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Combinatorial Synthesis of $Ni_{1-x-y}Mn_xGa_y$ Thin Films

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Contract Number: W7707-052899/001/HAL

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Defence R&D Canada – Atlantic

Contract Report
DRDC Atlantic CR 2005-190
September 2005

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Abstract

This research was conducted to evaluate the combinatorial synthesis approach and rapid characterization facilities (at Dalhousie University) for the development of Ni-Mn-Ga alloys. A combinatorial thin film of $Ni_{100-x-y}Mn_xGa_y$, where 20 < x < 35 (at. % Mn) and 18 < y < 30 (at. % Ga) was prepared by magnetron sputtering. To create such small composition ranges, new target masks had to be designed. The film was sputtered onto four different substrates; a Si(100) wafer, a masked Si(100) wafer sectioned into 49 discrete dots, a masked alumina plate sectioned into 49 discrete dots, and a Silicone polymer on glass. Microprobe results indicate that the actual ranges that were sputtered were 15 < x < 30 and 6 < y < 16. In general the films were more Ni-rich than expected and the sputtering masks must be redesigned or the power output to the targets must be adjusted. X-ray diffraction patterns on samples sputtered onto the Si(100) wafer showed the presence of a well defined peak consistent with the (220) reflection of the $L2_1$ phase of Ni-Mn-Ga and shows that the film has a crystalline structure.

Résumé

Effectuée dans le cadre de l’élaboration d’alliages Ni-Mn-Ga, notre recherche visait l’évaluation de la méthode de synthèse combinatoire et des installations de caractérisation rapide (de l’Université Dalhousie). À cette fin, nous avons préparé une couche mince combinatoire de $Ni_{100-x-y}Mn_xGa_y$, pour 20 < *x* < 35 (en pourcentage de Mn) et 18 < *y* < 30 (en pourcentage de Ga), par pulvérisation par magnétron. Pour obtenir une gamme si étroite de compositions, nous avons dû créer de nouveaux masques de cibles. La couche a été pulvérisée sur quatre substrats différents : une plaquette Si(100); une plaquette Si(100) masquée, sectionnée en 49 points discrets; une plaque d’alumine masquée, sectionnée en 49 points discrets; un polymère de silicone sur du verre. L’analyse par microsonde a indiqué que les pourcentages de Mn et Ga se situaient plutôt dans les intervalles 15 < *x* < 30 et 6 < *y* < 16 et, donc, que la teneur en Ni des couches dépassait généralement celles prévues. Ainsi, il sera nécessaire de concevoir de nouveaux masques de pulvérisation ou d’ajuster la puissance de sortie vers la cible. Les patrons de diffraction des rayons X sur les échantillons pulvérisés sur une plaquette Si(100) montrent des maximums bien définis, probablement causés par la réflexion (220) de la phase $L2_1$ du Ni-Mn-Ga, ce qui indique que la couche est cristalline.

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Executive summary

Introduction: Magnetic shape memory (MSM) alloys are a relatively new class of materials with potential applications as sensors or actuators. Ni-Mn-Ga alloys are among the most promising of this new class of materials and the focus of an extensive research program at Defence R&D Canada - Atlantic. The present investigation studies the use of a novel combinatorial sputtering approach to prepare an entire library of Ni-Mn-Ga compositions and for characterization by rapid analysis techniques. This work was contracted to and carried out by Norman Deschamps and Richard Dunlap of Dalhousie University (Department of Physics and Atmospheric Science).

Significance: This study is part of the ongoing development of Ni-Mn-Ga alloys by Defence R&D Canada and is intended to assess the combinatorial approach to preparation and characterization of ternary thin films. The combinatorial approach augments conventional means to design, explore and exploit material properties of new materials. This will enhance current materials research activities in the development of actuator/sensor materials, and will find application in other materials research streams as well.

Results: A combinatorial thin film of $Ni_{100-x-y}Mn_xGa_y$, where $20 < x < 35$ (at. % Mn) and $18 < y < 30$ (at. % Ga) was prepared by combinatorial sputtering. The creation of such small composition ranges required the design of new target masks for the sputtering apparatus. The film was sputtered onto four different substrates to allow for a variety of analysis techniques. Microprobe results indicate that the actual compositional ranges that were sputtered were $15 < x < 30$ and $6 < y < 16$. In general the films were more Ni-rich than expected and the sputtering masks must be redesigned or the power output to the targets must be adjusted. X-ray diffraction patterns on samples sputtered onto the Si(100) wafer showed that the film has a crystalline structure.

