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Gas cluster ion beam etching for etch-resistant materials

難エッチング材料加工のためのガスクラスターイオンビームエッチング技術

Noriaki Toyoda and Isao Yamada
豊田紀章, 山田公

Graduate School of Engineering, University of Hyogo
2167 Shosha, Himeji, Hyogo, 671-2280, Japan
兵庫県立大学大学院工学研究科　〒671-2280　兵庫県姫路市書写2167

Etching of etch-resistant materials using gas cluster ion beam (GCIB) with acetic acid circumstance was studied for future nonvolatile memory process. With acetic acid vapor supply during O_2-GCIB irradiation, etching depth of various etch-resistant materials (Pt, Ru, Ta, CoFe) showed 1.8 – 10.7 times higher values than those without acetic acid. High-pressure and high-temperature effects of GCIB enhance chemical reactions between reactive gas and substrate surface at room temperature. Thus, halogen free and room temp. etching of etch-resistant materials was achieved.

1. Introduction

Various next-generation nonvolatile memories have been developed in recent years. In these devices, exotic materials such as Pt, Ru, Ta, and CoFe are used. In general, there are many difficulties with current etching process for these materials. It is also desirable that etching process is performed at low-temperature, with low damage, without halogen.

Gas cluster ion beam (GCIB) has been developed in the past two decades. It can be used for various applications such as surface smoothing, low-damage etching, high-rate sputtering, thin film formations, surface analysis and so on [1-4]. As thousands of atoms or molecules bombard on areas of a few nm at the same time, 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 will occur.

We have reported Cu etching with O_2-GCIB irradiation under acetic acid vapor at room temperature without halogen gas [5]. In this study, we examined etching effects of Pt, Ru, Ta, CoFe, Si_3N_4, SiO_2 by Ar-GCIB or O_2-GCIB irradiation under acetic acid vapor. In addition, surface morphology, and surface composition analysis were carried out for Pt after O_2-GCIB irradiation with or without acetic acid in order to understand the etching process.

2. Experiment

Fig. 1 shows a schematic diagram of GCIB system with acetic acid vapor supply. Neutral Ar or O_2 cluster beams were formed by supersonic expansion of gas through a nozzle. Subsequently they were ionized by electron bombardments. Gas cluster ions were accelerated up to 20 kV. In this study, partial pressure of acetic acid gas was fixed at 10^{-5} Torr. Pt, Ru, Ta, CoFe, Si_3N_4, SiO_2 films were partially covered with stainless-mask, and etching depths were measured with a contact surface profiler. Surface morphologies after GCIB etching were observed with an atomic force microscope. In addition, Pt surface after Ar-GCIB or O_2-GCIB irradiation with or without acetic acid vapor were characterized with XPS. The acceleration voltage and ion dose were 10 kV and 1×10^{16} ions/cm^2, respectively.

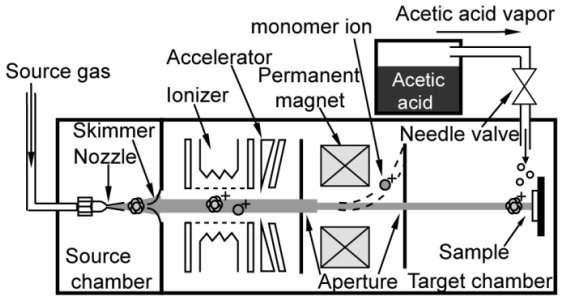

Fig. 1. GCIB system with acetic acid supply

3. Results and Discussions

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. Etching depth of Pt irradiated by 20kV O_2-GCIB without acetic acid was 18.4 times higher than that irradiated by Ar-GCIB. Also, etching depth of Ru by O_2-GCIB was 5.5 times higher than that irradiated by Ar-GCIB, because of volatile RuO_4 (M.P. 25.4^{o}C) formation.

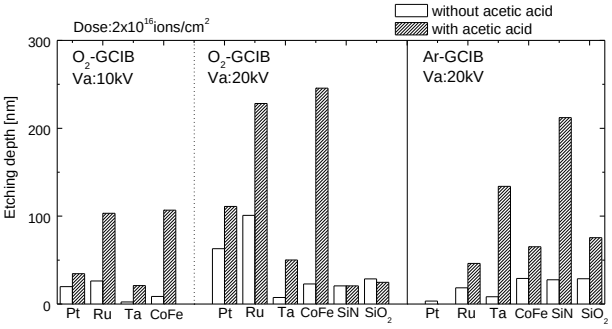

Fig. 2. Etching depth of Pt, Ru, Ta, CoFe, Si_3N_4, SiO_2 irradiated by Ar or O_2-GCIB with or without acetic acid

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.

