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Engineered magneto-optical response of cobalt ferrite thin films deposited on self-assembled colloidal crystal

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ABSTRACT

Oriented growth of patterned cobalt ferrite magnetic thin films on polymeric colloidal crystal films has been carried out employing a room-temperature pulse laser deposition method. The series of colloidal crystal films containing uniform polystyrene particles (180–420 nm) were prepared by self-assembly. Scanning electron microscopy and optical reflectometry were used to confirm the assembly of well-arranged colloidal crystal films. Magnetic films of different thicknesses were deposited. X-ray diffraction measurements confirmed the nano-crystalline structure of cobalt ferrite grown on the spherical-shaped surface. Magneto-optical effects of the patterned thin films were examined and the results illustrated that the increase in film thickness leads to the decrease in coercivity, while the saturation magnetization increases. Furthermore, the magnetic origin of the coercivity variation dependence on the colloidal diameter and film thickness are discussed. Our results suggest that the preparation conditions of the deposited films should be tailored to obtain perpendicular anisotropy in cobalt ferrite films. The adjustable magnetic anisotropy was obtained due to substrate-induced magnetic shape anisotropy.

1. Introduction

Shape-induced tunable magnetic anisotropy is an ongoing research trend in the field of nano-sensors, switches, and recording device fabrication [1–5]. A common practice in the fabrication of many of these devices is of the use of epitaxial growth or textured magnetic oxide materials; as promising techniques to achieve adjustable perpendicular magnetic anisotropy [6–8]. Such anisotropy has been obtained following the implementation of different frameworks including thin film hetero-structures [9] and other composite nanostructures [10]. Regarding these structure frameworks, numerous studies have been conducted to investigate the influence of the interface strain and the shape anisotropy on the modification of the magneto-crystalline anisotropy direction [11–14].

Shape anisotropy effects were well scrutinized for certain magnetic ferrite materials such as $CoFe_2O_4$ (CFO), thin film of which shows spiral structure [15], high resistivity [16], large permeability [16], high magnetostriction coefficient [17], tunable coercivity [18], and the highest magneto-crystalline anisotropy constant [17]. These features of CFO have been subjected to wide-range applications such as microwave devices [19], resistive switching [7,8,20], and magneto-optic media [21]. So far, the adjustability of the CFO strain, as well as the anisotropy, depends primarily on the choice of the substrate [22], thermal treatment process [23,24], post-deposition annealing [25], and deposition process [26] employed.

Among various deposition techniques, pulsed laser deposition (PLD) is employed as an advantageous method to grow magnetic films with large magnetic anisotropy and high perpendicular coercivity [3,7]. These films can be produced by magnetic thin film epitaxial growth along the magnetic easy axis perpendicular to the substrate [8]. To this end, a crystalline film growth is provided to overcome the film magnetic shape anisotropy energy [24]. Such crystalline films have been grown on various rigid solid substrates such as $Pt/TiO_2/SiO_2/Si$ [7], MgO/Si [8] and $SrTiO_3$ [3,27] with indispensable elevated substrate temperatures for spin-coating deposition, PLD, and pulsed laser molecular beam deposition, respectively, or post-deposition annealing. In contrast, the PLD technique at a deposition temperature of 300 K (room-temperature PLD) has been applied recently to produce crystalline oxide materials utilizing soft polymer substrates [28–30].

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The polymer materials are well-suited cost-effective substrates owing to their flexibility, high thermal expansion coefficient, and low heat conductivity [31]. Using multiple preparation conditions, these materials can be assembled in various shapes in particular using spherical colloid particles [32,33]. There are several ways to arrange these colloids to construct a colloidal crystal film [34,35]. It has already been demonstrated in our previous work that applying a colloidal film as a substrate, room-temperature PLD may be utilized to fabricate bismuth ferrite thin films [36]. In addition, a polymer, flexible substrate can induce stress on the film for tuning the optical and magnetic properties of ferrite thin films through strain-induced engineering of magnetic anisotropy.

In this manuscript, two series of experiments have been performed to investigate the effect of film thickness and the diameter of the colloidal substrate to further explain magnetic and shape anisotropy effects. The study confirms that the preparation conditions of CFO thin films can be tailored to obtain perpendicular anisotropy behaviour.

2. Experiments and methods

2.1. Preparation of colloidal crystals film

Anionic polystyrene (PS) spheres with 180 nm, 260 nm, and 420 ± 5 nm diameters were prepared using different weight percentages of Polyvinylpyrrolidone (PVP, Aldrich, K-30) emulsifier in terms of styrene (St, Aldrich, 99%) monomer in ethylene-propylene copolymer. It was heated to 70 °C, and the aqueous potassium persulfate (KPS, Merck Chemicals, 99%) initiator was added to the mixture to initiate the polymerization. The mixture was stirred for about 15 min at 300 rpm, whereupon St and PVP were added to the same amount of deionized water in a three-neck round-bottom flask in a water bath. For the spheres with 260 nm diameter, sodium bicarbonate ($NaHCO_3$) was also used. The reaction mixture was deoxygenated at room temperature for 30 min. When the temperature was increased to 75 °C, a solution of KPS was added to initiate polymerization. It was kept at this temperature (75 ± 5 °C) for 24 h. Finally, the mixture was kept in the lab to reach the room-temperature.

