University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Faculty Publications from Nebraska Center for
Materials and Nanoscience

Materials and Nanoscience, Nebraska Center
for (NCMN)

4-1991

Diffraction studies on Ni-Co and Ni-Cr alloy thin films

A. R. Sethuraman

Center for Applied Energy Research, 3572 Iron Works Pike, Lexington, Kentucky

R. J. De Angelis

University of Nebraska - Lincoln

P. J. Reucroft

Engineering, University of Kentucky, Lexington, Kentucky

Follow this and additional works at: <https://digitalcommons.unl.edu/cmrafacpub>

Part of the [Nanoscience and Nanotechnology Commons](#)

Sethuraman, A. R.; De Angelis, R. J.; and Reucroft, P. J., "Diffraction studies on Ni-Co and Ni-Cr alloy thin films" (1991). *Faculty Publications from Nebraska Center for Materials and Nanoscience*. 76.
<https://digitalcommons.unl.edu/cmrafacpub/76>

This Article is brought to you for free and open access by the Materials and Nanoscience, Nebraska Center for (NCMN) at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Faculty Publications from Nebraska Center for Materials and Nanoscience by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Diffraction studies on Ni-Co and Ni-Cr alloy thin films

A. R. Sethuraman

Center for Applied Energy Research, 3572 Iron Works Pike, Lexington, Kentucky 40511

R. J. De Angelis

Center for Materials Research and Analysis, University of Nebraska, Lincoln, Nebraska 68588

P. J. Reucroft

Department of Materials Science and Engineering, University of Kentucky, Lexington, Kentucky 40506

(Received 2 July 1990; accepted 11 December 1990)

Alloy films of Ni-Co and Ni-Cr of compositional ratios 1:1, 1:3, and 3:1 deposited by vapor deposition were studied by Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD). Results of TEM analysis on the Ni-Co alloy films indicated that the films were face-centered cubic (fcc) in structure. XRD results confirmed the TEM observations. TEM analysis of Ni-Cr alloy films showed that the films were body-centered cubic (bcc) in structure. With increase in the Cr content more than 25%, the material contained a higher fraction of an amorphous phase. XRD studies provide limited information owing to the quasi-amorphous structure of the films of high Cr content.

I. INTRODUCTION

The study of structural, surface/interface, and electrical properties of alloy thin films has attracted attention in recent years owing to their widespread applications in the fields of catalysis and microelectronics.¹⁻¹⁴ Ni-Co alloy films are of specific importance since they are currently being considered as an improved magnetic storage medium.¹⁻¹⁴ The Ni-Cr alloy films have been employed in microelectronics as thin-film resistors. The structure and electrical properties of Ni-Cr alloy films have been of interest for over a decade and numerous studies have been carried out to evaluate the influence of performance conditions on the behavior of these films.¹⁻¹⁴ Recent interest in surface and interface analysis of the Ni-Cr alloy films has been motivated by the recognition that oxide-induced processes affect the surface structure as well as the electrical properties—in particular, the temperature coefficient of resistance (TCR).

Toth *et al.*¹⁰ carried out electron microscopic and AES studies on 50% Ni–50% Cr thin films deposited on fused silica plates and SiO_x layers supported by microgrids from a NiCr 50/50 granule by flash evaporation. The substrates were at 400 K during evaporation. The films were studied in the as-evaporated state as well as after annealing at various temperatures and time periods. It was found that the temperature coefficient of resistance increased with the annealing temperature and that the structure of the film transformed from amorphous to crystalline.

Sethuraman *et al.*¹² investigated deposition of alloy films from a single source using a Ni-Co model alloy system. The Ni-Co evaporation source was synthesized

by electrodischarge compaction, and the films of the Ni-Co alloy with various compositions were deposited on a silicon substrate at room temperature. The films were analyzed using AES, XPS, XRD, and TEM. The results from the AES studied showed uniformity and homogeneity of the surface chemical composition.

Kington *et al.*¹⁵ investigated the structural and magnetic properties of evaporated films of 75% Co–25% Ni. Results indicated that the magnetic properties varied with substrate temperature and film thickness. The structural studies showed that at high temperatures, the films were fcc in structure. It was concluded that if deposition was carried out below the temperature of the martensitic transformation, the film structure transformed from fcc to hcp with increasing thickness. The authors also proposed that the 75% Co–25% Ni would normally be hcp at room temperature in the bulk form and fcc in the thin film form.

