Electron-Ion Mixed Conduction of Amorphous WO_{3-x} Thin Film Probed by Soft-X-Ray Spectroscopy

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Amorphous WO_{3-x} thin films with ~200 and ~600 nm thicknesses have been prepared on Pt/SiO₂ substrates by RF magnetron sputtering. The mixed valence states of W⁶⁺ and W⁵⁺ are observed in the photoemission spectroscopy (PES) spectra of W 4*d* core level. The electrical conductivities exhibit the thermal activation-type behaviors in the temperature region of 100~200°C. The activation energies of 200 and 600 nm films are 0.1 and 0.6 eV, respectively. The band gaps (*E_g*) of 200 and 600 nm films are ~2.6 and ~2.0 eV, respectively. The expanded PES in the *E_g* region and X-ray absorption spectra exhibit the W 5*d*-DOS at the Fermi level and defect-induced state at the bottom of conduction band, respectively. The above results indicate that the conducting carrier of amorphous WO_{3-x} thin film is closely related to the film thickness and oxygen vacancies.

Keywords: amorphous WO_{3-x} thin film, oxygen vacancies, electron-ion mixed conduction, electronic structure

1. INTRODUCTION

According to Moore's law, the performance of present current Flash memory will reach the physical limit in the near future. Among many candidates, the resistive random access memory (ReRAM), which is based on resistive switching effect of dielectric material, is expected as one of the most promising devices with high speed and low power consumption [1,2]. The switching effect has been observed in several dielectric oxide materials such as NiO [3,4], TiO₂ [5-7], Ta₂O₅ [8,9], and WO_{3-x} [10]. Furthermore, similar effect has been reported in Ag₂S and amorphous WO_{3-x}-based nanoionics devices by Terabe *et al.* [11-13]. In particular, the Pt/WO_{3-x}/Pt device structure exhibits the volatile and nonvolatile resistance states, which correspond to the human brain's forgetting process for short-time memory and long-term memory. The current response strongly depends on the magnitude and interval time applied voltage [12,13]. This device is realized through externally induced local migration of oxygen ions [13].

Tungsten oxide WO₃ with stoichiometric composition is a transparent insulator with a band gap (*E_g*) of 2.6 eV in the visible light region [14,15]. This material exhibits metallic conductivity and superconductivity by substitution of carrier element and formation of oxygen vacancies [16-17]. Therefore, the structural and electrical properties have been extensively studied in the single crystal and thin film forms. However, details of amorphous WO_{3-x} with oxygen vacancies, which can use as brain-type memory device, have not been clarified in term of solid state physics.

In this study, we have prepared the amorphous WO_{3-x} thin films with 200 nm and 600 nm thicknesses by RF magnetron sputtering. Since the thin films have high

resistivity at room temperature, the electrical conductivity was measured by AC impedance method. The conducting carrier was estimated from the slope value of the conductivity measured as a function of oxygen gas partial pressure [20,21]. The electronic structure, which is closely related to the conductivity, was studied using soft-X-ray spectroscopy. In this paper, we report about the electron-ion mixed conduction is important for the brain-type memory device using the amorphous WO_{3-x} thin film.

2. EXPERIMENTAL

The WO_{3-x} thin films were deposited on Pt/SiO₂ substrates by RF magnetron sputtering using WO₃ ceramic target. The target sizes had a diameter of 30 mm and a thickness of 5 mm. The crystallization was confirmed by X-ray diffraction (XRD) analysis.

The RF magnetron sputtering system has a symmetric configuration with rotating substrate holder for compositional uniformity [22]. During the deposition, the total flow rate of Ar gas and O₂ gas was approximately 20 sccm. The deposition pressure was fixed at 6.8 mTorr. The substrate temperature and RF power applying the target were fixed at room temperature and 50 W, respectively. The 200 and 600 nm films were prepared by controlling the deposition time. The prepared thin films are confirmed to be amorphous phase by XRD analysis.

In order to measure electrical conductivity, Pt top electrode with thickness of 100 nm was deposited on the film surface through a metal shadow mask by RF magnetron sputtering. The prepared Pt/WO_{3-x}/Pt/SiO₂ films were cross-point structure. The electrical conductivities of out-of-plane were measured by the AC

impedance method using frequency response analyzer (Solatron 1260) and amplifier (Solatron 1296) in dry atmosphere in a temperature region from room temperature to 200 °C. In order to characterize the conducting carrier, the conductivities were measured by changing the oxygen gas partial pressure (P_{O_2}) at 200 °C. The measurements frequency region was from 32M Hz to 10m Hz.

