

## Phase transformation in sputter-deposited PdMn and PdPtMn thin films

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The phase transformations of PdMn and PdPtMn films were investigated using differential scanning calorimetry (DSC), x-ray diffraction (XRD), and transmission electron microscopy (TEM). The enthalpy for the fcc to  $L1_0$  transformation in the PdMn and PdPtMn thin films has been measured by DSC as  $-5.4$  and  $-7.6$  kJ/mol at., respectively. The fcc to  $L1_0$  phase transformation was identified by XRD and TEM on as-deposited and annealed samples. The transition temperature for the PdPtMn is approximately  $40$  °C lower than that for PdMn. PdPtMn thin films have better corrosion resistance than PdMn. © 2006 American Institute of Physics. [DOI: [10.1063/1.2162988](https://doi.org/10.1063/1.2162988)]

### I. INTRODUCTION

One class of antiferromagnetic film materials widely used in giant magnetoresistance (GMR) reading heads are the  $L1_0$ -ordered tetragonal alloys such as NiMn,<sup>1-3</sup> PdMn,<sup>4,5</sup> PdPtMn,<sup>6,7</sup> and PtMn.<sup>8</sup> However, as-deposited thin films do not possess the antiferromagnetic  $L1_0$  crystal structure but have a chemically disordered, paramagnetic phase. Therefore, an annealing step is required during the processing of magnetoresistive devices to transform the film from its metastable, paramagnetic as-deposited state to its stable antiferromagnetic state. During this annealing step, processes detrimental to the GMR reading head structure may occur.<sup>9</sup> For example, interdiffusion between the multilayers and thermal roughening of the interfaces can degrade the properties of the GMR reading head.<sup>10-14</sup> Therefore, low-temperature short-time annealing is desired.

Though there are some reports using PdMn (Refs. 4,5) and PdPtMn (Refs. 6,7,15,16) thin films as an antiferromagnetic layer, detailed studies on the phase transformation of PdMn and PdPtMn thin films have not been found. Alloying in PtMn of Pd may affect the phase transformation temperature.<sup>17-19</sup> For example, favorable kinetics for the transformation in PtMn thin films were only found above  $260$  °C (Ref. 8) and a postdeposition annealing step at  $230$  °C for 1 h was reported for PdPtMn thin films.<sup>16</sup> Differential scanning calorimetry (DSC), combined with other techniques such as transmission electron microscopy (TEM) and x-ray diffraction (XRD), can offer both quantitative and qualitative information for the phase transformation in thin films.<sup>20,21</sup> In this study, the phase transformation in PdMn and PdPtMn films was investigated using DSC, XRD, and TEM. The difference in the transformation temperature for PdMn and PdPtMn thin films is discussed.

### II. EXPERIMENT

The PdMn and PdPtMn films used in this study were deposited by direct current magnetron sputtering of elemental component targets onto glass slides at ambient temperature in a 6 mTorr Ar atmosphere. The base pressure prior to the deposition was  $2 \times 10^{-7}$  Torr. Films of  $1$   $\mu\text{m}$  thick were deposited on glass slides for the DSC study. The composition of the films was controlled by adjusting the areas of Pd and Pt sheets covering the Mn target. The composition of the films was determined to be Pd<sub>52</sub>Mn<sub>48</sub> and Pd<sub>5</sub>Pt<sub>45</sub>Mn<sub>50</sub> by energy-dispersive x-ray spectrometry and electron probe microanalysis with an uncertainty less than 2 at. %. After deposition, the films were peeled off from the substrate and loaded into a copper pan in a Perkin Elmer DSC 7 for measurements. The DSC measurement was carried out in an atmosphere of 99.998% pure Ar, further deoxidized by an in-line Ti sponge gettering furnace, with a flow rate of 55 cc/min. In order to produce good signal-to-noise ratios, a sample mass of about 10 mg was used. The measurements were conducted between room temperature and  $600$  °C. The base line was established by repeating the measurements under identical conditions without removing the sample.

