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Mechanical properties of nickel fabricated by electroplating with supercritical CO_2 emulsion evaluated by micro-compression test using non-tapered micro-sized pillar

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ABSTRACT

This paper reports mechanical properties of nickel films fabricated by high pressure electroplating (HPE) and electroplating with supercritical CO_2 emulsion (ESCE). Structures and mechanical properties of the plated films were examined by TEM, electron backscattered diffraction analysis and micro-compression test using a non-tapered micro-sized pillar. The films were electroplated in an electrolyte composed of Watts bath, supercritical CO_2 and surfactant. Agitation in ESCE leads to the formation of many CO_2-in-water type micelles. The micelles would cause an effect called periodic plating characteristic, and this effect refined the microstructure of the plated nickel from 3 μm of columnar grained structure to 8 nm diameter of equiaxial grained structure. Mechanical properties were also improved to 3.5 GPa of compressive strength, which was five times higher than the HPE nickel. The high strength in ESCE is believed to be largely a result of grain refinement and carbon impurity.

1. Introduction

Recently, micro-sized materials with high strength to be used as mechanical components in micro-electro-mechanical systems (MEMS) are required for the development of MEMS. Electroplating is a good candidate to fabricate micro-components used in MEMS [1]. Incorporating the electroplating method with lithography enables fabrication of metallic micro-patterns. Microstructures such as crystallographic orientations and grain size can also be easily controlled by changing pH of electrolyte [2], usage of additives [3] or pulse plating method [4] to meet the favorable mechanical properties of the components.

We have developed an electroplating technique with supercritical CO_2 (sc-CO_2) emulsion (ESCE). Agitation with addition of surfactant enables an electrolyte and sc-CO_2 to form emulsions with CO_2-in-water (C/W) type micelles at a certain pressure and temperature [5]. C/W micelles could continuously bounce on the surface of working electrode while electroplating is in process, and which gives periodic plating characteristic (PPC). PPC is like pulse plating where the electroplating reaction is turned off when the surface of working electrode is in contact with the micelles and turned on when the micelles go away from the surface. Hydrogen gas bubbles evolved as a side reaction of electroplating could be immediately engulfed by the micelles because of high solubility of hydrogen in CO_2. These features given in ESCE can increase the quality of the film plated, such as grain refinement, film smoothening, and defect- and pinhole-free plating [5]. The physical properties of supercritical CO_2, such as high diffusivity and low surface tension also contribute to the ESCE. Yan et al. reported when CO_2 is substituted by *n*-hexane for formation of the emulsion, the surface condition of the plated nickel films became worse [6].

However, effects of the sc-CO_2 emulsion on the nickel films fabricated by ESCE, especially microstructure and mechanical property, have not been well studied. This paper focuses on the effect of agitation, which is needed for formation of the micelles, on microstructure of plated nickel films by comparing nickel films fabricated by ESCE and high pressure electroplating (HPE), which is without agitation. Mechanical properties were investigated by micro-compression test using a non-tapered micro-sized pillar with square cross-section. The micro-sized pillars were fabricated from the plated films by using focused ion beam (FIB) machine. This investigation examines the potential of the ESCE for applications in MEMS fabrication by clarifying the microstructures and mechanical properties of the plated film using micro-sized samples.

2. Experimental

2.1. Material fabrication

Copper substrate was pretreated with 10 wt.% degreasing solution (Ace Crean, Okuno Industry) and 10 wt.% HCl solution (Okuno Industry) for 1 min and 10 s, respectively. Nickel films were fabri-

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cated by ESCE and HPE. Composition of the additive-free Watts bath was $NiSO_4 \bullet 6H_2O$(300 g/l), $NiCl_2 \bullet 6H_2O$(50 g/l), and H_3BO_3 (50 g/l). The pH of the electrolyte is 3.49. High pressure experimental apparatus with reaction chamber was applied for sample preparation, details of which are described elsewhere [7]. Operating pressure was 15 MPa and 6 MPa for ESCE and HPE, respectively. A non-ionic surfactant, polyoxyethylene lauryl ether ($C_{12}H_{25}(OCH_2CH_2)_{15}OH$) purchased from Toshin Yuka Kogyo was used, and magnetic agitator with a cross-shaped magnetic stirrer bar was employed for the formation of the emulsion. The same electrolyte was used for HPE. Emulsion was not formed for HPE because agitation was not applied. Samples were electroplated for 3 h with constant current density of 2 A/dm^2 at temperatures of 323 K for both ESCE and HPE.

