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Grain Size Control of Bi-Substituted Garnet Films Crystallized by Multi-Step Rapid Thermal Annealing for Magneto-Optical Disks

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The sputtered Bi-substituted iron garnet films of improved microstructures are successfully grown using the optimized multi-step rapid thermal annealing (MSRTA). The concepts of the incubation time and the relaxation time in the MSRTA are applied to obtain good microstructures of garnet films. By repeating the optimized thermal cycle many times, the high density of nucleated grains can be obtained, and the grain size can be forced to be as small as it can be. This optimized MSRTA leads to a finer grain size of less than 0.1 μm and better surface morphology with higher grain density than a conventional annealing method. The crystallized sample shows good squareness and large remnant Faraday rotation.

KEYWORDS: magneto-optical disk, garnet film, multi-step rapid thermal annealing, Faraday rotation, sputtering, grain size

1. Introduction

Among several candidates for high density magneto-optical recording materials, Bi-substituted polycrystalline iron garnet films[1,2] are very promising. They have corrosion resistance and a large magneto-optic Faraday effect at short wavelengths less than 550 nm. Generally, they are prepared by RF sputtering on glass substrates, since sputtering provides good uniformity over a large deposition area. But RF sputtered iron garnet films have poor signal-to-noise ratio (SNR) caused by light scattering at grain boundaries.[3] Therefore, the control of film morphology and ricrostructure have been the most important issue for garnet films in general.[4,6]

It was reported that the conventional oven annealing at about 650 °C for several hours brings about inherently a high media noise caused by grains and surface roughness. Rapid thermal annealing (RTA) to crystallize as-deposited amorphous phase in Bi-substituted films is known to generate improved microstructure and surface morphology.[7-9]

This paper describes the crystallization behavior as a function of the parameters of multi-step rapid thermal annealing (MSRTA), such as the heating time, the cooling time, and the heating temperature. We propose and demonstrate an optimized MSRTA to obtain high density fine grains with good surface morphology by using the incubation time and the relaxation time.

2. Experiments

2.1 *Preparation of the samples*

Bi-substituted iron garnet thin films ($Bi_2Dy_1Ga_1Fe_4O_{12}$) are prepared by RF sputtering in an argon atmosphere on glass substrates (Corning 7059) held at ambient temperatures during the deposition process. Sputtering targets (5 cm diameter) are made by sintering at 950 °C. Sputtering parameters are of great importance to the properties of crystallized films.[10] Therefore, all the parameters of sputtering are made to be the same for the samples used in our experiment as given in Table I.

2.2 *Multi-step rapid thermal annealing (MSRTA)*

In comparison with conventional furnace annealing, MSRTA is useful to control grain size and film surface morphology. To optimize the MSRTA conditions for high density fine grains, we investigate the incubation time and the relaxation time at various crystallization temperatures. The incubation time is the heating time needed for the nucleation of the grain and the relaxation time is the cooling time for nearly nucleated grain (still embryonic state) to completely revert to an amorphous phase. The heating time (t_a) and the cooling time (t_c) of our MSRTA cycle are explained in Fig. 1.

MSRTA is performed in O_2 ambient (*in situ* RF sputtering chamber). The rapid heating is done using tungsten-halogen lamps. During the period of annealing, the temperature histories of all samples are traced directly by a K-type thermocouple as shown in Fig. 1.

Table I. Sputtering conditions.

Target composition	$Bi_2Dy_1Ga_1Fe_4O_{12}$
Base vacuum pressure	5×10^{-6} Torr
Sputtering gas/pressure	argon/20 mTorr
Sputtering substrate temperature	450 °C
RF power	350 W
Deposition rate	2.5 μm/h
Film thickness	3500 Å

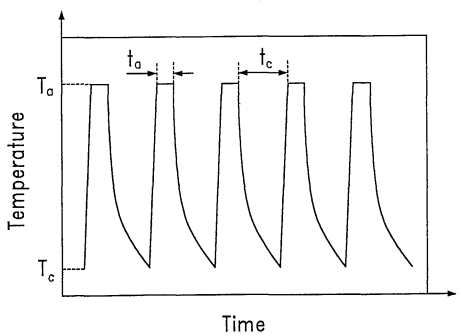

Fig. 1. Temperature history diagram of a multi-step rapid thermal annealing. (T_a; heating temperature, T_c; cooling temperature, t_a; heating time, t_c; cooling time)

The effects of heating time is studied at a fixed ramp-up rate of 40 °C/s limited by our system configuration.