The electronic structures were measured by X-ray absorption spectroscopy (XAS) and photoemission spectroscopy (PES) systems installed at the undulator beam line BL2A in Photon Factory (PF) at the High Energy Accelerator Organization (KEK) in Tsukuba, Japan [23]. The XAS spectra were measured in total electron yield mode. The kinetic energy of photoelectrons for PES was measured using the Gammatdata-Scienta SES-2002 hemispherical analyzer. The energy resolution s of PES and XAS were 100 and 60m eV, at $h\nu = 800$ eV. The energy axis was calibrated by measuring the Au film evaporated onto the manipulator in all the measurements.

3. RESULTS AND DISCUSSION

Figure 1(a) shows PES spectra in the W 4d core level of WO_{3-x} thin films with 200 nm and 600 nm thicknesses. The prepared thin films did not exhibit the XRD peaks, indicating the amorphous structures for WO_{3-x} thin film. Therefore, the valence states of W and O were characterized by PES spectra. The W 4d PES spectra consists of $4d_{5/2}$ and $4d_{3/2}$ by spin orbital splitting. The spectra shape and peak position of 200 nm thin film are similar to those of 600 nm thin film. However, the spectral shape of W $4d_{5/2}$ peak is non-symmetric like in both films. Here, the authors have analyzed the valence states by Gaussian fitting assumed the W^{6+} and W^{5+} as shown in Fig. 1(a). The fitting can reproduce the W $4d_{5/2}$ peak with non-symmetric structure. The W^{5+} peak intensity of 200 nm is ~ 1.07 times as strong as that of 600 nm thin film.

Figure 1(b) shows the O 1s PES spectra of the amorphous WO_{3-x} thin films with 200 nm and 600 nm thicknesses. The spectral shapes and peak positions of 200 nm thin film are in good agreement with those of 600 nm thin film. However, these spectra are asymmetric shapes. A broad shoulder structure at ~ 531 eV corresponds to the O-H bond as shown in dashed line obtained by Gaussian fitting. The existence of O-H bond has been observed in YSZ thin film with oxygen vacancies [24]. The O-H bond is not the molecules absorbed at the surface because such a molecules structure is observed as double peak structures or different peak position.

The O 1s PES spectra were normalized by beam current and measurement times. The O 1s peak intensity of 600 nm thin film is ~ 1.07 times as strong as that of 200 nm thin film. This is a direct evidence that the amount of oxygen vacancies is larger than in 200 nm thin film. Furthermore, the intensity ratio of O 1s peak accords with that of W^{5+} peak intensity in Fig. 1(a). These results indicate that the amorphous WO_{3-x} thin films has W^{5+} valence state created by oxygen vacancies in addition to W^{6+} valence state in the ground state.

Figures 2(a) and (b) show the Cole-Cole plots of

Fig. 1 (a) W 4d and (b) O 1s PES spectra of WO_{3-x} thin films with 200 nm and 600 nm thicknesses.

Fig. 2 Cole-Cole plots of WO_{3-x} thin films with (a) 200 and (b) 600 nm thicknesses at 150 °C.

Fig. 3 Arrhenius plots of the conductivities of WO_{3-x} thin films with 200 nm and 600 nm thicknesses in dry atmosphere.

Fig. 4 Conductivities of WO_{3-x} thin films with 200 nm and 600 nm thicknesses as a functions of oxygen partial pressure (P_{O_2}) at 200°C.

amorphous WO_{3-x} thin films with 200 and 600 nm thicknesses, respectively, at 150°C. Although the Cole-Cole plot of 200 nm exhibits one semicircle, that of 600 nm consists of one-semicircle and the tail of second semicircle. The resistivity, which corresponds to the intersection between the bottom axis and first semicircle, is $\sim 2.9 \text{ K}\Omega$ for 200 nm and $2.0 \times 10^{-5} \Omega$ for 600 nm. The small resistivity of 200 nm is generally interpreted as electron conduction. However, the contribution of electron conduction may be small in 600 nm due to the high resistivity. The details will be discussed in Fig. 4.

Figure 3 shows the Arrhenius plots of the conductivities of amorphous WO_{3-x} thin films with 200 nm and 600 nm thicknesses in dry atmosphere. These conductivities exhibit the thermal-activation-type behavior. The 200 nm thin film has high conductivity, which corresponds to semiconductor, and small activation energy (E_A) of 0.10 eV. On the other hand, the 600 nm thin film has low conductivity and large E_A of 0.61 eV, indicating that the species of the conducting carrier do not depend on temperature.

