

Magnetic CoPt Nanoparticles Deposition using Plasma Focus Device

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A 3.3 kJ pulsed plasma focus device (NX2) was used to deposit magnetic CoPt nano-particles on Si (100) substrates at a low charging voltage of about 8kv. The hydrogen was used as filling gas at different gas pressures (2, 4, 6, and 8 mbar) to investigate the morphological, structural and magnetic properties of nanostructure thin films, using scanning electron microscopy (SEM), X-ray diffraction (XRD), and vibrating sample magnetometer (VSM), for 25 focus shots depositions. It was observed that the nano-particles become more and more uniform and the particle-size decreases significantly with the increasing filling gas pressure. Magnetically hard fct phase CoPt nanoparticles, with high uniformity and narrow size distribution, were successfully synthesized by plasma focus device which may find application in high density data storage.

Keywords: CoPt, nanoparticles, plasma focus device(DPF)

1. Introduction

Equiatomic cobalt-platinum (CoPt) alloy films with an $L1_0$ -ordered structure have been attractive as ultra-high density magnetic recording media, because the thermal agitation of spins would be suppressed due to their very large magnetic anisotropy of about 4.9×10^7 erg/cc [1] to avoid the superparamagnetic behavior [2], even for particles with diameter of few nanometers. In particular, the interest on elemental and alloy magnetic particles is aimed at lowering down the particle size and to get uniform particle size distribution for the potential application in high density storage. CoPt nanoparticles have been produced using various techniques, mostly based on chemical methods [3] and physical thin film deposition techniques including pulsed laser deposition (PLD) [4], the radio-frequency (RF) sputtering [5], molecular beam epitaxy (MBE) [6]. In this paper, we used dense plasma focus device as a pulsed plasma deposition technique. The dense plasma focus device (DPF) [7-9] is a simple pulsed plasma device in which the electrical energy of a capacitor bank, upon discharge, is initially stored as the magnetic energy behind the moving current sheath as the sheath is accelerated along the coaxial electrode assembly. The duration of breakdown and axial rundown phase is about 1.3-1.5 μ s for NX2 device. A portion of this magnetic energy is then rapidly converted into plasma energy during the collapse of the current sheath towards the axis beyond the end of the central electrode resulting in the formation of a short lived (50-100 ns duration), but hot ($\approx 1 \sim 2$ keV) and dense ($\approx 10^{25-26}$ m⁻³) plasma. The focus

plasma column is then disrupted by $m=0$ instability accelerating energetic ions towards the top of the chamber and relativistic electrons towards the anode. More recently, the energetic ions of the plasma focus device have been used for inducing a change of phase in thin films [10], and for deposition of thin films [11]. The energetic electrons which move towards the anode ablate the anode top forming the plasma of the material whose thin film is to be deposited. L.Y. Soh et al. [12] have shown that the duration of ablated material plasma is of about 2 μ s. The use of plasma focus for thin film deposition purposes has shown that pulsed DPF possesses interesting features of high deposition rates and energetic deposition. In this paper, we report the deposition of nanostructured magnetic CoPt thin films at room temperature on Si substrates at different hydrogen filling gas pressures using repetitive pulsed plasma driver called plasma focus device. A systematic study of the structural, morphological and magnetic properties of the nanostructured CoPt thin films is presented.

2. Experiment Setup

In our investigation, a high performance low inductance capacitor bank based repetitive plasma focus machine designated as NX2 (Nanyang X-ray source 2) was employed. The schematic diagram of the deposition setup is shown in figure 1. The conventional central hollow copper anode was replaced by a high purity (50:50 at%; Kurt J. Lesker, 99.99%) solid CoPt tip fitted copper anode. The nanostructure CoPt thin films were deposited on Si