The Faraday rotation angle of about 1 degree is measured by a polarization modulation scheme using a Faraday rotator and a phase sensitive detection method. The net Faraday rotation hysteresis loops of garnet films are obtained by subtracting the linear contribution of the glass substrates from the hysteresis curves traced by the polarization modulation scheme. The film morphology is studied by analyzing scanning electron microscope pictures. The formation of crystal is confirmed by Faraday hysteresis loops and X-ray diffraction patterns.

3. Results and Discussion

When heating temperature of as-deposited garnet films is lower than 700 °C, the sample shows no remnant Faraday rotation and X-ray diffraction patterns exhibit the halo pattern as amorphous films. When annealing is carried out at temperature over 750 °C, the thin film is cracked by the thermal stress between the thin film and the substrate. The temperature to crystallize as-deposited amorphous films (crystallization temperature) is measured to be between 700 °C and 750 °C. From X-ray diffraction patterns, the single crystalline phase of the garnet film is confirmed.

To study the effects of O_2 gas pressure on crystallization, MSRTA is performed for various O_2 gas pressures in a vacuum chamber. The results reveal that the grain size, density, and remnant Faraday rotation angle increase with O_2 gas pressure. For comparison purposes, we also anneal samples in a vacuum condition (no oxygen). In this case, the Faraday hysteresis loop is not square and the surface morphology is slightly rough. Therefore, we set the O_2 gas pressure at the lowest possible value (50 mTorr) to obtain good surface morphology. All the samples in the experiments are annealed in 50 mTorr O_2 ambient.

Since the incubation time is the heating time needed for the nucleation, the incubation time could depend on the initial temperature of the sample. According to our measurement, about 6 minutes of cooling is found to be sufficient to obtain a constant initial temperature condition (250±10 °C). At the fixed cooling time of 6 minutes, various heating times are tried to determine the incubation time. The incubation time for nucleation of the grain at the annealing temperature of 700 °C is found to be about 75 seconds as shown in Fig. 2(a). If the heating time is longer than 80 seconds, the none of the crystalline phase reverts to the amorphous phase even after the long cooling. We confirm the formation

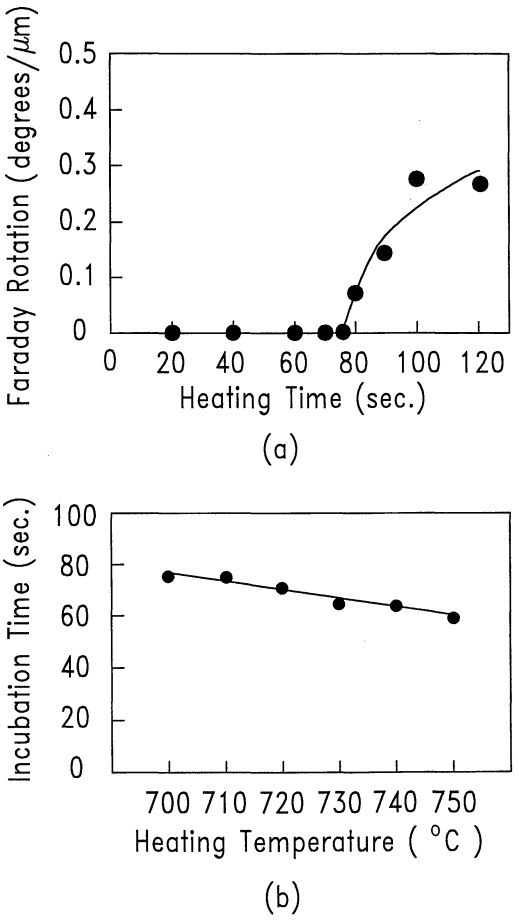

Fig. 2. (a) Remnant Faraday rotation angle versus heating time to determine the incubation time at 700 °C. (6 minutes cooling and 10 cycles annealing) (b) Annealing temperature dependence of the incubation time at crystallizable temperatures (700 °C~750 °C).