Wakai¹⁶ studied the improvement of corrosion resistance of NiCo alloy film on polyethylene terephthalate (PET) by surface passivation. The films were deposited using electron-beam evaporation from an 80% Co–20% Ni (by weight) prealloyed slug. XPS, RHEED, and friction measurement were employed to study the surface chemical structure and corrosion-resistance behavior. It was found that films passivated by a mild-oxidation method have superior resistance to moist atmospheric corrosion. It was concluded that their strong corrosion resistance can be attributed to very thin, amorphous cobalt (III) oxyhydroxide formed on the surface, containing a small amount of Co²⁺ ions.

In the present investigation, structural features of Ni-Co and Ni-Cr films have been studied and the re-

sults have been compared. The major objective of the study was to understand the effect of chemical composition on the structure of the thin films.

II. EXPERIMENTAL PROCEDURE

Pure Ni (99.99%), Co (99.99%), and Cr (99.99%) of approximately equal size distribution (-100 mesh) were obtained from Johnson-Mathey. Three compositions for the Ni-Co system, 25% Ni-75% Co, 50% Ni-50% Co, and 75% Ni-25% Co (wt. %), were weighed using a digital microbalance. Powders of Ni and Cr with the same compositions as the Ni-Co systems were weighed. The weighed powders were mixed in a mortar and pestle by a volume mixing method to ensure homogeneous mixing and synthesized into a compact. The details of the synthesis of the evaporation source can be found elsewhere.¹⁷

The deposition of thin films from a single source was accomplished by physical vapor deposition using a Veeco VE-7700 metal evaporator. A thickness monitor (Kronos QM-311) was attached to the evaporator. The sources were evaporated from a tungsten alumina crucible made by GTE Sylvania Emissive Products Division (CS-1008 series). These tungsten crucibles are coated with nonreactive alumina, thereby minimizing contamination. The crucibles were vacuum outgassed before every deposition cycle for 20 min at 1450 °C in a vacuum of about 1×10^{-7} Torr.

The substrates used were float zone silicon with a (111) orientation. Alloy thin films for TEM studies were deposited on copper grids coated with Formvar simultaneously. The silicon wafers were initially etched with HF, rinsed in de-ionized water, dried, and introduced into the evaporation chamber within about a minute to avoid excessive reoxidation. The source to substrate distance was 18 cm and the deposition was carried out on a line-of-sight method. The chamber was evacuated to 1×10^{-7} Torr and held there for about 15 min to remove any residual contaminants. The crucible was slowly heated to the required temperature so that the source melted and thin films were deposited on the silicon substrates to a thickness of about 700 Å. After the required thickness was deposited, the crucible was slowly cooled down. The wafers were maintained in vacuum for at least 30 min before they were removed from the chamber. A fresh source was used each time to avoid the oxide contamination that would be introduced if the same source was used again.

A. TEM analysis

The TEM samples were deposited on a carbon coated Formvar on a copper grid. The Formvar film anchored the grid to a borosilicate glass slide, and the alloy thin films were deposited on the film of Formvar

and were studied in a Hitachi H-800 TEM/STEM operated at 200 kV.

B. XRD studies

The thin films deposited on silicon were studied in a Rigaku x-ray diffractometer equipped with a diffracted beam graphite monochromator and a copper target x-ray tube. The films were studied in the range 34° – 56° (2θ). Higher angle reflections were also studied in the range 70° – 140° (2θ). The data were acquired using a PDP 11/23 system and the patterns were compared with Ni-, Co-, and Cr-containing entries in the JCPDS.¹⁸ In the Ni-Co system, previous work that has been carried out on Ni-Co bimetallic catalysts¹⁹ on silica and alumina support was compared with the results obtained in the present investigation. It was observed that the results of the Ni-Co system were similar to that of the Ni-Co bimetallic catalysts. However, the hcp Co/Co_xO_{1-x} lines that were observed in the catalyst samples were absent in the thin film samples.