Future Plans: Work is ongoing to characterize the Ni-Mn-Ga film to identify compositions that show the most promise for MSM applications. New thin films, over the desired compositional range, will be fabricated by adjusting the power output to each of the targets during sputtering and/or redesign of the sputtering masks. In addition, an investigation of the effects of heat treatment and magneto-mechanical training on the properties of sputtered films will be undertaken.

Deschamps, N. and Dunlap, R.A. 2005. Combinatorial Synthesis of $Ni_{1-x-y}Mn_xGa_y$ Thin Films. DRDC Atlantic CR 2005-190. Defence R&D Canada – Atlantic.

Sommaire

Introduction : Les alliages à mémoire de forme magnétique sont une classe de matériaux découverte depuis peu, qui pourraient être utilisés comme senseurs ou actionneurs. Parmi ceux-ci, les alliages Ni-Mn-Ga sont possiblement les plus prometteurs et ils ont fait l'objet d'un programme de recherches approfondies à R & D pour la défense Canada – Atlantique. Dans cet article, nous présentons nos travaux sur une nouvelle méthode de pulvérisation combinatoire, utilisée pour produire une série complète de nuances d'alliage Ni-Mn-Ga et sur leur caractérisation par des techniques d'analyse rapides. Ce travail a été réalisé sous contrat par Norman Deschamps et Richard Dunlap du Département de physique et des sciences atmosphériques de l'Université Dalhousie.

Importance : Cette étude contribue aux travaux continus d'élaboration d'alliages Ni-Mn-Ga par R & D pour la défense Canada et vise l'évaluation de la méthode combinatoire pour la préparation et la caractérisation de couches minces d'alliages ternaires. La pulvérisation combinatoire s'ajoute aux méthodes habituelles de conception, d'exploration et d'exploitation des propriétés des nouveaux matériaux. Elle profitera aux recherches actuelles sur l'élaboration de matériaux pour les actionneurs et les capteurs, ainsi qu'à d'autres activités de recherches en sciences des matériaux.

Résultats : Nous avons produit par pulvérisation combinatoire, une couche combinatoire de $Ni_{100\text{-}x\text{-}y}Mn_xGa_y$, pour $20 < x < 35$ (en pourcentage de Mn) et $18 < y < 30$ (en pourcentage de Ga). Pour obtenir une couche présentant une gamme aussi étroite de compositions, nous avons dû concevoir de nouveaux masques de cible pour le dispositif de pulvérisation. La couche a été pulvérisée sur quatre substrats différents adaptés aux différentes techniques d'analyse. L'analyse par microsonde a indiqué que la gamme réelle de composition se situait plutôt dans les intervalles $15 < x < 30$ et $6 < y < 16$ et, donc, que la teneur en Ni des couches dépassait généralement celle prévue. Ainsi, il sera nécessaire de concevoir de nouveaux masques de pulvérisation ou d'ajuster la puissance de sortie vers la cible. Le patron de diffraction des rayons X des échantillons pulvérisés sur une plaquette Si(100) indique que la couche est cristalline.

Travaux futurs : Les travaux de caractérisation des couches d'alliages Ni-Mn-Ga visant à découvrir les nuances d'alliages à mémoire de forme magnétique les plus prometteuses se poursuivent. Nous produirons de nouvelles couches minces dont la composition tombe dans la gamme souhaitée en ajustant la puissance de sortie pour chacune des cibles pendant la pulvérisation ou en redessinant les masques de pulvérisation. En outre, nous entreprendrons une recherche sur les effets sur les propriétés des couches pulvérisées, du traitement thermique et de leur « entraînement ».

Deschamps, N. et R.A. Dunlap, 2005. *Combinatorial Synthesis of* $Ni_{1\text{-}x\text{-}y}Mn_xGa_y$ *Thin Films* (Synthèse combinatoire de couches minces de $Ni_{1\text{-}x\text{-}y}Mn_xGa_y$). RDDC Atlantique CR 2005-190. R & D pour la défense Canada – Atlantique.

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1. Introduction

Magnetic shape memory (MSM) alloys are a relatively new class of sensor/actuator material that produces large strains (up to 10%) in response to an applied stress and/or magnetic field. Although strains offered by MSM alloys are similar to conventional temperature driven shape memory alloys, the faster response due to magnetic control makes them more promising for a variety of applications.