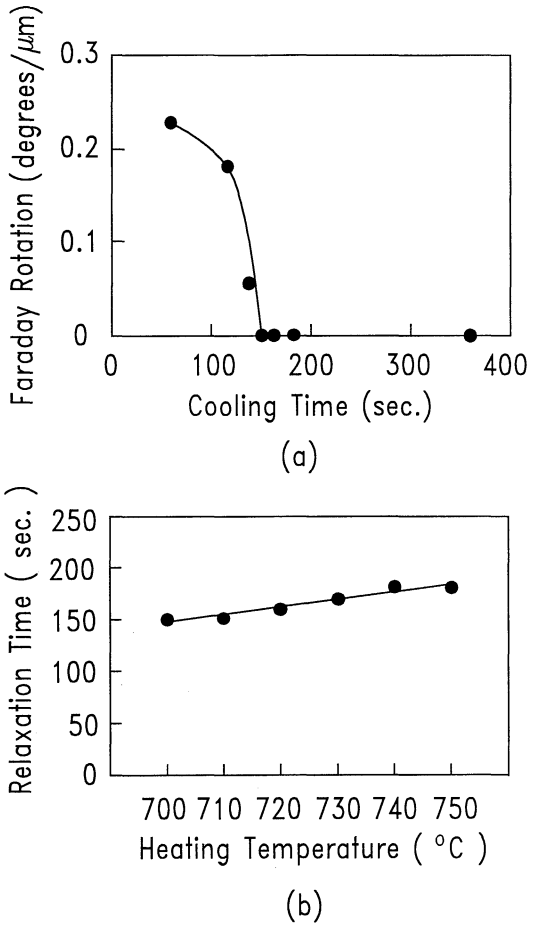

Fig. 3. (a) Remnant Faraday rotation angle versus cooling time to determine the relaxation time at 700 °C. (Heating time (t_a) is the same as the incubation time of 75 seconds, and 10 cycles annealing) (b) Annealing temperature dependence of the relaxation time at crystallizable temperatures (700 °C~750 °C).

of the crystalline phase from the X-ray diffraction data in addition to the Faraday rotation angle. Also, depending on the heating temperature, the incubation time changes as expected. As the heating temperature is increased from 700°C to 750°C, the incubation time is decreased from 75 seconds to 60 seconds, as shown in Fig. 2(b). From these observation, it can be argued that the grain grows faster at a higher temperature.

The relaxation time is the cooling time for nearly nucleated grain but still in an embryonic state to completely revert to an amorphous phase. To determine the relaxation time, it is necessary to vary cooling time at a fixed heating temperature and heating time. We set the heating time to be the same as the incubation time (75 seconds) and the heating temperature to be 700°C. By doing this, the sample is guaranteed to be nearly nucleated but still in an embryonic state. If the sample is cooled for more than 150 seconds, the embryonic grains completely relax to an amorphous phase. If the cooling time is shorter than 150 seconds, they don't relax to an amorphous phase but still remain in an embryonic state. By repeating this cycle many times, the embryonic grains are nucleated and grow. Therefore, the relaxation time at 700°C heating temperature is 150 seconds.

Initially, the relaxation time was assumed to be independent of the heating temperature, since those samples heated for duration equal to incubation time are likely to be in the same crystallization state. Contrary to our expectation, when the sample is annealed at a temperature higher than 700°C, the relaxation time tends to increase as shown in Fig. 3(b). This finding could be explained by assuming that the nuclei of the sample annealed at a higher temperature are somewhat larger than those annealed at a lower temperature. These results indicate that performing MSRTA at the lowest possible temperature will lead to grains of minimum size.

In order to investigate the effects of the heating time on grain size, various heating times are tried with sufficient cooling time of 6 minutes. When the heating times are longer than the incubation time (60 seconds) at a heating temperature of 750°C, the grains become nucleated and these grains remain in the nucleated state even after long enough cooling. As shown in SEM micrographs of Fig. 4, the grain size of the sample increases with the heating time, and so does the remnant Faraday rotation. The grain density does not increase greatly, since the nucleation of the grains is somewhat suppressed by sufficient cooling.

