Sputter-deposited, equiatomic PtMn thin films have application in giant magnetoresistive spin valves, tunneling magnetoresistive spin valves, and magnetic random access memory. However, the as-deposited films are found to be a disordered A1 phase in a paramagnetic state rather than an antiferromagnetic phase with L10 structure, which is needed for device operation. Therefore, a post-annealing step is required to induce the phase transformation from the as-deposited A1 face-centered-cubic phase to the antiferromagnetic L10 phase. The A1 to L10 metastable transformation was studied by x-ray diffraction and differential-scanning calorimetry. An exothermic transformation enthalpy of $-12.1 \text{ kJ/mol}$ of atoms was determined. The transformation kinetics were simulated using the Johnson-Mehl-Avrami analysis.

INTRODUCTION

The dramatic increase in the areal density of magnetic disk drives has been driven by the discovery of giant magnetoresistance (GMR)\textsuperscript{1-5} and magnetic tunnel junctions (MTJ)\textsuperscript{6-8} and their incorporation into spin valve read heads.

The recent development of MgO-based MTJ has stimulated great interest in the application of magnetic random access memory (MRAM),\textsuperscript{9} which has the potential to replace all computer memory RAM technologies in use today and can lead to instant-on computers and longer battery life for pervasive devices. Among the components of both the GMR and MTJ device, an essential part is the antiferromagnetic (AFM) material, which is used to pin the magnetic moment of adjacent ferromagnetic (FM) layer by the field cooling method. Within the category of AFM materials, the manganese-based alloys, such as FeMn, NiMn, IrMn, and PtMn are frequently used for this purpose. Of these materials, PtMn\textsuperscript{10-12} is a good candidate for the final commercial MR device because of its high pinning field at operating temperature, high blocking temperature, and good corrosion resistance.

However, there is a significant processing obstacle that arises in using PtMn as the AFM: the sputter-deposited form of PtMn is not antiferromagnetic but is a paramagnetic, chemically disordered, face-centered-cubic (fcc) A1 phase. A post-deposition anneal is needed to transform PtMn to an antiferromagnetic, L10 phase. The phase-transformation anneal can have detrimental effects on other parts of the sensor, such as interdiffusion and magnetic realignment, which are minimized by lower temperatures and shorter anneal times. The thermodynamics and kinetics of PtMn phase transformation from the metastable A1 phase obtained by sputter deposition to the stable L10 phase were studied in detail by x-ray diffraction (XRD) and differential-scanning calorimetry (DSC). With available thermodynamic phase equilibria and structure evaluation, a model was created by incorporating the Johnson-Mehl-Avrami (JMA) analysis. This technique can be used to find the ideal annealing conditions to complete the phase transformation while minimizing damage to other parts of the sensor.

Pulse-thermal processing (PTP) utilizing high-density plasma-arc heating has the ability to revolutionize the processing method of the functional materials. The high temperature and small exposure time allowed by the fast heating rate enable efficient thermal processing as compared to conventional furnace anneal. Pulse-thermal processing utilizing high-density plasma arc lamp technology at Oak Ridge National Laboratory (ORNL) with a heating rate of up to 600,000°C/s, which is orders of magnitude larger than the current state-of-the-art rapid-thermal anneal system, makes it possible to process functional material in a fraction of a second to seconds. Therefore, this technique will be a good candidate for the processing of the GMR and MTJ devices. In this paper, the anneal performance of PtMn by PTP utilizing high-density plasma arc lamp technology was evaluated by
ordered, antiferromagnetic L10 B2 phase; and a low-temperature, chemically disordered A1 structure forms. Therefore, there is no thermodynamic barrier to overcome by heating; the anneal just provides the necessary activation energy for atomic rearrangement. Furthermore, the irreversible heat signals from DSC scans shown later give sufficient evidence to believe the L10 phase is also the stable phase in the thin film samples investigated here.