Figure 4 shows the conductivities of amorphous WO_{3-x} thin films with 200 nm and 600 nm thicknesses as a functions of oxygen partial pressure (P_{O_2}) measured at 200°C. When the conductivity depends on P_{O_2} , the slope of the conductivity against P_{O_2} reflects electron or

Fig. 5 Valence bands and conduction bands of WO_{3-x} thin films with 200 nm and 600 nm film thicknesses obtained from PES and XAS, respectively.

Fig. 6 Expanded PES spectra in the band gap energy regions of WO_{3-x} thin films with 200 nm and 600 nm thicknesses.

ion or mixed conduction in terms of defect chemical analysis of oxide material. At the 200 nm thin film, the conductivity rapidly decreases with increasing P_{O_2} in low- P_{O_2} region of 0.05–0.3 atm. The slope value is estimated to be -2.86 , which indicates the electron conduction in low- P_{O_2} region. The slope value in high- P_{O_2} region above 0.3 atm is ~ 0 , indicating the ionic conduction. On the other hand, the conductivity of 600 nm thin film slowly decreases with increasing P_{O_2} . The slope value is estimated to be -0.12 , which corresponds to the electron-ion mixed conduction.

Figure 5 shows valence bands and conduction bands of amorphous WO_{3-x} thin films with 200 nm and 600 nm film thicknesses obtained from PES and XAS, respectively. The abscissa is the relative energy to Fermi level (E_F) at 0 eV. The E_F position of the O 1s XAS spectrum was determined from the O 1s PES peak. The E_F locates at the bottom of conduction band, which corresponds to n -type oxide semiconductor with oxygen vacancies. In the crystallized WO_3 thin film, the valence band consists of the O 2p states hybridized with W 5d state [25]. Although the hybridization states can not prove in the amorphous WO_{3-x} thin film, the authors expect that the valence band consists of O 2p and W 5d states. The peak position and spectral shape of 200 nm thin film accord with those of 600 nm thin film.

The energy separation between the top of the valence band and the bottom of the W 5d conduction band reflects the value of band gap (E_g). The E_g of 200 and 600 nm thin films are estimated to be ~ 2.0 and ~ 2.6 eV, respectively. Although the E_g of 200 nm thin film accords with that of WO_3 bulk crystal, the E_g of 600 nm is smaller than that of the bulk crystal. This originates to the existence of tail structure at the bottom of the conduction band. The tail structure might be the localized level created by oxygen vacancies in amorphous WO_{3-x} thin film.

Figure 6 shows the expanded PES spectra in the band gap energy region of amorphous WO_{3-x} thin films with 200 nm and 600 nm thicknesses. These spectra exhibit small and broad DOS. In $\text{TiO}_{2-\delta}$ [26] and $\text{SrTiO}_{3-\delta}$ [27], similar DOS is estimated as the localized Ti 3d donor states created by oxygen vacancies. Therefore, the broad DOS is considered to the small defect-induced W 5d states. The intensity of the broad-DOS is larger in 200 nm thin film with high electron conduction in Fig. 3. The high electron conduction contribute to the W 5d electron at E_F . The electron-ion mixed conduction of 600 nm thin film may be achieved by the W 5d electron at E_F and the oxygen ion trapped at the defect-induced state at the bottom conduction band through the thermal energy.

4. CONCLUSION

We have studied the structural and electrical properties of amorphous WO_{3-x} thin films with 200 and 600 nm thicknesses prepared by RF magnetron sputtering. The W 4d PES spectra exhibit the mixed valence states of W^{6+} and W^{5+} that is created by oxygen vacancies. The ratio of W^{5+} state is larger in 200 nm thin film. The 200 nm thin film exhibits the high conductivity above 10^{-3} S/cm and small E_A of 0.1 eV, although the 600 nm thin film exhibits the low conductivity and large E_A of 0.6 eV. The Po_2 dependence of the electrical conductivity and defect chemical analysis indicate the electron conduction for 200 nm and electron-ion mixed conduction for 600 nm. The E_g of 200 and 600 nm thin films are ~ 2.6 eV and 2.0 eV, respectively. The broad W 5d DOS in the band gap region is observed in both films. The defect-induced level at the bottom of the conduction band is observed in 600 nm thin film. These results indicate that the electron-ion mixed conduction of 600 nm thin film is achieved by W 5d electron at E_F and oxygen ion trapped at the defect-induced state.

ACKNOWLEDGEMENTS

We would like to thank Dr. Makoto Minohara, Koji Horiba and Hiroshi Kumigashira of the Institute of Materials Structure Science, KEK for their technical supports. This work at KEK was done under the approval of the Program Advisory Committee (Proposal No. 2016G003) at KEK.

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(Received January 11, 2018; Accepted February 21, 2018; Published Online April 1, 2018)