To obtain high density fine grains, the incubation and relaxation times are used in the optimized MSRTA. In this process, a sample is heated for the incubation time and cooled for a slightly (~10 s) shorter

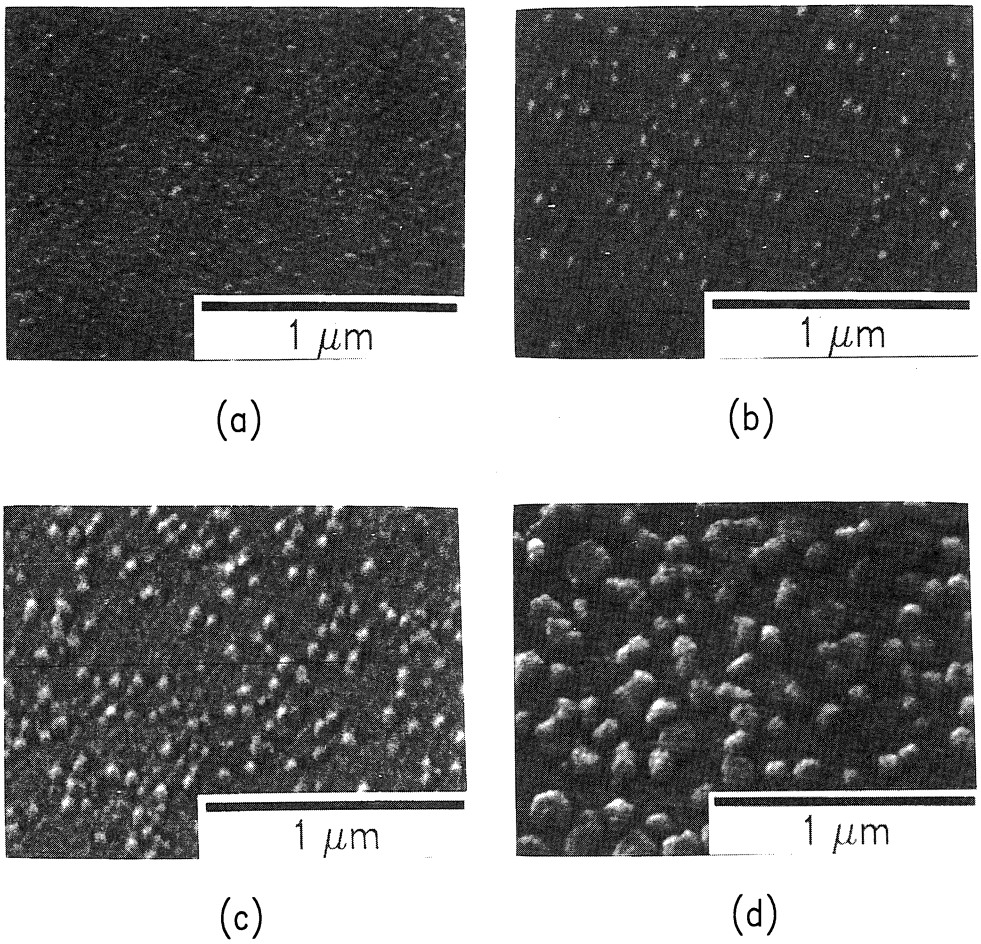

Fig. 4. SEM micrographs taken from the films annealed by using heating time longer than incubation time at 750°C. (T_a; 750°C, t_c; 6 min, 10 cycles annealing) t_a; (a) 1 min 10 s, (b) 1 min 30 s, (c) 2 min, (d) 3 min.

