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Effect of oxygen deficiency on electronic properties and local structure of amorphous tantalum oxide thin films

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ABSTRACT

The dependence of electronic properties and local structure of tantalum oxide thin film on oxygen deficiency have been investigated by means of X-ray photoelectron spectroscopy (XPS), Reflection Electron Energy Loss Spectroscopy (REELS), and X-ray absorption spectroscopy (XAS). The XPS results showed that the oxygen flow rate change results in the appearance of features in the Ta 4f at the binding energies of 23.2 eV, 24.4 eV, 25.8, and 27.3 eV whose peaks are attributed to Ta^{1+}, Ta^{2+}, Ta^{3+}/Ta^{4+}, and Ta^{5+}, respectively. The presence of nonstoichiometric state from tantalum oxide (TaOx) thin films could be generated by the oxygen vacancies. In addition, XAS spectra manifested both the increase of coordination number of the first Ta-O shell and a considerable reduction of the Ta-O bond distance with the decrease of oxygen deficiency.

1. Introduction

Recent years, the resistance random access memory (RRAM) has been intensively investigated due to its potential in future nonvolatile logic and memory devices [1]. RRAM composed of a metal/insulator/metal structure which can be reversibly switched between a high resistance states (HRS) and a low resistance state (LRS) by applying bias voltage [2,3]. High performance has been reported for resistive switching materials with good electrical properties, thermodynamic stability, fast write, low energy operation, and a lower cost of fabrication such as NiO, TiO_2, ZrO_2, HfO_2, and CuO_x [4–9]. Tantalum oxide (Ta_2O_5), particularly, can be one of the possible alternatives for RRAM application because of their high endurance, long retention, and fast switching speed which is related to the presence of the oxygen deficiency in Ta_2O_5 [10–12]. The oxygen deficiency is regarded as the cause of the defect in Ta_2O_5 and contributes to the formation of non-stoichiometric tantalum oxide (known as TaO_x) [13].

Jain et al. [14] investigated the effect of substrate heating on the stoichiometry and electrical properties of pulsed dc reactively sputtered tantalum oxide films. They showed that the partially oxidized of tantalum oxide films caused a lower breakdown field, higher leakage current density, and higher apparent dielectric constant and dielectric loss. Meanwhile, Yang et al.[15] reported the nonstoichiometric TaO_x films deposited by radio frequency sputtering on the prefabricated Pt/Ti/SiO_2/Si substrate as a multilevel resistance switching. They confirmed that the switching between the high resistance state and the intermediate resistance state originates from a phase transformation between Ta_2O_5 and TaO_2. In other study, Kimura et al. [16] reported the relationship between leakage current and local structure around the tantalum atom by EXAFS analysis and showed that the leakage current of tantalum oxide capacitors prepared with different process (using N_2 annealed, dry O_2 annealed, and O_2-plasma annealed), are strongly related to imperfection in the arrangement and deficiency of oxygen atom in tantalum oxide films. Hence, the oxygen content inside tantalum oxide plays a crucial role in altering the electrical properties [17–19]. However, so far, there are no detailed reports on the effect of oxygen deficiency on the electronic properties and the local structure of tantalum oxide thin films. In this study, we

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examine the electronic properties and local structure as a function of the oxygen flow rate during deposition for tantalum oxide films by utilizing REELS, XPS, and XAFS methods.

2. Experimental

The nonstoichiometric TaO_x thin films were deposited on prefabricated Pt/TiN(50 nm)/SiO_2/Si(001) substrate with the thickness of 15 nm by radio frequency sputtering method. Two different conditions were imposed out as follows: (1) The films were deposited with O_2 gas flow rate, which were varied at 9.5, 11, 12, 14, and 16 sccm (standard cubic centimeters per minute); (2) One film was prepared by O_2 plasma oxidation in order to get stoichiometry of tantalum oxide. XPS and REELS spectra were obtained by using a VG ESCALAB 210 equipment. XPS measurements were performed using a Mg Kα X-ray source and the energy analyzer pass energy of 20 eV. The binding energies were referenced to the C 1s peak of hydrocarbon contamination at 284.5 eV [20]. The REELS spectra were measured with the primary electron energy of 1.5 keV and with a constant analyzer pass energy of 20 eV. The incident and take-off angles of electrons from the surface normal were 55° and 0°, respectively. The full width at half maximum (FWHM) of the elastic peak was 0.8 eV. Local structure of TaO_x thin films was studied by means of X-ray absorption spectra (XAS) at 8C beam line in Pohang Light Source (PLS), South Korea, and with the electron storage performance of 2.5 GeV and 200 mA. The fluorescence mode with 7-element germanium solid-state detector (SSD) system was used in the XAS measurement and the data was collected and analyzed at the TaL_3-edge near 9881 eV using a suitable IFEFFIT program.

