Gas Cluster Ion Beam Stimulated Reaction with Adsorbed Molecules on Metal Surface

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Various next-generation non-volatile memories have been developed in recent years. In these devices, exotic materials such as Pt, Ru, Ta, and CoFe are generally used. These materials are typically difficult to etch with current etching processes. It is also desirable that etching process is performed at low-temperature, with low damage, without halogen.

In this study, we used gas cluster ion beam (GCIB) as novel etching technique for various metals. Since the energy per atom or molecule of GCIB is a few eV, GCIB can be used as ultra-low-energy ion beam. Although the energy/atom is low, the bombarded areas experience both high pressure and temperature. As a result, enhancement of chemical reactions among reactive gas, adsorbed molecules and substrate surface occurs. In addition, desorption of etching products is also promoted by GCIB bombardment.

In this study, we examined etching effects for materials used in non-volatile memories (Pt, Ru, Ta, CoFe, Si_3N_4, SiO_2) by Ar-GCIB or O_2-GCIB irradiation in acetic acid vapor. Fig. 1 shows a schematic diagram of GCIB system with acetic acid vapor supply. Ar or O_2 cluster beams were formed with a nozzle. Subsequently they were ionized by electron bombardments, and were accelerated up to 20 kV. In the target chamber, an acetic acid supply was equipped to control the partial pressure of acetic acid at 10^{-5} Torr during GCIB irradiations.

Fig. 2 shows the etching depths of Pt, Ru, Ta, CoFe, Si_3N_4, and SiO_2 with or without acetic acid vapor during Ar or O_2-GCIB irradiations. The acceleration voltages of O_2-GCIB were 10kV, 20kV, and 20keV for Ar-GCIB. The ion dose was 2×10^{16} ions/cm^2. With acetic acid vapor supply during 20kV O_2-GCIB irradiation, etching depths of various metals (Pt, Ru, Ta, CoFe) increased by 1.8 – 10.7 times than those without acetic acid. Etching depth of Ru, Ta, CoFe by Ar-GCIB with acetic acid showed 2.2–16.1 times higher than those without acetic acid. These results indicate that O_2 or Ar-GCIB bombardments enhance chemical reactions between acetic acid and target metals.

Fig. 3 shows cross-sectional TEM images and diffraction patterns of FeCo films before and after etching by O_2-GCIB with acetic acid background gas. The acceleration voltage and the ion dose were 20 kV and 2×10^{15}ions/cm^2, respectively. In the case of Ar-GCIB with acetic acid, the etching depth was 2nm, however, that by O_2-GCIB with acetic acid was 7 times deeper (14 nm) under the same irradiation conditions. Halogen free, low-damage and low-temperature reactive etching of FeCo is realized with O_2-GCIB irradiation in acetic acid environment.

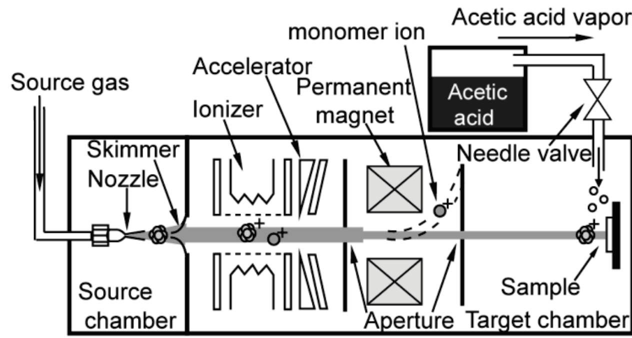

Figure 1: Schematic diagram of GCIB system with acetic acid gas supply.

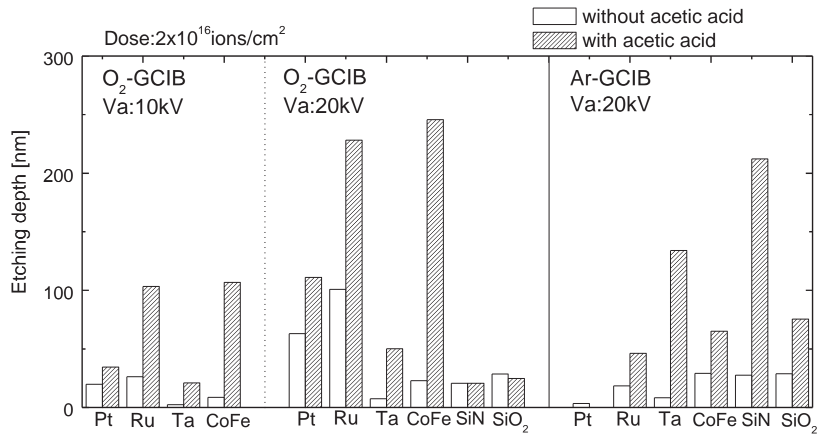

Figure 2: Etching depth of Pt, Ru, Ta, CoFe, Si_3N_4, SiO_2 irradiated by Ar or O_2-GCIB with/without acetic acid. (Accel. voltage: 20kV, Fluence: 2×10^{16} ions/cm^2)

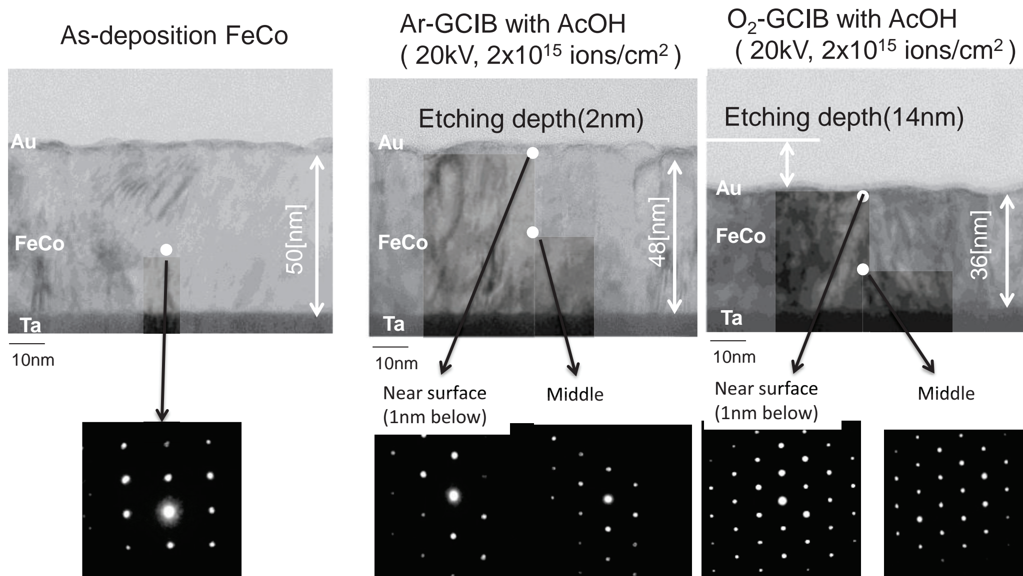

Figure 3: Cross-sectional TEM and diffraction pattern of FeCo films before and after Ar, O_2-GCIB irradiation in acetic acid environment.