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Structural and Magnetic Properties of Ag Nanoparticle (0.25%, 0.50% and 1%) doped YIG Thin Films

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This study investigated the structural, morphological and magnetic properties effects of silver (Ag) nanoparticle doping at low doping rates on $Y_3Fe_5O_{12}$ (YIG) thin films. In the first stage of the study, Ag nanoparticles were synthesized by polyol method. In the second stage, both undoped YIG and 0.25%, 0.50% and 1% doped YIG thin films were grown on thermally oxidized Si substrates using sol-gel method. All films were crystallized crack-free by a two-step heat treatment process. XRD patterns confirm the YIG crystal structure and the Ag crystal structure, which is embedded in the structure without bonding with the YIG components. SEM images revealed that the Ag NPs synthesized by the polyol method have a homogeneous distribution. The surface morphology of the thin films showed that Ag NPs doping formed small islands on the surface morphology. While the saturation magnetization (M_s) values of the samples were very close to each other regardless of the doping rate, the coercive field values (H_c) increased remarkably with Ag doping. This value tends to decrease as the doping ratio increases. 0.25% AgNPs sample has the highest H_c value. M_s values between in-plane and out-of-plane measurements of the films increased with Ag concentration. As a result of all analyses, it was observed that all crack-free thin films were successfully obtained by optimizing the production parameters of the sol-gel method, which is a relatively inexpensive and easy method. Silver nanoparticle doping was found to improve the structural and magnetic properties of YIG thin films. It is predicted that this improvement will contribute to other properties of YIG thin films used in magneto-optical applications.

1. Introduction

Yttrium Iron Garnet ($Y_3Fe_5O_{12}$; YIG) is a magnetic ceramic material that finds wide application area due to its high electrical resistance, excellent gyromagnetic performance, narrow resonance linewidth in microwave region, low magnetization damping value, good saturation magnetization and high radiation stability [1-4]. The magnetic and optical properties of YIG are due to the interactions between its sublattices. The Y^{3+} ions are considered as non-magnetic while Fe^{3+} ions are magnetic in the main lattice of YIG. The sublattice structures of YIG occupied as three Fe^{3+} ions in tetrahedral with 24 (d) sites and octahedral with 16 (a) sites correspond to the magnetization of YIG. The O^{2-} ions include 96 (h) sites in the YIG lattice [5]. Due to its unique properties, YIG has many applications in microwave devices, spintronic devices, magneto-optical applications, magnetic sensors, 5G communication technology, microwave device antennas, defense industry, medicine and telecommunications.

While many efforts to improve the properties of YIG are based on replacing ions in the crystal structure with other ions, it is important that the ions in the YIG crystal structure remain intact. This is because the magnetic properties of YIG are known to be part of this atomic order. Due to the effect of the orbital motion, which is opposite to the spin motion of yttrium, it makes the total magnetic moment of the yttrium atom parallel to the magnetic moment of iron. Therefore, instead of using an alternating doping for yttrium and iron atoms, it would make more sense to doping without disturbing the YIG crystal structure. Although many ion substitution studies have been carried out into the YIG crystal structure, Ibrahim et al. predicted that doping at low rates could have positive results on the structural properties of YIG [6]. Silver is a noble metal that has relatively reasonable price and is widely available in nature and preferred in optical

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applications. Therefore, Ag doping is considered to improve the properties of YIG thin film, a magneto-optical material. In addition, since silver is a noble metal, it is predicted to settle into the crystal structure without bonding with YIG components. [7]. Recently, a study was conducted to examine the effect of Ag and AgNPs doping on the properties of YIG thin film. It has been argued that doping silver in nanoparticle format will improve magnetic properties, regardless of the contribution rate [8]. It is important to investigate whether this effect of Ag nanoparticle will also occur at different doping rates. In some doping studies on YIG thin film, the importance of doping at low rates has been emphasised [9]. Therefore, in this study, we investigated the effect of lower amounts of Ag NPs on the structural and magnetic properties of YIG thin film. Studies on the crystal and morphological structure of YIG have gained great importance in recent years. Improving the structural properties of YIG thin films, which are frequently used in the field of spintronics, is very important for this field.

