Nitrogen-Doped Ge$_2$Sb$_2$Te$_5$ Films for Nonvolatile Memory

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Nitrogen-doped Ge$_2$Sb$_2$Te$_5$ (GST) films for nonvolatile memories were prepared by reactive sputtering with a GST alloy target. Doped nitrogen content was determined by using x-ray photoelectron spectroscopy (XPS). The crystallization behavior of the films was investigated by analyzing x-ray diffraction (XRD) and differential scanning calorimetry (DSC). Results show that nitrogen doping increases crystallization temperature, crystallization-activation energy, and phase transformation temperature from fcc to hexagonal (hex) structure. Doped nitrogen probably exists in the grain vacancies or grain boundaries and suppresses grain growth. The electrical properties of the films were studied by analyzing the optical band gap and the dependence of the resistivity on the annealing temperature. The optical band gap of the nitrogen-doped GST film is slightly larger than that of the pure GST film. Energy band theory is used to analyze the effect of doped nitrogen on electrical properties of GST films. Studies reveal that nitrogen doping increases resistivity and produces three relatively stable resistivity states in the plot of resistivity versus annealing temperature, which makes GST-based multilevel storage possible. Current-voltage (I-V) characteristics of the devices show that nitrogen doping increases the memory’s dynamic resistance, which reduces writing current from milliampere to microampere.

Key words: Phase change, nonvolatile memory, nitrogen doping, Ge$_2$Sb$_2$Te$_5$ (GST), multilevel storage, writing current reduction

INTRODUCTION

As the storage and portable application market rapidly expands, there is a great demand for a new kind of memory. The Ge$_2$Sb$_2$Te$_5$ (GST)-based nonvolatile memory has been regarded as one of the most promising candidates for the next generation memory because it has fast write/read speed, high-density storage capability, good endurance, and compatibility with complementary metal-oxide semiconductor technologies. The GST-based nonvolatile memory operates by converting a small volume of GST film back and forth between the polycrystalline and amorphous phases.1 There are high and low resistance states for the amorphous and polycrystalline GST, respectively, which can represent stable “0” and “1” in the storage technology.

However, there are some critical issues to be solved before its practical application. One of them is the reduction of writing current that should match the current limit of a nominal size negative-channel, metal-oxide semiconductor, field-effect transistor in a high-density GST-based nonvolatile random-access memory.2 Several different methods3 have been put forward to solve this problem. Among them, doping a small amount of nitrogen into the GST film seems to be a practical approach because nitrogen doping makes the GST dynamic-resistance increment, which leads to effective power delivery and results in writing current reduction.2 However, to the authors’ knowledge, most researches4–7 on nitrogen-doped GST film were focused on its optical properties and

(Received July 15, 2004; accepted September 20, 2004)
optical storage applications, while few articles relate to its electrical properties. In this study, nitrogen-doped GST films were prepared by reactive magnetron sputtering. Electrical properties and crystallization behavior of the films are discussed. Energy band theory is used to analyze the effect of doped nitrogen on electrical properties of GST films. The results indicate nitrogen doping not only reduces writing current but also is helpful to realize GST multilevel storage.

**EXPERIMENTAL**

Nitrogen-doped GST films were deposited on SiO$_2$/Si(100) wafers by direct-current (DC) reactive magnetron sputtering from a GST alloy target using argon and nitrogen gas. The argon partial pressure was fixed to 0.207 Pa, and the nitrogen dose in the films could be controlled by changing nitrogen partial pressure. The pure GST films were also prepared for comparison. All films are 200-nm thick. The detailed preparation parameters are listed in Table I. Specimen GST represents the pure GST film. Specimen NGST$_5$ and NGST$_{10}$ represent nitrogen-doped GST films with a nitrogen partial pressure ratio of 5.5% and 10.4%, respectively.

After deposition, specimens were annealed for 10 min at various temperatures under the protective argon atmosphere to crystallize the films. Doped nitrogen content of specimens NGST$_5$ and NGST$_{10}$ were determined to be 0.8 at.% and 1.3 at.%, respectively, using x-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) spectra and atomic force microscopy (AFM) were used to analyze the crystallography and morphology of the specimens. Differential scanning calorimetry (DSC) was employed to measure crystallization temperature and phase transformation temperature and to evaluate crystallization-activation energy ($E_a$). A four-point probe measurement was used to determine the sheet resistance of the films. The optical band gap ($E_{opt}^{opt}$) was measured using spectroscopic ellipsometer with a wavelength range from 200 nm to 1,200 nm. Current-voltage (I-V) characteristics of the devices could be obtained by using a simple structure shown in Fig. 1.

**RESULTS AND DISCUSSION**

**Crystallization Behavior and Morphology**

To know crystallization behavior and morphology of a material is helpful for a better understanding of its electrical properties. Figure 2 shows XRD spectra of the specimens annealed for 10 min at different temperatures. For the pure GST film, there are two peaks indicating the fcc structure in the XRD spectra of the 180°C annealed film, while only one fcc peak can be found for specimen NGST$_5$, but no clear XRD peaks can be observed for specimen NGST$_{10}$ annealed at 180°C. It can be deduced that the crystallization temperature increases with nitrogen dose increment. The first peak indicating hex structure appears on the XRD spectra of the pure GST film annealed at 280°C, which represents the phase transformation from fcc to hex structure. However, for specimen NGST$_5$, the first hex peak appears above 280°C and that of specimen NGST$_{10}$ appears at about 400°C. So the phase transformation temperature also increases with nitrogen dose increment.

Figure 3 shows DSC curves of specimens. There is at least one distinct exothermal peak on each curve. The first peak near 180°C indicates the occurrence of crystallization, and the second peak near 370°C represents the phase transformation from fcc structure to hex structure. It is clear that the crystallization temperature and the phase transformation temperature increase with nitrogen dose increment. For specimens with nitrogen dopant, there are two distinct peaks on each curve, but only one peak can be found for pure GST. The possible reason is that the phase transformation from fcc to hex structure of pure GST is a gradual process, which can also be demonstrated from the dependence of the resistivity on the annealing temperature shown in Fig. 6.

According to Kissinger’s equation,$^9$ the crystallization-activation energy can be calculated from the following equation:

$$\ln(T_p^{1/2}/\alpha) = A + (E_a/K_B)/T_p$$

where $T_p$ is the exothermal peak temperature, $A$ is a constant, $E_a$ is the crystallization-activation energy, $\alpha$ is heating rate, and $K_B$ is Boltzmann’s constant. A