Short wavelength compositionally modulated Ni/Ni-P films prepared by electrodeposition

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Compositionally modulated Ni/Ni-P films, with wavelengths between 2.1 and 4.0 nm and an average P content around 12 at. %, have been prepared by alternating electrodeposition in a simple and inexpensive apparatus consisting of two baths of different composition. X-ray diffraction showed a single (000) satellite at low angles due to the presence of the modulation.

I. INTRODUCTION

Artificial materials created by interleaving of very thin (0.5–10-nm) layers, also called “compositionally modulated materials” if the layer interfaces are very diffuse, are of much current interest because of their unique physical properties, their technological applications (such as x-ray mirrors), and because they allow atomic diffusion to be studied in a regime that is inaccessible by other techniques.^{1–4} Since 1940, when Dumond and Youtz⁵ made the first artificial x-ray mirror by dual source evaporation, these materials have been produced exclusively by atomic deposition from a vapor or plasma, as in evaporation, sputtering (dc, rf, or ion beam), or molecular-beam epitaxy.

The very first attempts at creating artificially layered materials, however, were made using electrodeposition. In 1923, Koeppe⁶ attempted to create an artificial x-ray mirror consisting of Cd and Ag layers by sequential dipping into two separate plating baths. In 1930, Deubner⁷ reported a similar attempt with Au and Ag layers. Both experiments were unsuccessful, in that no diffraction lines other than those corresponding to crystal lattice spacings were observed. In retrospect, their failure can be explained by the very rapid interdiffusion of the layers by atomic transport through the moving grain boundaries of the polycrystalline material.^{8,9}

Artificially layered materials can also be made in a single electroplating bath by modulating either the cathodic current or potential. Cohen *et al.*¹⁰ have produced Ag/Pd multilayers by this technique. The layer thicknesses in their materials, however, were rather large: only composition modulations with a repeat length (“wavelength”) greater than 100 nm could be obtained, which they attributed to electrokinetic limitations. As a result, these modulations cannot be observed by the standard x-ray diffractometer techniques. The long interdiffusion distance also puts a lower limit of about $10^{-23} \text{ m}^2 \text{ s}^{-1}$ on the interdiffusivities that can be measured, which is no better than can be obtained by a number of other techniques, such as Rutherford backscattering spectroscopy or sputter profiling.¹¹ Furthermore, many of the unique features of the physical properties of the artificial multilayers are often only present at short modulation wavelengths.^{12,13}

Given the relative simplicity and inexpensiveness of electrodeposition, combined with the unique compositions that can be obtained that way, it seemed desirable to develop a plating technique that can produce short wavelength com-

positionally modulated materials. The technique reported here is a variation on the two-bath attempts of the 1930's.

The Ni-P system was chosen for a number of reasons. First, its electrochemical deposition is well developed, beginning with the work of Brenner in the 1940's and 1950's.^{14–16} Second, the electron densities of Ni and P are sufficiently different, so that the layers have good x-ray contrast. Third, homogeneous Ni-P deposits with a P content above 18 at. % are known to be amorphous.¹⁷ As a result, the main reason for the failure of the early experiments with polycrystalline layers is avoided, since grain boundaries, which are conduits for short-circuit diffusion, are not present in an amorphous material. Amorphous metals also have a high hardness, which is an additional benefit in this technique. Finally, amorphous Ni-P is one of the earliest known and most widely studied amorphous metallic alloys.¹⁸ A study of the interdiffusion in this system by the modulated film technique¹¹ would be the first one on a binary metal-metalloid amorphous metal. For the purpose of demonstrating the preparation technique, however, these first experiments have been done on (nominally) pure Ni/Ni-P films, in order to obtain good x-ray contrast between the layers.

II. EXPERIMENT

Figure 1 is a sketch of the plating apparatus. It consists of two adjacent separate baths, 3 liters each, that are filled nearly to the top with two plating solutions, the temperature of which was kept at 65 °C by immersion heaters. The substrate cathode is a 0.5-mm-thick, 11-cm-diam copper disk that is exposed to the solutions through two windows in the shape of circular sections with a width of 16°. The anodes are 0.5-cm-diam Ni rods, placed behind each window at a distance of 7.5 cm. The substrate is attached to a brass wheel that is rotated by a high-torque electric motor at speeds between 12 and 20 rpm. The cathode is electrically isolated by Teflon insulator rings and sheets. Leakage of the solutions is minimized by pressing the substrate against the rubber gaskets around each window. The apparatus is made of aluminum lined with Plexiglas inside the baths, and is 32 cm wide, 37 cm long, and 15 cm high. The potentials to the baths are supplied by a single power supply with a voltage divider that allows independent control of the two plating processes.

