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Effect of bath types on sonoelectrodeposited Cu/Ni Multilayer at low temperature

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Abstract

Multilayer of Cu/Ni of average thickness of 870nm were synthesized, by electrodeposition using single bath with different electrolytes at sub-ambient temperature under potentiostatic condition .The deposition is carried out with super modulated effect of ultrasound. Multilayer was prepared by pulsed electrodposition on the graphite substrate with different solutions. The nano order grain size of the bilayers, corresponds to kinetic control of either mass transport or mixed control of mass and charge transport of the electrode reaction. Attainment of this procedure was done by control over composition of bath and by application of ultrasound. The microstructure of this multilayer is systematically compared by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersed spectroscopy (EDS). Microscopic results show the highly agglomerated and smooth layers of both the nanostructure phase. The average thickness and grain size of the bilayers have found to be strongly dependent on the temperature, composition of the bath and presence of ultrasound. XRD results conforms the high crystallinity of both copper and nickel with a slight indication of intermediate phases of copper and nickel.

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Introduction

There has recently been a growing interest in electrodeposited multilayer [1] especially since it has been demonstrated [2, 3] that they can exhibit a significant giant magnetoresistance (GMR) effect. Giant Magnetoresistance effect in nanoscale alternating magnetic/nonmagnetic metallic multilayer has tremendous interest worldwide. GMR sensors have potential applications in detection of land mines, anti-skid brakes in cars and trucks, electronic surveillance of international borders, missile guidance systems and extremely useful for ultra-high-density data storage in hard disk (RAM) of computers. Many technological applications such as cutting, abrading, polishing and coating put a high demand on materials with unusually high hardness.

Multilayer can be produced by various methods like physical vapor deposition, molecular beam epitaxy (MBE) ion assisted deposition and magnetron sputtering [4,5,6].Production of multilayer by electrodeposition has a number of advantages over other techniques such as low cost process, simple equipment, higher deposition rate, precise deposition control and highly reproducible and complicated geometries can be coated. More significantly electrodeposition is a low temperature process which in turn prevents interdiffusion in the multilayer during deposition, generating a specified interface. Higher solution temperature generally produces higher surface irregularities .An increase in the grain size with increasing solution temperature is closely related to improved supply of metal ions, the increased diffusion distance of cations and the increased surface diffusion distance of adatoms[7].The kinetic control of the depositing species plays an important role in the layer deposition .Control over both composition and kinetics of the deposit significantly affected by the application of ultrasound . Ultrasound and electrochemistry provide a powerful combination for several reasons. Ultrasound is well-known for its capacity to promote heterogeneous reactions, mainly through increased mass transport, interfacial cleaning, and thermal effects. The formation of the deposit is time and flux dependent. Fast mass transport causes the formation of many nucleation sites (small overlapping diffusion spheres) and the high flux of material to increase rapidly.

The deposition can be of two types whether it is in the form of bilayers or alloy type. It is known that the alloy type is more sensitive to thermal load than the bilayer type .It has been already clearly establish that the GMR amplitude showing disappearing compared to bilayer type as the temperature increases [8].So the keen interest of fabrication is concerned on the fabrication of multilayer in the form of alternate layers of metals.

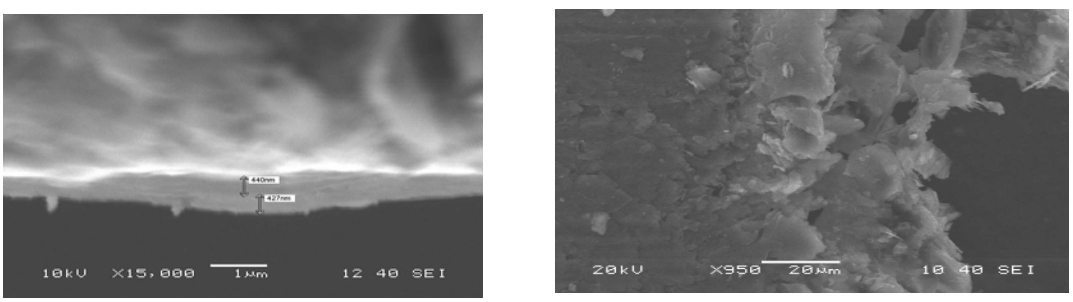
Experimental section

In this paper we have studied the deposition of bilayers in single bath with different type electrolyte (sulphate and chloride) bath on the substrate of copper and graphite at different temperature with the effect of ultrasonic vibration. The keen focus was centered on the synthesis of Cu/Ni multilayer by this sonoelectrochemical deposition. Among different types microstructure characterization of multilayer thin films the deposition of layers by different baths and the microstructure difference are investigated.
The experimental setup for the production of multilayered deposits consists of a single-compartment glass vessel. The deposits were produced on graphite and copper substrate use as the working electrode. Counter electrode was aluminum and reference electrode

