JOURNAL OF MATERIALS SCIENCE 29 (1994) 3993–3996

Thermal and X-ray studies of the pyrolysis process for bismuth-substituted iron garnet films

J. CHO*
Data Storage Systems Center, Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

The thermal decomposition and crystallization processes of two types of films with various thicknesses prepared by spin-coating aqueous and acetylacetonic solutions made by dissolving metal nitrate hydrates of appropriate ratios for the garnets, are described. It was found that the aqueous films decomposed with endothermic reactions over a broad temperature range from 80–500 °C, while the acetylacetonic films decomposed at two strong exothermic reactions at temperatures of 130 °C and 250°–400 °C. Both films decomposed to become amorphous oxides, which then began to crystallize at a temperature of about 600 °C. It was also found that when the amorphous oxide films were thinner than 0.3 μm, the garnets were formed directly from the amorphous oxides. When the films were thicker than 0.3 μm, intermediate orthoferrites were formed which, upon further heating, transformed to the garnets. Differential thermal analysis, thermogravimetry, and X-ray diffraction data in the temperature range 20–750 °C are given and discussed.

1. Introduction

Bismuth-substituted iron garnet films are of interest because of their use for magneto-optic and microwave devices [1–4]. These films have been prepared by spin coating followed by thermal decomposition and crystallization or by pyrolysis [5, 6]. Pyrolysis, in addition to its simplicity, has an advantage over vacuum processes, in that it permits a precise control of chemical composition of the films [1] and hence may be used to fine tune the properties of the films for specific applications by doping various ions.

Previous studies [7, 8] have shown that the aqueous and acetylacetonic solutions used in this study to prepare the films have the following features. The aqueous solutions are stable but do not wet the glass substrates well, because of their high surface tension. Wetting can be improved by pretreatments of the substrates by techniques such as air plasma bombardment. The acetylacetonic solutions form stable metal chelates and wet the glass substrates well, but the quality of the films prepared by this solution is rather sensitive to the heat treatment.

Although the preparation of the films by pyrolysis using the solutions has been reported [5, 6], little is known about the thermal decomposition process itself. This is essential information if one wishes to optimize the heat treatment and quality of the films.

This paper discusses thermal and X-ray data obtained during heating of the films prepared from the two types of solutions to clarify how the films are decomposed and how the garnet phases are formed by pyrolysis.

2. Experimental procedure

Aqueous and acetylacetonic solutions were prepared by dissolving metal nitrate hydrates of appropriate ratios for the garnets in water and acetylacetone ($CH_3COCH_2COCH_3$). Table I shows the molar ratios of the metal nitrate hydrates used. The solutions were spin-coated on to glass substrates and dried for 5 min at 80 °C. The coated substrates were then broken into small pieces and used for thermal and X-ray analyses. The thicknesses of the films were varied by changing the concentration of the solutions and spinning speed.

Differential thermal analysis (DTA) and simultaneous thermogravimetry (TG) were performed in the temperature range 20–750 °C with a heating rate of 10 °C min^{-1}. For X-ray analysis, the samples were heated at the same rate in a furnace and taken out as soon as they reached certain temperatures. They were then quenched by placing on a cold aluminium plate and examined at room temperature using an X-ray diffractometer.

3. Results

Fig. 1 shows DTA and TG curves for the aqueous films with various chemical compositions. As shown, the overall shapes of the DTA and TG curves are not

---

* *Present address*: Department of Electronic Materials Engineering, Gyeong Sang National University, 900 Gazwa-Dong, Chinju-Shi, Kyong Nam, Korea.

0022–2461 © *1994 Chapman & Hall*

TABLE I Molar ratios of the metal nitrate hydrates used to prepare aqueous (1–4) and acetylacetonic (5) solutions

	Sample no.				
	1	2	3	4	5
$Y(NO_3)_3 6H_2O$	1.5	1.5	–	–	–
$Dy(NO_3)_3 5H_2O$	–	–	1.5	1.5	1.5
$Bi(NO_3)_3 5H_2O$	1.5	1.5	1.5	1.5	1.5
$Fe(NO_3)_3 9H_2O$	5.0	4.0	5.0	4.0	4.0
$Al(NO_3)_3 9H_2O$	–	1.0	–	1.0	1.0
Solvent	Water	Water	Water	Water	Acetylacetone[a]

[a] $CH_3COCH_2COCH_3$.