Defence R&D Canada - Atlantic has recently completed a project on magnetic shape memory (MSM) alloys, in particular, Ni-Mn-Ga alloys. As part of the ongoing development of Ni-Mn-Ga alloys, Richard Dunlap (Dalhousie University) was contracted to employ the combinatorial sputtering approach for rapid, cost-effective production of thin-film libraries. This is intended to map compositional ranges of Ni-Mn-Ga for selection of compositions that reflect key material properties.

In particular, this study focused on the preparation of thin films of $Ni_{100-x-y}Mn_xGa_y$ in the range of $20<x<35$ and $18<y<30$ using the combinatorial sputtering system supplied by Jeff Dahn at Dalhousie University [1]. Figure 1 is a representation of the targeted composition range on a 3" x 3" square substrate.

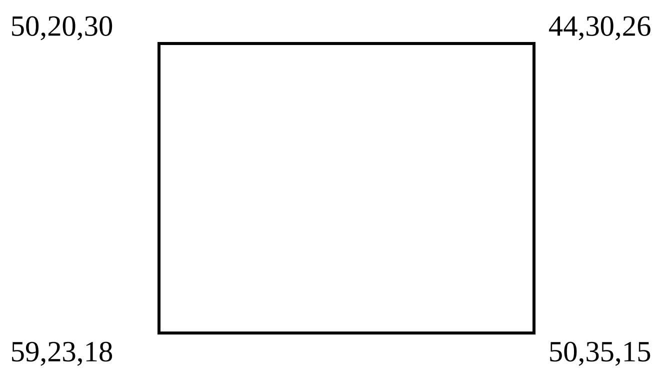

Figure 1. *Targeted Ni-Mn-Ga composition range: numbers represent the expected composition at that point in terms of Ni, Mn, and Ga content, respectively.*

2. Sputtering Mask Design and Construction

To create a ternary combinatorial film within the desired composition listed in Figure 1, new target masks had to be created for the Dahn sputtering system. The initial design of the masks is based purely on the theoretical model as described by Dahn [2]. The paper describes how the sputtered material follows a Gaussian distribution along a ring shaped area of the circular sputtering table between 8.33 cm and 18.33 cm from the centre of the sputtering table.

A Maple work sheet was created to numerically solve the required integral for the creation of the mask profiles. Three different masks were required to achieve the desired ternary composition: A 50 to 100 linear in mask, a 57 to 100 linear in mask, and a 100 to 60 linear out mask[1].

The mask profiles were calculated with a total of 40 points along each side of the mask. The mask profiles were then cut out of aluminium discs using an industrial wire electrical discharge machine at Fleet Maintenance Facility Cape Scott on the Canadian Forces Base Halifax.

When these masks were used for sputtering, it was found that they did not produce the desired linear change in composition for each element. Figure 2 shows the results of the sputtering using these masks based on sputtered mass measurements.

To develop masks that provided the correct linear composition changes, the difference between the desired linear model and the measured mass was determined at each point. This was then used to adjust the mask profile by the same percentage at each point. These adjusted masks profiles can be seen in Figure 3. Note that these adjusted mask profiles differed from the profile of the version 1 masks by no more than 8% at various points.

[1] Without a mask a Gaussian-shaped mass profile is produced. A linear in mask produces a film where the mass increases linearly from the outside in towards the center of the sputtering chamber. Linear out is the opposite and the maximum mass is deposited furthest from the center of the sputtering chamber.

