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New dual-bath technique for electrodeposition of short repeat length multilayers

L. M. Goldman, C. A. Ross, W. Ohashi, D. Wu, and F. Spaepen
Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

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An electrodeposition technique for making multilayered thin films, based on controlled deposition from two different solutions, is described. Ni/NiP_x and NiP_x/NiP_y multilayered thin films with repeat lengths as low as 20 Å have been prepared. They show up to three low-angle x-ray peaks corresponding to the electron density modulation.

Multilayered thin films, consisting of alternating layers of two different materials, have been studied extensively because of their unusual properties.[1] Multilayers with repeat distances of 100 Å and below are of particular interest because they can be used to measure diffusivities to high accuracy,[2] as well as demonstrating anomalous properties such as the supermodulus effect.[3] Metal multilayers can be made by several processes including sputtering and evaporation, but the earliest attempts to make them were by an electrodeposition process.[4] However, full advantage has not been taken of electrodeposition as a multilayer fabrication process, despite its relative simplicity, speed, and economy compared to the more conventional vacuum processes.

Two approaches have been used to make electrodeposited metal multilayers. In most of the experimental work, a single-bath technique using an electrolyte or plating solution containing two different metal ions is used. The plating current or potential is periodically altered between two values so that alternate layers are deposited, rich in one metal or the other. The technique is limited, however, to specific bimetallic pairs by the need for an electrolyte from which both materials can be deposited, and it is difficult to obtain both metals in a highly pure form.[5] An alternative technique is one in which the substrate is moved between two different electrolyte baths. This method has the advantage that, in principle, any two materials can be deposited from standard plating baths without the need for a compatible electrolyte. The method is mechanically more complex because the substrate must be transferred between the solutions, and this may allow undesirable surface reactions.

Several types of multilayers have been made by single-bath electrodeposition; the most common is Cu/Ni[5–9] with wavelengths as low as 36 Å. Other systems include α/β brass multilayers with repeat lengths of 4000 Å,[10] Ag/Pd with repeat lengths of 1000 Å and above,[11] Ni/Mo alloys with repeat lengths of 1170 Å and above,[12] and multilayered NiP_x/NiP_y with a 200 Å repeat length.[13] The Ag/Pd study suggested that modulations of 500 Å and finer could not be made in this system by the single-bath technique, although x-ray diffraction demonstrated that repeat lengths in the range 36–100 Å[6,8] could be achieved in the Cu/Ni system.

We have previously shown that a two-bath technique can be used to produce repeat lengths in the range 21–40 Å in the Ni/NiP_x system.[14] X-ray diffraction revealed the presence of a single (000) satellite at low angles. This electrodeposition technique has the drawback that the substrate (which rotates as the multilayer is deposited) is in contact with gaskets surrounding the plating windows within which deposition occurs, and this could damage a soft deposit. In this letter we present a new two-bath method which eliminates this problem, and we demonstrate the use of the method to produce short repeat length Ni/NiP_x and NiP_x/NiP_y multilayers of sufficient quality to give several x-ray satellites.

The electrodeposition apparatus[15] operates by confining the two plating solutions to certain regions of the substrate by suitably designed plating nozzles (Fig. 1). Deposition occurs only in the areas of the substrate exposed to the solutions. The substrate (cathode) is a copper disk of 11 cm in diameter which rotates horizontally over the two plating nozzles. The nozzles are wedge shaped and contain platinum wire anodes. The substrate is suspended over the nozzles on three ball bearings and is turned by a motor; the nozzle-substrate distance is adjusted to ~0.5 mm. The electrolytes are held in 3 ℓ reservoirs at a constant temperature and are continuously circulated through the nozzles. The small sep-

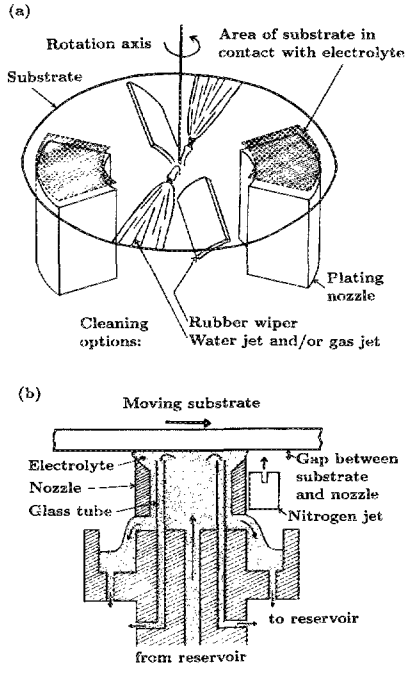

FIG. 1. (a) Schematic diagram of the electroplating apparatus and (b) detail of a plating nozzle in cross section.

