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Transition Metal Complex Reaction Etching for MRAM Applications using Neutral Beam and Its Mechanism Investigated by First-Principles Calculation

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Abstract

We performed a theoretical investigation to understand the mechanism of recently reported new etching method of transition metal using ethanol gas and oxygen and argon neutral beams at low temperature. The process was entirely new and mechanism has not been known besides that the oxygen neutral beam caused oxidation of the metal surface and the oxidation is needed for the etching process. First-principle calculations based on density functional theory and cluster models were adopted for the investigation. As a result, it was found that adsorption of ethanol on both of tantalum oxide and metallic tantalum. Then "hydrogen movement" reaction can occur by argon neutral beam bombardment in case of oxide surface. It is concluded that (1) oxidation of metal surface, (2) adsorption of ethanol, and (3) hydrogen movement, are the key processes to proceed the etching and the hydrogen movement is the reason why oxidation is needed for etching. Especially, the "hydrogen movement" is the reason why oxidation is needed. Such understanding should be useful to design new etching processes using transition metal complex.

1. Introduction

STT-MRAM (spin transfer torque magnetic random access memory) attracts much attention due to its superior performance. However, its commercialization is not yet possible because anisotropic and damage-free etching process of its MTJ (magnetic tunnel junction) structure is not yet available. It is generally difficult to etch transition metals (especially, magnetic materials used in MTJ) with conventional plasma etching, and Ar ion milling has been widely used which causes problems such as damage, redeposition, poor selectivity, etc.

Recently Gu et al. reported [1] that anisotropic and damage-free etching of transition metals (Ta, Ru, and Pt) is realized using transition metal complex reaction, by using a neutral beam apparatus [2] shown in Fig. 1. It is an entirely new method, i.e., the metals were etched by exposing the surface with ethanol gas and oxygen + argon neutral beams, as shown in Fig. 2. It is expected the process proceeds as following (Fig. 3): (1) the metal surface is oxidized by bombardment of oxygen neutral beam (neutral beam oxidation [3]), (2) ethanol molecules adsorb at the surface, and (3) metal complexes like $Ta(OC_2H_5)_5$ are formed by argon neutral beam bombardment. However, detail of the mechanism was not clear. Especially, it is known [1] that elimination of oxygen neutral beam resulted in no etching, i.e., oxidation of the metal surface is inevitable for this etching process, but the reason is unknown.

To understand the etching mechanism, computational investigation was performed. Classical molecular dynamics calculation has been widely used in simulation of various plasma-surface reactions, but we thought it cannot be applied to this process because it is an entirely new process including metal complex reaction. Therefore we performed first-principles calculation.

2. Calculation

Calculations based on density functional theory were performed using Gaussian09 software running on a SGI UV1000/2000 system in Institute of Fluid Science, Tohoku University.

Figure 4 shows cluster models used in the calculation. Tantalum was adopted for this investigation. Since it is known that irradiation of oxygen neutral beam causes oxidation of the surface in low temperature [3], models representing tantalum oxide were prepared.

Calculations were performed based on the expected mechanism shown in Fig. 3. Thus, we first calculated adsorption of ethanol on the surface. Comparison with metallic tantalum surface was also performed. Then, we investigated possible reaction which may occur after the adsorption of ethanol. Finally we investigated whether such a reaction can occur by argon neutral beam irradiation.

3. Results and Discussion

First, adsorption of ethanol molecule on these clusters were investigated. As a result, it was found that the adsorption reactions of ethanol on both of tantalum oxide and metallic tantalum were both exothermic and had no energy barriers. It means that ethanol adsorbs spontaneously on both surfaces and that adsorption step (step 2 in Fig. 3) is

not a reason why oxidation is needed for the etching.

Then, we investigated possible reaction which may occur after the adsorption of ethanol. It was found that O–H bond in the adsorbed ethanol can be dissociated and the dissociated H atom can be bonded to an oxygen atom in the metal oxide (hydrogen movement). This causes elongation and weakening of Ta–O bonds in the tantalum oxide from about 1.9 Å to about 2.1 – 2.2 Å. Also, the adsorbed ethanol was changed into an ethoxy group. It means that adsorption of ethanol followed by the hydrogen movement occurs results in Ta–OC_2H_5 (ethoxy group) structure and weaker Ta–O(–Ta) bond. Thus, if this reaction occurs several times, the assumed volatile product, $Ta(OC_2H_5)_5$, can be generated and etching can progress. Note that this process can occur only in case of oxide surface, not metallic surface, because the metallic surface does not have oxygen atom which can accept the hydrogen atom from the adsorbed ethanol. This explains why oxidation of the surface is needed for transition metal etching.