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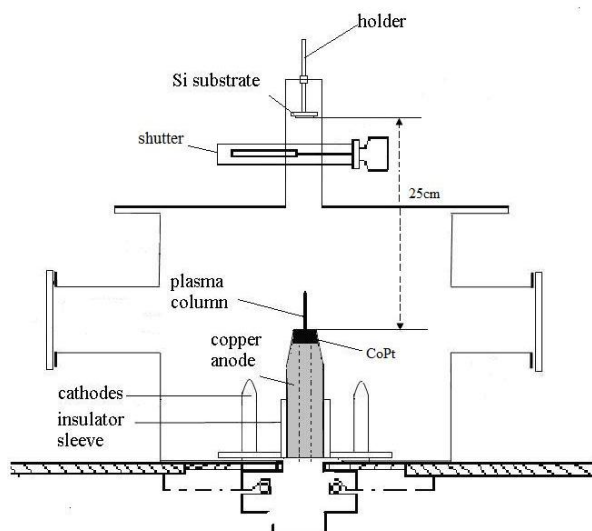


Fig. 1 Schematic of plasma focus based deposition setup.

substrates at room temperature by NX2 plasma focus device. Si substrates were placed along the anode axis at a distance of 25 cm as shown in figure 1. Hydrogen is used as the filling gas for deposition. It is well known that plasma focus operation varies from shot to shot. However, a very good consistency in focus operation, as judged from the intense peak in voltage probe and steep dip in current probe signals, was obtained over the range of filling gas pressure used in this experiment. A shutter was used, between the anode and the sample holder, to avoid deposition during the initial three to five conditioning shots. Once strong focus peak is observed in voltage probe signal the shutter was removed and thin film was deposited using a designated number of depositions. To investigate the effects of ambient gas pressure we deposited the nanostructured CoPt at different gas pressures (from 2 to 8 mbar) using 25 plasma focus deposition shots at a fixed repetition rate of 1 Hz during the entire set of investigation. The distance between the substrate holder and the anode top was fixed at a relatively bigger distance of 25 cm and the plasma focus machine was operated at the lowest focus voltage of 8 kV for entire set of depositions to achieve uniform depositions. As-deposited thin films were then annealed in a vacuum furnace at 500 °C and 650 °C for 1 hour duration.

The morphology of magnetic CoPt nanostructured thin films was measured by a JOEL JSM-6700F scanning electron microscope. X-ray diffraction (XRD) spectra of the CoPt thin films were measured by a Rigaku D/MAX-rA X-ray diffractometer with $\text{CuK}\alpha$ radiation. A LakeShore 7400 vibrating sample magnetometer (VSM) with maximum applied field of 10 kOe was used to measure the magnetic properties of the samples.

3. Results and discussion

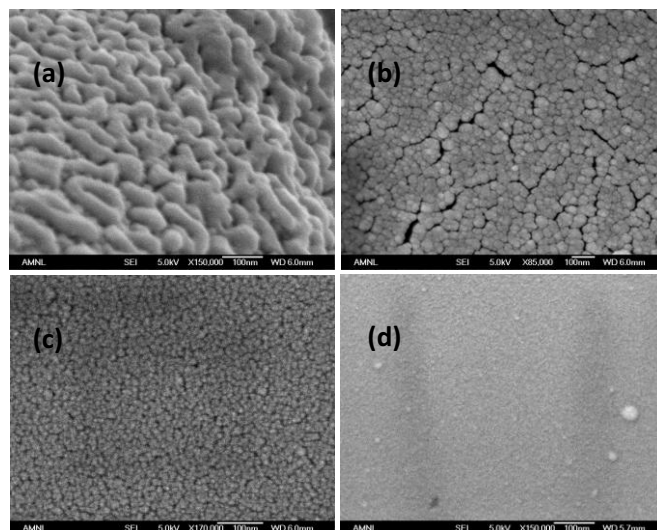


Fig. 2 SEM images of CoPt nanostructures synthesized at different gas pressures. From (a) to (d): 2, 4, 6 and 8mbar.