was a saturated calomel electrode (SCE). The electrodes are polished by 1μm size sand paper and then it is mirror polished with diamond paste and washed and dried. The three electrodes were connected to a potentiostat (EG&G, Model-362) and the whole system was put in an ultrasonic cleaner. For maintenance of different temperature a cryogenic chamber was used. Two types of baths are used, basically sulphate and chloride bath are taken. The bath composition of different metal salts for sulphate bath is 280g/l of $NiSO_4.6\text{-}7H_2O$,8g/l of H_3BO_3, 32g/l of Na_2SO_4, 4g/l of $CuSO_45H_2O$ and for chloride bath 68g/l of $NiCl_26H_2O$,8g/l of H_3BO_3,29g/l of NaCl the temperature 20˚C the deposit was prepared. The deposition potential for coppers deposition was maintained at -0.3-0.6V, then was hold and then the potential was changed to 0.9-1.2V for Ni deposition. The scan rate was maintained at 1mV/s. Then the deposition was washed with distilled water and dried.

Results and discussion

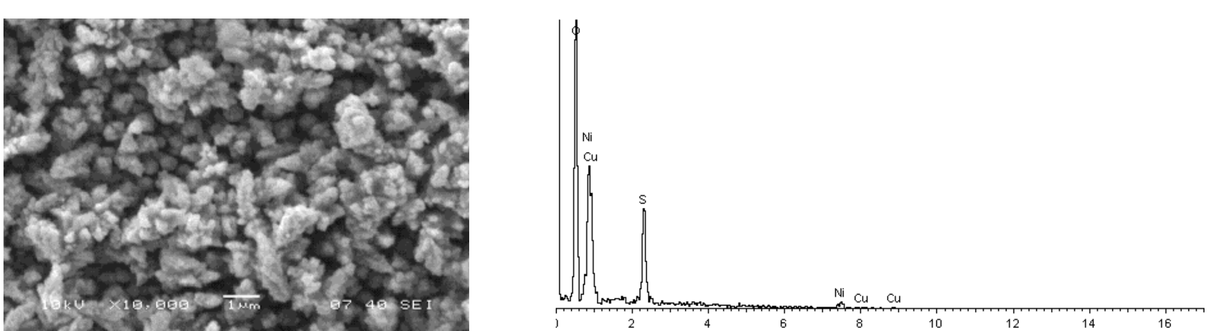
Scanning electron micrographs of cross section of the deposits of different baths are shown Fig-1. These graphs showing the thickness of the multilayer for sulphate bath is around 870nm and for sulphate bath and micron level for chloride bath. The electron micrograph shows the formation of multilayer parallel to the substrate, although the increase of the deposition time promotes the development of roughness surface increase.



(a) (b)

Fig-1 SEM images of electrodeposits at room temp with ultrasound (a) sulfate bath (b) chloride bath

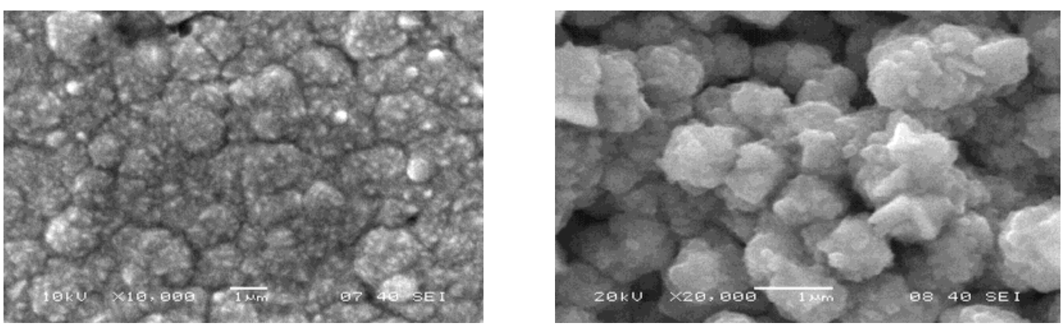
For silent condition and sulphate bath SEM graphs of Fig-2(a) shows the dendritic growth of the grain of the deposits. Figure-2(b) shows the corresponding compositional analysis by EDS. On quantification analysis, it confirms presence of equal amount of each phase with some concentration of oxygen and sulfur.