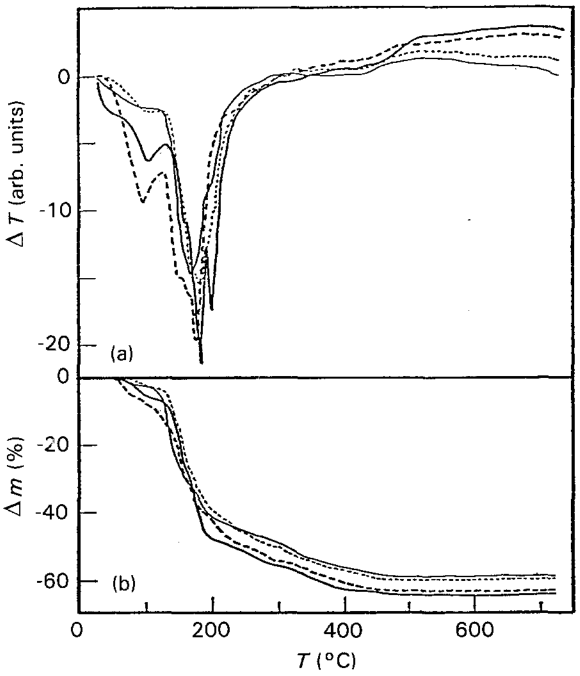

Figure 1 (a) DTA and (b) TG diagrams of aqueous films. Sample: (——) 1, (– – –) 2, (——) 3, (- - - -) 4.

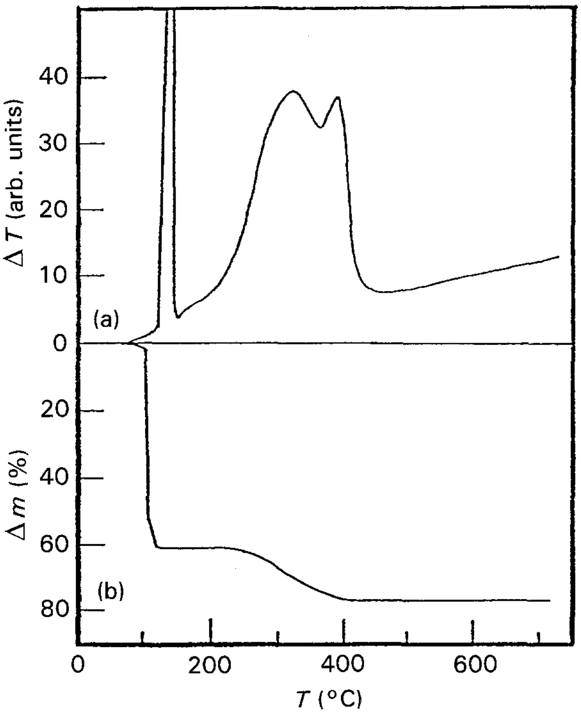

Figure 2 (a) DTA and (b) TG diagrams of an acetylacetonic film (Sample 5).

sensitive to the film composition. Note that endothermic reactions are observed at temperatures of 100 °C ($\Delta T = -10$ °C), 180 °C ($\Delta T = -25$ °C), and 400 °C ($\Delta T = -2$ °C) in the DTA curves and corresponding weight losses at temperatures of 80–120 °C ($\Delta m = -5\%$), 120–200 °C ($\Delta m = -45\%$), and 200–500 °C ($\Delta m = -15\%$) in the TG curves. This indicates that the films mostly decompose in the temperature range 120–200 °C and then gradually decompose at temperatures up to 500 °C.

Fig. 2 shows DTA and TG curves for the acetylacetonic film. A sharp, very strong exothermic reaction ($\Delta T = 80$ °C) and corresponding large weight loss ($\Delta m = -60\%$) are seen at the temperature of 130 °C. This is then followed by broad strong exothermic reactions at temperatures of 300 °C ($\Delta T = 40$ °C) and 400 °C ($\Delta T = 40$ °C) and corresponding weight loss at temperatures of 250–400 °C ($\Delta m = -20\%$).

DTA and TG curves for the individual metal nitrate hydrates are shown in Fig. 3. The major intermediate and end products assigned based on the weight-loss ratios in the TG curves are shown in Table II. From Fig. 3 and Table II, note that bismuth, iron, and aluminium nitrate hydrates sharply decompose at the relatively low temperature of 180 °C and form their subnitrates, which then decompose to form their oxides at temperatures up to about 550 °C for the bismuth subnitrate, and 400 °C for the iron and aluminium subnitrates. However, yttrium and dysprosium nitrate hydrates gradually decompose at temperatures from 100–300 °C to form their anhydrous nitrates, which then change to their subnitrates at the relatively high temperature of about 400 °C, and finally become their oxides at a temperature of about 500 °C.