X-Ray Diffraction Results

Figure 2 shows the sequence of Bragg XRD scans for as-deposited films and films annealed at 260°C for 175 min., 225 min., 360 min., and 480 min., respectively. It can be seen that the (111) planar spacing changes between the as-deposited and fully volume-transformed sample is minimal; only a slight 2θ shift from 39.88° to 40.25° is observed. In between, the decrease in intensity is due to a combination of grain size change associated with the transformation of A1 phase to the L10 phase and a small degree of reorientation from the (111) texture. The full-width half-maximum reaches a maximum at approximately 50% transformed phase, and then decreases to a value similar to the as-deposited state as the volume phase transformation completes. This is due to the superimposing effect of the A1 and L10 phases that contribute to the total (111) PtMn peak. The (111) textured L10 phase that dominates the growth appears to consume the small amount of reoriented L10 phase present at the completion of the volume phase transformation as further annealing takes place. Thus, the final L10 phase consists primarily of (111) texture that matches the parent phase.

The shift in 2θ with annealing time was used to give an approximate measure of the degree of transformed phase for these samples. The termination of the shift of the 2θ value marks the completion of the volume phase transformation. Approximately 45% of the PtMn film is transformed to L10 after annealing for 175 min. After 6 h the volume phase transformation is nearly complete, but it takes more than 8 h to fully saturate the 2θ value. This shows that the samples are difficult to fully transform at 260°C, and long annealing times are required. It is important to note that the XRD peak shift correlation to degree of phase transformation is merely an approximation, due to the complications of reorientation and particle size that certainly have effects on the intensity and breadth of the individual contributions to the observed peaks.

**RESULTS AND DISCUSSION**

**Phase Equilibria Investigation**

The PtMn phase diagram as calculated by Mahler et al. (Figure 1) shows three polymorphs at the equiatomic concentration: a high-temperature liquid phase; a mid-temperature, chemically ordered, B2 phase; and a low-temperature, chemically ordered, antiferromagnetic L10 phase. It is clear that the as-deposited A1 (fcc) structure is metastable and does not appear on the equilibrium phase diagram at the equiatomic concentration. However, the adjacent platinum and γ-Mn phases are both A1 and would likely join and form a chemically disordered A1 phase as visualized by drawing metastable extensions if the ordered B2, L10, and L12 phases were suspended from the phase diagram. During sputter deposition, vapor atoms condense to form solid thin films. The thermodynamic effect is a rapid removal of the heat of sublimation. The kinetic effect is a quench rate that is too high for the formation of the ordered PtMn structures and the chemically disordered A1 structure forms. Therefore, there is no thermodynamic barrier to overcome by heating; the anneal just provides the necessary activation energy for atomic rearrangement. Furthermore, the irreversible heat signals from DSC scans shown later give sufficient evidence to believe the L10 phase is also the stable phase in the thin film samples investigated here.

**EXPERIMENTAL PROCEDURES**

The samples used for the Johnson-Mehl-Avrami (JMA) model development consist of PtMn and ferromagnetic layers (permalloy of Ni81Fe19 wt.% or a single A1 phase of a few percent iron in cobalt) direct-current magnetron-sputter-deposited from compound targets onto thermally oxidized silicon substrates with a thin seed layer preceding the stack deposition. The x-ray diffraction samples consist of single PtMn/ferromagnetic bilayers with a PtMn layer thickness of 250 Å. These samples are also capped with 50 Å of the seed material to protect the bilayer during annealing.

The films were annealed in a commercial dispatch oven at 260°C in order to induce various states of order in the resulting PtMn layer. The structural characterization was done with a Phillips XPert x-ray diffractometer (XRD) utilizing Cu Kα radiation. The differential-scanning calorimetry (DSC) samples consist of 74 repeats of the PtMn/ferromagnetic bilayer with the PtMn layers being 150 Å thick. In order to produce good signal-to-noise ratios in the DSC, 10–20 mg of the repeating bilayer stack were needed. The DSC was done with a Perkin Elmer DSC 7 system using both aluminum and copper pans.

The samples for pulsed-thermal processing (PTP) utilizing the plasma arc lamp were co-sputter deposited onto thermally oxidized silicon substrate from platinum (99.99%) and manganese (99.9%) targets. The compositions of the films was calibrated by Rutherford backscattering spectroscopy to produce PtMn with a 1:1 ratio. The films underwent various PTP conditions and were studied using XRD on a Stoe diffractometer to determine the PtMn phase transformation fraction.