Electrodeposition of Ni-W Alloys into Deep Recesses

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Introduction

Tungsten alloys are of interest due to their excellent corrosion, mechanical and tribological properties.[1] Nickel-tungsten alloys have the capability to significantly enhance the wear resistance of microstructures, coupled with very high thermal resistance.[2] In addition, the mechanism of Ni-W electrodeposition is fascinating, since pure tungsten cannot be electrodeposited from aqueous electrolytes without the aid of codepositing iron-group elements such as nickel.[3] Different aqueous plating baths have been proposed for Ni-W electrodeposition, including sulfamate[4] and aqueous ammoniacal citrate baths.[5] But there are several challenges that need to be addressed in order to adapt any of these electrolytes for depositing into deep recesses for MEMS applications, such as avoidance of gas evolving side reactions, local pH rise, and diffusional limitations of soluble reactant and product species.

Pulse electrodeposition with different ramping schemes has been investigated here for the adaptation of thin film Ni-W plating formulations to deposits into deep recesses for MEMS. It will be shown that pulsing with an appropriate relaxation time is a requirement for Ni-W deposition into 500 micron deep recesses in order to minimize hydroxyl ion gradients in the cavity and thus pH.

Experimental

Substrates for Ni-W deposition are prepared by exposing 500 μm PMMA sheets attached to copper plates to synchrotron x-ray lithography with a pattern of 200 μm diameter hole or square mask and then developing. Ammoniacal citrate bath at 70°C and pH 10 was used for electrodeposition. Current is pulsed using an EG&G potentiostat and function generator. The morphology of microposts was obtained from a scanning electron microscope (JEOL, JSM-840A). Composition along the length of the post was analyzed using WDS x-ray analysis with 1 μm spot size resolution. Rotating cylinder electrode experiments were also carried out to characterize the induced codeposition phenomenon.

Results and discussion

Ni-W deposits with 5 to 12 weight percent W and 90 % current efficiency were obtained on rotating cylinder Cu electrodes at various rotation rates. Despite the high current efficiency, direct current deposition of Ni-W under identical conditions into deep recesses was not possible. The central problem was in maintaining the pH in the cavity, which lead to undesirable precipitation products. Even moderate pH rises affect the induced codeposition mechanism and thus composition. Since microcavities are convective hindrances, this problem cannot be addressed by improved mixing in the bulk. Pulse current schemes have been considered to manage local pH rises.

Figure 1 shows a Ni-W deposit obtained from Ni-W citrate bath by galvanostatic pulsing with 10 sec "on" and 30 sec "off" times. The "on" current was varied as shown in Figure 2. The measured composition is shown in Figure 3. The tungsten concentration in the micropost depends on the applied current density as well as the depth of the recess. As the alloy grows, the boundary layer thickness decreases, and in this example, leads to a reduction of the tungsten alloy content. The results presented here have been used as a combinatorial design tool.

Figure 1. Ni-W microposts, 500 μm tall

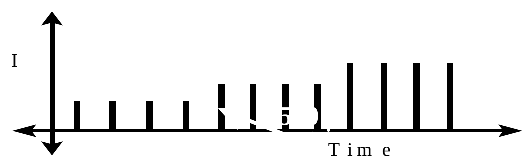

Figure 2. Galvanostatic pulsing scheme with step ramping

A key feature to adapt conventional Ni-W plating baths to deep recess plating is the use of long relaxation times in pulses. A ramp in pulsing current can be used as a combinatorial tool and shorten the time required to plate into deep recesses.

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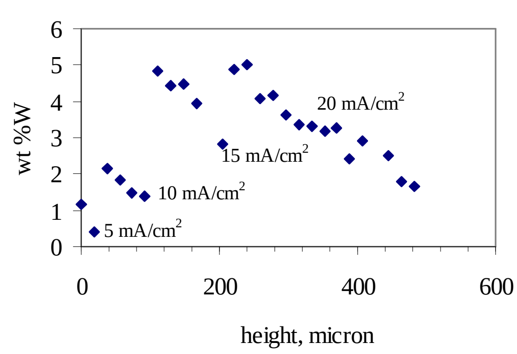

Figure 3. Wt % W along the length of the microposts

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