Sequential deposition of Cu–Ni by electron beam evaporation and its characterisation

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Sequential deposition of Cu–Ni was carried out on glass and mild steel substrates by electron beam evaporation technique. The films were vacuum annealed at 200°C for 1 h. A smooth deposit with 7·8 μm thickness was observed using a profilometer. The polycrystalline nature with FCC structure of the films was determined with X-ray diffraction analysis. The uniform coverage of film surface was observed with atomic force microscopy (AFM). X-ray fluorescence (XRF) showed a change in composition for the vacuum annealed Cu–Ni film. A high transmittance in the visible region and a very low transmittance in the infrared region were observed for these films. Corrosion behaviour of the evaporated Cu–Ni films in 3·5% w/v NaCl solution was examined.

Keywords: Metallic coatings, PVD, Electron beam evaporation, Corrosion Nyquist plot

Introduction

Plating of Cu has generated considerable interest because of the use of this material in semiconductor metallisation. Copper as an interconnect material has low resistance and high electromigration resistance.[1] Many Cu alloys are more resistant to corrosion than copper itself owing to the incorporation of corrosion resistant metals such as nickel.[2] There has been growing interest in metallic multilayers owing to the unusual physical and magnetic properties observed in multilayers of nanometric bilayer thicknesses.[3] One such property, giant magnetoresistance (GMR), has been the prime focus of many researchers because of its potential importance in magnetic sensors.[4,5] The Cu–Ni system has been chosen because it is a model multilayer system and Ni/(Cu)/Cu[6] deposits wherein, a small amount of copper impurity in the layer is represented as (Cu), are industrially useful. Multilayer systems, Co(Cu)/Cu[7], Ni–Co(Cu)/Cu[8], etc., have been fabricated from a variety of electrolytes.

Thin coatings of various thicknesses of the noble metal Cu and the transition metal Ni were prepared by electron beam evaporation technique at different deposition rates and substrate temperature. Electron beam evaporation is one of the physical vapour deposition (PVD) techniques, which is faster and less complex than sputtering.[9,10] Basically, this is a physical process of vacuum evaporation, whereby a vapour flow is created using the kinetic energy of accelerated electrons directed towards the evaporators. Copper and nickel are face centred cubic metals and form a continuous series of solid solutions.[11] The preferred orientation (texture) of the crystalline grains of polycrystalline metals influences their physical, chemical and mechanical properties (hardness, elastic and abrasive resistance, magnetic penetrance, chemical activity, etc.).[12] In the present paper, the material properties of evaporated thin Cu–Ni metallic coatings on glass substrates and mild steel are reported.

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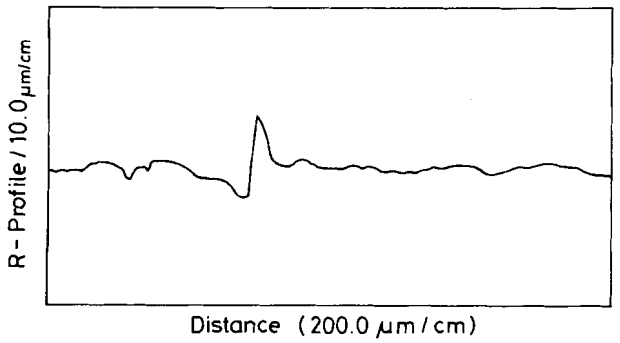
Experimental

The substrates used were ordinary 1 mm thick microscope slides and mild steel. Coating on to glass substrates was performed to study the optical properties. Microscope slides were cleaned with acetone, alcohol, a hot detergent solution and distilled water, and finally dried with lint free paper. Mild steel substrates were mechanically polished and degreased with acetone followed by electrocleaning and drying. The substrates, six at a time, were mounted in a standard 12 inch Hind Hi Vac vacuum chamber. Each substrate was normal to the line of sight from the evaporation source at a different polar angle to avoid shadow effects. The distances varied from 15 to 20 cm. Copper and nickel of 99·9% purity were used as the starting materials. The evaporations were sequentially performed without breaking the vacuum. A vacuum of 1×10^{-6} torr was set up using rotary and diffusion pumps. During evaporation, the film thickness was measured by a Quartz crystal thickness monitor. Annealing of the samples was performed in vacuum at 200°C for 1 h. XRD studies were carried out using a Jeol JDX 803a X-ray diffractometer. Surface morphology of the coatings was analysed using a Molecular Imaging atomic force microscope. The composition of the sequentially plated Cu–Ni coatings was analysed by Horiba X-ray analytical microscope XGT-2700. The optical characterisation of the films was carried out using a Cary 5E UV-vis-NIR spectrophotometer in the wavelength region of 300–2500 nm.