The morphological features of CoPt nanostructures synthesized at various hydrogen gas pressures are shown in figure 2. It can be clearly observed that two layers have been formed with the top layer sintering together to form island-like structure and some agglomerates can also be found between the nanoislands on the sub layer for the sample deposited at 2 mbar, as shown in figure 2(a). Obviously, as the gas pressure increases from 2 to 4 mbar, CoPt nanoparticles coalesced together so that only agglomerates can be observed with the average agglomeration size of 35 ± 6.0 nm, measured by the SMileView © 2000JEOL software, which were made up of small size nano-particles. Figure 2(c) shows numerous highly uniform nanoparticles, with smaller size distribution, are formed homogeneously and distinctly isolated from

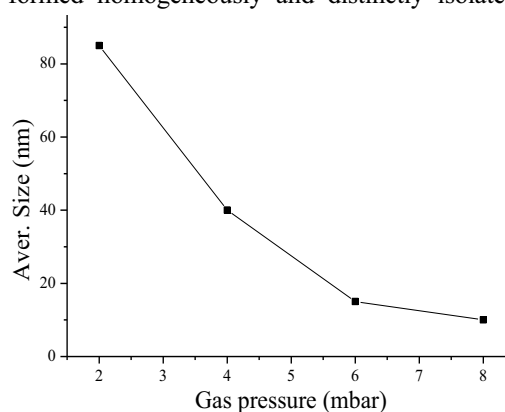


Fig. 3 The size variation with different hydrogen gas pressures each other on the sample deposited at 6 mbar. The average size of these nanoparticles is around 15 ± 3.0 nm. The smaller nanoparticles of about 10 ± 2.0 nm are observed on the samples deposited at the gas pressure of 8 mbar, seen in figure 2(d), with a few bigger size agglomerate particles on the surface. The change in the size of nanoparticles and

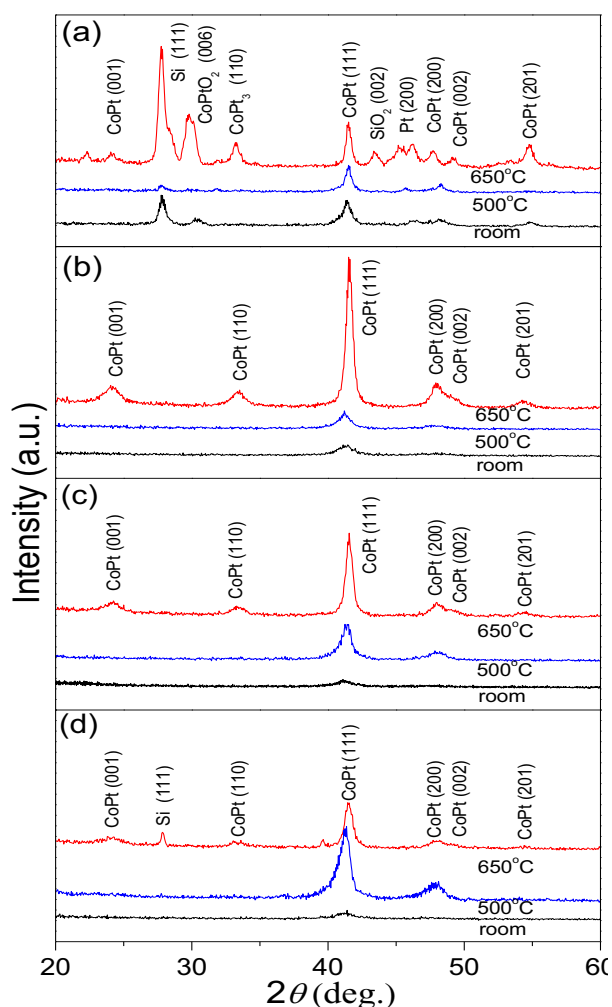


Fig. 4 XRD spectra of CoPt nanostructures synthesized at different gas pressures and annealed at different temperatures. From (a) to (d): 2, 4, 6 and 8 mbar.

nanoparticle agglomerates with increasing filling gas pressure is shown in figure 3.