Both the as-deposited and annealed PdMn and PdPtMn films were investigated by XRD to characterize the crystal structure. XRD studies were conducted using a Stoe diffractometer with Cu  $K\alpha$  radiation at 40 kV and 25 mA. Scans were typically taken over a  $2\theta$  range of  $20^\circ$ – $90^\circ$  using a scan step of  $0.02^\circ$ .

For TEM samples, a single layer alloy film with a thickness of 50 nm was deposited onto a glass slide coated with a polymer. After floating the film off the glass substrate in ethanol, the film was soaked/filtered/rinsed with ethanol at least ten times to remove the traces of polymer residue and then captured on Cu grids yielding plan-view TEM samples. TEM study was carried out on a Philips CM200 operating at an accelerating voltage of 200 keV.

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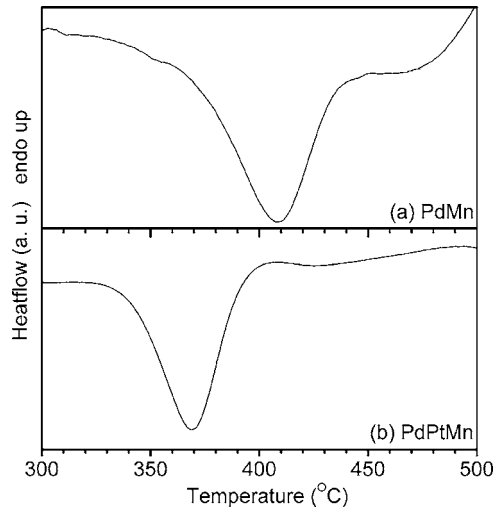


FIG. 1. DSC traces of PdMn (a) and PdPtMn (b) thin films with a heating rate of 30 °C/min.

### III. RESULTS

Figures 1(a) and 1(b) show the typical constant-heating-rate DSC traces at 30 °C/min from 1- $\mu\text{m}$ -thick PdMn and PdPtMn films. Only one exothermic peak was observed at around 410 and 370 °C for PdMn and PdPtMn, respectively, which is similar to PtMn (Ref. 8) and Pd<sub>3</sub>In (Ref. 22) thin films but rather different from the NiMn (Refs. 2,3) thin films obtained with a similar technique. The transition peak temperature for PdMn and PdPtMn films is higher than that in the PtMn (Ref. 8) (330 °C) thin films with the same scanning rate. The enthalpy of transformation was calculated from the DSC scan with a value of  $-5.4$  kJ/mol at. for PdMn and  $-7.6$  kJ/mol at. for PdPtMn, which are lower than that for PtMn (Ref. 8) thin films ( $-12.1$  kJ/mol at).

In order to relate the DSC signal to the structure change, the PdMn and PdPtMn films on glass slides were heated at 30 °C/min from room temperature to 500 °C in a DSC. Figures 2(a) and 2(b) show the XRD patterns of the as-deposited and annealed PdMn and PdPtMn thin films. It can be seen in Fig. 2 that both of the as-deposited PdMn and PdPtMn thin films have a face-centered-cubic (fcc) structure, which is different from the NiMn (Refs. 2,3) thin films prepared under the similar conditions. After being heated to 500 °C, extra peaks were observed for both materials. The appearance of (001), (110) peaks, and (200)/(002) and (220)/(202) doublets indicates the phase transformation from the disordered fcc to the ordered  $L1_0$  phases. No MnO peaks were observed in the XRD patterns of the annealed PdMn and PdPtMn thin films, which is contrast to our previous studies in NiMn thin films.<sup>2,3</sup>

