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Modification of Nanoparticle Films with Inductively-Coupled High-Pressure RF Plasmas

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We have tried modification of $Y_3Fe_5O_{12}$ nanoparticle films in high-density RF plasmas sustained at high operating gas pressure. Experiments for pure Ar plasma showed phase separation which occurred by oxygen deficiency and no phase transformation to YIG. Modification by adding Ar gas to oxygen gas results in significant structure change. These results suggest that the plasma sustained for $Ar+O_2$ mixture gas have enough enthalpy for phase transformation. The addition of oxygen in Ar plasmas is effective for suppression of phase separation and enhancement of phase transformation to YIG. Rate of phase transformation in high-density plasma is fast compared to that in conventional annealing using electric furnace which requires for 30 min at 900 °C to transform to YIG.

Key words: Yttrium iron garnet, nano-composite, plasma treatment, ceramics, deposition

1. INTRODUCTION

Yttrium iron garnet (YIG, cubic $Y_3Fe_5O_{12}$) have attracted considerable attention as functional materials in the variety of applications to photo catalysts, gas sensors, microwave devices and magneto-optical devices [1-5]. Particularly, YIG nanoparticles with < 100 nm are expected to enhance their functionalities and/or to improve their performance when nano-composite materials are formed with inclusion of the nanoparticles. Nano-composite materials of YIG are applicable to media for high-density magnetic or magnetooptical information storage [6,7].

Synthesis of YIG nanoparticles from corresponding oxides (Y_2O_3 and Fe_2O_3) and production of YIG nanoparticles by modification of yttrium iron oxide nanoparticles [6] requires high annealing temperature. Especially the modifications of yttrium iron oxide nanoparticles using the conventional annealing processes involve problems associated with agglomeration nature of nanoparticles, which hinders retention of functional nano structure mainly due to easiness of sintering and formation of complex oxide compounds. Therefore development of techniques to prevent problems associated with agglomeration nature of nanoparticles is required.

To meet these requirements, we developed nanoparticle modification techniques in high-density RF plasmas sustained at high operating gas pressure. The new technologies for modification of nanoparticles were suitable for controlling phase structures and chemical states of surfaces without coagulation.

In this paper, for production of YIG nanoparticles by modification of yttrium iron oxide nanoparticles, modifications of phase structures of $Y_3Fe_5O_{12}$ nanoparticle films are demonstrated to exhibit modification capabilities of nanoparticles by high-density plasmas. Furthermore effects of discharge gas on phase structures of $Y_3Fe_5O_{12}$ nanoparticle films are also reported.

2. EXPERIMENTAL

2.1. Preparation of $Y_3Fe_5O_{12}$ nanoparticle films

In this study, $Y_3Fe_5O_{12}$ particles (Hosokawa Micron Corporation) with hexagonal phase, an average size of 30nm were used for precursor of YIG nanoparticles. $Y_3Fe_5O_{12}$ nanoparticle films were prepared on Si substrate by electrophoretic deposition. Figure 1 shows experimental set-up of an electrophoretic deposition (2007) system. Electrophoretic deposition is a combination of two processes: electrophoresis and deposition. Electrophoresis is the motion of charged particles in a suspension under the influence of an electric field. The electrophoretic deposition was employed an ethanol suspension of 5 wt% $Y_3Fe_5O_{12}$ particles. Si substrate and

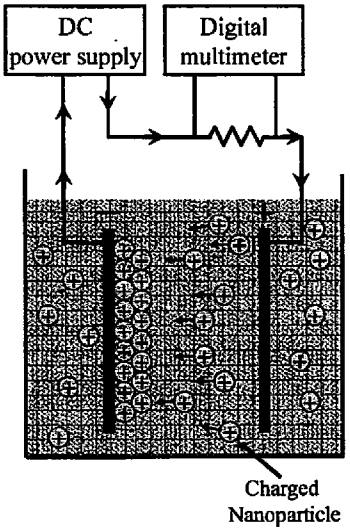

Fig. 1. Schematic diagram of electrophretic deposition system.

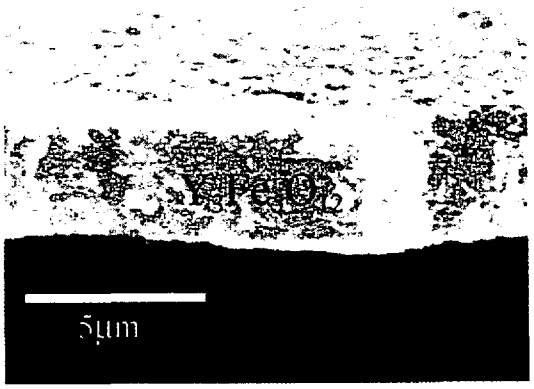

Fig. 2. Cross-section SEM image of $Y_3Fe_5O_{12}$ films deposited by electrophoretic deposition