X-ray studies revealed that both types of film decomposed to become amorphous oxides, which then began to crystallize at the temperature of 600 °C. When the amorphous oxide films were thinner than 0.3 μm, the films crystallized to form the garnet phases. When the films were thicker than 0.3 μm, the films crystallized to form intermediate the orthoferrite phases which transform to the garnet phases only after further heating for 3 h at 750 °C. Fig. 4 shows X-ray diffraction diagrams of two films with the same chemical composition but different thicknesses after being quenched from 700 °C. Note that diffraction lines of the garnet phase are only seen for the thinner film, while those of the orthoferrite phase are seen for the thicker film.

TABLE II Major intermediate and end products of metal nitrate hydrates: assigned based on the ratio of weight loss in TG diagrams

	Temperature (°C)					
	100	200	300	400	500	600
$Y(NO_3)_36H_2O$ →			→ $Y(NO_3)_3$	→ $YONO_3$	→ Y_2O_3	
$Dy(NO_3)_35H_2O$ →			→ $Dy(NO_3)_3$	→ $DyONO_3$	→ Dy_2O_3	
$Bi(NO_3)_35H_2O$ →		→ $BiONO_3$				→ Bi_2O_3
$Fe(NO_3)_39H_2O$ →		→ $FeONO_3$		→ Fe_2O_3		
$Al(NO_3)_39H_2O$ →		→ $AlONO_3$		→ Al_2O_3		

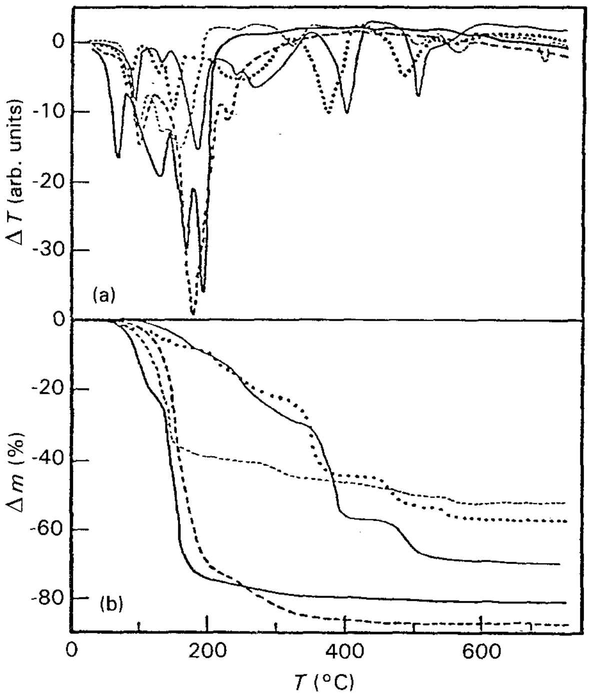

Figure 3 (a) DTA and (b) TG diagrams of individual metal nitrate hydrates. (——) $Y(NO_3)_36H_2O$, (●●●) $Dy(NO_3)_35H_2O$, (– – –) $Bi(NO_3)_35H_2O$, (——) $Fe(NO_3)_39H_2O$, (– – –) $Al(NO_3)_39H_2O$.

4. Discussion

Based upon the observations for the metal nitrate hydrates (Fig. 3 and Table II), one can interpret the DTA and TG data (Fig. 1) obtained for the aqueous films investigated as follows. The endothermic reactions observed at 100 °C may be due to the evaporation of the remaining water. The endothermic reactions corresponding to the rapid weight loss at the temperature of about 180 °C result from the decompositions of iron, aluminium, and bismuth nitrates to their subnitrates. The following gradual decomposition as the temperature is increased up to 500 °C is ascribed to the decompositions of yttrium and dysprosium nitrates and iron, aluminium and bismuth subnitrates to their oxides.

In contrast to the aqueous solutions, the acetylacetonic films examined show totally different thermal behaviour (Fig. 2). The sharp exothermic reaction and weight loss at 130 °C is probably due to the decomposition of the acetylacetone, because this is an oxidation reaction. The following strong, exothermic reactions with a gradual weight loss at the temperature range from 250–400 °C probably result from the decompositions of chelates to oxides. These strong exothermic reactions probably make the chemical homogeniety of the acetylacetonic films sensitive to the heat treatment during the film preparation.