The plan-view bright field TEM images and selected area diffraction (SAD) patterns of the as-deposited and annealed PdMn and PdPtMn thin films are shown in Fig. 3. The crystalline structure of the as-deposited films are indexed as fcc, shown in the selected area diffraction patterns in Fig. 3(a) (PdMn) and Fig. 3(b) (PdPtMn). This is different from the previous study of NiMn (Refs. 2,3) films, in which a coexistence of an amorphous and fcc phases in the as-deposited films was found. It can be seen in Fig. 3(c) (PdMn)

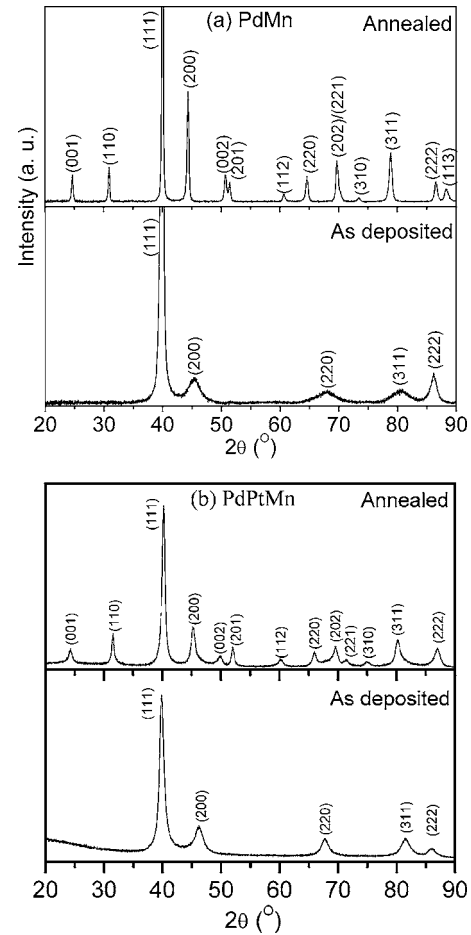


FIG. 2. XRD patterns of PdMn (a) and PdPtMn (b) thin films showing a fcc phase in the as-deposited state and a  $L1_0$  phase in the samples heated to 500 °C.

and Fig. 3(d) (PdPtMn) that, after annealing, the grain sizes become larger; grain boundaries become straighter and sharper. Some small black spots were observed on the surface of the grains in PdMn thin films, which is due to the oxidation of Mn, as indexed in the SAD pattern in Fig. 3(c). The major phase in the annealed PdMn thin films can be indexed as  $L1_0$ , indicating a disorder/order phase transformation from fcc to  $L1_0$ , which is consistent with XRD results. The grain sizes in the annealed PdPtMn thin films are much larger than those in annealed PdMn thin films, however, no MnO was observed, suggesting better corrosion resistance in the PdPtMn thin films. Twins were observed to form in both PdMn and PdPtMn thin films to accommodate the lattice strain generated during the fcc to  $L1_0$  ordering phase transformation.<sup>23</sup>

### IV. DISCUSSION

The transformation temperatures of PdMn and PdPtMn films are about 80 and 40 °C higher than that in PtMn films. The addition of Pd into PtMn thin films increases the phase transformation temperature, which is similar to the addition of Co to FePt thin films.<sup>17</sup> The phase transformation temperature is about 120 °C higher in CoPt thin films than in FePt thin films.<sup>24</sup> The transformation temperature for ternary alloy thin-film Fe<sub>30</sub>Co<sub>28</sub>Pt<sub>42</sub> lies between the two end mem-