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aration between the substrate and nozzles ensures that the plating area does not extend outside the nozzle rim. Solution and evolved hydrogen are sucked back to the reservoir by fine glass tubes just inside the perimeter of the nozzles. Suitable choice of the plating currents through each nozzle, together with selection of the rotation speed of the substrate (between 10 and 30 rpm), allows a multilayer of desired repeat length to be deposited.

Contamination of one electrolyte by the other can be a problem since solution may remain on the substrate as it rotates between the nozzles. To reduce this, fine jets of nitrogen gas were directed upwards at the trailing edges of the nozzles. Additionally, the cathode was cleaned as it passed between the nozzles by rinsing with a jet of water or the solution in the next nozzle, and drying with a jet of air. Alternatively, the substrate could be dried by a silicone rubber wiper pressing very gently against the surface, and this in fact gave the highest quality multilayers. Cross-sectional scanning electron microscopy (SEM) of thick, crystalline nickel deposits shows the same columnar microstructure irrespective of whether the deposit was made with the substrate rotating or stationary, i.e., whether the Ni was deposited as discrete layers or continuously.

Films were made from crystalline Ni/amorphous NiP_x and also from fully amorphous NiP_y with a modulation in the phosphorus concentration. Multilayers with repeat lengths down to 20 Å and individual layers as thin as 5 Å have been produced. Ni was deposited from a high chloride Watts bath[16] and amorphous NiP_x from a bath developed by Brenner[17] and Cargill.[18] The electrolyte compositions are given in Table I. The amount of phosphorus incorporated into the NiP_x is a function of plating conditions, particularly the current density[17,19] and rotation speed of the substrate, and it is therefore possible to deposit a NiP_x/NiP_y multilayer from a single bath by, e.g., varying the current density.[13] NiP_x is known to be amorphous above 18.6 at. % P.[20] Deposits of 25 at. % P were produced in this apparatus with a current density of 700 Am^{-2} and a rotation speed of 20 rpm, while the composition was 10 at. % at 2100 Am^{-2} and 20 rpm. A strong correspondence was found between the cathodic plating efficiency and the composition of the NiP_x. For instance, the low current density films with 25 at. % P generally plated at an efficiency near 10%, while the high current density films with 10 at. % P plated at an efficiency near 30%. The correlation between the NiP_x composition and the current density is in agreement with a previous investigation.[19]

TABLE I. Composition of electroplating solutions.

Ni electroplating bath		NiP_x electroplating bath	
$NiSO_4$	195 g/ℓ^{-1}	H_3PO_3	30 g/ℓ^{-1}
$NiCl_2$	174 g/ℓ^{-1}	H_3PO_4	35 m/ℓ^{-1}
H_3BO_3	40 g/ℓ^{-1}	$NiCO_3$	26 g/ℓ^{-1}
		$NiCl_2$	46 g/ℓ^{-1}
		$NiSO_4$	154 g/ℓ^{-1}
pH3.5 45 °C		pH1.5 68 °C	

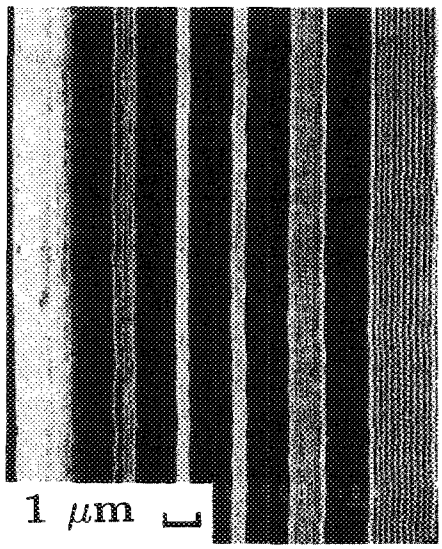

FIG. 2. SEM image of groups of NiP_x layers of thicknesses 2000 Å and below (white) in a crystalline Ni matrix (dark) on a copper substrate (not shown).