III. RESULTS AND DISCUSSION

A. Ni-Co alloy system

The x-ray diffraction patterns of all the three different compositions of the Ni-Co alloy films are shown in Fig. 1. The three x-ray diffraction patterns contain no evidence of the presence of either pure Ni or Co phases. To establish that there was no evidence that either of the two pure metal phases was present, the scans were compared with standard powder diffraction line data of Ni (denoted by dotted vertical lines on the plot) and Co (denoted by solid vertical lines on the plot) (see Fig. 1). The Co phase that was compared was hcp Co since it is the room temperature form. However, even if one were to compare the data from fcc Co,

FIG. 1. X-ray diffraction spectrum of all three alloy compositions.

the lines would be adjacent to the Ni lines and there is no definite indication of their presence.

The sample of 75% Ni-25% Co composition did indicate a possible trace of Ni present as a single phase; see, for example, a small increase of less than 1 c/s in the diffracted intensity at the Ni(200) position; the amount of Ni that would give rise to that peak is estimated to be about 1%. Except for this result, the XRD patterns indicate the presence of an alloy phase.

The samples were studied in a Hitachi H-800 electron microscope operated at 200 kV. The TEM micrographs are given in Figs. 2 to 4. The bright-field images obtained indicate that the films have a uniform fine-grained structure. The electron diffraction patterns shown in Figs. 2 to 4 are characteristic of crystalline

(a)

(b)

FIG. 2. (a) Electron diffraction pattern and (b) bright-field image at 100 000 $\times$ of 75% Ni-25% Co alloy film.

(a)

(b)

FIG. 3. (a) Electron diffraction pattern and (b) bright-field image at 100 000 $\times$ of 50% Ni-50% Co alloy film.

materials, which implies that the films are not amorphous. Further, the diffraction patterns do not show characteristics resembling patterns from either Co or Ni. There is no definite evidence of pure Ni or Co phases being present in the film. This is indicative of an alloy film and the diffraction patterns are that of a face-centered cubic alloy. The diffuse appearance of the rings may be said to be due to the small grain size of the films. The grain size was estimated to be ≈ 400 Å.

B. Ni-Cr alloy system

The x-ray diffraction patterns from Ni-Cr alloy films were diffraction amorphous. Addition of Cr has been proposed to be the reason for the small size of the crystallites.¹⁰⁻¹⁴ Also, the patterns suggest that there is a predominance of an amorphous phase in the films.

(a)

(b)

FIG. 4. (a) Electron diffraction pattern and (b) bright-field image at 100 000 $\times$ of 25% Ni-75% Co alloy film.

This structure is due to the presence of the amorphous chromium oxide, believed to be Cr_2O_3 , in the alloy film. Crystallization of the amorphous films has been reported to occur on heating in UHV at temperatures in the range of 800 $^{\circ}\text{C}$ for about 100 h.⁶ In the present investigation, the available equipment was only a high vacuum chamber with a 500 $^{\circ}\text{C}$ capability. Working at the highest possible temperature at high vacuum had no effect on the film structure. For example, the films were annealed in high vacuum at about 480 $^{\circ}\text{C}$, in an attempt to crystallize the amorphous film, for 18 h with no success.

The films were studied by TEM with the microscope operating at 200 kV. The results are shown in Figs. 5 to 7. It can be seen that with decreasing amount of Ni the diffraction rings lose clarity and become more

(a)

(b)

FIG. 5. (a) Electron diffraction pattern and (b) bright-field image at 150 000 $\times$ of 25% Cr-75% Ni alloy film.

diffuse. This is due to the increase in the amount of the Cr_2O_3 in the film. The patterns suggest that the films contained extremely small particles of sizes ≤ 50 $\text{\AA}$. The patterns were solved as being due to a body-centered cubic material. The patterns do not indicate the presence of any pure Ni or pure Cr. The results in this study are in agreement with those of earlier investigators.⁶⁻¹¹ This suggests that the film is an alloy of Ni and Cr with a bcc structure. The diffuse appearance of the rings is due to the smaller grain size of the material and also the presence of Cr_2O_3 . The bright-field images of films shown indicate that the films possess a uniform grain structure with a very small grain size. It can also be seen that with an increasing amount of Cr the structure as seen in the micrographs does not have much definition. The grain size can be estimated to be ≈ 100 $\text{\AA}$.

