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FePt clusters synthesized by thermal pyrolysis of Fe and Pt compounds in an organic solvent

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A simple synthetic procedure involving the pyrolysis of Fe and Pt acetylacetonates mixed in trioctylamine results in the formation of alloy clusters with an average cluster around 4.2 nm and narrow size distribution. When the clusters are dispersed onto silicon wafers and heated under the protection of forming gas or nitrogen, the fcc structured clusters transform into hard magnetic FePt clusters with L1₀ chemical order. Coercivity values as high as 23 kOe are reached after rapid thermal annealing at 750 °C for 5 min. © 2006 American Institute of Physics.

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I. INTRODUCTION

FePt clusters with face centered tetragonal ordered L1₀ structure possess high magnetocrystalline anisotropy ($K_u \sim 7 \times 10^7$ erg/cm³). This may permit the use of thermally stable particles with sizes down to 3–4 nm as the ultimate unit for producing ultrahigh density magnetic recording media. The interest in FePt clusters, together with their counterparts, CoPt and FePd, has been very strong. Sun *et al.* have prepared FePt clusters by the reduction of platinum acetylacetonate in combination with the thermal decomposition of iron pentacarbonyl in the presence of organic surfactants.¹ FePt nanoparticles with partial chemical order were produced by resorting to a high boiling-point solvent of hexadecylamine using a modified solution phase reaction.² Direct synthesis of fct-FePt nanoparticles was also reported by the polyol reduction process, but the coercivity is quite low.³ Recent research on chemical reduction of metal salt mixtures within porous alumina templates by hydrogen gas has demonstrated that hydrogen reduction is a universal approach for producing CoPt, FePt, and FePd clusters.^{3–6} It is also a clean, one-step method for producing L1₀ ordered clusters with high chemical order. Furthermore, these hard magnetic FePt clusters can be released and capped with organic surfactants and organized into ordered arrays by template mediated self-assembly. Anisotropic magnetic properties can be reached when the self-assembly is carried out under external magnetic field.⁵

The above-mentioned results indicate that there remains much work to be done in both the synthesis and the manipulation of FePt clusters with narrow size distribution. In this study, a novel and simple approach, thermal pyrolysis of Fe and Pt acetylacetonates mixture in trioctylamine, is introduced to produce FePt clusters. When the proper mixture of Fe and Pt organometallic compounds is dissolved in a high-boiling-point trioctylamine, and fluxed at 330 °C for 4 h, FePt clusters with narrow size distribution are produced

without performing any size selection. The structure, phase transformation and magnetic properties are presented and discussed.

II. EXPERIMENTAL METHODS

The synthetic experiments were carried out using Fe(acac)₃ and Pt(acac)₂ without further purification. First, a 0.7 mmol Fe and Pt acetylacetonates mixture was dissolved in 10 ml trioctylamine at 70 °C. It was transferred to a three-neck flask with reflux attachment and placed on a heating mantle under rigorous magnetic stirring, and heated to 330 °C at a constant rate of 10 °C/min. During this stage, the brown color solution turned black indicating the formation of fine FePt clusters. The clusters were precipitated by adding alcohol and centrifugation. X-ray diffraction (XRD) analysis was carried out with Cu K_α radiation. Heat treatment was performed using rapid thermal annealing (RTA) technique. Magnetic properties were measured by a superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSION

A. Preparation of FePt L1₀ clusters

After heating the Fe and Pt acetylacetonate mixture in trioctylamine at 330 °C for 4 h, the black precipitation collected by centrifugation is dispersed in hexane. A drop of dilute suspension of these clusters is assembled onto a TEM grid coated with a 10 nm carbon film. Figure 1 is a TEM image of the assembly of FePt clusters on the carbon film. FePt clusters are well isolated which means that there is an organic layer around them.

Figure 2 is the histogram of cluster size distribution and its log-normal fitting. The clusters have an average size about 4.2 nm and a rms standard deviation of about 0.7 nm, indicating a relatively narrow size distribution ($\sigma/d_{av} \cong 0.17$). Energy-dispersive x-ray spectroscopy (EDX) composition analysis revealed that the clusters have a composition of nearly equal Fe and Pt atomic ratio. In comparison with the pyrolysis of the mixture of Fe and Pt complexes, Fe and Pt

