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Beam study of plasma-surface interactions for etch resistant materials
ビーム実験による難エッチング材料のプラズマ表面相互作用

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In an attempt to develop low-damage, highly selective etching techniques for difficult etching materials such as magnetic thin films, surface reactions of thin films exposed to reactive ions have been studied with the use of a mass selected ion beam system. Especially focused is etching of Pt, Ni, Co and Ta films by CO^+, C^+ and O^+ irradiation. It is found that, with CO^+ ion irradiation, etching of Pt, Ni, Co proceeds whereas etching of Ta hardly occurs due to the formation of an oxidation layer. The results suggest etching mechanisms of carbon monoxide or methanol based plasmas and also possibilities of developing a selective etching technique by reactive plasmas.

1. Introduction

Recently magnetic thin films have become materials of choice for some specific microelectronics applications such as magnetic random access memory (MRAM). However, it is well known that magnetic films are difficult to etch because they hardly react with gaseous species that are present in plasmas. Therefore Ar ion milling seems to be almost the only etching technique in the current manufacturing processes. However, capabilities of Ar ion milling for anisotropic and selective etching of magnetic films are severely limited and therefore new technologies of reactive ion etching for magnetic films are now seriously sought [1][2][3].

Reactive ion etching based on noncorrosive CO based gas (CO/NH_3 or CH_3OH etc.) are candidates of magnetic film etching. However, the mechanism for etching reactions has not yet been clearly understood. In this study, we have focused on etching processes of Pt, Ni, Co and Ta (typical material of had mask) thin films and examined their surface reactions caused by energetic CO^+, C^+, and O^+ ions, which are generated in CO based gas plasmas. Specifically we evaluated etching yields of the samples and examined chemical states of ion irradiated sample surfaces, using a mass-selected ion beam system equipped with multiple *in-situ* diagnostic systems.

2. Experimental

The ion beam system can inject mono-energetic single-species ions (e.g., CO^+, C^+ or O^+ ions) to a sample (e.g., Pt, Ni, Co or Ta) film surface in ultra-high vacuum conditions[4][5][6]. The reaction chamber, where the sample is placed, is equipped with a quadrupole mass spectrometer (QMS), and an X-ray photoelectron spectroscopy (XPS) (Fig.1). The QMS is used for the detection of desorbed products during ion beam injection and XPS is used for *in-situ* chemical analyses of the irradiated sample surface. The ion beam energy used in this study was in the range of 300-1000eV. The etching yield was determined from the depth profile of a beam-irradiated surface, which was measured by stylus profilometry. For each sample, a 200nm thick film of the sample material was deposited on Si substrates by sputtering.

3. Results

Etching yields of Pt, Co and Ta films by CO^+ and O^+ irradiation are shown in Fig.2, Fig.3 and Fig.4. The etching yields of Pt by CO^+ ions are in agreement with the yields of equivalent physical sputtering (indicated by the blue straight line in Fig.2), which are estimated from interpolation of sputtering yield data of inert atom ions (He^+, Ne^+, Ar^+, Kr^+ etc.)[7][8]. The etching yields of Co by CO^+ ions are higher than that by O^+ ions but slightly smaller than the yields of equivalent physical sputtering. On the other hand, the etching yields of Ta by CO^+ ions are far smaller than the yields of equivalent physical sputtering and almost the same as that by O^+ ions. When C^+ ions irradiate Ni and Co surfaces, no etching took place and a:C layer grew.

From XPS measurements of Ni2p, Co2p and Ta2p for Ni, Co and Ta surfaces after exposure to various ions, it is found that Ta is oxidized, which suggests that the oxide layer on a Ta film prevents etching by ions listed here. It is also found that oxidation occurs on a Ni and Co surface under O^+

ion irradiation. On the other hand, the oxide layer on Ni or Co is shown to be removed by CO^+ ion irradiation.

4. Conclusions

It has been found that CO^+ ions etch Pt, Ni and Co without oxidation whereas O^+ ions hardly etch Ni and Co due to oxidation of the surface. On the other hand, CO^+ ions hardly etch Ta, forming a oxidation layer on the Ta surface. The etching yields of Ta by CO^+ and O^+ are far smaller than the yields of equivalent physical sputtering. Thus it has been found that high selectivity of Pt, Ni and Co etching against Ta by CO^+ irradiation arises from the prevention of etching by Ta oxidation.

References

[1] I. Nakatani: IEEE Trans. Magn, 32, (1996) 448.

[2] N. Matsui, K. Mashimo, A. Egami, A. Konishi, O. Okada, and T. Tsukada: Vacuum 66 (2002) 479

[3] K. Kinoshita, H. Utsumi, K. Suemitsu, H. Hada, and T.Sugibayashi: Jpn. J. Appl. Phys. 49 (2010) 208JB02.