The first bath contained a solution for plating pure Ni; its composition is listed in Table I.¹⁹ The cathode efficiency during the plating of modulated films was determined to be 85%, and the cell was run at a current density between 2.7

FIG. 1. Schematic diagram of the plating apparatus.

and 4 A dm^{-2} . The second bath contained a solution, listed in Table II, for plating of Ni-20 at. % P at current densities between 15 and 20 A dm^{-2} , as developed by Brenner,¹⁴⁻¹⁶ Bagley,²⁰ and Cargill.¹⁷ This composition was checked by deposition of homogeneous films. The cathode efficiency was determined to be 15% during deposition of the modulated films. For both baths the cathode efficiency was found to be a strong function of the pH. The modulation wavelength and individual layer thicknesses could be selected by adjusting the current densities in the plating cells and the rotation speed of the substrate.

The films were studied by x-ray diffraction, using a standard diffractometer with $\text{CuK}\alpha$ or $\text{CrK}\alpha$ radiation. The wavelength of the composition modulation was determined from the position of the (000) satellite.¹¹ The atomic scale structure was characterized by high angle θ - 2θ and Ω scans, and by in-plane transmission electron microscopy on specially deposited transparent multilayers. The overall composition of the films was determined by electron microprobe analysis.

III. RESULTS

A number of films with wavelengths between 2.1 and 4.0 nm and with total thickness of about $1 \mu\text{m}$ were prepared. The total plating time for a film was between 15 and 30 min. The surface of most films was reasonably smooth; the hard-

ness of Ni-P may have been a benefit in minimizing possible "scratching" by the gaskets or embedded particles in the Teflon. Figure 2 shows a typical example of a (000) satellite, corresponding to a modulation wavelength of 3.9 nm. The wavelengths calculated based on the current densities measured during deposition agreed with the measured wavelengths to within 5%.

The overall phosphorus content was between 11.0 and 13.9 at. %. Since homogeneous films plated from the Ni-P solution contain 20 at. % P, the thicknesses of the individual Ni and Ni-P layers are about equal, in agreement with the selected current densities. The width of the modulation satellites (0.25° FWHM in Fig. 2, for example) shows that the variation in the layer thickness over the course of a deposition is about 10%. The intensity of the satellite is similar to that obtained for other amorphous metals prepared by dc sputtering,²¹⁻²³ as is the absence of higher order satellites. This indicates that the composition profile is close to sinusoidal, and that the nominally purer Ni films contain some P. This can be the result of either interdiffusion during the deposition process, or leaking between the baths. Deposition of a homogeneous film from the Ni bath after it had been used once for the multilayer deposition did indeed reveal the presence of about 1 at. % P. The gasket design is being improved to minimize the leakage.

TABLE I. Composition of the Ni plating bath (from Ref. 19).

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	: 300g/l
H_3BO_3	: 30 g/l
pH	: 2.0

TABLE II. Composition of the Ni-P plating bath.

H_3PO_3	: 30.0 g/l
H_3PO_4 (84%)	: 35.0 ml/l
NiCO_3	: 26.3 g/l
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	: 46.0 g/l
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	: 153.8 g/l

FIG. 2. Low-angle x-ray diffractometer trace, using $\text{CrK}\alpha$ radiation, of a Ni/Ni-P compositionally modulated film. The position of the (000) satellite corresponds to a modulation wavelength of 3.9 nm.

The high angle θ - 2θ scans showed only broad peaks, characteristic of the amorphous phase. An Ω scan with the detector at the 2θ position corresponding to the (111) peak of Ni did not reveal any crystallinity either. Dark-field electron microscopy and electron diffraction, however, revealed a mixture of amorphous material and very small crystals (< 5 nm). Presumably, the low-P layers are polycrystalline, with a grain size on the order of the layer thickness. That the layer structure is still very stable—no change in the satellite intensity has been observed over at least half a year at room temperature—is probably due to the alternating amorphous Ni-P layers, which contain no grain boundaries and in which the bulk diffusivity is low.

IV. CONCLUSION

We have demonstrated that it is possible to use electrodeposition to produce artificially layered materials with a wavelength short enough so that it can be observed easily in a conventional x-ray diffractometer. The method is simple and inexpensive, and allows deposition of materials that cannot easily be obtained by other methods. For example, by raising the average P content of the samples they can be made entirely amorphous, which makes it possible to use them for interdiffusion measurements in a binary metal-metalloid system. Differences in diffusion behavior and relaxation²⁴ between liquid-quenched and electrodeposited amorphous metals can also be investigated, since the atomic

transport properties, such as diffusivity, are very sensitive indicators of small structural differences.

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