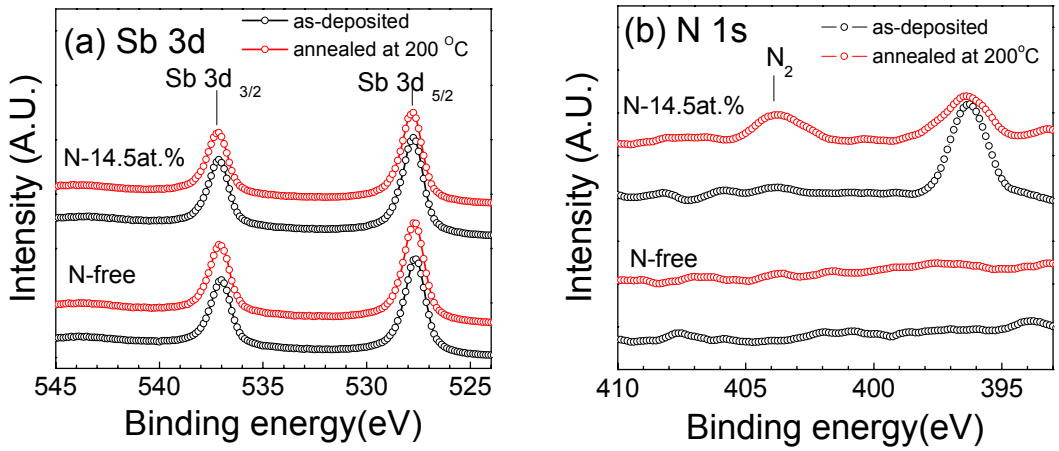


Figure 7. (a) Sb 3d and (b) N 1s core level XPS spectra of the as-deposited and the annealed Sb films of two different nitrogen contents.