(a)

(b)

FIG. 6. (a) Electron diffraction pattern and (b) bright-field image at 150 000 $\times$ of 50% Cr-50% Ni alloy film.

(a)

(b)

FIG. 7. (a) Electron diffraction pattern and (b) bright-field image at 150 000 $\times$ of 75% Cr-25% Ni alloy film.

IV. CONCLUSIONS

The structural studies by XRD and TEM indicated that the structure of the Ni-Co alloy film was fcc by XRD studies and the same was confirmed by TEM results. There were no indications of the presence of pure

metal phases. The grain size from the bright-field images was estimated to be ≈ 400 Å.

In the Ni-Cr system, attempts to obtain an x-ray diffraction pattern using a conventional diffractometer from the films were unsuccessful due to the very small crystallite size. The results from XRD suggested the

presence of an amorphous phase. Annealing for 18 h in high vacuum at 480 °C did not crystallize the amorphous phase. TEM studies showed evidence of a crystalline phase. The electron diffraction pattern showed diffuse rings with an amorphous halo. This halo is attributed to the presence of Cr₂O₃ oxide. Ni content over 25 wt. % reduced the amorphous halo and increased definition in the diffraction rings. The diffraction pattern was found to be bcc in structure, in agreement with previous investigations. The grain size from the bright-field images was estimated to be ≈ 100 Å.

ACKNOWLEDGMENT

Financial assistance for one of the authors (A. R. Sethuraman) from the University of Kentucky Graduate School is gratefully acknowledged.

REFERENCES

- ¹R. W. Bicknell, H. Blackburn, D. S. Campbell, and D. J. Stirland, *Microelectron. Reliability* **3**, 61 (1964).
- ²J. G. Swanson and D. S. Campbell, *Thin Solid Films* **1**, 183–202 (1967).
- ³P. W. Palmberg, *J. Vac. Sci. Tech.* **9** (1), 160 (1971).
- ⁴R. K. Jain and B. R. Marathe, *Thin Solid Films* **14**, 155–159 (1972).
- ⁵T. M. Nenadovic, Z. B. Fotiric, T. S. Dimitrijevic, and M. D. Adamov, *Thin Solid Films* **10**, 45–56 (1972).
- ⁶L. Lassak and K. Hieber, *Thin Solid Films* **17**, 105–111 (1973).
- ⁷W. R. Hardy and D. K. Murti, *Thin Solid Films* **20**, 345–362 (1974).
- ⁸S. Hoffmann and A. Zalar, *Thin Solid Films* **39**, 219–225 (1976) and references therein.
- ⁹G. Nocerino and K. E. Singer, *Thin Solid Films* **57**, 343–348 (1979).
- ¹⁰L. Toth, A. Barna, M. Menyhard, and T. Koranyi, *Vacuum* **33** (1/2), 111–115 (1983).
- ¹¹M. Koltai, I. Trifonov, and M. Czermann, *Vacuum* **33** (1/2), 49–52 (1983).
- ¹²A. R. Sethuraman, P. J. Reucroft, R. J. De Angelis, D. K. Kim, and K. Okazaki, *J. Vac. Sci. Tech. A* **8** (3), Pt. II (1990).
- ¹³A. R. Sethuraman, P. J. Reucroft, R. J. De Angelis, and K. Okazaki, *Proc. of the 37th National Symposium of the American Vacuum Society* (to be published).
- ¹⁴P. Gadenne, C. Sella, M. Gasgnier, and A. Benhamou, *Thin Solid Films* **165**, 29–48 (1988) and references therein.
- ¹⁵B. W. Kington, R. Pascual, and M. Prutton, *Thin Solid Films* **6**, 267–275 (1970).
- ¹⁶K. Wakai, *J. Appl. Phys.* **61** (8), 3822 (1987).
- ¹⁷A. R. Sethuraman, Ph.D. Dissertation, University of Kentucky, 1990.
- ¹⁸JCPDS—International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081.
- ¹⁹H. Woo, R. Srinivasan, L. Rice, R. J. De Angelis, and P. J. Reucroft, *J. Mol. Catalysis* (in press).