The changes in morphology and the reduction of agglomerate size with the increasing filling gas pressure are essentially controlled by two factors; (i) the decrease in focusing efficiency with increasing gas pressure which resulted in lesser number of ablated ions from the anode target with lower kinetic energies, and (ii) with the increase ambient gas pressure collision frequency between the ablation ions and the ambient gas will increase which causes the ablated ions to lose more energy during its movement to substrate from the anode. Vice versa, at lower gas pressure the ions/particles reach the substrate surface with greater energy as efficient focusing generates energetic ablated species and less ambient pressure causes fewer collisions during movement from anode to the substrate. This will result in greater mobility (due to higher energies) of impinging ions/particles on the substrate surface causing nanoparticle coalescence to form agglomerates (in figure 2(b)), and islands shown in figure

2(a). That is the reason that nanoparticles deposited at 2 mbar almost sintered together and form island-shape morphology, and still agglomerated significantly at 4 mbar. When the gas pressure is 8 mbar, the particles become smaller and more uniform. Few agglomerates of particles on the sample surface at the gas pressure of 8 mbar might be because the collision between the ablated Co or Pt ions and dense gas ions which cause the Co and Pt ions to rebound and combine together with lower energy during the movement and then falling on the surface.

Figure 4 represents the XRD results of the samples deposited at different gas pressures and annealed at 500 °C and 650 °C. Samples deposited at 2 mbar shows CoPt (111) peak with Si (111) peak in figure 4(a). It might be because that the gas pressure was very low that the ablated species ion carried very high energy which significantly affected not only the morphology but also the structure of the deposited thin film. After annealing at 650 °C, there are some other diffraction peaks which appear and are identified as Si (111), CoPtO₂ (006), CoPt₃ (110), SiO₂ (002), and Pt (200). Figure 4(b), (c) and (d) show XRD spectra for the samples deposited at 4, 6 and 8 mbar respectively and annealed at 500 °C and 650 °C. All as-deposited CoPt nanostructures exhibit fcc phase with a broad and weak peak of (111) at about 41°. After annealing at 500 °C, all the samples shows that the (111) peak remains at same position but the peak intensity slightly increases. In addition to (111) peak a (002) peak also appears, indicating the enhancement of crystallinity. As the annealing temperature increases further to 650 °C, the appearance of superlattice diffraction peaks (001) and (110) at around 24° and 33°, as well as the slight splitting of (200) and (002) peaks, reveals the phase transition of CoPt from disordered fcc phase to order fct phase [13]. It indicates as-deposited samples consist of a randomly oriented distribution of nanoparticles, and the ordering process is efficiently promoted during the annealing. It is observed that the intensity of the fundamental and

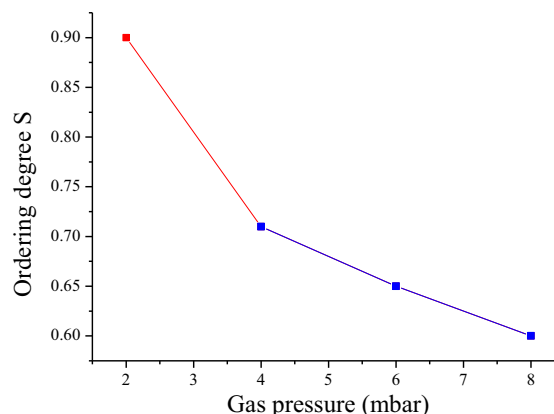


Fig. 5 The ordering degree, S, variation with hydrogen gas pressure.