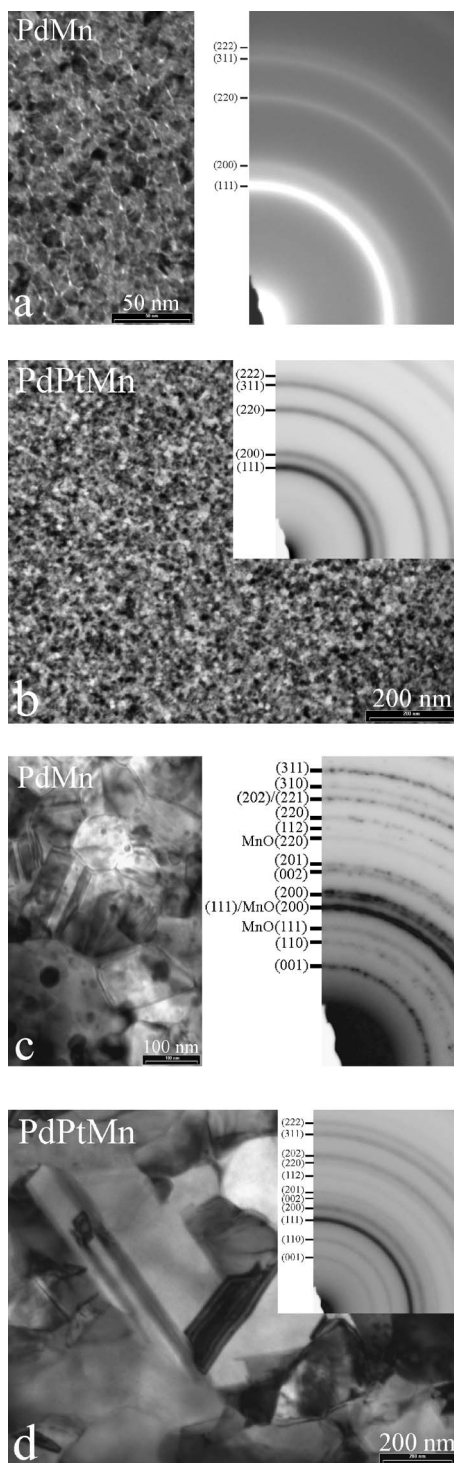


FIG. 3. Bright field TEM images together with the SAD patterns of the PdMn [(a) and (c)] and PdPtMn [(b) and (d)] thin films, showing a fcc phase in the as-deposited [(a) and (b)] and a  $L1_0$  phase in the annealed samples [(c) and (d)], respectively.

bers FePt and CoPt thin films.<sup>17,24</sup> Similarly, the transition temperature for the PdPtMn thin films most likely lies between those of PdMn and PtMn thin films as the case in this study.

The fcc structure obtained by sputter deposition is metastable and does not appear on the equilibrium phase diagram with a composition close to the equiatomic concentration. Growth of thin films in a sputter machine is a nonequilibrium

phenomenon governed by a competition between kinetics and thermodynamics. The thermodynamic effect is a rapid removal of the heat of sublimation and minimization the total free energy. The kinetic effect is a quench rate that is too fast to allow the formation of the ordered  $L1_0$  structure and the chemically disordered fcc phase forms.<sup>25</sup> Upon annealing enough activation energy is required to overcome the nucleation barrier for the transformation from the metastable fcc to the stable  $L1_0$  phase. The larger enthalpy of phase transformation in PtMn thin films than those in PdMn and PdPtMn thin films means larger driving force for phase transformation, resulting in the lower transformation temperature in PtMn thin films.

No MnO was observed in both of the XRD and TEM results of PdPtMn thin films. The formation of MnO on the surface of TEM sample but not in the XRD sample of PdMn indicates that PdMn has better corrosion resistance than NiMn thin films, in which MnO was found in both of the annealed TEM and XRD samples. Therefore, considering the phase transformation temperature and corrosion resistance, PtMn thin films are one of the best candidates as the antiferromagnetic film materials.

## V. CONCLUSION

In summary, investigations have been carried out on the phase transformation in sputter-deposited PdMn and PdPtMn films with DSC, XRD, and TEM. A disordered fcc phase was found in the as-deposited films. The transformation into the  $L1_0$  phase upon heating through the DSC peak was characterized by XRD and TEM. The addition of Pd in PtMn thin films increased the transformation temperature. PdPtMn has better corrosion resistance than PdMn.

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