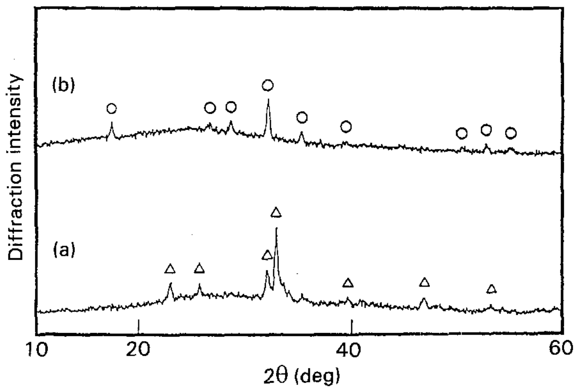

Figure 4 X-ray diffraction diagrams of two films with the same chemical composition (Sample 1) but different thicknesses, after being quenched from 700 °C. (a) $t = 0.6$ μm, (b) $t = 0.2$ μm. (○) Garnet, (△) orthoferrite.

After the thermal decompositions, the films become amorphous oxides, which then crystallize the temperature of about 600 °C. The intermediate orthoferrites observed in the thicker films (Fig. 4) may result from the chemically inhomogeneous segregations as the viscosity of the films increases during the decompositions of the bismuth and iron nitrates or acetylacetone, since both cases are accompanied by a large weight loss (Figs 1 and 2). These segregations seem to result in chemically inhomogeneous amorphous oxides after the decompositions are completed. Previous studies [9, 10] have shown that the iron ions diffuse faster than the yttrium ions. Therefore, once the inhomogeneous oxides are formed, they crystallize to orthoferrites. The following example reactions for Solution 1 (see Table I) are

$$\underset{\text{(amorphous)}}{1.5Bi_2O_3} + \underset{\text{(amorphous)}}{1.5Y_2O_3} + \underset{\text{(amorphous)}}{5Fe_2O_3} \xrightarrow{600\,^{\circ}\mathrm{C}} \underset{\text{(crystalline)}}{6(Bi,Y)FeO_3} + \underset{\text{(amorphous)}}{2Fe_2O_3} \quad (1)$$

As the diffusion proceeds further, the orthoferrite $(Bi,Y)FeO_3$ transforms to the garnet $(Bi,Y)_3Fe_5O_{12}$ by absorbing more iron ions.

$$\underset{\text{(crystalline)}}{6(Bi,Y)FeO_3} + \underset{\text{(amorphous)}}{2Fe_2O_3} \xrightarrow{750\,^{\circ}C} \underset{\text{(crystalline)}}{2(Bi,Y)_3Fe_5O_{12}} \qquad (2)$$

The orthoferrites hinder the garnets from forming directly from the amorphous oxides at low temperature. While not shown, the orthoferrite was not observed even in the films thicker than 0.3 μm prepared by multiple spin-coating thin layers.

5. Conclusions

The thermal decomposition and crystallization processes of aqueous and acetylacetonic films have been investigated. It was found that the aqueous films decompose with endothermic reactions over a broad temperature range from 80–500 °C, while the acetylacetonic films decompose with strong exothermic reactions at temperatures of 130 °C and 250–400 °C. Both films decomposed to become amorphous oxides, which then began to crystallize at about 600 °C. It was also found that when the amorphous oxide films were thinner than 0.3 μm, the garnets were formed directly from the amorphous oxides. However, when the films were thicker than 0.3 μm, intermediate orthoferrites were formed, which upon further heating transformed to the garnets.

References

1. T. MIZUNO and M. GOMI, *IEEE Trans. Magn.* **MAG-22** (1986) 1236.
2. W. E. ROSS, J. CHO, A. FARMER, D. N. LAMBETH, T. LE, S. SANTHANAM and D. STANCIL, *Proc. SPIE* **1704** (1992) 26.
3. R. WOLFE, E. M. GYORGY, R. A. LIEBERMAN, U. J. FRATELLO and S. J. LICHT, *Appl. Phys. Lett.* **60** (1992) 2048.
4. P. PAROLI, *Thin Solid Films* **114** (1984) 187.
5. J. CHO, M. GOMI and M. ABE, *J. Appl. Phys.* **70** (1991) 6301.
6. A. ITOH and K. NAKAGAWA, *Jpn J. Appl. Phys.* **31** (1992) L 790.
7. J. CHO, M. GOMI and M. ABE, *ibid.* **28** (1989) 1593.
8. *Idem, J. Magn. Soc. Jpn* **13** Suppl. (1989) 723.
9. A. SZTANISZLAW, E. STERK, L. FETTER, M. FARKAS-JAHNKE and J. LABAR, *J. Magn. Magn. Mater.* **41** (1984) 75.
10. V. P. CHALYI and K. P. DANIL'CHENKO, *Inorg. Mater.* **10** (1974) 933.

Received 25 June 1993
and accepted 19 January 1994