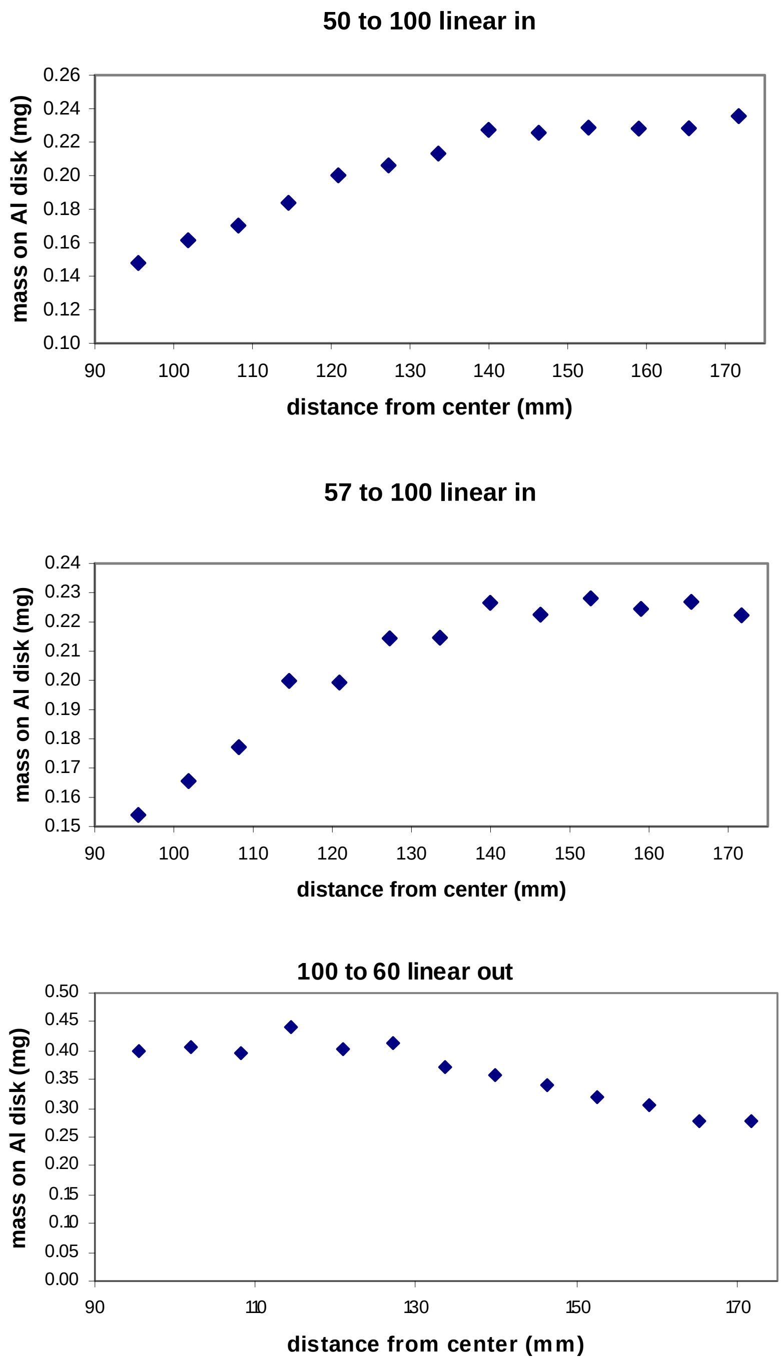

Figure 2. *Results of sputtering using Version 1 masks*

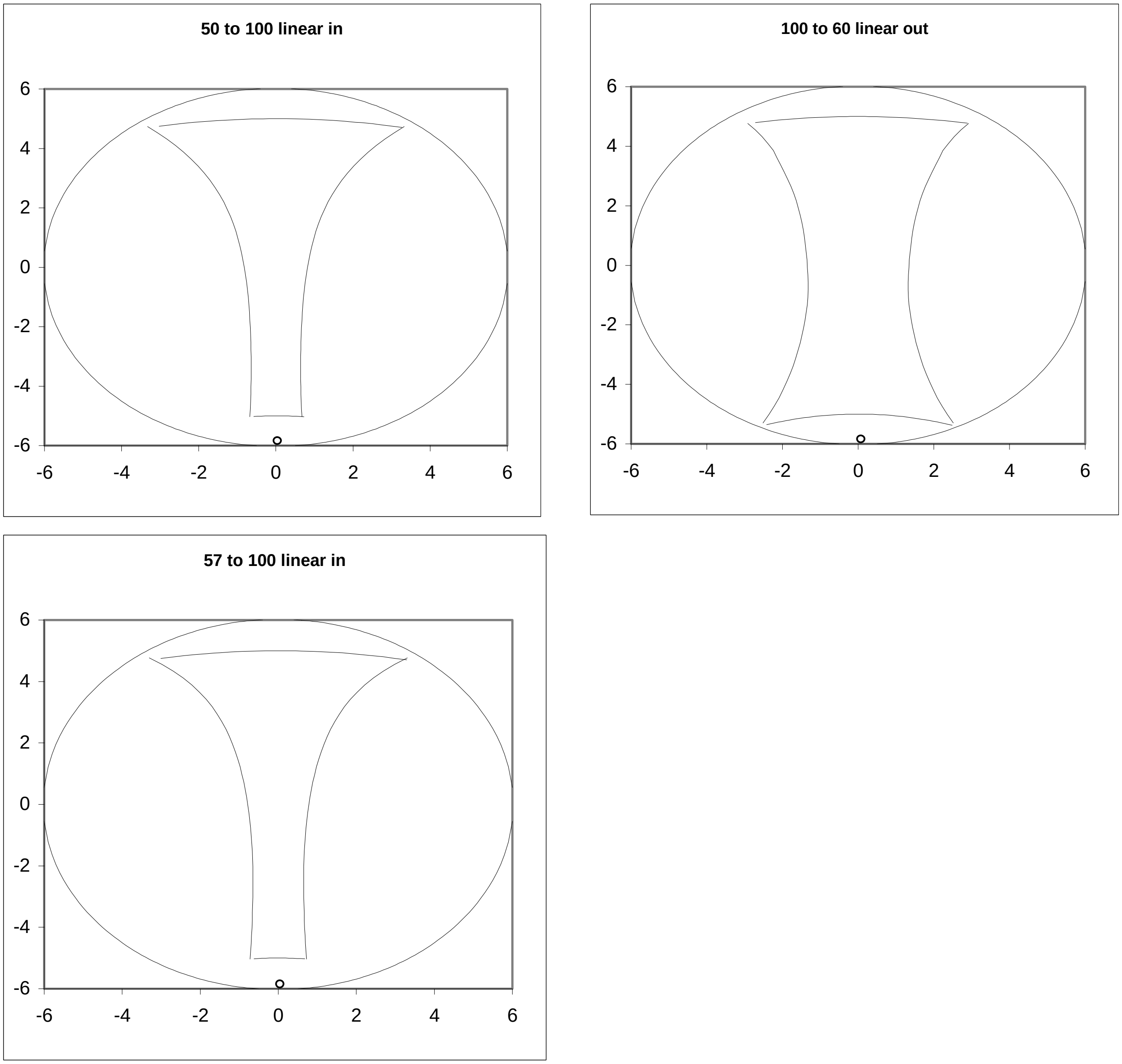

Figure 3. *Version 2 mask profiles*

3. Analysis of Sputtered Film

One ternary $Ni_{100-x-y}Mn_xGa_y$ combinatorial thin film was sputtered using the Dahn sputtering machine. The film was sputtered onto four different substrates; Si(100) wafer, a masked Si(100) wafer sectioned into 49 discrete dots, a masked alumina plate sectioned into 49 discrete dots, and a Silicone polymer on glass. Each of the sputtered substrates corresponded to a roughly 3" x 3 "square.

The Silicone film did not stay adhered to the glass plate during sputtering. Subsequently, it rolled into a tight cylinder at some point during the sputtering and fell onto the floor of the sputtering chamber, rendering it useless for any analysis. This may have resulted from the heat generated in the chamber during sputtering