2.2. Analysis

Cross-sectional slices of the sample were prepared by electronic discharge machine and were thinned down to the thickness of 50 μm by mechanical polishing and chemical polishing. Microstructure observation was conducted using scanning electron microscope (FEG-SEM, Hitachi: S-4500SE) equipped with electron backscattered diffraction pattern detector (Oxford instruments: INCA Crystal software) and transmission electron microscopy (TEM, Philips: CM200). Samples were prepared by FIB (Hitachi: FB2100) and ion milling machine (Fischone: Model 1010) using argon ion accelerated at 2 kV for to remove damaged layer. TEM investigations were performed at an acceleration voltage of 200 kV. The impurity content in the plated films was analyzed by a glow discharge optical emission spectrometer (GDOES, Rigaku: GDA750).

2.3. Micro-compression test

Micro-sized compression pillars were fabricated from the plated nickel films. FIB was used to fabricate the compression pillar as schematically shown in Fig. 1. In the beginning, pillar with the thickness of the sliced sample was fabricated as shown in Fig. 1a. The ion irradiation at an angle of 45 degree from the thin plate whittled the pillar down to smaller one as shown in Fig. 1b. Finally, as shown in Fig. 1c, the pillar was thinned down to the final shape of square cross-section with 20 μm on a side and 40 μm in height. Ion beam current was reduced to 300 pA in final step to minimize ion bombardment damage. The compression tests were conducted using a test machine designed for micro-sized specimen [8]. Loading directions were set to be parallel to nickel/substrate interface. Flat-ended diamond indenter equipped to a load cell was used as a compression platen, and controlled at constant displacement rate of 0.1 μm/s using piezo-electric actuator. Force and displacement data were recorded every 33 ms.

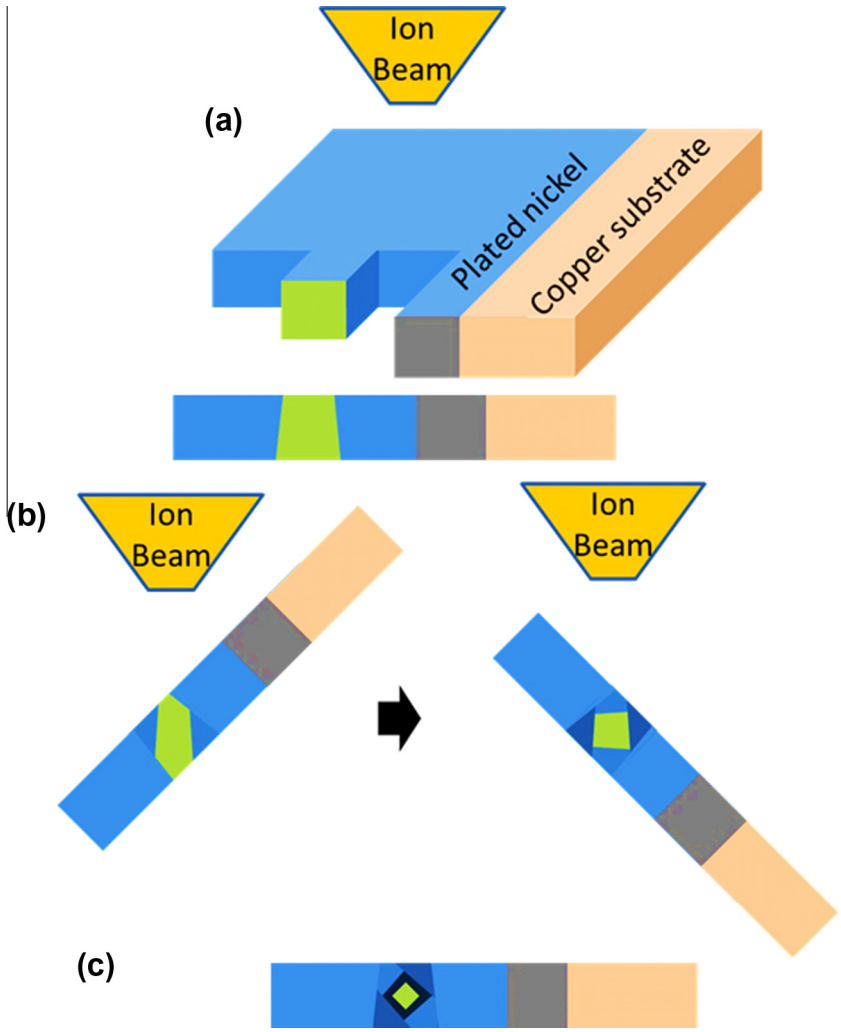

Fig. 1. Schematic images showing fabrication flow of the pillar. (a) Fabrication of the pillar with size as thickness of the sliced sample. (b) Size reduction of the pillar. (c) Finishing process using ion beam with low current at a tilt angle of ± 2.3.