superlattice lines is strongest for the sample deposited at 4 mbar after annealing at 650 °C as compared with annealed samples deposited at 6 and 8 mbar. It decreased with the increasing gas pressure. It is also noticed that Si (111) peak appears at the sample deposited at 8 mbar and annealed at 650 °C, which might confirm that nanoparticles on the samples deposited at 8 mbar are well separated. The average crystallite size can be calculated using Scherrer's formula $t=0.9\lambda/(\beta\cos\theta_\beta)$, with CuK α radiation $\lambda=1.5406\text{\AA}$ and β is FWHM at the diffraction angle of θ_β . The average crystallite size of samples deposited at 2, 4, 6 and 8 mbar are estimated to be about 15.6, 12.0, 12.3 and 11.6 nm using the most preferred (111) CoPt peak respectively. These results appear reasonable and are supported by the HRSEM results, which also confirms that nanoparticles are not sintered together when the gas pressure reach a certain value. The ordering degree of annealed samples are calculated from the ratio of peaks intensity of $I_{(001)}/I_{(002)}$ in XRD spectra. The ordering parameter can be calculated using $I_{(001)}/I_{(002)}=(28S^2)/15\approx 1.87S^2$ [14], where S is the long-range-ordering parameter. The ordering degree parameters are about 0.90, 0.71, 0.65 and 0.60 for the 650 °C annealing samples deposited at 2, 4, 6 and 8 mbar respectively. The ordering parameter is plotted in figure 5 and shows that for the samples deposited at 4, 6 and 8 mbar,

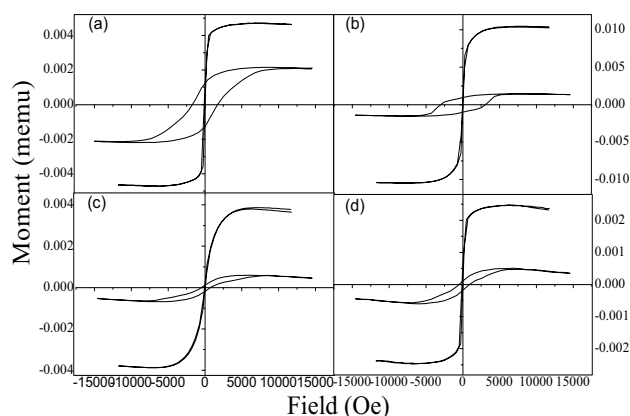


Fig. 6 Hysteresis loops for CoPt nanostructures synthesized at different gas pressures and annealed 650 °C. From (a) to (d): 2, 4, 6 and 8 mbar.

which have uniform nanoparticles or nanoparticle agglomerates, the ordering degree decrease linearly with the increase of the gas pressure.

Figure 6 shows hysteresis loops for as-deposited CoPt samples synthesized at different gas pressures and the samples annealed at a temperature of 650 °C. As-deposited samples without annealing show very weak coercivity, since they are in soft fcc phase which was noticed in corresponding XRD spectra. The coercivity of the samples after annealing were significantly enhanced to about 1700, 3014, 618 and 696 Oe for samples deposited at 2, 4, 6 and 8 mbar respectively. The enhanced coercivity after

annealing is due to phase transition from low magnetic anisotropy disordered fcc phase to ordered fct phase which exhibits a high magnetic anisotropy. It was also noticed that the coercivity after annealing was decreased with the increasing gas pressure, which is due to the reducing ordering degree trend shown in figure 5.

4. Conclusions

CoPt nanoparticles are successfully synthesized by DPF at relatively bigger distance of 25cm and the lowest charging voltage of 8kv at different gas pressures (2, 4, 6 and 8 mbar). The morphological features observed on plane-view SEM image show that the size of agglomerates and separated nanoparticles depends strongly on the filling hydrogen gas pressure if the other parameters are kept constant. Hence it provides a possibility to control the CoPt nanoparticles size by simply changing the operating gas pressure of DPF system. As-deposited CoPt nanoparticles were in magnetically soft fcc phase and an annealing temperature of 650 °C was required for phase transition to magnetically hard fct phase which can be used for data storage applications. Coercivity was greatly enhanced after annealing at 650 °C due to phase transition to fct phase upon annealing. The decreasing trend of coercivity for the samples deposited at 4, 6 and 8 mbar found to be due to the different degree of crystallization and the ordering degree of phase transition of the samples.

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