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PULSED LASER DEPOSITION OF $NiFe_2O_4$ THIN FILMS

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Thin $NiFe_2O_4$ ferrite amorphous and crystalline films were grown on different substrates. The energy of the laser beam, the O_2 pressure, the substrate temperature, and the distance between the target and the substrate were varied in order to establish the optimal deposition conditions for the thin films. The microstructure of the thin films was characterized by XRD, SEM, EDX and AFM analysis. The characteristics of the investigated specimens were interpreted in terms of the role of the post annealing condition on the microstructure, on stoichiometry and on the magnetic properties of the $NiFe_2O_4$ thin films.

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1. Introduction

Bulk ferrites are widely used in electronics. Soft magnetic thin films with high electric resistivity are needed for developing microinductors and microtransformers [1]. The ferrites are also used in discrete microwave devices. For integrated planar circuits operating at high frequencies however, designs based on thin ferrite films are expected to have important application. Generally, magnetic properties of ferrite films are more sensitive to crystalline disorder than those of metal films, such as permalloy. An important step in realization of planar ferrite devices is the study of the influence of the microstructure on the magnetic properties.

In the 80’s for Ni ferrite characterized by ultrafine particles was observed a small low temperature magnetization and very high saturation field [2]. Recent studies have revealed similar effect in thin films [3]. Margulies consider that the reduced magnetization with only asymptotic saturation observed in their sputtered Ni ferrite films may be due to anisotropy caused by comprehensive strain to the thin film plan. This is the result of the differences between the lattice constants of the MgO substrate and of Ni ferrite thin film. Using same RF sputtering procedure was grown Ni ferrite films at 600 ^oC on $SrTiO_3$ substrate [4]. The films consist of small crystalline grains surrounded by thin region of amorphous material. These disordered regions strongly affect the magnetic behavior, resulting in extremely high saturation fields and giving rise to unidirectional anisotropy when the films are cooled in a field. Postdeposition annealing at 1000 ^oC improves the crystallinity of the films, at the same time reducing the field required for saturation [5]. Was observed that the interlayer exchange coupling increases when the bilayer is annealed at temperatures below 600 ^oC. At higher annealing temperature the overlayer crystallize and becomes ferrimagnetic with the bulk magnetization of Ni ferrite.

The last years demonstrate a growing interest in plasma laser deposition (PLD) of Ni ferrite films. The deposition of multilayer thin films alternating ferrimagnetic and antiferomagnetic phases it is an actual research field [6,7]. The interest is justified also by wide variety of the multilayers deposited by this technique [8-10] and by their application. The stoichiometry of the target is faithfully reproduced in the films if the conditions of the PLD of the thin film are judiciously picked. The deposition “in situ” of the oxide materials without predeposition processes is an important advantage of the PLD technique, which is also simple, and with low cost. Another advantage of is the

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deposition of the multi-layers thin films carried out by changing the gas pressure or the substrate temperature or the target. Oriented Ni ferrite films with different orientation on different substrate have been reported [11] ten years ago. Sputtered films growth usually requires a postdeposition annealing to develop the spinel structure and preferential (h h h) textured structure of the ion beam sputtered films were observed after thermal treatment [12].

Single step deposition of single phase $NiOFe_2O_3$ ferrite films prepared by PLD on different substrate from bulk ferrite targets were reported [13]. Single crystal (111) oriented Ni ferrite film were grown onto C-plane sapphire substrate. Polycrystalline highly (400) textured Ni ferrite film were grown onto R-plane sapphire substrates. The interest it is to obtain films having the easy direction of the magnetization perpendicular to the film plane. For Ni ferrite the easy direction of the magnetization is along the (111) direction.

In many cases the main interest is to obtain highly structured films on silicon, glasses or quartz substrates for electronic devices. In such cases the temperature of the substrates and the post deposition thermal treatment temperature is limited. The temperature of the substrates is a very important factor and the microstructure of the films depends on this. The main purpose of this work was to clarify the influence of the substrate and of the temperature of the substrate on the microstructure of the Ni ferrite films.

2. Experimental results

An KrF excimer laser (λ = 248 nm, 20 ns pulse duration, 10 Hz repetition rate) model Lambda Physik, COMPex 102 and PLD chamber made by hand in Chang Hua University facility has been used to deposit Ni ferrite films on various substrate. The laser beam was directed at 45° from the target normal and focused on a 3.5×0.5 mm^2 area of the ablated target. A simple mechanical system was used to raster over the target surface the laser beam. Different substrates as (100) silicon, (100) Al_2O_3, (100) MgO, and glass were used. The substrate size was 10 mm $\times$ 20 mm for silicon and glass and 10mm x 10mm for Al_2O_3 and MgO substrate.