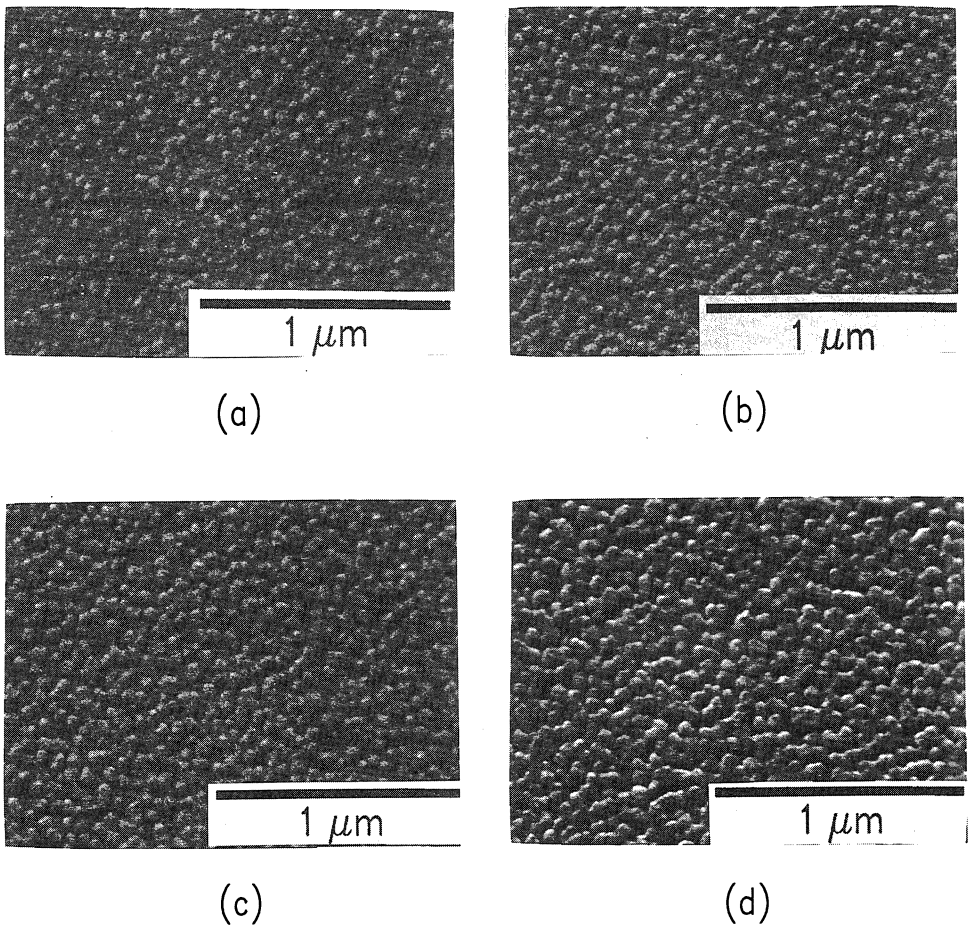

Fig. 5. SEM micrographs taken from the films prepared by our optimized MSRTA. Heating time equals the incubation time and cooling time is slightly shorter than the relaxation time. (T_a; 700°C, t_a; 75 s, t_c; 140 s) (a); 10 cycles annealing, (b); 20 cycles, (c); 30 cycles, (d); 40 cycles.

time than the relaxation time. During this first cycle, some grains are generated in an embryonic state. In the subsequent cycles, the additional new embryonic grains will be generated, while the most of the former grains still remain in an embryonic state. Consequently, the high density nucleated grains can be formed from, this high density grains in an embryonic state. When Fig. 5 is compared with Figs. 4(c) and 4(d), it is clear that the grain density in Fig. 5 is higher than those in Fig. 4 but the grain size is smaller, which supports the validity of our optimized MSRTA.

A typical hysteresis loop of a crystallized iron garnet film prepared by our optimized MSRTA is traced by using a polarization madulation method. The sample shows good squareness and the remnant Faraday rotation angle (θ_F) is about 1.4 deg/μm at 633 nm wavelength. The coercivity (H_c) of the film is about 1.3 kOe.

4. Conclusion

We propose and demonstrate an optimized MSRTA method to obtain iron garnet films with improved microstuctures. Bi-substituted iron garnet films of fine grains of less than 0.1 μm diameter with high grain density are successfully obtained using an RF sputtering method adapting the MSRTA processes based on the concepts of the incubation time and the relaxation time. Crystallization temperature of iron garnets is found to be 700°C. For heating temperature 700~750°C, the incubation time is 75~60 seconds and the relaxation time is 150~180 seconds. If the sputtering parameters are optimized and the heating ramp-up rate is increased, the smaller grains will be obtained by this optimized MSRTA. The optimization in MSRTA could be applied to the other magneto-optic garnet films of different composition.

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