Applied Surface Science 346 (2015) 366–371

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Sb–Te alloy nanostructures produced on a graphite surface by a simple annealing process

Masashi Kuwahara[a,*], Hideaki Uratsuji[b], Maho Abe[c], Hayato Sone[d], Sumio Hosaka[d], Joe Sakai[e], Yoichi Uehara[c], Rie Endo[f], Tohru Tsuruoka[g]

[a] Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan
[b] Shibaura Eletec Co., Yokohama 247-0006, Japan
[c] Research Institute of Electrical Communication, Tohoku Univ., Sendai 980-8577, Japan
[d] Department of Electronic Engineering, Gunma Univ., Kiryu, Gunma 376-8515, Japan
[e] Groupe de Recherche en Matériaux, Microélectronique, Acoustique et Nanotechnologies (GREMAN), UMR 7347 CNRS/Université François Rabelais de Tours, Tours 37200, France
[f] Department of Metallurgy and Ceramics Science Graduate School of Science and Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan
[g] International Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

ARTICLE INFO

Article history:
Received 16 January 2015
Received in revised form 30 March 2015
Accepted 30 March 2015
Available online 4 April 2015

Keywords:
Phase change materials
Narrow gap semiconductor
Sb_2Te_3
Nanoparticles
Nanoneedles

ABSTRACT

We have produced Sb–Te alloy nanostructures from a thin Sb_2Te_3 layer deposited on a highly oriented pyrolytic graphite substrate using a simple rf-magnetron sputtering and annealing technique. The size, shape, and chemical composition of the structures were investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM), and energy dispersive X-ray spectrometry (EDX), respectively. The shape of the nanostructures was found to depend on the annealing temperature; nanoparticles appear on the substrate by annealing at 200 °C, while nanoneedles are formed at higher temperatures. Chemical composition analysis has revealed that all the structures were in the composition of Sb:Te = 1:3, Te rich compared to the target composition Sb_2Te_3, probably due to the higher movability of Te atoms on the substrate compared with Sb. We also tried to observe the production process of nanostructures in situ using SEM. Unfortunately, this was not possible because of evaporation in vacuum, suggesting that the formation of nanostructures is highly sensitive to the ambient pressure.

1. Introduction

Chalcogenides have been attracting many researchers for a long time, not only because the materials have proved useful as recording materials [1,2] but also because they show unique physical and chemical properties. The structural, optical, thermal, and electrical properties of bulks and thin-films of chalcogenides are still the subjects of intensive research [3–18]. Recently, the size of memory cells for phase change memory (PCM) has been driven down further and further in order to reduce power consumption. The understanding of their physical and chemical properties in nanoscale forms is therefore important for the design and development of PCM. There is also a substantial interest in the physical and chemical properties resulting from size effects in nanostructured chalcogenides. Chalcogenides are categorized as semi-metals or narrow band-gap semiconductors, in which the size effects on their properties in nanoscale range have been studied insufficiently, in contrast to a number of studies of nanostructured metals or semiconductors. Fabrication and characterization of chalcogenide nanostructures have been reported by several groups. The shape, crystal structure, *I–V* characteristics, and chemical composition were investigated for chalcogenide nanostructures with several hundreds of nanometers in diameter obtained by catalyst assisted growth [19,20,22], electrochemical deposition [23,24], or ball milling [21]. However, the diameters of these structures were too large to investigate size effects. Smaller-sized nanostructures are required to clarify their basic properties and allow the development of new electric or optical memory devices that go beyond current capabilities.

In this study, we fabricated nanostructures of a chalcogenide material using a simple combination of rf-magnetron sputtering and annealing techniques without catalysis or any complicated

* Corresponding author at: Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan. Tel.: +81 298612950.
E-mail address: kuwaco-kuwahara@aist.go.jp (M. Kuwahara).

http://dx.doi.org/10.1016/j.apsusc.2015.03.199
0169-4332/

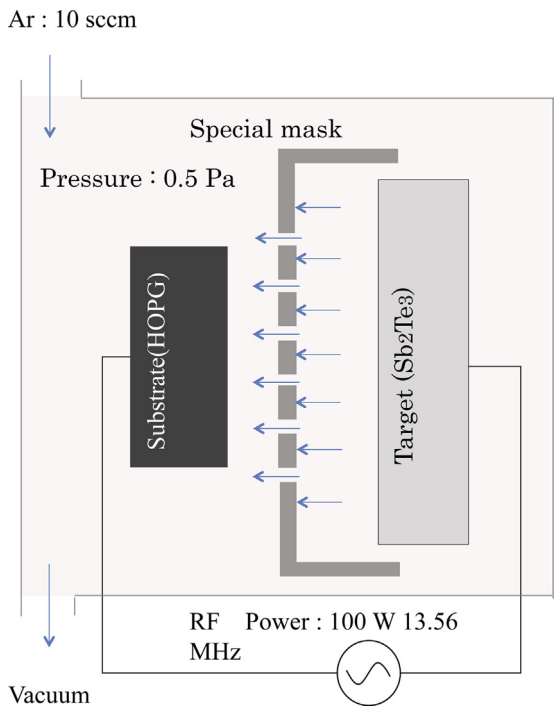

Fig. 1. Schematic diagram of the rf-sputtering setup used in this study. A special mask with small holes was inserted between the target and the substrate to control the deposition rate precisely.

procedures. We selected an Sb–Te alloy as a representative chalcogenide material, and highly oriented pyrolytic graphite (HOPG) as the substrate material, expecting that Sb and Te atoms would be mobile on it, and that nanostructures are easily recognized on its atomically flat surface. We report the production of nanoparticles with approximately 10–20 nm in diameter and nanoneedles with approximately 20–50 nm in diameter and several hundred nanometers in length, as well as their morphological and compositional analyses. We also discuss the importance of ambient pressure for the formation of nanostructures.

