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High thermal stability of the amorphous structure of $Ge_xNbTaTiZr$ ($x=0.5$, 1) high-entropy alloys

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ABSTRACT

Two $Ge_xNbTaTiZr$ ($x=0.5$, 1) compositions were designed to show excellent thermal stability in amorphous structure. Both amorphous structures in the deposited thin film can be retained after one-hour vacuum annealing at 700 °C and 750 °C, respectively. Thermodynamic, topological and kinetic factors governing this excellent thermal stability are discussed via high entropy effect, atomic size differences and sluggish diffusion phenomena.

1. Introduction

Metallic glass (MG) is an amorphous material without long range order. With proper design of composition, MG could have outstanding mechanical and/or magnetic properties for advanced applications [1,2]. Nevertheless, the crystallization temperatures of reported MGs are low and might place a limitation when applied at higher temperatures [3–5]. Since crystallization would eliminate the merits of amorphous structure, developing MGs with higher crystallization temperatures is always the important issue. In 2004, high-entropy alloys (HEAs) were defined as having at least five major metallic elements in which each has an atomic percentage between 5% and 35% [6–8]. In HEAs, the high mixing entropy could enhance the stability of solid solution at high temperatures, and the large lattice distortion as well as sluggish diffusion effects could reduce the phase transformation rate [8]. In case of amorphous solid solutions, the present study proposes that the tendency of crystallization at high temperatures could be reduced by using the advantages of high entropy, lattice distortion and sluggish diffusion effects. This thinking route is using high entropy effect to enhance the mixing of composing elements, using the significant atomic size difference to cause the topological instability, and using higher melting point elements and sluggish diffusion effect to slow down the crystallization of amorphous structure. By this concept, $Ge_xNbTaTiZr$ ($x=0.5$, 1) alloys were designed in which Nb, Ta, Ti and Zr have small mixing enthalpy between each other but Ge have similar large negative enthalpy with the four metal elements [9]. These comparable mixing enthalpies would let Ge mix well with the four elements through high entropy effect. In addition, the required significant atomic size difference and higher melting point of composing elements are also fulfilled. Sputtering deposition method was chosen to fabricate the homogeneous amorphous films and rapid thermal annealing (RTA) at different temperature was used to estimate the thermal stability of the amorphous structure. Excellent thermal stability was anticipated for verifying the design route.

2. Experimental procedure

The 2-inch sputtering targets of $Ge_xNbTaTiZr$ ($x=0.5$, 1) alloys were prepared with high-purity Ge, Nb, Ta, Ti, and Zr elemental raw materials via vacuum arc-melting in a water-cooled crucible. Sapphires were utilized as the substrate for the deposition of $Ge_xNbTaTiZr$ ($x=0.5$, 1). The deposition method is direct current (DC) magnetron sputtering operated at a target power of 150 W under a base pressure better than 5×10^{-6} Torr and a working pressure of 5×10^{-3} Torr with an argon gas flow of 40 sccm. The as-deposited samples were further placed in a quartz plate at the center position of a quartz tube furnace and subjected to rapid thermal annealing below 3×10^{-7} Torr. Six infrared heating lamps

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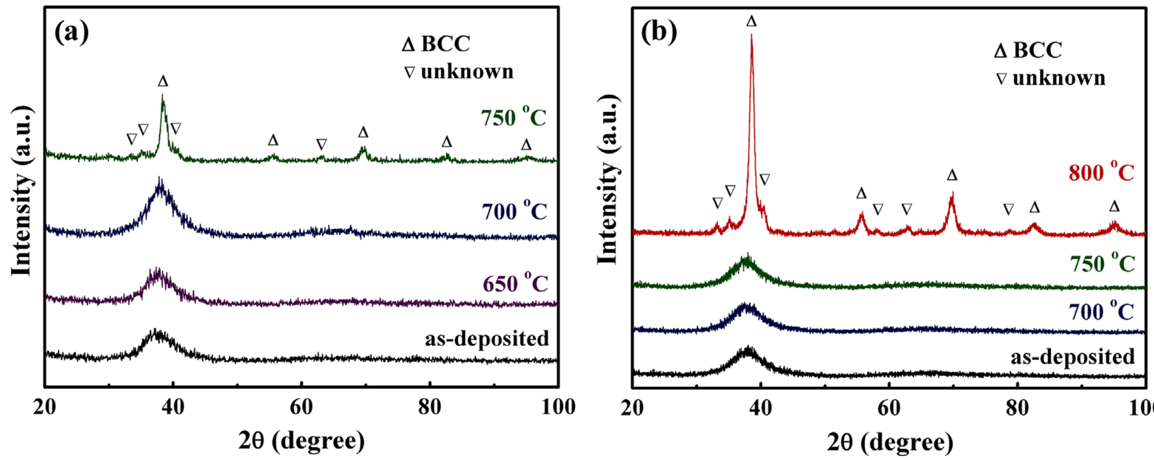

Fig. 1. XRD patterns of (a) $Ge_{0.5}NbTaTiZr$ and (b) GeNbTaTiZr thin films in the as-deposited and as-annealed states.