and the manner that the film was attached to the glass plate. At this time there has also been no analysis done on the thin films sputtered onto the masked Si(100) and alumina substrates.

3.1 Microprobe Analysis

Microprobe analysis was done on the film deposited on the Si(100) substrate to determine the composition at various points along the film. For this analysis the JEOL 8200 microprobe with an energy dispersive spectrometer (EDS) and a wave dispersive spectrometer (WDS), in the Department of Earth Sciences at Dalhousie University, was used. The microprobe analysis was performed with a 10 micron spot size on a 10 by 10 grid with the points spaced 8.6 mm apart. Figure 4 shows a ternary diagram showing the expected (red area) and measured (crosses) compositions of the thin film.

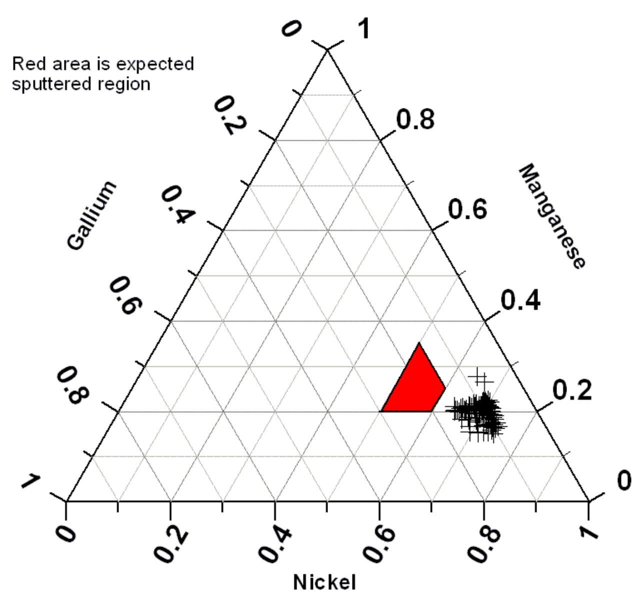

Figure 4. *Ternary diagram of the sputtered film: crosses represent sputtered compositions*