The deposition of the Ni thin films was done in a high-vacuum chamber, which was evacuated to a base pressure lower of 1×10^{-6} Torr by means of a turbo-molecular pump. The gas pressure inside the PLD chamber was measured using a cold cathode gauge and adjusted via an electronic mass flow controller. Flowing O_2 gas pressure ranging between 1 and 200 mTorr was used.

To diminish the occurrence of ferrite drops, which might be splashed out from the target during laser ablation, the process was done under 70mJ constant energy of the laser beam. The ablation spot was permanently rastered on the target surface to ablate fresh material and avoid the effects of target cratering.

The substrate temperature during deposition was between 400 – 600 °C. Before deposition, the substrates were cleaned for 15 min in acetone in an ultrasound bath, then rinsed and soaked. In all the reported experiments the target-to-substrate distance was 4 cm. The deposition time was increased from 30 min to 2 hours. *Ex situ* post deposition thermal oxidation was performed at 1100 ^{o}C, for 2 h, under the conditions of rapid heating up and cooling down rates (15 °C/min).

The film structure before and after annealing process was determined by X-ray diffraction using the SCINTAG DMS 2000 XRD equipment in a θ-2θ configuration, using the Fe K_α radiation (λ = 1.93604 Å). Lower O_2 pressure resulted in film exhibiting α-Fe and impurity phases. The film thicknesses was measured by profile meter with 5 Å resolutions. Film morphology and composition were evaluated from SEM and EDX measurements performed on a Hitachi S3000N microscope, equipped with a Horiba electron microprobe.

Spectral measurements have been performed using an UV/VIS/near-IR spectrophotometer (JASCO-V570). The optical transmittance of the samples deposited onto polished transparent glass, MgO and Al_2O_3 substrates were monitored in the range 250-2000 nm. From the optical transmittance spectra, the wavelength dependence of the refractive index and optical absorption coefficient was inferred using the transmittance envelope method [14, 15]. The optical band gap for the Ni ferrite thin films (ΔE_g) was calculated from $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plots [16]. Magnetic measurements have been made using a vibrating–sample magnetometer located at University of New Orleans.

3. Results and discussion

As shown in Fig. 1, the Ni thin films feature a smooth surface on the nanometer scale, with no grain boundaries and few sub micron droplets. The occurrence of these few ferrite droplets is the result of incomplete elimination of target splashing during laser ablation, in spite of lower energies of laser beam. High repetition rate of the laser pulses, which is required to assure high deposition rate, may cause droplets and cluster aggregates occur during ablation. We found that 5 Hz is an optimum repetition rate for growing good quality Ni ferrite thin films. The deposition rate was about 2nm/min.

Fig. 2 shows the EDX spectrum of a Ni thin film deposited on a Si substrate. The Ni, Fe and O peaks appear along with a large Si substrate peak. A very small C and significant Au peaks, due to the metallization process, was detected in the EDX spectrum. These results demonstrate that the thin film reproduces the stoichiometry of the target. Similar results were found for Ni ferrite thin films deposited on glass, MgO and Al_2O_3 substrates. The evolution of the oxygen peak in the EDX spectra showed increasing values for the oxygen signal after thermal oxidation at 1100 °C and an increasing of the grain size by nucleation.

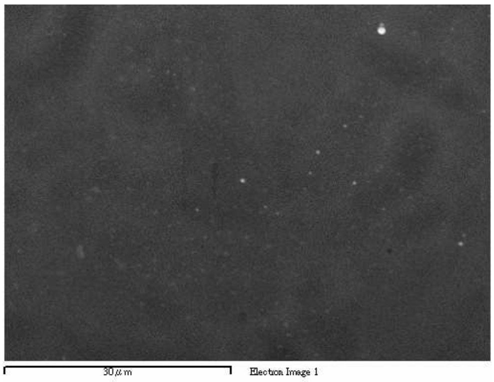

Fig. 1. A surface SEM image of a PLD Ni ferrite thin film grown on Si.