Results and discussion

Thickness

A profilometer was used to measure the step height between a base substrate and the adjacent coating. A



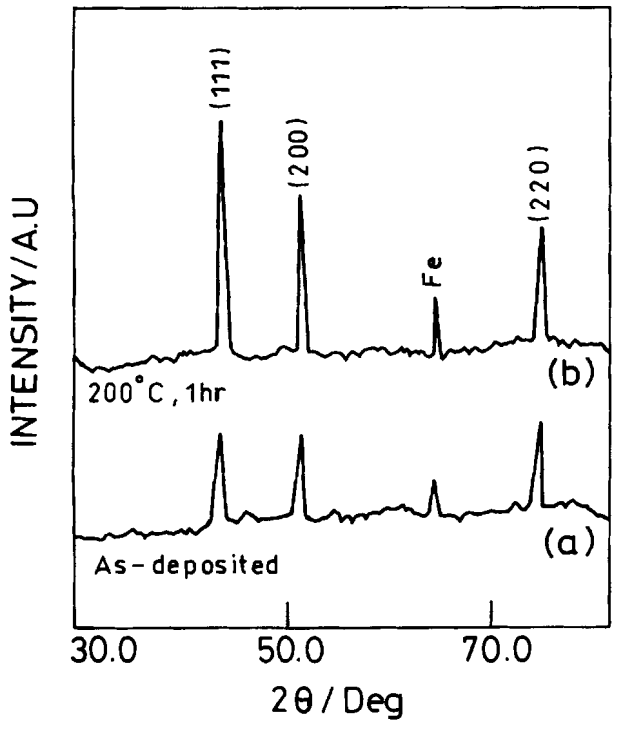
1 Roughness profile of as evaporated Cu–Ni film

stylus was drawn across the step from the substrate to the coating and both the vertical and horizontal motion of the stylus was amplified and recorded. A region of the substrate was masked before evaporating the elements. The uniform nature of the Cu–Ni films prepared by electron beam evaporation was observed from Fig. 1 and a thickness of 7·81 μm was obtained. Thickness of these coatings was also measured by an *in situ* quartz thickness monitor during evaporation and found to be 8·02 μm.

Structural and microstructural analysis

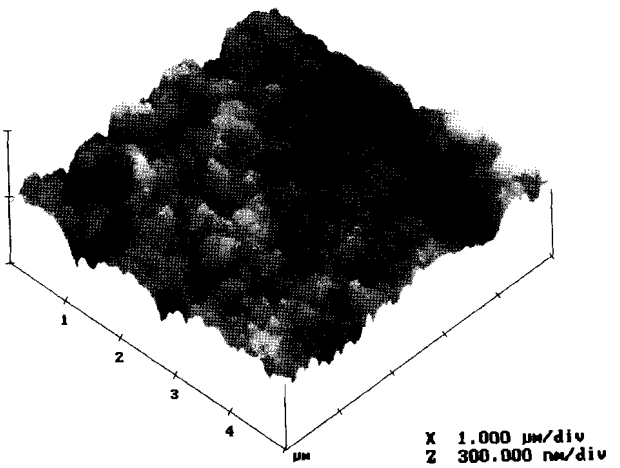
X-ray diffraction patterns of the Cu–Ni films as a function of heat treatment temperature are shown in Fig. 2. The polycrystalline nature of the as 'evaporated' and 'vacuum annealed' Cu–Ni films on mild steel substrates with orientations corresponding to face centred cubic structure was observed.

The observed d values of hybrid Cu and Ni from XRD pattern were found to be in good agreement with values reported earlier by Ishikawa *et al.*[13] The peak



a as evaporated; *b* vacuum annealed

2 X-ray diffraction patterns of Cu–Ni films



3 Representative AFM picture of as evaporated Cu–Ni film

height was found to increase for the film vacuum annealed at 200°C for 1 h, which indicates the grain growth of Cu–Ni deposit. The presence of the Fe peak due to substrate showed the thin nature of coating. The lattice parameter a was calculated as 3·608 and 3·616 for the 'as evaporated' and 'vacuum annealed' coatings respectively.