2. Results and Discussion

2.1. Microstructural Analysis

To observe the effect of Ag doping on the crystal structure of YIG thin films, XRD measurements were performed between 20°- 60°, then analyzed using X-Pert High-Score Plus software. Figure 1(a-d) shows the XRD profile of YIG, 0.25%, 0.50% and 1% Ag doped YIG thin films, respectively. The XRD patterns of the YIG thin film shown in Fig. 1a exhibit the characteristic YIG diffraction peaks with garnet structure of (400), (420) and (422) located at 2θ=28.63°, 32.13° and 35.34°, respectively. It confirms that YIG films grown on Si/SiO_2 substrate crystallize in a single-phase cubic garnet structure. For Ag-doped YIG films, in addition to the YIG crystalline peaks, a metallic Ag peak oriented at 2θ=38.25° and 44.49° (200) is clearly visible in the XRD patterns. In the XRD patterns of all samples from the substrate, a peak corresponding to Si (200) is observed at approximately 33°. The observation of both characteristic YIG peaks and Ag peaks in the XRD patterns of the thin films confirms that the samples were obtained in the desired crystal structure.

SEM images of YIG, 0.25%, 0.50% and 1% Ag NPs samples are shown in Fig. 2. Fig. 2(a-d) shows the surface morphology of the samples and Fig. 2e shows the cross-sectional image of the samples. According to the surface morphology of the thin films, all samples were grown without cracks and nucleation. With the doping of Ag NPs, small islands

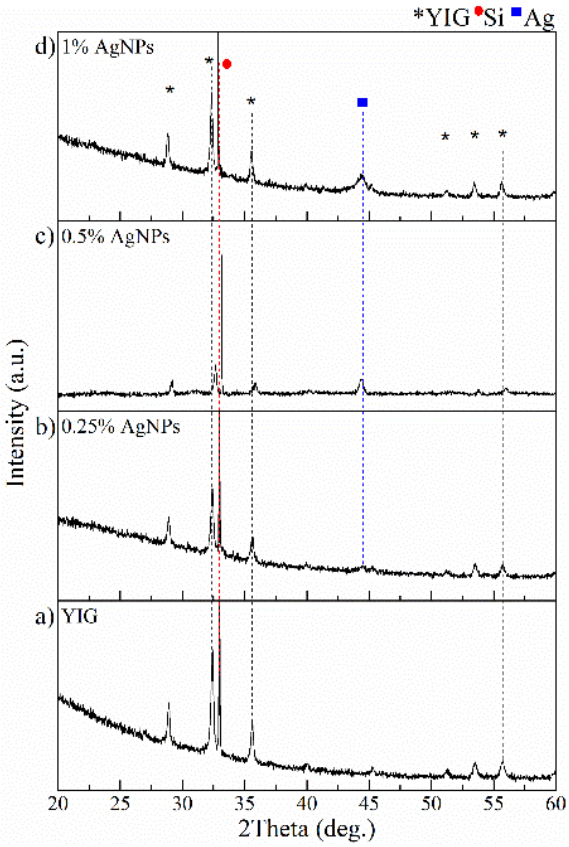

Figure 1. XRD patterns of a) YIG, b-d) 0.25%, 0.50%, 1% Ag NPs doped YIG thin films, respectively.

appeared on the film surfaces. These islands are thought to be due to the metallic nature of Ag nanoparticles. According to the cross-sectional images, the thickness of the YIG thin film is 94.44 nm, 0.25% and 1% Ag NPs doped samples have a thickness of 101.2 nm and 0.50% Ag NPs doped sample has a thickness of 91.24 nm. The non-linear variation of the film thicknesses is thought to be due to the production process of the films.

