Thin Solid Films 552 (2014) 92–97

Contents lists available at ScienceDirect

Thin Solid Films

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

Gravity-assisted pulsed laser ablation for fabrication of compositional gradient thin film

Takashi Nishiyama [a,*], Takashi Kajiwara [a,b], Sachi Morinaga [a], Kunihito Nagayama [a]

[a] Department of Aeronautics and Astronautics, Kyushu University, Motooka 744, Nishi-ku, Fukuoka, 819–0395, Japan
[b] Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka, 819–0395, Japan

ARTICLE INFO

Article history:
Received 13 March 2013
Received in revised form 18 December 2013
Accepted 19 December 2013
Available online 28 December 2013

Keywords:
High gravity field
Pulsed laser ablation
Compositional gradient
Selective reevaporation

ABSTRACT

A compositional gradient thin film of Fe/Si was fabricated by gravity-assisted pulsed laser ablation under a gravity field of 5.3×10^4 m/s^2. Systematic experiments were conducted by varying the values of several parameters including the gravity, distance between the target and the substrate, and laser fluence.

The atomic fraction of Fe was measured by scanning electron microscopy/energy dispersive X-ray spectroscopy. We found that the atomic fraction of Fe increases along the gravity direction, i.e., it exhibits an apparent spatial gradient.

We also found the optimal laser fluence at which a thin film having the largest possible spatial compositional gradient is obtained. It is shown that the surface energy density on the substrate surface is the key parameter to control the compositional distribution. The relatively high laser fluence as well as the very narrow space between the target and the substrate are found to be essential to sputter the film material. A plausible model is presented to explain the experimental data.

1. Introduction

In an acceleration field, a body force directly acts on each atom according to its weight and size. Heavier and smaller atoms in condensed media experience a stronger force along the acceleration direction. Therefore, an atomic-scale graded structure will be generated in a two-component solid material system under very high gravity field. Mashimo et al. developed super centrifuges [1,2] and showed that atomic-scale diffusion due to an acceleration field could occur even in crystalline solids, although the acceleration field strength required in this case might be close to or above 9.8×10^6 m/s^2 [3–5]. Thus far, several diffusion theories have been reported to explain the effect of the gravitational field [6,7].

A centrifugal field has also been used for materials processing. Kinemuchi et al. developed a unique apparatus for sintering ceramics under a gravity field of over 9.8×10^3 m/s^2 in a high-temperature environment [8,9]. In another study, Abe et al. developed a high-gravity chemical vapor deposition apparatus for the deposition of thin films and reported that the film properties were influenced by a gravity field of 98 m/s^2 [10].

Nishiyama et al. proposed a gravity-induced compositional gradient formation process. This process employs a combination of a high gravity field and the pulse laser ablation (PLA) method [11,12]. PLA is a process in which a cloud of high-energy particles is produced by instantaneous laser energy absorption on a solid material target. Pulsed laser deposition (PLD) is one of the established thin film fabrication methods in which high-energy particle species produced from a target material by PLA are deposited onto a substrate [13,14]. This could possibly result in nonequilibrium deposition. Under such circumstances, it is expected to achieve a compositional gradient of thin film materials at a much lower acceleration field and temperature than those used in the case of bulk materials by Mashimo et al. We call this method gravity-assisted PLA (GAPLA). Although achieving compositional modulation on thin films should require a much smaller gravity field than that for bulk materials, appreciable energy density will still be required on a substrate surface. This study adopts somewhat extreme experimental laser ablation conditions that have rarely been used in various examples of thin film deposition by laser ablation. We chose a very narrow space between the ablation target and the moving substrate and very large laser fluence at the target surface. These conditions are explained in detail later.

In this study, a series of systematic experiments were conducted by varying several parameters such as the gravity, target–substrate distance, and laser fluence for a typical $FeSi_2$ sample. Furthermore, a plausible scenario was proposed to explain the experimental results.

2. Experimental setup

We designed an apparatus for depositing a thin film with a concentration gradient by using a combination of PLA and a gravity field [11,12]. Fig. 1(a) shows a schematic illustration of the designed

---

* Corresponding author at: Department of Aeronautics and Astronautics, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819–0395, Japan. Tel.: +81 92 802 3016; fax: +81 92 802 3017.
E-mail address: nishiyama@aero.kyushu-u.ac.jp (T. Nishiyama).

0040-6090/$ – see front matter. Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.12.048