Table 1
Characteristic parameters of $Ge_xNbTaTiZr$ (x=0.5, 1) thin films. Calculation methods can be seen in Ref. [10,11,20].

Composition	*d*/K	ΔH_{mix} (kJ/mole)	δ	ΔS_{mix} (J/mole K)	T_m (K)
$Ge_{0.5}NbTaTiZr$	0.821	−17.58	0.046	13.15	2384.8
GeNbTaTiZr	0.816	−29.92	0.050	13.38	2264.1

acting as heat sources are symmetrically distributed around the quartz tube. The heating rate is 10 °C/s. Annealing for 1 h was done at temperatures from 773 K to 1073 K with an interval of 50 K in order to evaluate the thermal stability of $Ge_xNbTaTiZr$ (x=0.5, 1) thin films. The error of annealing temperature is controlled within ±0.5 °C by the temperature controller 'EUROTHERM 3504' equipped with a thermal couple whose probe tip is placed at the side of samples to monitor and ensure the accuracy of annealing temperature. Surface morphology was observed with field-emission scanning electron microscope (FESEM, SU8010, Hitachi). The crystallographic structures of films were probed by a glancing incident angle X-ray diffractometer (TTRAXIII, Rigaku, Japan) using Cu Kα radiation at 50 kV, 300 mA and the incident angle of 1°. The structures of films were investigated with transmission electron microscope (TEM, JEM-2100F, JEOL).

3. Results and discussion

The XRD patterns of $Ge_xNbTaTiZr$ (x=0.5, 1) films in Fig. 1 show that all samples possess single diffused humps except 750 °C-annealed $Ge_{0.5}NbTaTiZr$ film and 800 °C-annealed GeNbTaTiZr film. This indicates that $Ge_{0.5}NbTaTiZr$ and GeNbTaTiZr could preserve

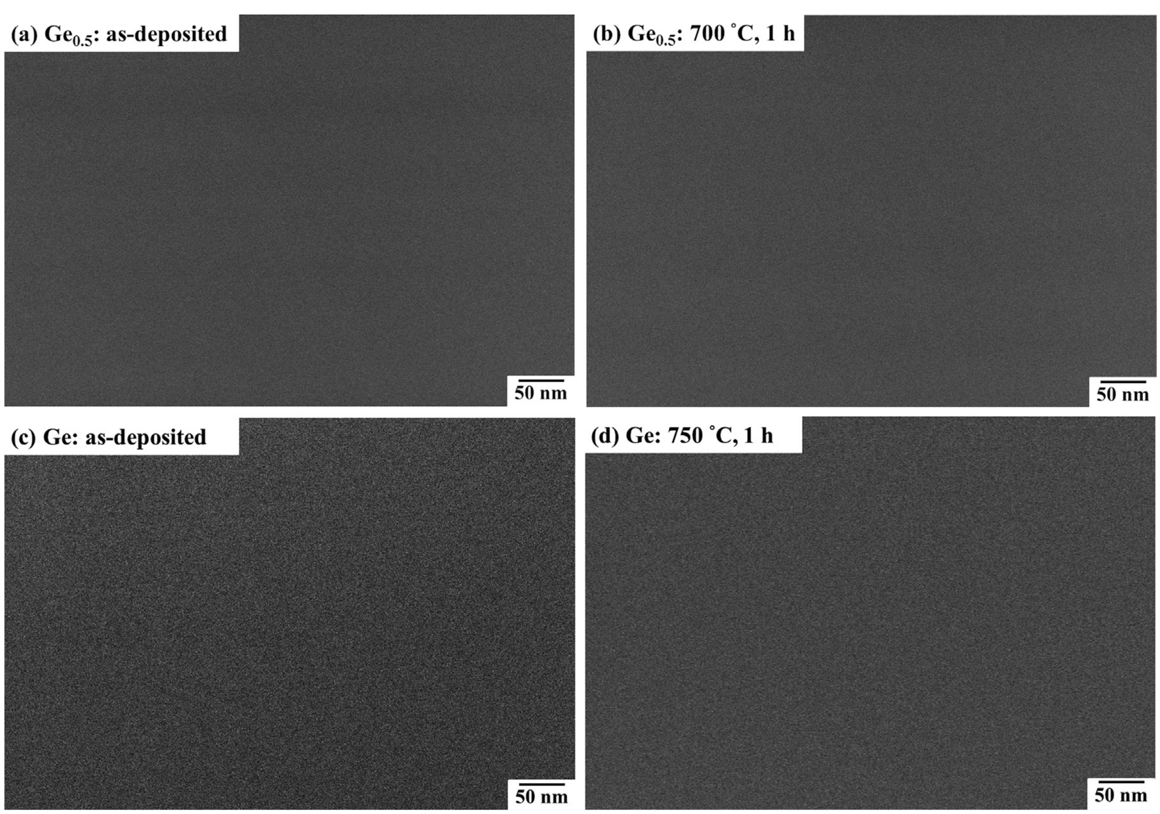

Fig. 2. FE-SEM images of (a) as-deposited, (b) 700 °C-annealed $Ge_{0.5}NbTaTiZr$ and (c) as-deposited, and (d) 750 °C-annealed GeNbTaTiZr thin films.