2.2. Magnetic Properties

Magnetic properties of YIG and Ag-NPs doped YIG thin films were investigated by using VSM system. The magnetic hysteresis measurements were carried out in two different ways by applying an in-plane (IP) and out-of-plane (OOP) magnetic field to the film surface at room temperature. Figure 3(a-d) shows the hysteresis curves of YIG and Ag-NPs doped YIG thin films. In all samples, the diamagnetic contribution from the substrate is subtracted from the raw hysteresis curves. It is clearly observed that the Ag doping, independent to the doping process, makes the films magnetically isotropic. M_s, H_c, H_a and K values extracted from hysteresis curves are demonstrated in Table 1.

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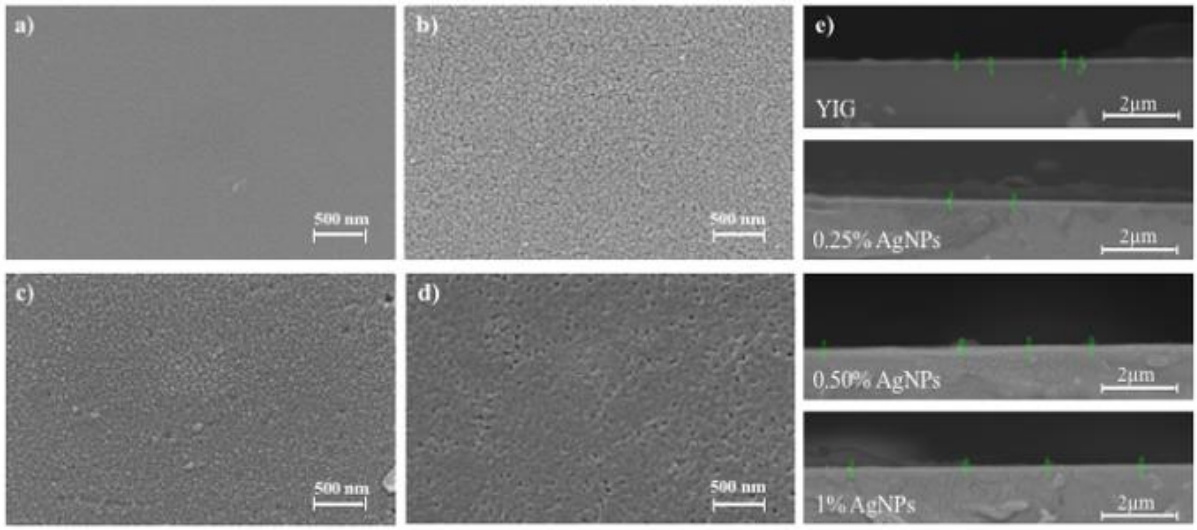

Figure 2. SEM images of a) YIG, b-d) 0.25%, 0.50%, 1% Ag NPs doped YIG thin films, respectively and e) cross-sectional SEM images of YIG and 0.25%, 0.50%, 1% Ag NPs doped YIG thin films respectively.

Although the hysteresis curves are similar, it is observed that the films exhibit isotropic properties with Ag NPs doping. An overall low coercive field (H_c) (see Table 1) is observed in the hysteresis curves of all samples, indicating that the samples are soft magnetic (ferromagnetic) at room temperature. However, the H_c values increased with Ag NPs doping and showed a decreasing trend with increasing doping ratio. This may be due to the small islands formed by the Ag doping on the film surfaces, as can be seen from the SEM images (see Fig. 2). Although Ms values of the samples were close to each other, Ms values between in-plane measurements increased with Ag concentration. Magnetic anisotropy energy values (K) are calculated using $K=M_sH_a/2$ relation and shown in Table 1. According to the calculated K values, the anisotropy energy of the undoped YIG thin film is the lowest. Silver doped samples have higher anisotropy energy values compared to the YIG sample. However, this value decreases linearly with the doping rate of Ag NPs. It is clearly seen that Ag doping makes the films magnetically isotropic, regardless of the doping process.

Table 1. Saturation magnetization, coercive field and anisotropy energy values of undoped and Ag NPs doped YIG thin films.