3. Results and discussions

The chemical states of TaO_x thin films grown in different oxygen flow rate were investigated by using XPS. Fig. 1(a) shows that the binding energies of the doublet Ta4f photoelectron core-level spectra are at around 27.40 and 29.29 eV for Ta $4f_{7/2}$ and Ta $4f_{5/2}$, respectively, with the spin-orbit splitting of 1.89 eV. These peaks correspond to the binding energy of fully oxidized stoichiometric Ta_2O_5, which are in good agreements with other works [21,22]. No change of binding energy for Ta $4f_{7/2}$ and Ta $4f_{5/2}$ was found in different oxygen flow rate, except the intensity increased with increasing in oxygen flow rate. The Ta 4f spectra of tantalum oxide were decomposed by Gaussian-Lorentzian (with 20% Lorentzian) line shape with a Shirley background and a fixed spin-orbit splitting (which is 1.9 eV) in the doublet spectra. The oxygen deficit rate of the film results in the appearance of component non-stoichiometric state Ta4f which are located in the lower binding energy region at binding energies of about 23.3, 24.5, 25.8, and 27.4 eV, these peaks are attributed to Ta^{1+}, Ta^{2+}, Ta^{3+}/Ta^{4+}, and Ta^{5+}, respectively [21]. We carried out X-ray diffraction measurements on all TaO_x films to investigate the diffraction peaks of the films (which is not shown here), which showed that all samples including deposited with O_2 plasma are amorphous. The detailed information about the binding energies, FWHM values, atomic ratios of [O]/[Ta] atom (with absorbing oxygen and carbon contamination on the surface taken into consideration), and percentages concentration for the Ta 4f components are given in Table 1. The [O]/[Ta] atomic ratio determined from XPS results for the films prepared with O_2 plasma, is 2.5 which is similar to that of the stoichiometry for Ta_2O_5. The nonstoichiometric TaO_x films were grown by varying oxygen flow rate. Hence, the presence of nonstoichiometriy from *a*-TaO_x thin films could be generated by

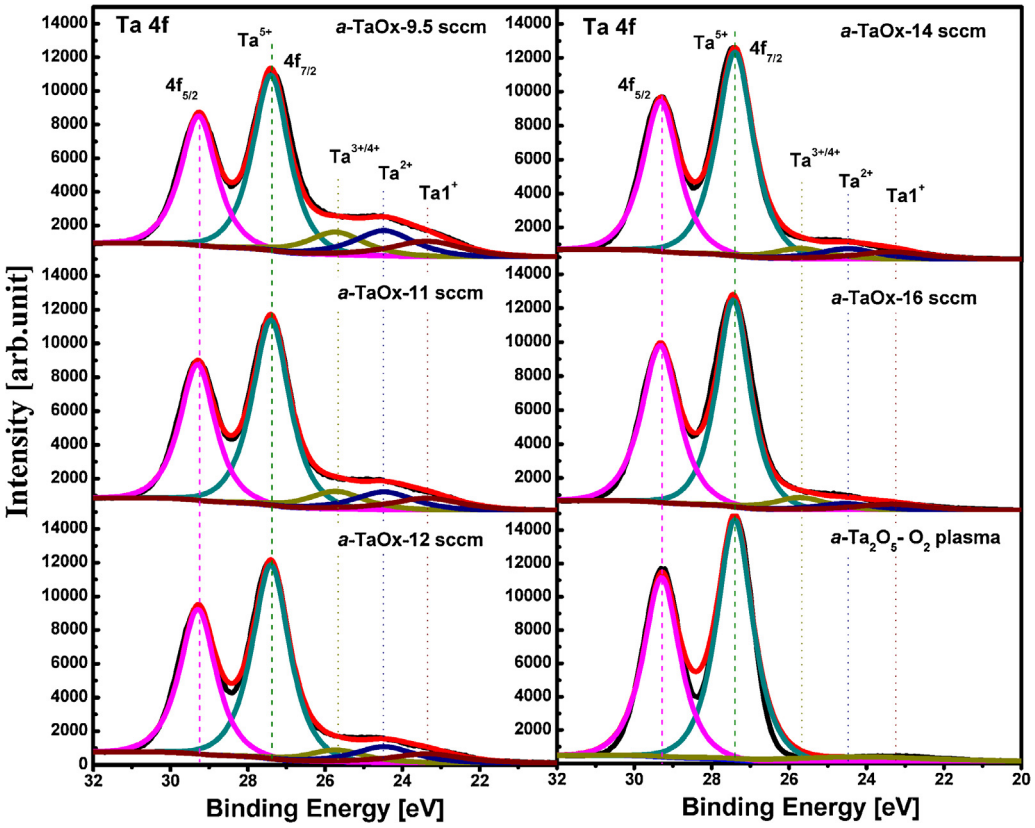

Fig. 1. XPS spectra of Ta 4f for tantalum oxide thin films in different oxygen flow rate as well as O_2 plasma oxidation including the curve-fitting of the core level Ta 4f with a Gaussian-Lorentzian function and a fixed spin-orbit splitting of doublet spectra Ta $4f_{7/2}$ and Ta $4f_{5/2}$.