[4] K. Karahashi, K. Yanai, K. Ishikawa, H. Tsuboi, K. Kurihara, M. Nakamura: J.Vac. Sci.Technol. A**22** (2004) 1166.

[5] K. Karahashi, and S. Hamaguchi: J.Phys. D: Appl. Phys, 47 (2014) 224008.

[6] K. Ishikawa, K. Karahashi, H. Tsuboi, K. Yanai, and M. Nakamura: J. Vac. Sci. Technol. A**21** (2003) L1.

[7] N. Laegreid, and G. K. Wehner: J. Appl. Phys. **32** (1961) 365.

[8] D. Rosenberg, and G. K. Wehner: J. Appl. Phys. **33** (1962) 1842.

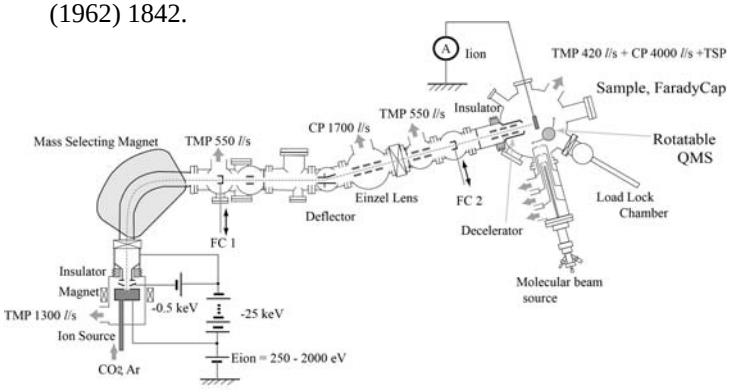

Fig.1.(a) A schematic diagram of Mass selected ion beam system

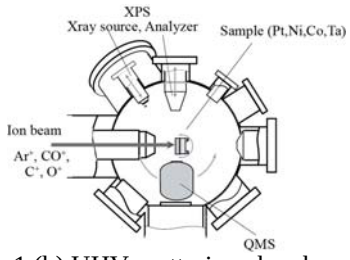

Fig.1.(b) UHV scattering chamber

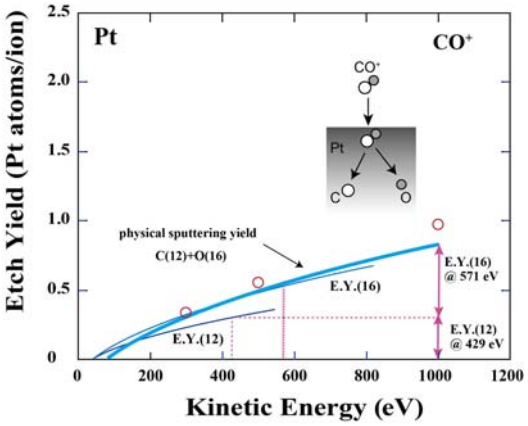

Fig.2. Etching yield of Pt by CO^+

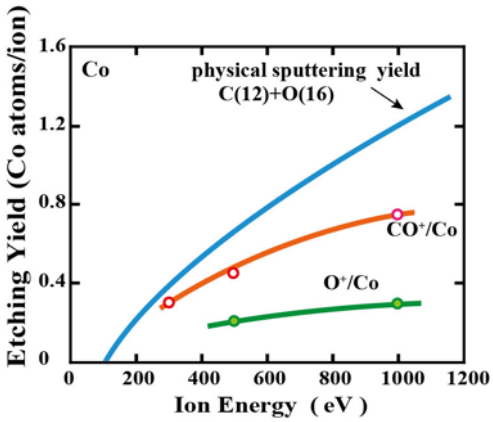

Fig.3. Etching yield of Co by CO^+ and O^+

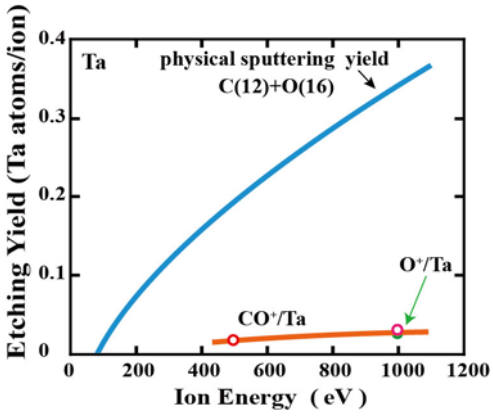

Fig.4. Etching yield of TA by CO^+ and O^+