On the other hand, the etching depths of SiO_2 and Si_3N_4 by O_2-GCIB didn't change either with or without acetic acid, which means that there is no chemical reaction enhancement. Therefore, these can be used as mask materials.

Surface morphology of Pt irradiated by O_2-GCIB with or without acetic acid was examined. Fig.3(a) shows the AFM image of the virgin Pt surface. The average roughness (R_a) and root mean square roughness (R_q) were 1.85 nm and 2.39 nm, respectively. Fig.3(b) shows AFM of Pt after O_2-GCIB irradiation without acetic acid. Fig.3(c) shows that with acetic acid. Acceleration voltage and ion dose of O_2-GCIB were 20 kV and 5×10^{15} ions/cm^2, respectively. R_a of Pt after O_2-GCIB irradiation without or with acetic acid were 1.00 nm, and 0.96nm, respectively. Although the etching depth was 1.8 times deeper than that without acetic acid, there was no surface roughening by O_2-GCIB etching with acetic acid.

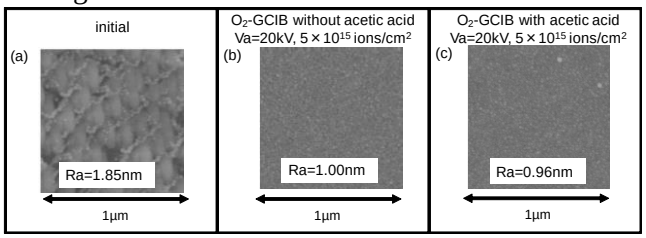

Fig. 3. AFM images of virgin Pt (a), O_2-GCIB without acetic acid (b), O_2-GCIB with acetic acid (c).

Next, Pt surface after irradiation of Ar-GCIB and O_2-GCIB with or without acetic acid were characterized with XPS. Fig.4 (a)-(d) show the XPS of Pt $4f_{7/2}$ before irradiation (initial) (a), after irradiation by Ar-GCIB without acetic acid (b), O_2-GCIB without acetic acid (c) and O_2-GCIB with acetic acid (d). Acceleration voltage and ion dose were 10 kV and 1×10^{16} ions/cm^2, respectively. After irradiation of Ar-GCIB without acetic acid (Fig.4(b)), spectrum was identical to the initial one (Fig.4(a)). After irradiation of O_2-GCIB without acetic acid (Fig.4(c)), Pt, PtO and PtO_2 peaks appeared. In contrast, after O_2-GCIB irradiation with acetic acid (Fig.4(d)), PtO_x peaks were very weak, and the spectrum was almost the same as the initial one. PtO_x layer was formed by O_2-GCIB irradiation. However, PtO_x reacted with acetic acid at the same time. Consequently, etching enhancement by removal of PtO_x layer was observed. Therefore, oxidation of Pt by O_2-GCIB is necessary in order to etch Pt.

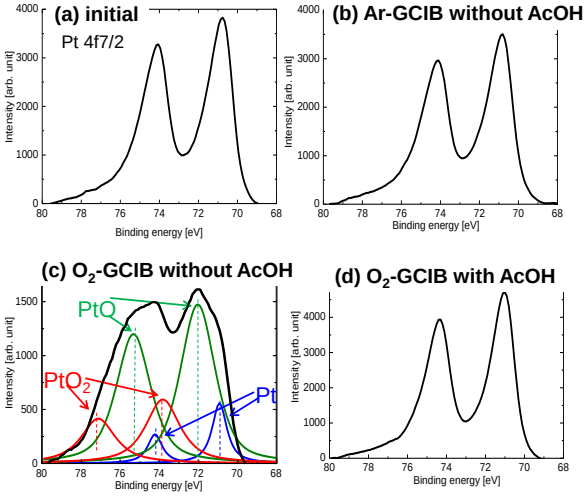

Fig. 4. Pt $4f_{7/2}$ XPS on initial Pt (a), Ar-GCIB without acetic acid (b), O_2-GCIB without acetic acid (c), O_2-GCIB with acetic acid (d)

Acknowledgments

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