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The effect of substrate temperature on the etching properties and the etched surfaces of magnetic tunnel junction materials in a CH_3OH inductively coupled plasma system

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ABSTRACT

The etching characteristics of the magnetic films (PtMn, CoFe) and hard mask materials (W, Ta) forming a magnetic tunnel junction (MTJ) stack in a CH_3OH inductively coupled plasma (ICP) system were investigated. We examined the etch rates of the metal films as a function of substrate temperature, and assessed the microstructures of the etched surfaces using high resolution transmission electron microscopy (HR-TEM). We also analyzed the surface states using X-ray photoelectron spectroscopy (XPS) and TEM electron energy loss spectroscopy (TEM-EELS). The PtMn and CoFe etch rates increased as the temperature increased, whereas the etch rates of W and Ta decreased slightly. Therefore the etch selectivity increased linearly with increasing substrate temperature. The CH_3OH plasma formed nonvolatile etching byproducts with the magnetic films and hard mask metals. In the case of PtMn and CoFe, the surface composition of the etching byproducts changed with increasing temperature; the relative concentration of pure metal compared with metal oxide or carbide increased as the substrate temperature rose. The etch rate was determined by the sputtering yield of the materials formed on the etched surface; accordingly the etch rates of those magnetic films would increase due to the higher sputtering yield of pure metal.

1. Introduction

MRAM (magnetic RAM), PCRAM (phase change RAM), and ReRAM (resistive RAM) have been widely investigated as candidates for a universal memory [1,2]. Among these, MRAM based on tunneling magneto resistance (TMR) has several important advantages, including nonvolatility and a fast writing speed (2–4 ns) comparable to that of DRAM; as such, this technology has the potential to replace DRAM and NOR flash memory. However, conventional MRAM is inherently limited in its scalability due to its use of an induced magnetic field in the writing method [3,4]. The recently discovered spin transfer torque (STT) switching could overcome the scaling limit of conventional MRAM. The magnetization of the free layer aligns toward the magnetization of the pinned layer, via the momentum transfer of spin polarized electrons when the current density is greater than a critical value, J_c [5,6]. The amplitude of the torque per unit area is proportional to the injected current density; the writing current therefore decreases proportionally with the cross-sectional area of the structure, which is beneficial for scalability [7]. Consequently, many groups have dedicated their research efforts to the development of STT-MRAM [8–12]. In STT-MRAM, the main data are stored in a magnetic tunnel junction (MTJ) device that consists of a bottom electrode, an MTJ multilayer and a top electrode. In a typical MTJ stack, an antiferromagnetic layer (e.g., a PtMn alloy) is located on the bottom electrode. A thin Al_2O_3 or MgO barrier layer separates the ferromagnetic free layer (e.g., a CoFe or NiFe alloy) from the antiparallel Ru coupled ferromagnetic sandwich layers.

To allow the commercial application of MTJ devices as mass storage devices, the device dimensions must be reduced to less than 50 nm, which is comparable to the dimensions of conventional DRAM. The critical engineering challenge for the fabrication of STT-MRAM is the development of an MTJ etching process, which largely determines the device characteristics and yields. Typical methods used to etch an MTJ stack consisting of magnetic films are physical etching, using ion milling, and reactive ion etching (RIE), which combines physical and chemical etching. In reactive ion etching, the discharge supplies both etchants and energetic ions to the surface. The combined effect of the etchant atoms and the energetic ions can be much larger in producing volatile etching byproducts than those produced by either pure chemical etching or by sputtering alone [13]. RIE is very helpful in enhancing the etch rate and etch selectivity to the mask. A Ta or W film located on the MTJ stack is used as both the top electrode and a hard mask protecting the MTJ during MTJ etching.

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The key issues in MTJ etching are as follows. The typical etching gases used in RIE are fluorine- or chlorine-containing gases such as Cl_2, BCl_3, SF_6, and CF_4. Etching a magnetic material is difficult, due to the nonvolatility of the etching byproducts when used with a typical halogen gas at practical processing temperatures. The nonvolatile etching byproducts therefore typically remain on the substrate surface and the sidewall of the MTJ pattern. In addition, etching selectivity to the hard mask material is very poor. Conventional reactive ion etching using Cl_2-based chemistry causes corrosion, due to the presence of residual amounts of atomic chlorine after MTJ etching [14]. Recently, several groups have explored the use of an MTJ etch technique using noncorrosive etching gases such as CH_3OH and CO/NH_3 [15–18]. The original concept for using CH_3OH gas was proposed by Osada et al. in 2004 [15]; they reported that CH_3OH plasma could etch MTJ stacks with good selectivity to a Ta hard mask. Otani et al. [16] found that an MTJ device etched in CH_3OH plasma showed better electrical characteristics compared with an MTJ device etched via Ar ion milling, and Peng et al. [17] observed that nonvolatile etching byproducts remained on the MTJ sidewall after etching in CH_3OH plasma.