From Figure 4 it is apparent that the nickel content of the sputtered thin film was higher than desired and the gallium and manganese contents were much lower than desired. This difference in composition may not require a redesign of the masks. From the diagram we can see that there was a 10 % change in the nickel, manganese, and gallium contents, respectively, which is the percentage change in the elements that were hoping to achieve. It may be possible to shift the entire sputtered region into the desired region on the ternary diagram by adjusting the power to each of the targets during sputtering rather than redesigning the masks.

Figures 5, 6, and 7 show how the nickel, manganese, and gallium respectively change as a function of X-Y coordinate. Ideally these should be linear changes throughout. While the composition of nickel does seem to change relatively linearly, the manganese and gallium contents show a curve in the composition change, as well as two severe peaks (manganese) and troughs (gallium). The two peaks/troughs may be simply anomalous points and measurements of the composition made using EDS at the same time as the WDS measurements seem to support this hypothesis.

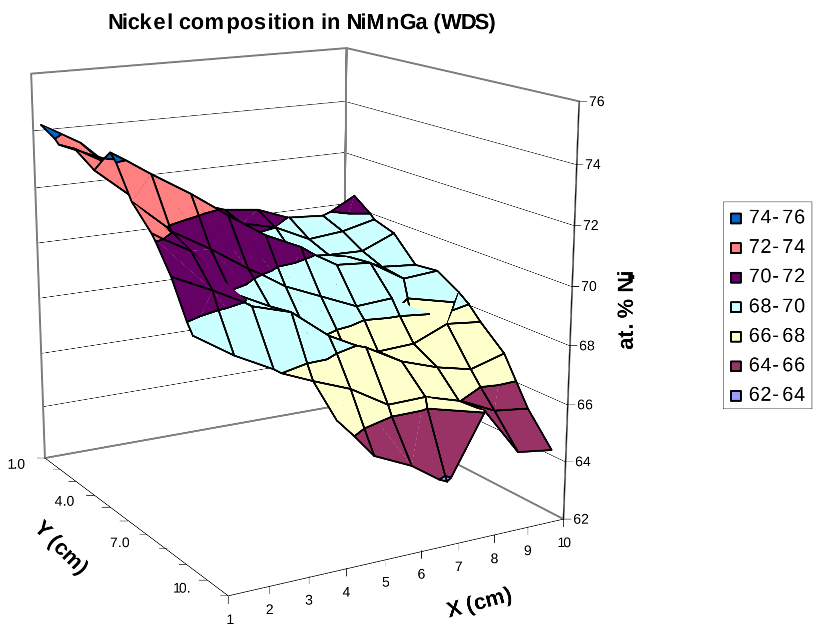

Figure 5. *Nickel content in the thin film as a function of X-Y position on the substrate*

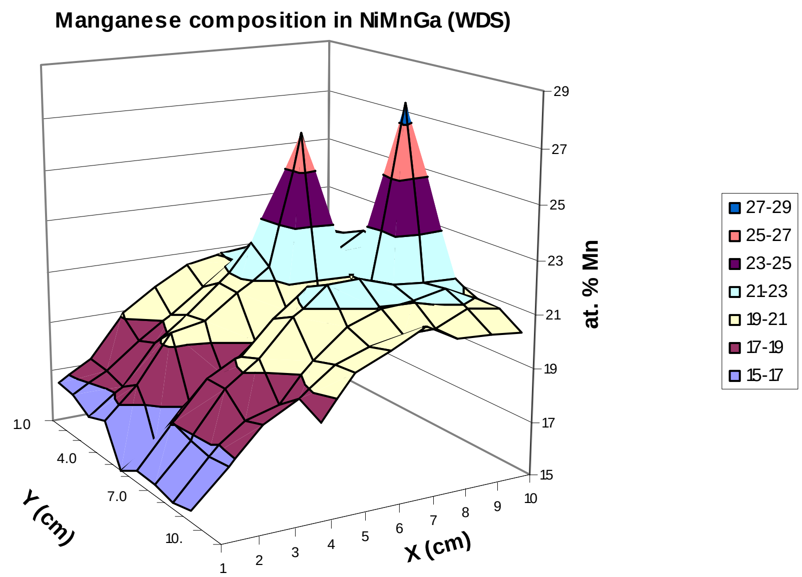

Figure 6. *Manganese content in the thin film as a function of X-Y position on the substrate*