Because the composition of the NiP_x films varied with current density, the repeat length and composition of a multilayer are adjustible only within narrow limits if both nozzles are plating simultaneously. To make a wider range of multilayers possible, the apparatus was modified such that the plating currents to each nozzle are turned on alternately, and can be left on for a chosen number of revolutions of the substrate (detected by a sensor) so that thicker layers of each material can be built up. The multilayer can then have thicker individual layers than are available from a single revolution of the substrate. This also allowed production of NiP_x/NiP_y multilayers from a single nozzle with a periodically varying current density.

The copper substrates were polished using metal polish (Brasso), cleaned in acetone, polished on 1, 0.3, and 0.05 μm alumina grit, and washed in distilled water and methanol. The plating efficiency from each electrolyte was measured from the weight change of the substrate after a fixed plating time. Multilayer deposition took between 10 and 60 min to produce a total thickness of ~ 1 μm. X-ray diffraction was

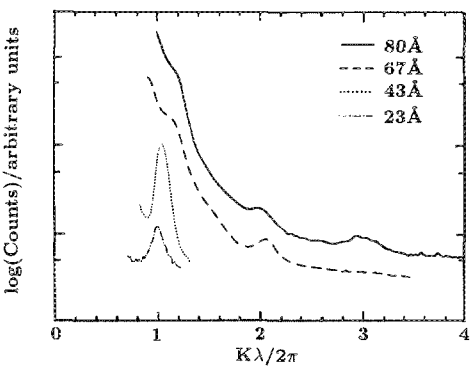

FIG. 3. X-ray traces at low angles, offset vertically, from three Ni/NiP_x multilayers with repeat lengths $\lambda = 80$, 43, and 23 Å and a NiP_x/NiP_y multilayer with $\lambda = 67$ Å. The horizontal axis is plotted in units of $K\lambda/2\pi$, equivalent to the order of reflection, where K is the magnitude of the scattering vector of the multilayer, $2k \sin\theta$ (k is the x-ray wave number).

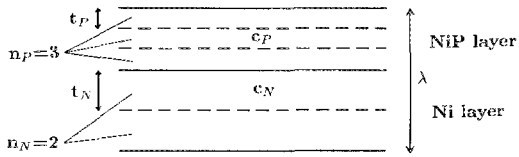

FIG. 4. Diagram of a unit cell of a multilayer.

performed in a θ-2θ scan using a GE diffractometer with Cr K_α radiation. Samples were examined by cross-sectional SEM after spark cutting, polishing, and etching in 1:3 acetic: nitric acid. Figure 2 shows a SEM image of a film consisting of groups of Ni/NiP_x layers separated by thicker Ni layers. The Ni is etched preferentially and the NiP_x appears brighter. Isolated individual layers down to 100 Å can be imaged using this method, and appear to be uniform in thickness. Average film compositions were determined by electron microprobe analysis.

For the shorter repeat lengths, x-ray diffraction at low angles showed strong (000) satellite peaks (Fig. 3), allowing determination of the repeat length, which agreed with measurements from cross-sectional transmission electron microscopy. The width of the x-ray peaks, typically $\Delta(2\theta) = 0.3°$ at $2\theta = 3°$, demonstrates that the average layer spacing remained constant to within 10% along the film normal. The highest order reflection that can be observed in any film corresponds to a spatial frequency of about 20 Å. This means that the rms interfacial roughness is <7 Å.[21] The positions of the three reflections from the 80 Å multilayer in Fig. 3 give an average refractive index of $(1-\delta) = 1 - (3.2\times10^{-4})$ from the modified Bragg equation, used at low angles.[22]

X-ray diffraction at high angles from Ni/NiP_x multilayers shows a broad peak in the position where the Ni (111) crystalline peak would be expected. The peak width is generally 2°–4° and increases as the repeat length decreases, corresponding to a crystallite size similar to the thickness of the nickel layer.

A series of Ni/NiP_x multilayers was made in which the individual Ni and NiP_x layer thicknesses were adjusted by altering the number of revolutions of the substrate per individual layer of the multilayer. The repeat lengths and average compositions of the multilayers were determined. If the number of revolutions per layer of Ni is n_N, the thickness of Ni deposited per revolution is t_N, its P content is c_N, and n_P, t_P, and c_P are the corresponding values for the NiP_x layer (Fig. 4), the repeat length λ, and the average P content c of the film are given by