Dry etching of the MTJ stack is the most critical step in STT MRAM fabrication. The basic advantages of the CH_3OH etching process, such as the fine etch profile resulting from the high selectivity between the magnetic metal and Ta, were already known in this field. Despite this, research on the etching characteristics of magnetic films such as PtMn and CoFe when using CH_3OH plasma is still in its early stages, and the etching mechanism of these films is not clearly understood. It is also important to understand the etching mechanism of hard mask materials such as Ta and W, which show relatively high etching selectivity in CH_3OH plasma. However, there have been few reports on the CH_3OH plasma etching mechanism of metal films that include magnetic materials and hard mask materials. Furthermore, it is hard to find any in-depth discussion of the etching selectivity between magnetic films and hard mask metals.

In the present study, we investigated the etching characteristics and etching mechanism for the magnetic metals PtMn and CoFe (that form the MTJ stack) and the hard mask metals Ta and W. The effect of substrate temperature on the etching rate of the metal films was examined in the range of 20–120 °C. We also investigated the surface reactions with various physical/chemical post-etch analytical techniques. Based on these surface analytical results, we discuss the temperature dependence of the etching behavior, and seek to provide a detailed explanation of the etching mechanism of magnetic films in CH_3OH plasma, as well as the etching selectivity to the hard mask metal. A fully integrated MTJ stack was fabricated, and its etching behavior is interpreted in terms of the proposed etching mechanism.

2. Experimental

Fig. 1 shows a schematic illustration of the ICP etching system for MTJ etching. The etching system consisted of an ICP antenna, a vacuum chamber, a power supply and matching system, an electrostatic chuck (ESC), a gas injection system, and vacuum pumps. The equipment used in this test was a commercial etching system and its plasma source type was inductively coupled plasma (ICP). The ESC was designed to endure high temperature up to 180 °C, which would be helpful to etch nonvolatile metals. Optical emission spectroscopy attached to chamber could monitor etching process in chamber. 27.12 MHz ICP power was applied to the dual-coil flat-type antenna on top of the chamber, and 2 MHz bias power was applied to the electrostatic chuck (ESC) on the bottom. Dual-coil flat antenna, which has separated inner and outer coil in a plasma source part, could improve etch uniformity within a wafer by controlling the currents of the coils independently. In this study, a 300 mm Si wafer was used as the substrate.

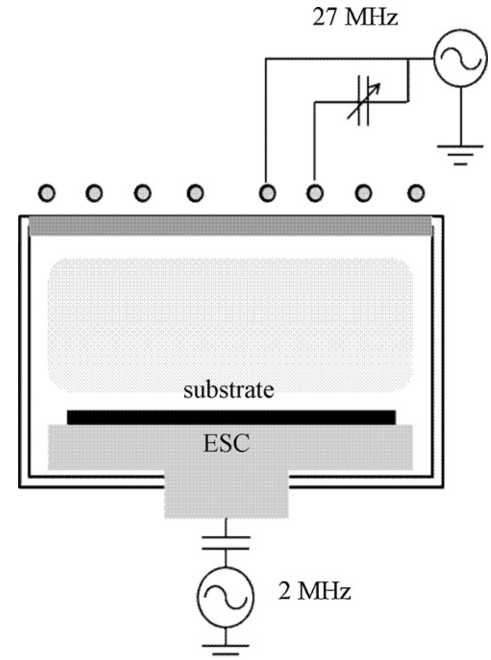

Fig. 1. Schematic diagram of ICP chamber system for MTJ etching.

First, the etching characteristics and mechanisms of each MTJ material were studied in CH_3OH plasma. CoFe and PtMn (the magnetic films forming a MTJ multilayer), and W and Ta (the hard mask materials for patterning), were deposited on Si wafers by physical vapor deposition. The etch rate of each film, the etch selectivity, and the formation of byproducts on the etched surface were carefully investigated as the substrate temperature was increased from room temperature to 120 °C. The stoichiometry of the CoFe and PtMn sputter targets were 90% Co and 10% Fe, and 60% Pt and 40% Mn, respectively, in terms of atomic concentration.

A high-resolution transmission electron microscope (HR-TEM, JEM-3000F, Jeol, with 0.17 nm resolution) was used to observe the thickness and the surface structure of each metal sample, before and after etching. The etch rate was calculated for each film from the thicknesses measured from the TEM images. The elemental profile and surface bonding structure were analyzed with high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), energy dispersive spectroscopy (EDS), and electron energy loss spectroscopy (EELS). TEM specimens of the etched metal films were covered by a thick epoxy film, then dimpled and ion-milled in sequence (PIPS, Gatan). The EELS analysis of the etched surfaces was performed by a Cs-corrected TEM (Cs-titan 80-300, FEI) under the following conditions: probe size of 0.3 nm, camera length of 38 mm, and entrance aperture of 2 mm. An EDS detector (EDAX) with 134 eV energy resolution and 0.3 nm probe size was used for the EDS analysis. X-ray photoelectron spectroscopy (XPS, Quantum2000, Ulvac-Phi) was employed to analyze the surface bonding structures and etching byproducts on the etched surface. As an X-ray source, 1486.7 eV of Al Kα was applied during XPS analysis, and 1253.6 eV of Mg Kα was substituted for Al Kα in the experiments measuring the XPS spectra of Fe in the CoFe etched surface.

The etching characteristics of the MTJ stack were also investigated through nano-patterning. To fabricate the MTJ device, an MTJ stack consisting of CoFe, PtMn, and MgO was deposited sequentially on the Si substrate, following the deposition of TiN/Ta as a bottom electrode. After the deposition of the Ta hard mask as a