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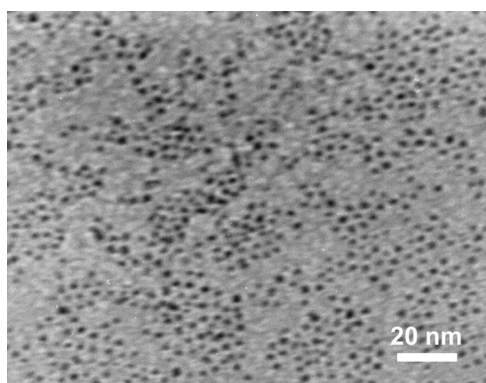


FIG. 1. TEM image of FePt clusters assembled on a copper grid coated with 10 nm carbon.

acetylacetonate were heated separately in trioctylamine. It was found that pure Fe particles with size around hundreds of nanometers are formed after heating in trioctylamine at 210 °C for 4 h. Similarly, pure Pt particles with size around tens of nanometers and large size distribution are formed after heating 250 °C for 4 h. The pyrolysis temperatures Fe acetylacetonate is lower than that of the Pt complex. The results of the separate pyrolysis of Fe and Pt acetylacetonates are not presented in this paper. It is surprising to note that the pyrolysis of the mixture of two complexes results in the formation of alloy clusters with very small size and narrow size distribution.

In the synthesis of FePt clusters using the polyol process, it was claimed that the Fe and Pt ions have to be reduced simultaneously in the polyol process.³ The differences of the particle sizes and the pyrolysis temperatures indicate that FePt clusters are unlikely to form by the simultaneous thermal decomposition of Fe and Pt acetylacetonate. The mechanism of the nucleation and growth is still under investigation. Our speculation about this chemical reaction is that an intermediate organometallic complex containing both Fe and Pt is formed after dissolving Fe and Pt acetylacetonate in trioctyl-

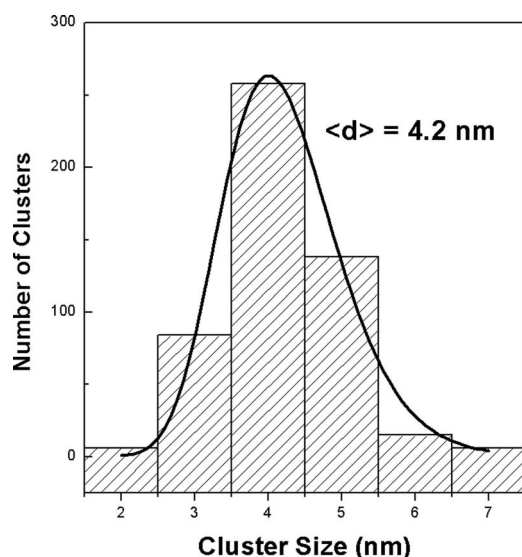


FIG. 2. Histogram of cluster size distribution and fitted curve following log-normal function.

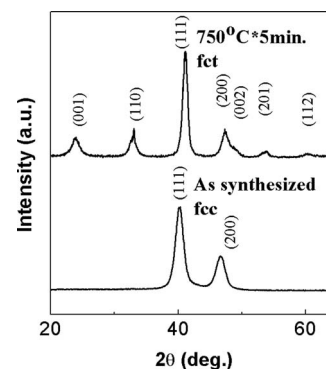


FIG. 3. XRD patterns of the FePt cluster assembled onto the silicon oxide substrate before (a) and after (b) heating at 750 °C for 5 min.

amine. Further heating leads to the pyrolysis of this intermediate organometallic complex followed by rapid nucleation of FePt clusters and slow growth. Thus small and homogeneous FePt alloy cluster are formed, rather than big and inhomogeneous element clusters. We also speculate that the generation of carbon monoxide during the pyrolysis of the complex is partially responsible for the reduction of Fe and Pt ions to pure elements.⁷

B. Structural change and magnetic properties

Figure 3 is the XRD of the FePt cluster assembled onto a silicon substrate before and after heat treatment using RTA in forming gas (consisting of 2% hydrogen, balance argon). Before annealing, the clusters have the chemically disordered fcc structure, heat treatment lead to the structural change from fcc to fct, and high coercivity is induced. Figure 4 shows the coercivity versus annealing temperature. The initial temperature for the structural change from fcc to fct structure is about 550 °C, which has a coercivity of about 3 kOe. The room temperature coercivities increase with the increase of annealing temperatures, and reach a maximum value of 23 kOe after heating at 750 °C for 5 min. Further annealing lead to the decrease of coercivity due to excessive