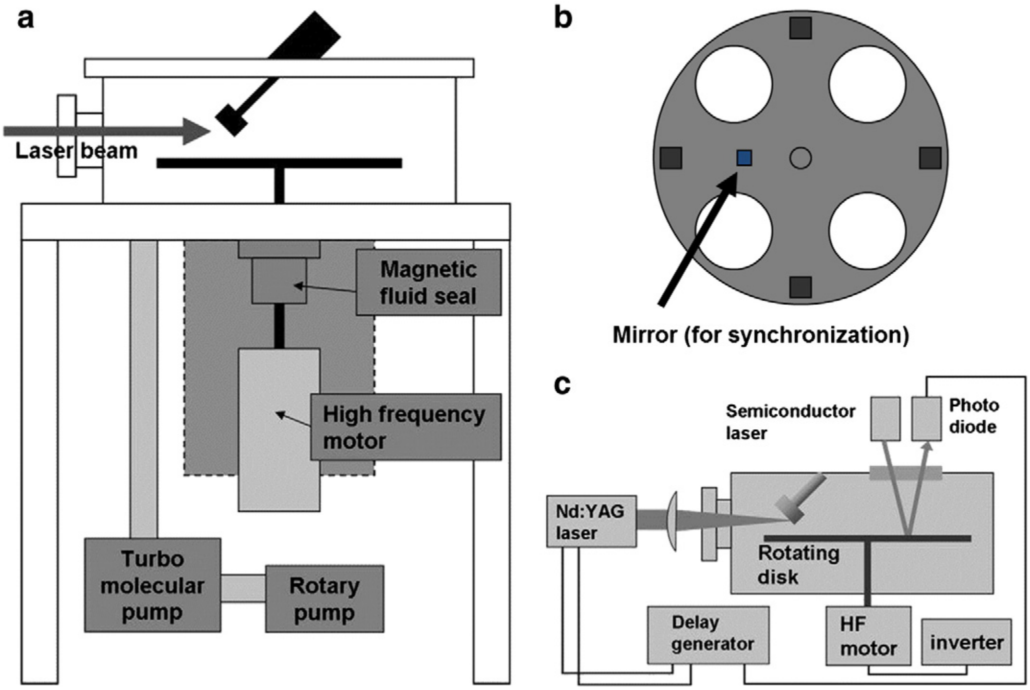

Fig. 1. Schematic illustration of the apparatus: (a) overview, (b) geometrical positions of the substrate plates on the disk, (c) block diagram of the experimental system.

apparatus. A 300-mm-diameter high-speed rotating circular disk made of pure titanium, which is known to have sufficient rigidity up to a temperature of 400 °C, was installed inside a vacuum chamber. A pulsed laser beam was introduced into the chamber through an optical glass window and focused on the target. The apparatus was designed solely for the synthesis of thin films. Four substrate sections having a size of 10 mm × 10 mm were positioned symmetrically near the outer periphery of the disk. The angle between the target plate and the substrate was 45°, and therefore, the incident angle of the ablation plume onto the target surface was also 45°. Fig. 1(b) shows the geometrical positions of the substrate plates on the disk. The weight balance of the titanium disk was tuned for high-speed rotation after its installation in the chamber. The substrate plates were fixed in each experiment; it was found that their small mass did not disturb the rotation balance. However, identical specimens were placed symmetrically to maintain the balance; therefore, at least two specimens could be used simultaneously. Fig. 1(c) shows a block diagram of the experimental system. A mirror was placed on the disk to reflect the semiconductor laser light for synchronizing the rotation with the laser ablation. The reflected light was detected using a photodiode that triggered laser radiation. Laser ablation and plume deposition were considered to be almost instantaneous as compared to the movement of the specimen by disk rotation, which ensures accurate compilation of the thin film structure at the very same position of the substrate plate.

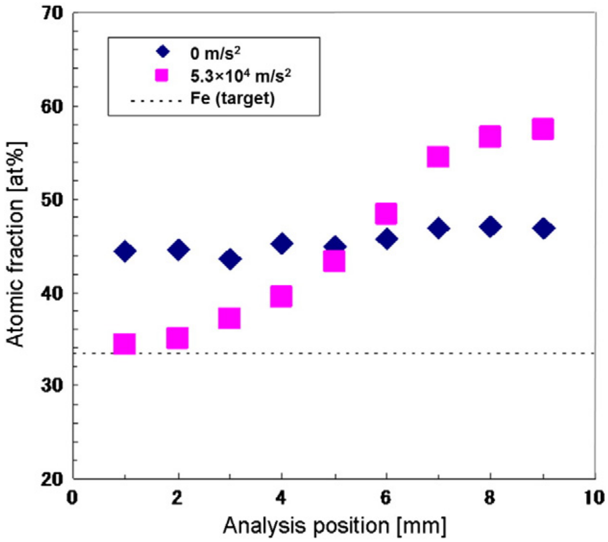

Fig. 2. EDX analysis results of graded thin films prepared by GAPLA with laser fluence of 10 J/cm^2 under a gravity field of 0 m/s^2 and 5.3 × 10^4 m/s^2. The dashed line shows the atomic fraction of Fe in the target material.

In this study, in our first attempt at compositional gradient formation, we chose $FeSi_2$ as a target material. $FeSi_2$ has a relatively high melting temperature of 1212 °C; this enabled us to demonstrate that one of the advantages of the GAPLA process is that it can be applied to any material that has a very high melting temperature. Furthermore, the constituent atoms of $FeSi_2$ have largely different atomic weights, although we recognized that this difference may not be a crucial factor in the formation of a compositional gradient in the GAPLA process. The change in the composition of the deposited film is considered to occur not because of their weight difference but because of their sputtering properties.

We used an Nd:YAG laser of fundamental frequency as the ablation energy source. The pulse duration and typical pulse energy were 4 ns and 100 mJ/pulse, respectively. We used a sapphire plate as the substrate on which the thin film was deposited. Great care must be taken to choose a substrate material whose constituent elements are not the same as those of the target material.

In this experiment, a thin film was produced with ≥1 μm thickness to ensure that the film properties could be precisely evaluated. The apparatus had to be continuously operated for more than an hour to prepare a thin film of this thickness, and all the reported experiments were conducted under high-vacuum conditions. The substrate surface was not subjected to additional heating.

The most striking features of the experimental conditions adopted in this experiment are (i) the very narrow space between the ablation target and the moving substrate surface and (ii) the appreciably large laser fluence for ablation as compared with that in normal PLD experiments. In this study, the dependences of the thin film properties on the target–substrate distance and on the laser ablation fluence were