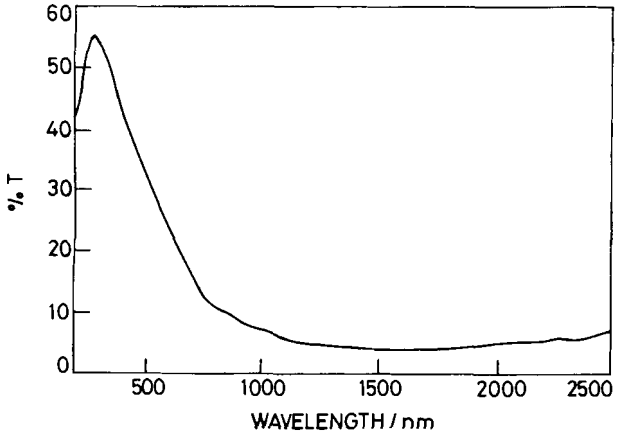
Surface characterisation of the 'as evaporated' sample was carried out using atomic force microscopy (AFM). The advantage of AFM is its capacity to probe the minute details related to the individual grains and intergrain regions as well in three-dimensional form. Figure 3 shows the representative AFM scan over an area of 5×5 μm. It shows the presence of hill-like structures on the top of a homogeneous granular background surface. The surface root mean square roughness R_{rms} was found to be 20 nm, which showed that the surface was more uniform without much projection of the grains above the average surface.

Composition analysis

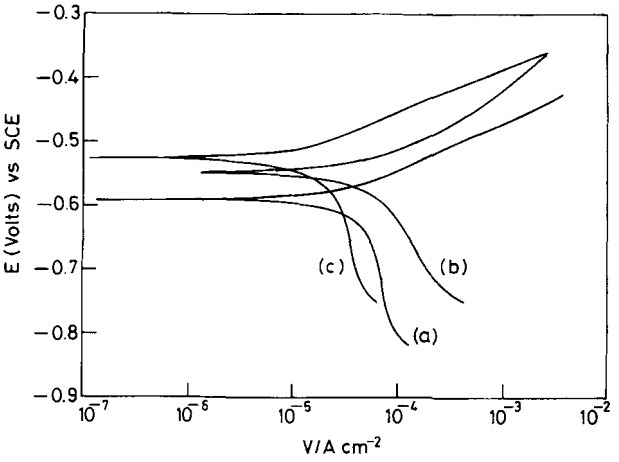
The composition of the coatings obtained from X-ray fluorescence (XRF) is shown in Table 1. The colour of the deposits depends on the composition. Deposits containing <40% nickel as observed from XRF were pink and appeared copper-like while deposits containing >40% nickel were silvery white in appearance which is the characteristic colour of nickel. The presence of Mn and Fe observed on as evaporated and vacuum annealed Cu–Ni films is due to the substrate, which indicated the thin nature of coating. The vacuum annealed sample showed change in composition which may be due to the diffusion of copper atoms into the nickel lattice during heat treatment.

Table 1 Composition analysis obtained from XRF

Sample	Element	Mass percentage/%
'As evaporated' Cu–Ni film	Mn	0·09
	Fe	1·15
	Cu	40·64
	Ni	49·12
'Vacuum annealed' Cu–Ni film	Mn	1·07
	Fe	2·42
	Cu	55·09
	Ni	41·42



4 Optical transmission spectra obtained for as evaporated Cu–Ni film



5 Polarisation measurements of *a* pure mild steel, *b* copper on mild steel and *c* nickel on copper in 3·5%NaCl (w/v)

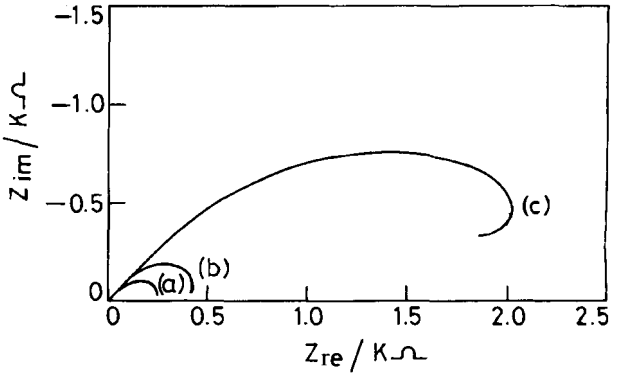
Optical and electrical properties

Figure 4 shows the optical transmittance spectrum obtained for the evaporated Cu–Ni films on glass substrates. A high transmittance in the visible region and a low transmittance in the infrared region indicate that these coatings are suitable in a window system where good heat insulating properties are required.

