Modulation of electrical mobility in Au ion irradiated titanium oxide with crystal field splitting

2016 Jpn. J. Appl. Phys. 55 115701

(http://iopscience.iop.org/1347-4065/55/11/115701)

Japanese Journal of Applied Physics **55**, 115701 (2016)
http://doi.org/10.7567/JJAP.55.115701

REGULAR PAPER

Modulation of electrical mobility in Au ion irradiated titanium oxide with crystal field splitting

Hyun-Woo Park[1], Byung-Hyuk Jun[2], Dukhyun Choi[3], and Kwun-Bum Chung[1*]

[1]*Division of Physics and Semiconductor Science, Dongguk University, Seoul 100-715, Korea*
[2]*Division Division of Neutron Utilization Technology, Korea Atomic Energy Research Institute, Daejeon 34057, Korea*
[3]*Department of Mechanical Engineering, School of Engineering, Kyung Hee University, Yongin, Gyeonggi 446-701, Korea*

*E-mail: kbchung@dongguk.edu

Received August 8, 2016; accepted September 5, 2016; published online October 17, 2016

Electrical modulation of radio frequency (RF) sputtered TiO_{2-x} films were investigated as a function of Au swift heavy ion irradiation dose at room temperature. The prepared TiO_{2-x} films were irradiated with 130 MeV Au swift heavy ion in the range from 1×10^{11} to 5×10^{12} ions/cm^2. As the Au ion irradiation dose increased up to 1×10^{12} ions/cm^2, the electrical mobility of TiO_{2-x} films were dramatically increased 3.07×10^2 cm^2 V^{-1} s^{-1} without the change of carrier concentration. These changes in electrical properties of Au irradiated TiO_{2-x} film, are related to the modification of electronic structure such as crystal field splitting of Ti 3d orbital hybridization and sub-band edge states below the conduction band as a function of Au swift heavy ion irradiation dose.

1. Introduction

Thin film transistors (TFTs) using transparent oxide semiconductor (TOS) such as indium–gallium–zinc-oxide (IGZO) have garnered considerable interest for next generation active matrix displays, flexible and transparent electronics applications due to high mobility of these material, despite their amorphous structure (>10 cm^2 V^{-1} s^{-1}), high transparency in the visible light region caused by wide band gap (>3.5 eV), and device fabrication even at low temperature.[1,2] Also, TOS-TFTs are representative candidates to replace the conventional amorphous/poly Si-TFTs, since they have thermal and chemical stability.[3,4] Although IGZO-TFTs can satisfy the requirements as active channel layer of switching in devices due to their high mobility and high transparency, the high cost of indium and gallium in IGZO channels remains a critical drawback.[5–7] Several research groups have suggested titanium oxide (TiO_{2-x}) as a cost effective n-type semiconductor, due to simple stoichiometry, high transmittance in the visible region, a high dielectric constant, and multifunctionality.[8–11] Moreover, the photoelectric properties of TiO_{2-x} have allowed to be used in a variety field applications, such as a solar cells, optical filters, and photocatalyst.[12–14] However, if these applications are to be realized, key issues related to the modulation method of TiO_{2-x} electrical properties, such as the carrier concentration and the mobility at low temperature, should be considered. In order to modulation of TiO_{2-x} electrical properties, various research groups have investigated to modify the electric and optical properties of the TiO_{2-x} thin films using the impurities doping, ion implantation, thermal annealing under the various ambient.[15,16] Unfortunately, these methods are not suitable for active channel layer because of physical structural damage, needs a subsequent curing process, and requires high temperatures to transform the crystal structure, which can generate unnecessary and uncontrollable defect states. Among the various post process methods, ion irradiation using light or heavy ion, is an suitable method to modify the structural, the electrical and the optical properties of the material at room temperature.[17,18] Especially, in the case of heavy ions lose their energy by elastic collisions with the target nuclear in the materials as well as by inelastic collisions that result in the electronic excitation of the target atoms in the materials, thus, those can effectively transfer and control the larger energy under the smaller irradiation dose and the minimization of ion collision damage, compared to light ion irradiation.[19–21]

In this study, the electrical mobility of swift heavy Au ion irradiated TiO_{2-x} films are modulated by Au ion irradiation dose at the room temperature, and the relevant material properties such as physical and electronic structures are also analyzed. Origins of change in electrical mobility of TiO_{2-x} films are investigated by the crystal field splitting and sub-band edge states below the conduction band as a function of Au ion irradiation dose.