We also found there was an energy barrier of about 0.6 eV in the hydrogen movement reaction. Thus, we investigated irradiation of argon neutral beam. It was found that irradiation of argon neutral beam to the ethanol-adsorbed surface caused the hydrogen movement, as shown in Fig. 5. It means that the hydrogen movement reaction and possibly tantalum etching can occur in the experimental condition under argon neutral beam irradiation.

4. Conclusions

The mechanism of the new etching process with transition metal complex reaction by using neutral beam, proposed by Gu et al., was investigated by first principle calculation. The mechanism is like following: (1) oxidation of the metal surface by oxygen neutral beam, (2) adsorption of ethanol, and (3) argon neutral beam irradiation causes the hydrogen movement reaction and generation of ethoxy complex. Such a new mechanism will open door to the new field of beam-assisted metallic complex reaction.

References

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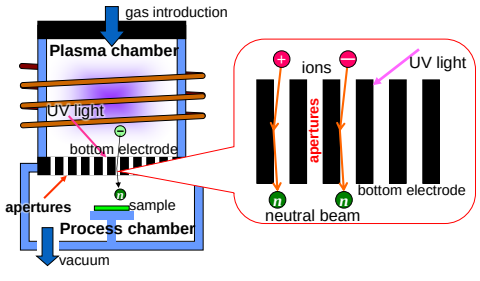

Fig. 1 Neutral beam apparatus.

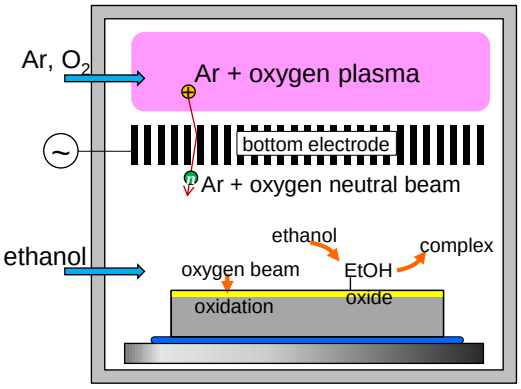

Fig. 2 Experimental setup using neutral beam to etch transition metals.

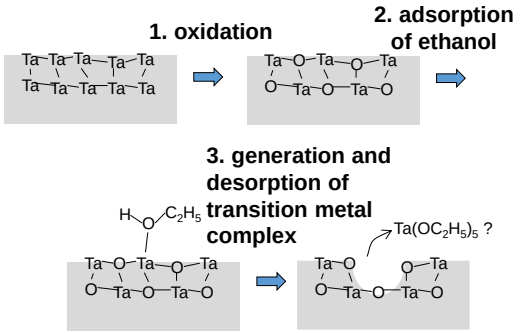

Fig. 3 Assumed mechanism of etching process.

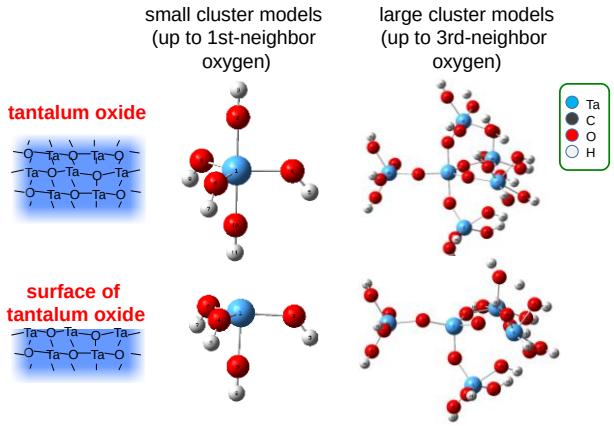

Fig. 4 Cluster models used for the calculation.

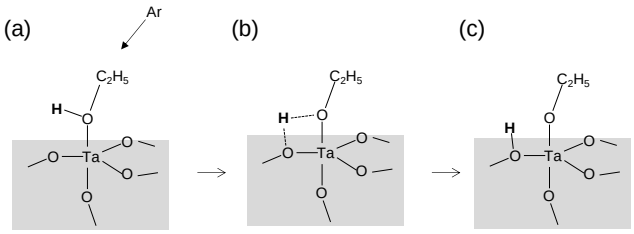

Fig. 5 Hydrogen movement reaction by argon bombardment.