Electrical resistivity measurements for this coating on glass substrates were performed using a four probe method at room temperature. The resistivity was found to be ~45 μΩ cm for the 'as evaporated' and the 'vacuum annealed' Cu–Ni films. These values are in good agreement with the resistivity values reported earlier for hybrid films of electroless Cu–Ni films and multilayered Cu/Ni films by Ishikawa *et al.*[13]

Potentiodynamic polarisation and ac impedance spectroscopy

Corrosion resistance measurements were performed using a three electrode assembly. The samples were masked with lacquer to expose an area of 1 cm^2 on one side of the working electrode. A platinum foil and a saturated calomel electrode were employed as auxiliary and reference electrodes respectively. Polarisation studies were carried out in 3·5% neutral NaCl (w/v) solutions. Typical polarisation curves obtained for the corrosion behaviour of the samples are shown in Fig. 5. Table 2 includes the values of the corrosion potential E_{corr}, the corrosion current density j_{corr}, the anodic and cathodic Tafel slopes during polarisation in 3·5%NaCl (w/v) and the corrosion rate. The positive shift in E_{corr} and the decrease in j_{corr} for the Ni on Cu samples observed from the values of copper on mild steel and pure mild steel panel are indicative of an increasing corrosion resistance with Ni on Cu sample. This will also be due to reduction in porosity at increased coating thickness.



6 Nyquist plots for corrosion of *a* pure mild steel, *b* copper on mild steel and *c* nickel on copper in 3·5% w/v NaCl solution

The same three electrode cell assembly, as used for the potentiodynamic polarisation experiments, was employed for the AC impedance investigations. Impedance measurements were performed at open circuit potential (OCP) applying an AC signal of 10 mV in the frequency range 10 Hz–1 MHz. Figure 6*a–c* shows the complex impedance spectra (Nyquist plot) of pure mild steel of area of 1 cm^2, copper on mild steel and Ni evaporated on copper base respectively. The impedance data were analysed using software provided with the impedance system where the dispersion formula was used (equation (1)). For a simple equivalent circuit model consisting of a parallel combination of a capacitor C_{dl} and a resistor R_{ct}, representing the solution resistance, the electrode impedance Z is represented by

$$Z = R_s + \frac{R_{ct}}{1 + (2\pi f R_{ct} C_{dl})^{\alpha}} \quad (1)$$

where α denotes an empirical parameter ($0 \leqslant \alpha \leqslant 1$) and f

Table 2 Corrosion parameters obtained from polarisation studies in 3·5%NaCl (w/v)

Sample	VS SCE/mV	Tafel slope, V/decade^{-1} b_c	b_c	j_{corr}, $\times 10^{-5}$ A cm^{-2}
Pure mild steel	−590	0·073	−0·529	9·59
Cu on mild steel	−547	0·104	−0·263	6·2
Ni on Cu/mild steel	−526	0·066	−0·420	1·3

Table 3 Corrosion parameters obtained from impedance measurements (Nyquist plot)

Sample	OCP/vs SCE mV	R_{ct}/Ω	C_{dl}/F
Pure mild steel	−0·607	315·15	$1{\cdot}97 \times 10^{-3}$
Cu on mild steel	−0·556	471·07	$6{\cdot}66 \times 10^{-4}$
Ni on Cu/mild steel	−0·534	2511·86	$8{\cdot}412 \times 10^{-5}$

is the frequency in Hz. The above relation is known as the dispersion formula and takes into account the deviation from the ideal resistance capacitance (RC) behaviour in terms of a distribution of time constants due to surface inhomogeneties, roughness effects and variation in properties or composition of surface layers.[14]

Table 3 gives the values of OCP, charge transfer resistance R_{ct} and the double layer capacitance C_{dl}. The measured R_{ct} of this sample was the highest at 2·5 kΩ. Consequently, the double layer capacitance would be at a minimum for this deposit and it was found to be $8{\cdot}4 \times 10^{-5}\ \Omega^{-1}$. Because the OCP is the most positive for the Ni on Cu film, this suggests that this deposit should be the most resistant to corrosion.

Conclusion

Sequential evaporation of Cu–Ni on glass and mild steel substrates was performed using electron beam evaporation technique. The polycrystalline nature of the coatings with face centred cubic structure was observed from XRD studies. Uniform coverage of the coating surface with fine grains was observed from atomic force microscope. A change in composition for the vacuum annealed Cu–Ni film was observed from XRF analysis. The positive shift in E_{corr} and the decrease in j_{corr} values for the Ni on Cu over mild steel substrate showed its highly corrosion resistant nature.

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