2. Experimental methods

TiO_{2-x} thin films with ~50 nm were deposited without the substrate heating by radio frequency (RF) sputtering system on thermally grown SiO_2 (100 nm)/heavy doped p-type Si wafers. An oxygen-deficient 3-in. TiO_x target (dark grey color) was used for the sputtering, at an RF power and process pressure of 75 W and 10 mTorr, respectively. Then, TiO_{2-x} films were irradiated with 130 MeV Au ion beam at room temperature using 15UD Tandem Accelerator at Inter University Accelerator Centre (IUAC), New Delhi, India, with different Au ion irradiation dose of the 1×10^{11}, 5×10^{11}, 1×10^{12}, and 5×10^{12} ions/cm^2, respectively. The swift Au ion irradiation was performed under high-vacuum condition (base pressure 2×10^{-6} Torr) and the beam current was kept very low (at 0.1 pnA) to avoid heating and the ion beam was uniformly scanned over 1 cm^2 area using a magnetic scanner. Incident angle of the ion beam was kept slightly away from surface normal of the sample to avoid the channeling effects. Figure 1 are the simulated approximate temperature as a function of Au ion acceleration energy. These results were calculated by the simulation of phonon scattering energy based on nuclear and electron cross section of stopping, using stopping and range of ions in matter (SRIM) code. The Au irradiated TiO_{2-x} film with the acceleration energy at 130 MeV could be induced by the local activation with the approximate temperature of 441 °C.

The electrical properties such as carrier concentration, mobility and resistivity of as-deposited and irradiated TiO_{2-x} films were examined by using Hall measurement system with

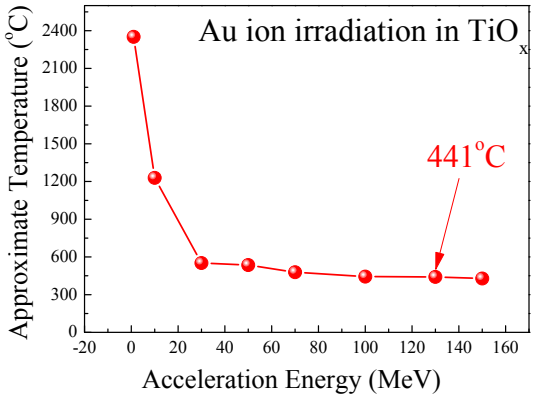

Fig. 1. (Color online) Approximate calculation of process temperature as a function of Au ion acceleration energy.

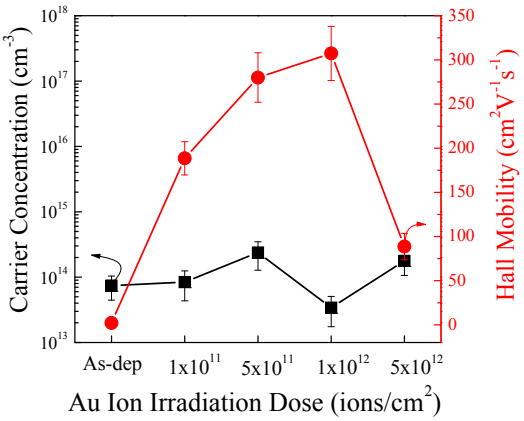

Fig. 2. (Color online) Electrical properties, including carrier concentration, and mobility for as-deposited and irradiated TiO_{2-x} films as a function of Au ion irradiation dose.

the permanent magnet of 0.55 Tesla at room temperature. The changes of physical properties, including crystallization, chemical composition was measured by X-ray diffraction (XRD), and Rutherford backscattering (RBS). The surface morphology was studied using an atomic force microscope (AFM) and scan area was each $5 \times 5\,\mu m^2$ at a scanning frequency of 0.5 Hz. The detailed electronic structures, related to changes in conduction band and band edge state below the conduction band, were investigated by synchrotron X-ray absorption spectroscopy (XAS) with total electron yield (TEY) mode in the 10D soft X-ray beam line at the Pohang Accelerator Laboratory in Korea. Sub-band edge states below the conduction band were examined at incident angles of 65, 70, and 75° at photon energies of 0.75–6.4 eV by using spectroscopic ellipsometry (SE) with a rotating analyzer system and an auto retarder.