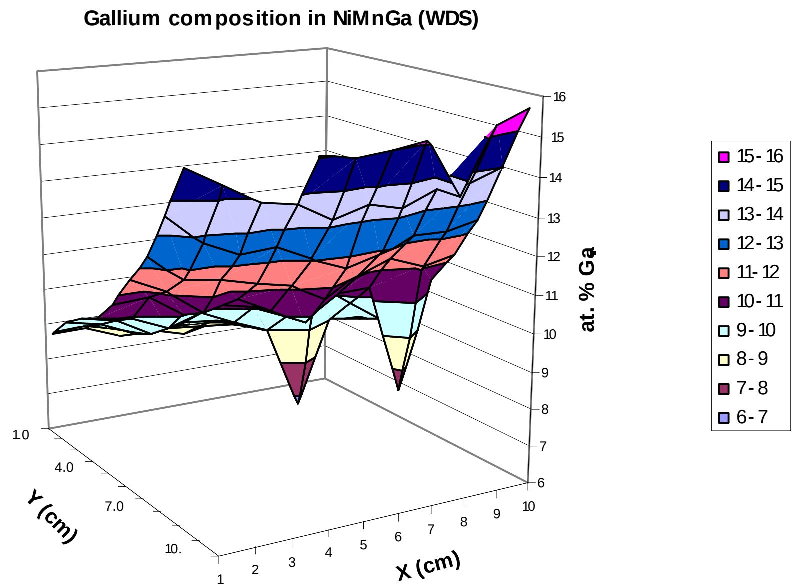

Figure 7. *Gallium content in the thin film as a function of X-Y position on the substrate*

3.2 XRD Analysis

XRD measurements were done on the Si(100) substrate using the INEL CPS120 curved detector system in the Dahn lab at Dalhousie University. This instrument allows for rapid X-ray diffraction measurements of the entire combinatorial film. The substrate was analyzed at intervals of 7.6 mm using a 10 x 10 grid through a 2θ range of 0° to 120°. Figure 8 shows the results of the XRD scan. The geometry of the detector only permitted for analysis of one 6 by 6 array of compositions at a time (depicted by different colors).

