1. Introduction

A spin transfer torque magnetoresistive random access memory (STT-MRAM) attracts attention as next generation memory device of a non-volatile random access memory because it is high-speed operation and high density. It is difficult to etch a magnetic tunnel junction (MTJ) which is an element of MRAM by using conventional plasma for metal etch, because of metal corrosion, compounds deposition again and negative effect of re-sputtering. Thermal etching in a solvent is a way to solve these problems if soluble byproducts are formed. The studied processes might also be promising for sidewall cleaning after conventional patterning.

A supercritical CO$_2$ fluid is a high pressure solvent that has low viscosity, excellent diffusivity, and zero surface tension. Thermal etching of Cu oxide in supercritical CO$_2$ has been reported [1]. In this study, we attempted to etch metal thin films (Cu, Ni) in supercritical CO$_2$ fluid.

2. Experimental procedure

A 50-nm-thick polycrystalline Cu or Ni thin films were deposited on glass substrates using magnetron sputtering. The metal/glass stacks were etched using hexafluoroacetylacetone (Hfzac) dissolved in a supercritical CO$_2$ fluid. The temperature and the total pressure were fixed at 200°C and 10 MPa, respectively. The etching time was changed from 30 to 60 min.

After the etching, the film thicknesses were measured with a surface profilometer. The films were characterized using an optical microscope and atomic force microscope (AFM).

3. Results and discussion

After supercritical CO$_2$ possessing, either Cu or Ni film became more transparent, which indicates film thickness decrease or significant film agglomeration. Figure 1 shows relationship between film thickness and etching time. Clear thickness decrement of Cu and Ni films was observed and the thicknesses decreased with increasing etching time. This indicates that Cu and Ni films were etched in supercritical CO$_2$ fluid.

Figure 2 shows AFM images of Ni surface (a) before and (b) after the etching. Surface of as-sputtered Ni was very smooth [Fig. 2(a)]. After the etching, the surface became rougher than that before the etching. The void formation was also observed at the Cu surface [Fig. 2(b)]. We observed the same tendency for Cu etching. Although the nominal thickness decrease looks small (Fig. 1), the Cu surface roughened significantly without a thickness increase. This also evidences Cu etching but not significant agglomeration.

The etching reactions are thought to be ignited by metal surface oxidation. The chelating reagent (hfac in our case) makes the oxide soluble in CO$_2$. This reaction forms H$_2$O as a byproduct and this H$_2$O works as an oxidizing agent. Etching uniformity can be sensitive the initial surface condition and the control of water amount is left as an interesting subject to study.

Fig. 1 Thickness of Cu and Ni films vs etching time.

Before Ni etching

Ni etching (60 min)

Ra = 1.7 nm

Ra = 2.8 nm

(a) (b)

Fig. 2 Ni surface (a) before and (b) after etching. The scan area is 10 x 10 μm. The z axis height is 100 nm

Reference