$$\lambda = n_N t_N + n_P t_P \tag{1}$$

and

$$c\lambda = t_N c_N n_N + t_P c_P n_P. \tag{2}$$

A graph of λ/n_N vs n_P/n_N gives an intercept at $t_N = 16.6 \pm 1$ Å and a slope $t_P = 6.1 \pm 0.6$ Å (Fig. 5) for several films made with n_N and n_P between 1 and 6. A graph of $c\lambda/t_N n_N$ vs $t_P n_P/t_N n_N$ gives an intercept at $c_N = 1.3 \pm 1.2$ at. % P and a slope of $c_P = 26.7 \pm 2$ at.% P. These films were plated at 30 rpm with current densities and plating efficiencies respectively, of 350 Am^{-2} and 80% for Ni and 700 Am^{-2} and 16% for NiP_x. The substrate was not washed between the nozzles but was cleaned with the rubber wiper, which could account for the inclusion of small amounts of P in the Ni. The linearity of the graphs indicates that the same thickness of each material is deposited on each revolution of the substrate, and that its composition remains constant. This allows precise control of the dimensions and composition of the multilayer.

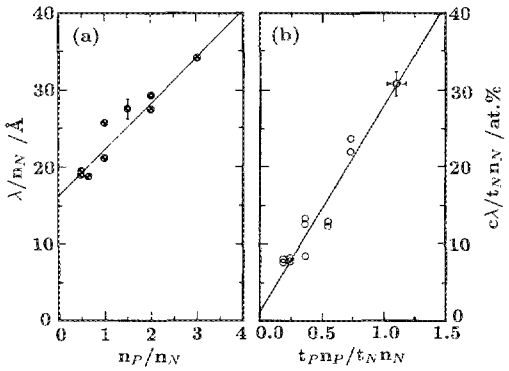

FIG. 5. Graphs with typical error bars of (a) λ/n_N vs n_P/n_N and (b) $c\lambda/t_N n_N$ vs $t_P n_P/t_N n_N$ for a series of multilayers.

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[1] *Synthetic Modulated Structures*, edited by L. L. Chang and B. C. Giessen (Academic, New York, 1985).
[2] A. L. Greer and F. Spaepen, in *Synthetic Modulated Structures*, edited by L. L. Chang and B. C. Giessen (Academic, New York 1985), p. 419.
[3] R. C. Cammarata, Proc. Mater. Res. Soc. **103**, 315 (1988).
[4] H. Koeppe, dissertation, Universitat Giessen, 1923.
[5] J. Yahalom and O. Zadok, J. Mater. Sci. **22**, 499 (1987).
[6] D. S. Lashmore and M. P. Dariel, J. Electrochem. Soc. **135**, 1218 (1988).
[7] D. Tench and J. White, Metall. Trans. A **15A**, 2039 (1984).
[8] S. Menezes and D. P. Anderson, J. Electrochem. Soc. (to be published).
[9] S. Menezes, in *Proceedings of the 7th Australian Electrochemistry Conference, Kensington, New South Wales, Australia, Feb. 1988*, edited by T. Tran and M. Skyllas-Kazakos (Royal Australian Chemical Institute, Electrochemistry Division, Australia, 1988), p. 79.
[10] R. Weil, C. C. Nee, and J. W. Chang, Metall. Trans. A **19A**, 1569 (1988).
[11] U. Cohen, F. B. Coch, and R. Sard, J. Electrochem. Soc. **130**, 1987 (1983).
[12] C. C. Nee, W. Kim, and R. Weil, J. Electrochem. Soc. **135**, 1100 (1988).
[13] B. Blanpain, M.S. thesis, Katholieke Universiteit Leuven, 1985.
[14] Lee M. Goldman, B. Blanpain, and Frans Spaepen, J. Appl. Phys. **60**, 1374 (1986).
[15] Lee M. Goldman, W. Ohashi, and Frans Spaepen, U.S. Patent No. 4 781 800 (November, 1988).
[16] *Metals Handbook Ninth Edition*, edited by W. G. Wood (American Society for Metals, Ohio, 1982), Vol. 5, p. 199.
[17] A. Brenner, *Electrodeposition of Alloys: Principles and Practice* (Academic, New York, 1963), Chap. 35.
[18] G. S. Cargill, III, Ph.D. thesis, Harvard University, 1969.
[19] D. S. Lashmore and J. F. Weinroth, Plat. Surf. Fin. **72**, 72 (1982).
[20] G. S. Cargill, III, J. Appl. Phys. **41**, 12 (1970).
[21] T. W. Barbee, Opt. Eng. **25**, 898 (1986).
[22] M. Sugawara, M. Kondo, S. Yamazaki, and K. Nakajima, Appl. Phys. Lett. **52**, 742 (1988).