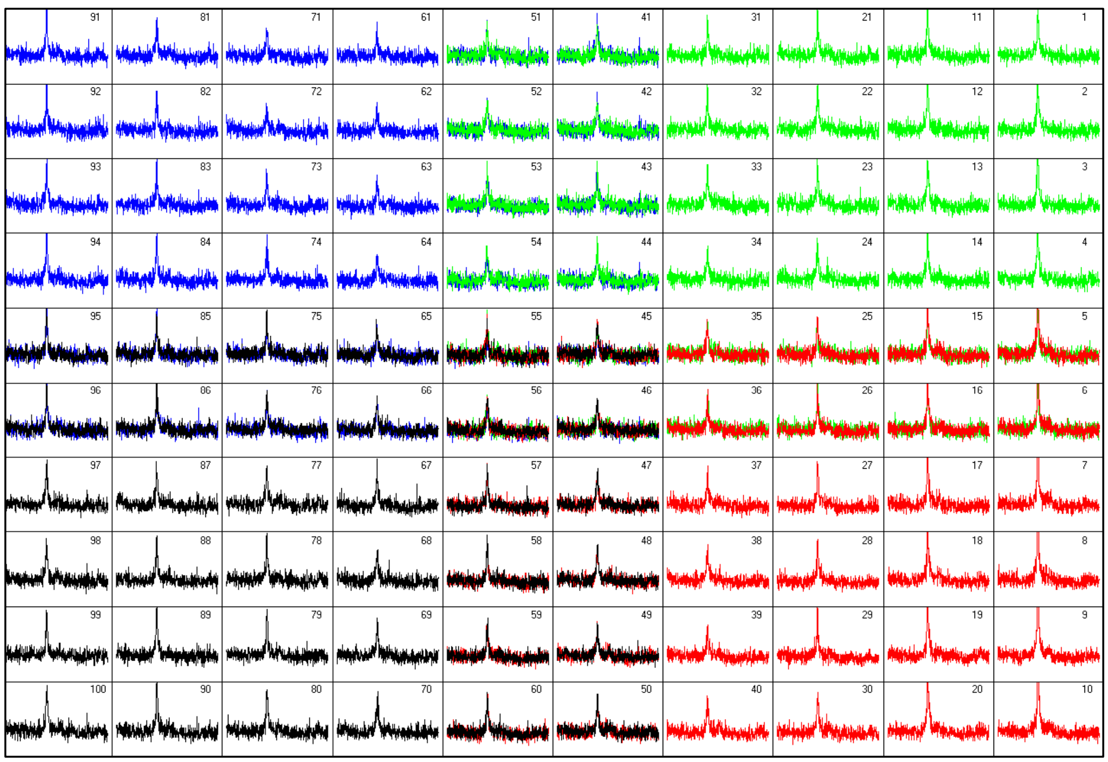

Figure 8. *XRD Scans of the $Ni_{1-x-y}Mn_xGa_y$ thin film on Si(100) substrate*

The peak near 44° is consistent with the Ni-Mn-Ga (220) reflection of the austenite $L2_1$ structure [3]. The broadening of the peak is similar to ground or milled samples of Ni-Mn-Ga that have retained residual stresses. The appearance of additional lower intensity reflections near this peak is suggestive of reflections observed for different martensite structures and may indicate the presence of the martensite phase. It is interesting that the film exhibits crystalline properties even before annealing. Annealing experiments on Ni-Mn-Ga powders and single crystals show similar results to that observed in Figure 8. The structure didn't become apparent until after heat-treatment. This is a crucial step to determining the structure of the phases that are present.

4. Conclusions and Future Work

The first sputtering of the Ni-Mn-Ga film did not produce the desired composition range. Microprobe analyses show that there is a nonlinear change in composition with position on the film. However, the change is smooth and continuous, apart from two anomalous points in the manganese and gallium compositions. This is a good first attempt and the film is still suitable for assessment of combinatorial analysis techniques and heat treatments.

XRD patterns indicated that the film has a crystalline structure, similar to as cast bulk Ni-Mn-Ga alloys. Similarily, it should be expected that an appropriate heat treatment schedule should permit resolution of XRD pattern reflections and structure determination for each composition. However, care must be taken to avoid compositional changes and oxidation of the film during heat-treatment.

Since the actual compositional spread is similar to the targeted range and the compositional change is relatively uniform, new films will be fabricated after adjustment of the power settings to each of the sputtering targets. If this fails, a complete redesign of the masks would be warranted.

Once problems with compositional variation are corrected, investigation of the effects of different heat treatments and annealing conditions on the structure of the film will begin. In addition, measurements on the magnetostrictive properties and resistivity of the films will then begin.

5. References

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[2] Dahn, J., Mask design for the production of continuous range of stoichiometries in sputtered samples, *internal lab document*, (2000).

[3] Ahn, J., Cheng, N., Lograsso, T., & Krishnan, K.M. (2001) Magnetic Properties, Structure and Shape-Memory Transitions in Ni-Mn-Ga Thin Films Grown by Ion-Beam Sputtering. *IEEE Transactions on Magnetics*, **37(4)**, 2141-2143.

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This research was conducted to evaluate the combinatorial synthesis approach and rapid characterization facilities (at Dalhousie University) for the development of Ni-Mn-Ga alloys. A combinatorial thin film of $Ni_{100-x-y}Mn_xGa_y$, where $20 < x < 35$ (at. % Mn) and $18 < y < 30$ (at. % Ga) was prepared by magnetron sputtering. To create such small composition ranges, new target masks had to be designed. The film was sputtered onto four different substrates; a Si(100) wafer, a masked Si(100) wafer sectioned into 49 discrete dots, a masked alumina plate sectioned into 49 discrete dots, and a Silicone polymer on glass. Microprobe results indicate that the actual ranges that were sputtered were $15 < x < 30$ and $6 < y < 16$. In general the films were more Ni-rich than expected and the sputtering masks must be redesigned or the power output to the targets must be adjusted. X-ray diffraction patterns on samples sputtered onto the Si(100) wafer showed the presence of a well defined peak consistent with the (220) reflection of the $L2_1$ phase of Ni-Mn-Ga and shows that the film has a crystalline structure.

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