3. Results and discussion

Figure 2 shows the carrier concentration, and mobility of the irradiated TiO_{2-x} films as a function of Au ion irradiation dose. In as-deposited TiO_{2-x} film, the carrier concentration and mobility were $7.41 \times 10^{13}\,cm^{-3}$ and $2.2\,cm^2\,V^{-1}\,s^{-1}$ with n-type semiconductor characteristic, respectively. As the Au ion irradiation dose is increased until 1×10^{12} ions/cm^2, the mobility was increased to $3.07 \times 10^2\,cm^2\,V^{-1}\,s^{-1}$. However, when the Au ion irradiation dose increased up to 5×10^{12} ions/cm^2, the mobility was dramatically decreased to $8.86 \times 10^1\,cm^2\,V^{-1}\,s^{-1}$ with small deviation of carrier concentration (10^{13}–$10^{14}\,cm^{-3}$). Therefore, the variation of mobility is main factor of enhancement of electrical properties as a function of Au ion irradiation dose. These remarkable changes in electrical properties could be associated to the changes of various film properties by Au ion irradiation, such as physical properties, chemical composition, and electronic structure.

Changes in physical structure and composition of TiO_{2-x} films depending on Au ion irradiation dose, were investigated using XRD and RBS measurements, as shown in Figs. 3(a) and 3(b). The preferred orientations and their qualitative comparison are comparable, because all of XRD spectra were measured by θ–2θ X-ray diffractometer and normalized by Si(400) from Si(200) substrate, regardless of Au ion irradiation dose. These indicate that the different Au ion irradiation dose have no effects on the change of physical structure, preserving the amorphous structure. Similarly, the physical composition of Ti and O (Ti : O = 32.2 : 67.8 at. %) has no changes depending on the Au ion irradiation dose within the detection limit of RBS. Surface morphology measured by AFM shows the smooth surface for as-deposited and irradiation films with root mean square (RMS) roughness of ~1 nm, as shown in Fig. 3(c). As a result, the changes of electrical properties have no dependence on the physical properties and composition, regardless of Au ion irradiation into TiO_{2-x} films.

Figure 4 show the electronic structure for O K edge in the conduction band measured by XAS. The normalized intensities of O K-edge spectra of TiO_{2-x} films directly reflect the molecular orbital hybridization between Ti orbital with 3d, 4sp states and O orbital with 2p states based on the local atomic bonding symmetry.[22] The qualitative energetic order of the corresponding hybridized molecular orbital between Ti 3d, 4sp, and O 2p are characterized, as $2t_{2g}$ (Ti 3d; O 2pπ) < $3e_g$ (Ti 3d; O 2pσ) < $1a_{1g}$ (Ti 4s; O 2pσ) < $3t_{1u}$ (Ti 4p; O 2p).[23] As Au ion irradiation dose increased, the ratio of orbital hybridization was changed with the enhancement of e_g in 3d orbital and a_{1g}, t_{1u} in 4sp orbital under the crystal-field splitting. In order to determine the detailed molecular orbital ratio as a function of Au ion irradiation dose, Fig. 4(b) represents the relative ratio of $e_g/(e_g + t_{2g})$ and 4sp/(3d + 4sp) based on the fitted results with Gaussian peaks comprised of two 3d orbital states and two 4sp orbital states. The interesting finding is that the noticeable crystal-field splitting of conduction band states was observed in the 3d, 4s, and 4p orbital of TiO_{2-x} layers even in the amorphous phase semiconductor, which had a relatively larger e_g states and 4sp states with the increase of Au ion irradiation dose up to 1×10^{12} ions/cm^2, then, the crystal-field splitting was reduced in case of more Au ion irradiation dose, similar to as-deposited film. The increase of the e_g states indicates the enhancement of molecular orbital symmetry of z^2 and $x^2 - y^2$ in 3d orbital, which induce the uniform distribution of d orbital states, compared to as-deposited TiO_{2-x} film. This change of d-orbital ordering can enhance the charge transport due to the symmetric distribution of unoccupied states in the 5-fold directional 3d orbital.[24,25] The other increase of relative ratio of the 4sp orbital also could cause an increase in the possibility of charge transport in terms of an enhancement