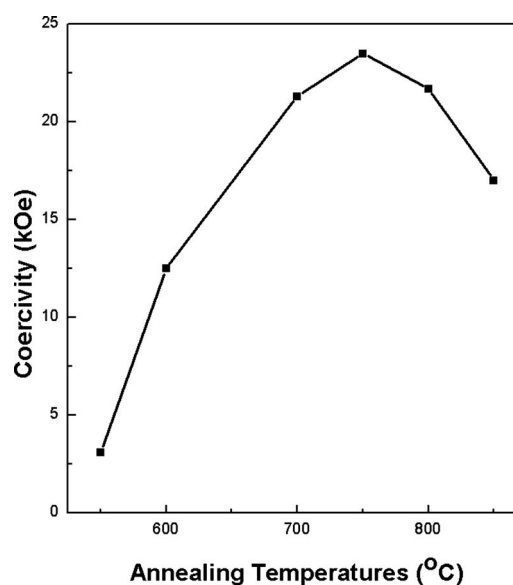


FIG. 4. Coercivity at room temperature versus annealing temperature curve.

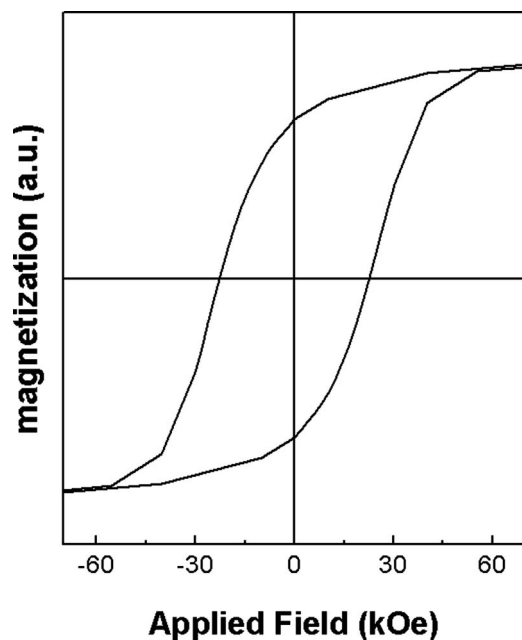


FIG. 5. Hysteresis loop measured at room temperature by SQUID on a sample heated at 750 °C for 5 min.

agglomeration of the clusters and the magnetic reversal mechanism is also changed. Figure 5 is a hysteresis loop measured by SQUID on samples after heat treatment at 750 °C for 5 min.

In order to verify if hydrogen is involved in the structural change, the forming gas was switched to high purity nitrogen as a protective gas during rapid thermal annealing. Little difference is observed in structure and magnetic properties between clusters annealed in forming gas and pure

nitrogen, suggesting that hydrogen does not play a significant role in the formation of the fct structure, although previous research indicate that the presence of hydrogen will accelerate the phase transformation from fcc to the fct ordered structure.^{4,5}

IV. SUMMARY

FePt clusters with average sizes about 4.2 nm and narrow size distribution can be produced by simply heating Fe(acac)₃ and Pt(acac)₂ in trioctylamine for 4 h. Coercivity values as high as 23 kOe are reached after annealing at 750 °C for 5 min. Further work on size selection and self-assembly is in progress.

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¹S. H. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, *Science* **287**, 1989 (2000).

²S. Kang, Z. Jia, S. Shi, D. E. Nikles, and J. W. Harrel, *Appl. Phys. Lett.* **86**, 062503 (2005).

³B. Jeyadevan, K. Urakawa, A. Hobo, N. Chinnasamy, K. Shinoda, K. Tohji, D. D. J. Djayaprawira, M. Tsunoda, and M. Takahashi, *Jpn. J. Appl. Phys., Part 1* **42**, L350 (2003).

⁴Y. Sui, L. Yue, R. Skomski, X. Z. Li, J. Zhou, and D. J. Sellmyer, *J. Appl. Phys.* **93**, 7571 (2003).

⁵Y. C. Sui, W. Liu, X. Z. Li, J. Zhou, R. Skomski, and D. J. Sellmyer, *J. Appl. Phys.* **97**, 10J304 (2005).

⁶Y. C. Sui, K. D. Sorge, R. Skomski, and D. J. Sellmyer, *APS March Meeting, Montreal, Quebec, Canada. Part 2*, W37, 1359 (2004).

⁷S. U. Son, Y. Jang, J. Park, H. B. Na, H. M. Park, H. J. Yun, J. Lee, and T. Hyeon, *J. Am. Chem. Soc.* **126**, 5025 (2004).