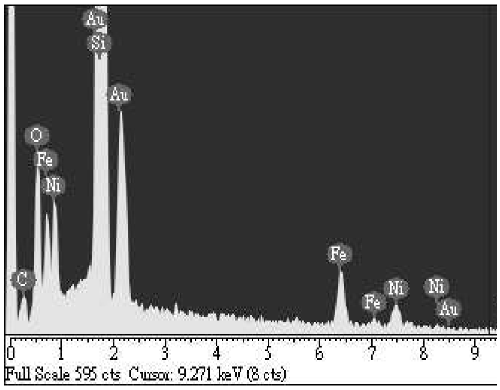

Fig. 2. The EDX spectrum of a PLD Ni ferrite thin film grown on Si.

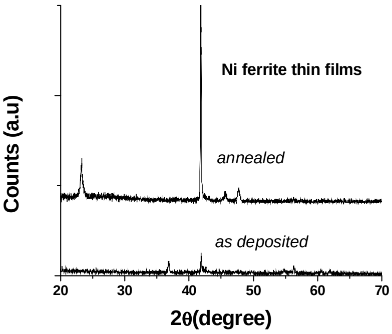

Fig. 3. A XRD pattern for a PLD Ni ferrite thin film grown on Si.

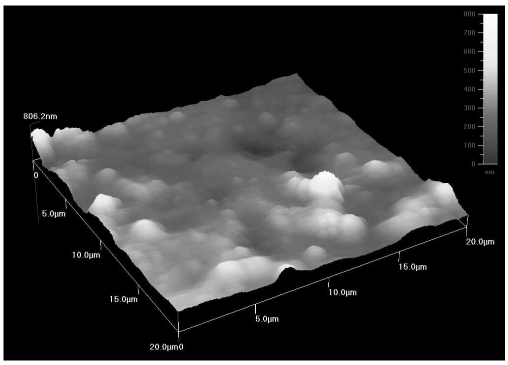

Fig. 4. The AFM picture of a PLD Ni ferrite thin film grown on Si and annealed in oxygen for 2 hours at 1100 °C.

The x-ray diffraction patterns for plasma laser deposition Ni ferrite thin film as deposited and annealed are shown in Fig. 3. The XRD patterns after annealing process straddle for phase transformation. The spinel structure becomes evident for oxidized samples. Ni ferrite films deposited onto silicon substrates exhibited predominantly (400) textured growth for temperature of the substrate ranging between 450 °C and 650 °C. In the case of Ni ferrite grown onto glass substrate an amorphous hump near 22° was observed. Similarly synthesized Ni ferrite films made onto Al_2O_3 substrates exhibited small and broadened diffraction lines, which could only be sharpened by subsequent heat treatments of the films. The AFM picture for the annealed sample, suggest a nucleation process of thin ferrite films. The microstructure of the sample deposited in oxygen at 50 mTorr for 1hour and annealed for two hours in oxygen at 1100 °C is presented in Fig. 4. The as deposited film is smooth, while the microstructure of the annealed sample becomes more rugged. Room-temperature magnetic hysteresis loops were measured for the as deposited and annealed films.

The as deposited films are amorphous and the hysteresis loops have a paramagnetic behavior. The annealed Ni ferrite films are textured structures and show magnetic behavior. The (400) Ni ferrite textured film grown on oriented silicon substrate indicates a coercive field of 389 Oe measured perpendicular to the film plane and 100 Oe measured in the plane of the films. The saturation flux density, $4\pi\ M_s$, was 2.3 kG as deduced from the approach to saturation of the perpendicular magnetization.

4. Conclusions

We investigated the morphological, structural, and magnetically properties of Ni ferrite thin films grown by PLD on various crystalline and amorphous substrates at different substrate temperature under an O_2 gas pressure ranging from of 1 mTorr to 200 mTorr. After annealing the amorphous Ni ferrite thin films become textured. The texture is influenced by the conditions of the deposition process, by the nature of the substrate and by the thermal treatment. Highly crystalline Ni ferrite thin films can also be prepared by annealing the PLD grown Ni ferrite films on quartz or silicon, on glass or Al_2O_3 substrate. The thermal oxidation at temperatures over 1000 °C results in good-quality and crystalline Ni ferrite thin films. As deposited thin films are paramagnetic at room temperature. The annealed ferrite thin films feature magnetic properties. The coercive magnetic field measured perpendicular to the film is higher that the coercive magnetic field measured in the plane of the films. More and detailed studies on the electrical and magnetically properties of the samples will be carried out in the near future.

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