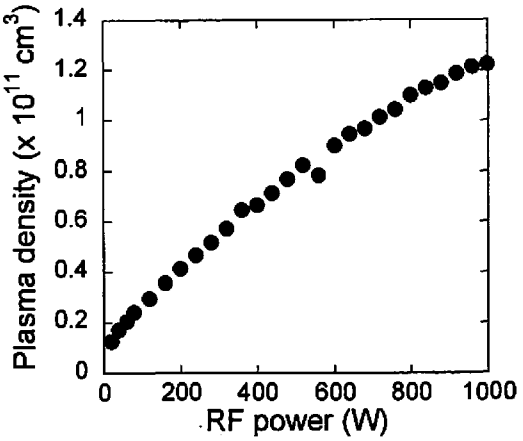

Fig. 4. RF power dependence of plasma density for argon plasmas at pressure of 26.6 Pa.

Pt plate were used for the deposition electrode and for the counter electrode. The supplied voltage was 10 V and deposition time was for 1 min. The thickness of $Y_3Fe_5O_{12}$ nanoparticle films was about 3 μm. Figure 2 shows cross-section SEM image of $Y_3Fe_5O_{12}$ nanoparticle films deposited by electrophoretic deposition.

2.2. Modification of $Y_3Fe_5O_{12}$ nanoparticle films using high-density plasma

The Schematic diagram of chamber for modification of $Y_3Fe_5O_{12}$ nanoparticle film by plasma exposure is shown in Fig.3. A water-cooled copper coil antenna (five turns) was looped around alumina discharge tube 17 mm in outer diameter and 13 mm in inner diameter. The antenna is coupled to a 600 W RF power generator at 13.56 MHz via a matching network. Pure Ar and Ar+O_2 mixture gases were supplied from upstream of the discharge tube. The total pressure was 26.6 Pa. Si substrates with $Y_3Fe_5O_{12}$ nanoparticle films were located at downstream side of 20 mm from the copper coil antenna.

Plasma density was measured with a cylindrical Langmuir probe which was located at downstream region 150mm from grounded side of antenna. The crystalline structure of $Y_3Fe_5O_{12}$ nanoparticle films was analyzed using X-ray diffractometer (XRD: JEOL JDX-3530M). Cross-section and surface morphology of nanoparticle films were studied with a scanning electron microscope (SEM: ELIONIX ERA-8800FE).

3. RESULTS AND DISCUSSIONS

To investigate characteristics of plasmas for modification of $Y_3Fe_5O_{12}$ nanoparticle films, plasma density at downstream region 150mm from grounded side of antenna was measured at an Ar pressure of 26.6 Pa. Figure 4 shows RF power dependence of plasma density for argon. The plasma density increased with increasing RF power and the density as high as 10^{10}-10^{11} cm^{-3} was observed at downstream region. From this result, plasma density at generation region is expected to be higher than that at downstream region.

Using the high-density plasmas, we have tried modification of $Y_3Fe_5O_{12}$ nanoparticle films deposited by electrophoretic deposition. Figure 5 shows XRD patterns of $Y_3Fe_5O_{12}$ films exposed by pure Ar plasmas sustained at RF power of 600W for 10 s. The XRD pattern showed no existence of YIG and a separation to orthorhombic, Fe_2O_3, Y_2O_3 and Fe phases. The presence of Fe phase is considered to be due to deficiency of oxygen in the

