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Evolution of the Structural and Electrical Properties of GeTe Under Different Annealing Conditions

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GeTe films were found to exhibit chemical, structural, and electrical changes depending on the crystal structure and annealing atmosphere. Amorphous GeTe was converted to cubic crystalline GeTe after annealing treatment at 400°C. Subsequent annealing in air induced phase transitions in the cubic GeTe, resulting in the formation of Ge oxide as the major phase and metallic Te as the minor phase. However, GeTe films deposited at 200°C maintained the rhombohedral structure regardless of the annealing time or atmosphere.

Key words: GeTe, phase change, oxygen, x-ray diffraction, annealing

INTRODUCTION

Under appropriate heating and cooling conditions, Ge-Sb-Te mixed alloys in phase-change memories exhibit sharp contrasts in electrical resistivity when switched between a highly resistive amorphous state and a conductive crystalline state. The binary compound GeTe has recently attracted a great deal of attention for high-temperature applications, since it presents a significant improvement in data retention at high temperature when compared with the commonly used $Ge_2Sb_2Te_5$. In addition, excellent contrast in terms of the electrical resistivity is observed between the amorphous and crystalline forms of GeTe.[1–9] In phase-change memory applications, electrical power provides the heat necessary for transformations between the amorphous and crystalline states. Thus, phase-change materials can degrade during repeated switching cycles due to structural and chemical instability. Oxygen can also easily penetrate into chalcogenide alloys during switching cycles. Unfortunately, few studies have been devoted to phase-change characteristics associated with oxygen.[8–11]

In the present work, we specifically investigated the structural changes of GeTe alloys. Such changes are dependent on the initial structure, annealing time, and annealing atmosphere. Depending on the deposition conditions, GeTe chalcogenide alloys can crystallize into two different phases: a NaCl-type cubic phase and a rhombohedral phase.[12,13] The oxygen diffusivity should exhibit a dependency on the crystal structure, and thus device stability could also show a different tendency according to the initial crystal structure, annealing time, and annealing atmosphere.

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EXPERIMENTAL PROCEDURES

GeTe films were grown on silicon wafers by radiofrequency sputtering from a GeTe target at room temperature and 200°C. The base pressure was 4 mPa, and the working pressure was adjusted to 400 mPa by introducing argon gas through a mass flow controller. The deposition rate was 0.2 nm/s. Samples deposited at room temperature and at 200°C are denoted as C-GeTe and R-GeTe, respectively. All films were annealed at 400°C in either air or N_2 atmosphere for 10 min, 100 min, and 1000 min; the heating rate was 2°C/s. After annealing, the films were gradually cooled to room temperature. The sheet resistance (R_s) of the films was measured by the four-point probe method.

The structural states of the samples were investigated by x-ray diffraction (XRD), secondary-ion