To fabricate good quality colloidal crystals, monodisperse PS particles were well-dispersed in a water solution and the colloidal suspension was then dried on a glass substrate. A three-dimensional order of the colloidal crystal films emerged owing to the inter-particle electrostatic repulsive force. To control the water evaporation rate, the 25 mm × 25 mm glass substrate was placed in a watch glass. The prepared colloidal suspension was thereafter stirred and dropped on the substrate. To avoid coffee ring defects, the upper surface of the substrate was accurately covered with a low viscosity liquid silicone (Grade: SF1000NFX010, KCC Silicone, Korea). The colloidal suspension was dried on the glass sheets at 32 °C. For transmission and reflection spectroscopy of the colloidal crystal films, a fibre optic UV–VIS-IR spectrometer (Ocean Optics Co.) was used and scanning electron microscopy (SEM) and optical microscopy (Axio Cam Co.) were conducted to characterize them. These measurements confirmed the large-area assembly of the three-dimensional colloidal crystal films.

2.2. Deposition of CFO film

To deposit the simple magnetic ferrite thin film, a particularly apt method using the room-temperature PLD was previously reported [36]. Applying a similar methodology, CFO thin films on polymer colloidal crystals and a glass (to compare) were deposited. The features of the studied samples are given in Table 1. Except for the deposition time, the CFO films were deposited in the same deposition parameters.

Table. 1
Characteristics of different $CoFe_2O_4$ thin films prepared on various deposition time, nominal thickness and colloidal crystal diminutions.

Samples	Colloidal diameter (nm)	CFO film thickness (nm)	Deposition time (min)
C0	180	40	1.5
C1	180	80	2.5
C2	180	160	4
C3	260	160	4
C4	420	160	4

An optimized repeatable deposition condition for an epitaxial growth was achieved using the third harmonic of Nd: YAG pulse laser beam at 10 Hz and a vacuum chamber (4.5×10^{-5} Pa). The laser pulse fluence was selected to be 2 J/cm^2 and the target to substrate distance was held at 3 cm. The deposition rate was approximately 0.5 Å/pulse. By exploiting the deposition rate and the relative differences of the deposition time, nominal CFO thicknesses were estimated within the experimental error (10 nm).

2.3. Characterization and magneto optical measurement of CFO films

The magnetic properties of the CFO thin films were investigated using a magneto-optical (MO) Faraday and longitudinal Kerr setups (error $= \pm 0.001°$) [37]. The setups included a modulated laser beam ($\lambda = 635$ nm), a lock-in amplifier, and a balanced amplified photodetector. The polarization state of the incident beam was carried out by a quarter wave plat between two sheet polarizers and the polarization state of the transmitted light was separated by a Wollaston polarizing prisms. A DC magnetic field from −500 to 500 mT (15 mT steps) has been exerted to the sample using a programmable power source station with LabVIEW interface. The output of lock-in amplifier was simultaneously recorded by a general propose interface bus. To increase the accuracy of the experimental data in MO loop, measurements were performed for at least four sets of magnetic field sweeps. Finally, MO response of the glass substrate was subtracted from all output data.

3. Results and discussion

3.1. Structural characterization

To characterize polymer colloidal crystal films whose periodic lengths are several hundred nanometres of the light wavelength, the photonic band-gaps (PBGs) can be visualized as Bragg reflection colours. Fig. 1 shows the normal-incidence reflection spectrum of the bare synthesis colloidal crystals, which consists of distinct spherical colloid diameters. The maximum reflection wavelength (MRW) is numerically expressed by Bragg's equation with Snell's law [38]. The well-arranged 180 nm spherical PS colloids (Fig. 1a) show two centres of MRWs at 415 and 234 nm for a beam impinging on an (111) plane of the fcc structure which agrees completely with Bragg's reflections 402 nm and 201 nm, respectively. In addition, the center of MRW is at 600 nm for 260-nm colloidal crystal (Fig. 1b) and 978 nm in 420-nm colloidal crystal (Fig. 1c). These Bragg reflections are consistent with the calculated ones (582 nm for 260-nm colloidal crystal and 940 nm for 260-nm colloidal crystal). Moreover, the right-hand panels of Fig. 1(d, e, f) show SEM images of the monodisperse spherical PS particles of the different colloidal crystal substrates.

The thickness dependence of optical response in CFO patterned films coated on colloidal crystal films has been studied. The normal transmittance spectra of 40 nm and 80 nm CFO thin films on the same 180 nm colloidal film substrates have been shown in Fig. 2. The spectrum of the CFO film with the 80 nm CFO thin film on a glass was depicted to demonstrate CFO layer transmittance curve. It is found that the increase of the magnetic material thickness in colloidal films leads to a decrease in transmissivity and a change in their PBG appearance owing to the dominance of the CFO layer transmittance curve.

The nano-crystalline CFO thin films which were grown on different substrates with the same deposition time (4 min) were characterized by the typical wide-angle $\theta - 2\theta$ XRD and small incident angles i.e.