(a) (b)

Fig-2 SEM images of electrodeposits at 20°C temp without ultrasound (a) sulfate bath (b) corresponding EDS graph

For ultrasonic condition the grains in sulphate bath are showing homogeneous, spherical, and agglomerated and a compact deposit as shown in Figure. 3(a) under same resolution. In case of chloride bath the deposition at ultrasonic condition shows deposition with homogeneously dispersed spheroids of 1μm size and is seem to loosely bind to the substrate.



(a) (b)

Fig-3 SEM images of electrodeposits at 20°C temp with ultrasound (a) sulfate bath (b) Chloride bath

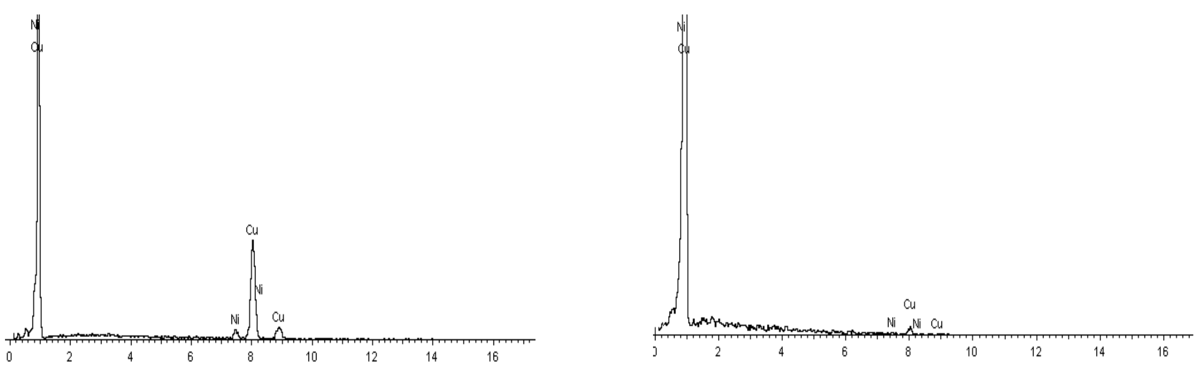


Fig-4 EDS images of electrodeposits at 20°C temp with ultrasound (a) sulfate bath (b) chloride bath

The EDS results shown in fig. 4 confirm the composition of the deposit. The EDS results show less sulphur in case of ultrasonic condition of the deposit as compared to silent condition. From the above SEM and EDS micrographs it can be conformed that the deposition at ultrasound condition showing more crystallinity as compared to the silent condition.

XRD plot of the deposit for the silent and ultrasonic condition are shown on the Fig. 5. The plot gives the crystalline phase confirmation of both the phases from their corresponding planes.

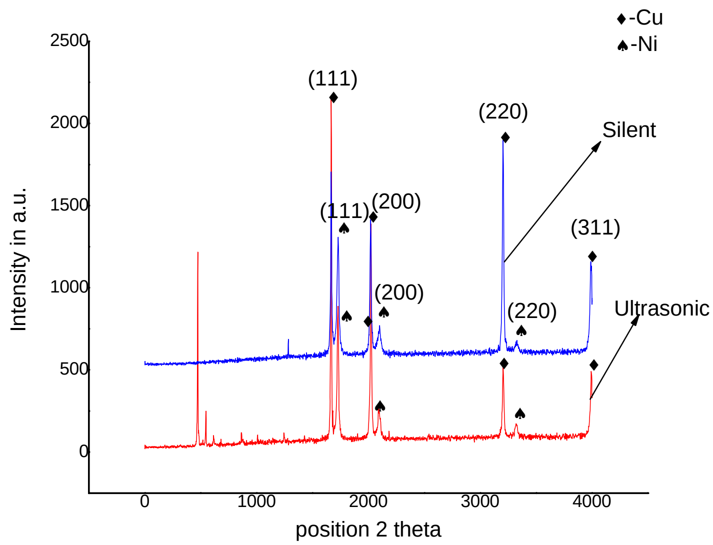


Fig-5. XRD plot of Cu/Ni deposition blue graph for ultrasonic condition and red graph for silent condition are shown.

Conclusion

All the experimental data conforms the multilayer structure. The above data clears that the multilayer structure can be formed at low temperature as compared to the established papers higher temperature with different baths like sulphate and chloride bath. But it is well searched from the above data that sulphate bath is giving better crystallinity layer structure than chloride bath at low temperatures graphs with XRD characterization matching the conformation towards the crystallinity structure for the bilayer deposition. The composition modulation confirms the Ni and Cu deposition.

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