Samples	H_c (Oe) ∓5%		H_a x10^{-2} (kOe) ∓5%	M_s (emu/cm^3) ∓10%		K ×10^4 (erg/cm^3) ∓10%
	OOP	IP		OOP	IP	OOP
YIG	11.1	20.0	6.7	45.4	55.1	1.9
0.25%AgNPs	68.6	81.5	37.5	16.2	55.6	10.4
0.50%AgNPs	32.6	78.9	30.9	34.1	56.1	8.6
1%AgNPs	28.5	41.5	12.9	17.1	56.7	3.6

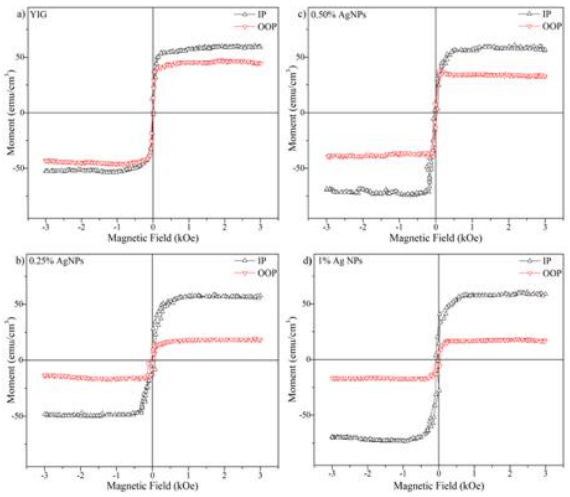

Figure 3. In-plane and out-of-plane magnetic hysteresis curves of a) YIG, b)0.25% AgNPs, c)0.50% AgNPs and d)1% AgNPs YIG thin film. All magnetic hysteresis measurements are performed at room temperature.

3. Conclusions

In summary, this study examined the effect of doping the nanoparticle form of silver, a noble metal, at low rates into the structure of the YIG thin film, on the structural, morphological and magnetic properties of YIG thin films. Ag nanoparticles were successfully produced by the polyol method, then they were added to YIG by the sol-gel method and thin films were grown on Si/SiO_2 substrates by the spin coating method. Both characteristic YIG peaks and metallic Ag peaks were observed in the XRD patterns, thus confirming that Ag settled into the

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YIG crystal structure without forming a secondary phase. The results of magnetic measurements revealed that doping Ag NPs at low rates did not significantly change the Ms value of the YIG thin film, but increased the H_c values remarkably. It was also observed that Ag NPs doped samples exhibited isotropic behavior compared to the undoped YIG sample. This trend is a result consistent with the literature [8]. The ability to successfully produce low-rate Ag NPs-doped YIG thin films grown on Si substrates in a non-vacuum environment with a low-cost production method will pave the way for their widespread use in magnetic devices. Based on this study, it is thought that by examining the optical properties of the samples, a broader idea can be obtained on the optical and magneto-optical properties of YIG by doping Ag NPs at low rates, and thus YIG thin films with low production and doping costs can be developed.

Method

Experimental Procedure

Ag-nanoparticles doped YIG thin films were produced by sol-gel and spin coating method. Ag nanoparticles to be used in doping were synthesized using the polyol method. The sol-gel method was then used to synthesize Ag NP doped YIG thin films.

Synthesis of Ag nanoparticles by Polyol Method

Figure 4a shows the production scheme of Ag nanoparticles. In this method, silver nitrate ($AgNO_3$) was used as starting salt, ethylene glycol (EG) as solvent and polyvinylpyrrolidone (PVP) as coating agent to adjust the shape and size of nanoparticles.
All steps shown in Figure 4a are listed as follows:
1. PVP in predetermined cytokiometric ratios was dissolved in ethylene glycol at 120 °C 600 rpm for 30 minutes (solution color turned light yellow).
2. When the temperature reached 120 °C, $AgNO_3$ dissolved at room temperature in ethylene glycol in an ultrasonic bath was transferred into a three-necked flask. The solution was allowed to stir at 160 C for 4 hours (solution color changed from brown to black).
3. The solution was cooled to room temperature.
4. Ag nanoparticles were centrifuged at 9000 rpm using acetone and ethanol.
SEM images of Ag nanoparticles obtained at the end of the process are shown in Figure 4b.