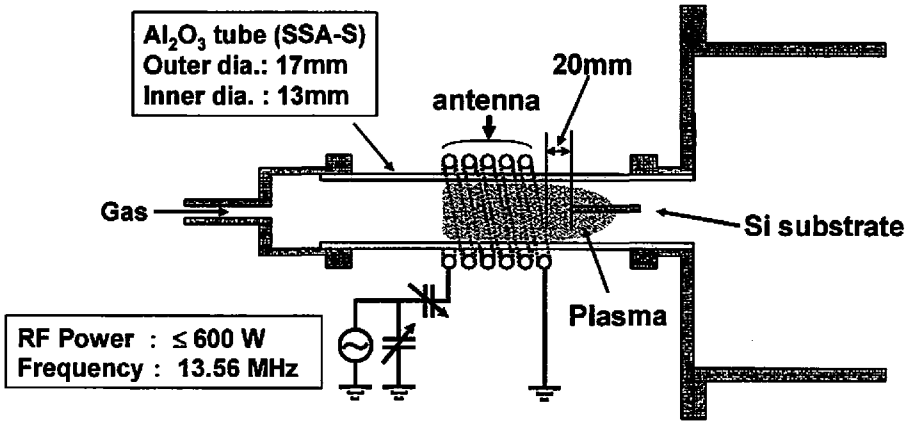

Fig. 3. Schematic diagram of chamber

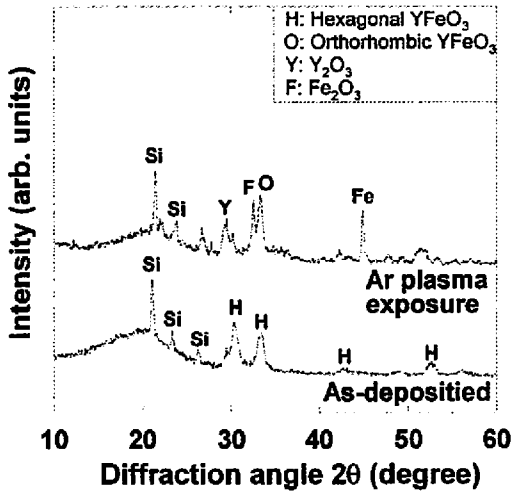

Fig. 5. XRD patterns of $Y_3Fe_5O_{12}$ films exposed by Ar plasmas.

plasmas since both high temperature and low oxygen partial pressure generally favor the reduction of oxide materials [8]. Therefore, theses results indicate that the phase separation occurred by shortage of oxygen.

Based on these results, we demonstrated modification of $Y_3Fe_5O_{12}$ nanoparticle films exposed by plasmas sustained for $Ar+O_2$ mixture. Figure 6 shows XRD patterns of $Y_3Fe_5O_{12}$ nanoparticle films exposed by $Ar+O_2$ mixture plasmas sustained at a RF power of 600W for 10 s. The XRD results for samples exposed by

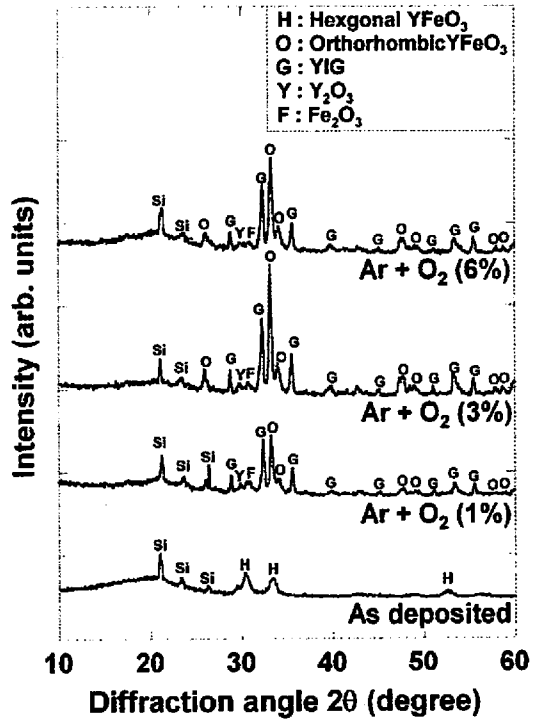

Fig. 6. XRD patterns of $Y_3Fe_5O_{12}$ films exposed by plasmas sustained for $Ar+O_2$ (1,3,6%)

plasmas sustained at $Ar+O_2$ mixture gases showed existence of YIG and suppression of phase separations to Fe_2O_3, Y_2O_3, and Fe phase was not observed from the XRD results. These results exhibit that addition of oxygen in Ar plasmas is effective for suppression of phase separation and enhancement of phase transformation to YIG. Furthermore this structure change suggests that these plasmas have enough enthalpy for phase transformation to YIG. However the XRD results for $Ar+O_2$ mixture gases also showed orthorhombic phase. The presence of orthorhombic phase indicates that $Y_3Fe_5O_{12}$ nanoparticle films melted due to heating at high temperature above 1800°C by plasma exposure for 10s [8, 9].

Variation of phase structure of $Y_3Fe_5O_{12}$ nanoparticle films on exposure time to plasmas was investigated. The XRD result for sample exposed by plasma for 5 s showed phase transformation to only YIG (not shown here). This result exhibits that the $Y_3Fe_5O_{12}$ nanoparticle film was heated to a temperature required for phase transformation to only YIG by the plasma exposure for 5 s. The rapid heating is considered to be caused by which the nanoparticle films are heated by bombardment of incident ions to the films from the high-density plasmas. Rate of the phase transformation in the modification using high-density plasmas is fast compared to that in conventional annealing using electric furnace which requires for 30 min at 900 °C to transform to YIG.

4. CONCLUSIONS

We have tried modification of $Y_3Fe_5O_{12}$ nanoparticle films in high-density RF plasmas sustained at high operating gas pressure. Experiments for pure Ar plasma showed phase separation which occurred by oxygen deficiency and no phase transformation to YIG. Modification by adding Ar gas to oxygen gas results in significant structure change. These results suggest that the plasma sustained for $Ar+O_2$ mixture gas have enough enthalpy for phase transformation. The addition of oxygen in Ar plasmas is effective for suppression of phase separation and enhancement of phase transformation to YIG. Rate of phase transformation in high-density plasma is fast compared to that in conventional annealing using electric furnace which requires for 30 min at 900 °C to transform to YIG.

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