2. Experiments

Nanostructures were produced by annealing a 5 nm-thick Sb_2Te_3 ultra-thin film deposited on the HOPG substrate. Fig. 1 shows the configuration of the sputtering machine (Shibaura Mechatronics CFS-4ES), with the substrate, an Sb_2Te_3 target, and a special mask. Here, the mask with 80 holes of 3 mm-diameter formed within a 100 mm-diameter area was inserted between the sputtering target and the substrate in order to lower the deposition rate. With the mask, the deposition rate of Sb_2Te_3 is reduced to 0.018 nm/s, one fortieth of that without the mask (0.73 nm/s), allowing precise control of the thickness of ultra-thin layers. The sputtering conditions were as follows; 10 sccm of argon gas flow rate, 0.5 Pa of ambient pressure, and 100 W of rf magnetron power, without intentional heating of the substrate. Following deposition, the sample was annealed in a heat stage unit (LINKAM LK-600PN), under argon atmosphere of 1 atm to avoid oxidization. The stage temperature was raised in a heating rate of 10 °C/min to the annealing temperature, which was 200 or 250 °C, and then held for 2, 5, or 60 min.

The morphology and the chemical composition of the nanostructures were evaluated by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). We used several SEM machines such as Jeol JSM-6700F, JSM-7000F, and Hitachi SU6600, while for EDX, Oxford Instruments INCA E350 and Jeol EX-37001 were used. The acceleration voltage was set to 5–10 kV and 8 kV for the analysis of sample morphology and chemical composition, respectively. The *Lα* line peaks of Sb and Te, which are located at 3.605 and 3.769 keV, were used to determine the chemical compositions. An atomic force microscopy (AFM; SFT-3500, Shimazu Co.) with a silicon cantilever (OMCL-AC160TN, Olympus Co.) was used for obtaining height information of nanostructure. We note here, in order to avoid misleading, that all Sb–Te alloy nanostructures obtained in this study were of Te-rich composition.

3. Results and discussion

3.1. Observation of the shape of the nanostructures

Fig. 2 shows SEM images and diameter distributions of Sb–Te alloy nanoparticles after annealing under various conditions. Fig. 2a and b shows nanoparticles obtained after annealing at 200 °C for 2 and 5 min, respectively. Nanoparticles with several tens of nanometers in diameter are clearly seen. The diameter distribution histogram is shown below each SEM image. The number of nanoparticles between 10 and 15 nm in diameter is largest in both cases. With the longer annealing time, the number and the size of the nanoparticles tend to increase. On the other hand, after the substrate was annealed at 250 °C, nanoneedle structures appeared. Fig. 3a and b shows SEM images of samples annealed at 250 °C for 2 and 5 min, respectively. The formation of nanoneedles can be seen in both cases, in a tendency that their size becomes longer and thicker for the longer annealing time. The length and thickness of nanoneedle structures are estimated to be tens to hundreds of nanometers and 15–50 nm, respectively. These needles grow in parallel to or tilting against the substrate surface. We also carried out prolonged annealing for 60 min at both 200 and 250 °C. The resulting SEM images are shown in Fig. 4a and b. Under prolonged annealing at 200 °C, nanoneedles grow from the nanoparticles, but not at 250 °C. Indeed, the shape of the nanostructures obtained strongly depends on both the annealing temperature and time. The effects of annealing conditions on the shape of the resultant structure are complicated. This will be the subject of a future investigation.

We also performed AFM measurements to obtain information on the detailed three-dimensional structure of the produced nanostructures. Fig. 5a shows a typical AFM image of the same sample in Fig. 3a. In this image, a nanoneedle with a length of 300 nm is clearly seen. The cross-section at the A–B line across the nanoneedle, as indicated in Fig. 5a, is depicted in Fig. 5b. This line profile suggests that the width and the height of the structure are 34 and 45 nm, respectively, and that the top face of the nanoneedle consists of a very flat 34 nm-wide terrace. Slopes seen on both sides of the nanoneedle, indicated by black arrows in Fig. 5b, are artifacts caused by a tip shape effect. These results suggest that the nanoneedles have rectangular cross-sections. We also tried to study the shape of the nanoparticles by AFM, but no reliable and reproducible AFM image was obtained because the AFM probe easily wipes the nanoparticles across the surface.

Being highly interested in how the nanostructures grew on the HOPG surface, we tried to observe the morphology of an Sb_2Te_3 thin film in situ during annealing, using SEM (S-2700; Hitachi High-Tech Science Co.) equipped with current feed-throughs. A Ta film deposited on a SiO_2 substrate was used as a heater, on which the sample was pasted. We were not able to directly measure the temperature of the sample due to a mechanical limitation in the SEM chamber; however, approximate values were obtained from the previously measured relationship between the temperature and electric voltage in the Ta heater. The sample was a 20 nm-thick