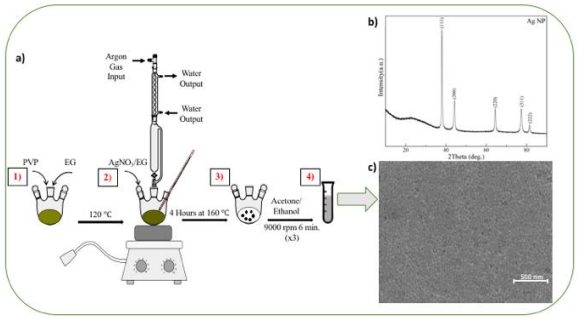

Figure 4. Schematically illustrated of a) Ag NPs synthesing process, b) XRD pattern of Ag NPs and c) SEM image of Ag NPs

Fabrication of Ag Nanoparticles Doped YIG Thin Films

The chemical solution of YIG films was prepared as follows; in appropriate stoichiometric ratios of yttrium (III) nitrate tetrahydrate ($N_2O_6Y{\cdot}4H_2O$) with purity 99.99% (Aldrich), iron (III) nitrate nanohydrate ($Fe(NO_3)_3{\cdot}9H_2O$) with purity 98.0% (Alfa Aesar) were separately dissolved in 2-methoxyethanol. Then both solutions were mixed and allowed to stir for 48 hours at 50 °C. (100) oriented Si is the most commonly used substrate in growhting YIG thin films [10-12]. Therefore, we used thermally oxidized Si substrate to be a buffer layer between YIG and Si [13]. Two-stages spin-coating process was used to grow YIG films that the solution is dropped on the substrate and it releases to accelerate to 1000 rpm in 10 s and then accelerate immediately to 3000 rpm for 59 s. Then, grown films were dried at 110 °C for 30 min in ambient atmosphere to burn off the organic solvents. For Ag nanoparticle doped YIG; The synthesized Ag nanoparticles were added to the YIG solution (see Figure 5a). The mixture was stirred for 48 hours. From now on, the same growth process that we applied to the YIG thin films was used.

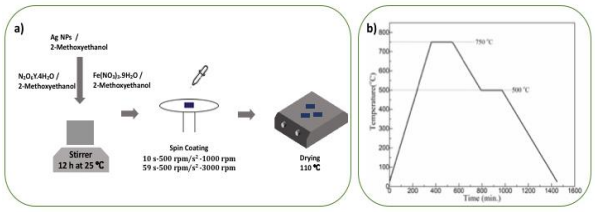

Figure 5. Schematically illustrated of a) Ag-doped YIG thin film production steps, b) Heat treatment stages for the final thin films.

Figure 5b shows a representative graph of the applied two-stage heat treatment process. The films

were heated to 750 °C with a heating rate of 2 °C/min and kept at this temperature for 3 hours. Afterwards, the films were cooled to 500 °C with a cooling rate of 1 °C/min and kept at this temperature for 3 hours. Finally, it was cooled to room temperature with a cooling rate of 1 °C/min. Thus, no crack formation is observed in the films thanks to the gradual cooling process.

Characterization Techniques

X-Ray Diffraction (XRD) with Cu-Kα radiation was used to determine the phase formation and the structural properties of the films. The microstructure and surface properties were studied by Scanning Electron Microscope (SEM). Physical Properties Measurement System (PPMS) with Vibrating Sample Magnetometer (VSM) head was used to characterized the magnetic properties of samples at room temperature.

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Conflicts of Interest

The authors stated that did not have conflict of interests.

Author Contributions

ND: Performed experiments/data collection, data analysis and interpretation, drafted the paper, provided grammatical revisions to manuscript, provided revisions to scientific content of manuscript.
MA: Performed experiments/data collection, data analysis and interpretation, provided grammatical revisions to manuscript, provided revisions to scientific content of manuscript.
FK: Data analysis and interpretation, provided grammatical revisions to manuscript, provided revisions to scientific content of manuscript.
AE: Data analysis and interpretation, edited the paper, provided grammatical revisions to manuscript, provided revisions to scientific content of manuscript.

Data Availability Statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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