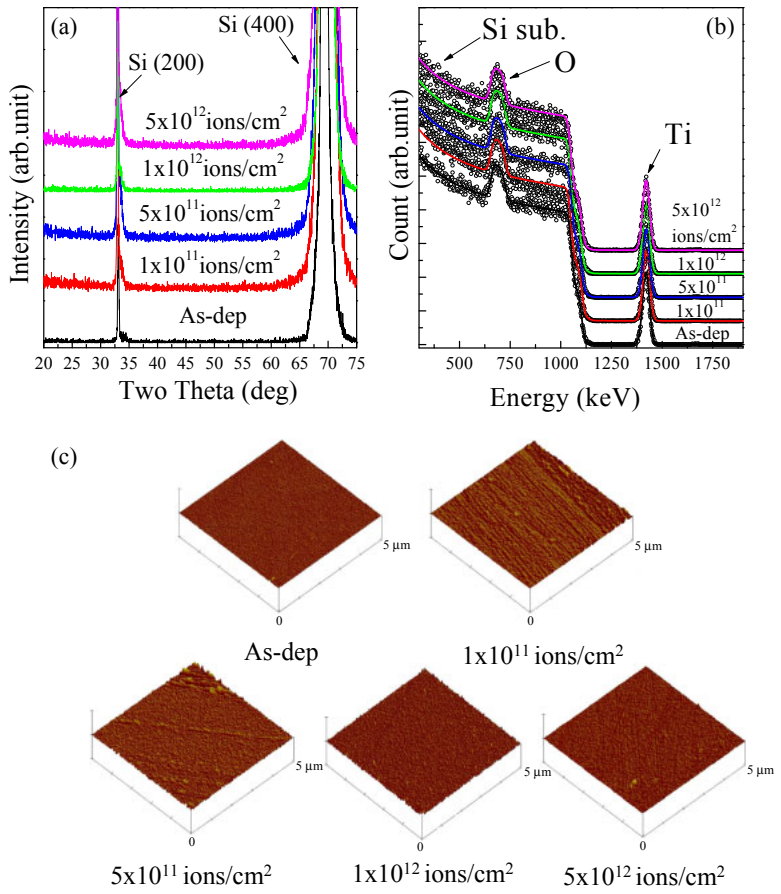

Fig. 3. (Color online) (a) XRD patterns, (b) RBS spectra, and (c) surface morphology using AFM for the as-deposited and irradiated TiO_{2-x} films as a function of Au ion irradiation dose.

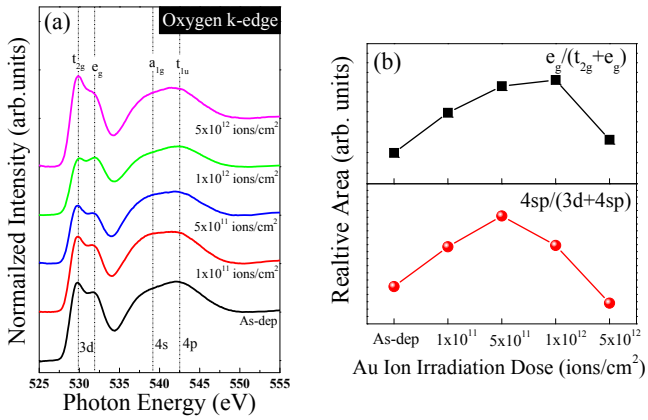

Fig. 4. (Color online) (a) Normalized O K-edge XAS spectra, (b) relative $e_g/(e_g + t_{2g})$ states ratio of Ti 3d and relative 4sp/(3d + 4sp) molecular orbital ratio of calculated by the Gaussian fitting results as a function of Au ion irradiation dose.

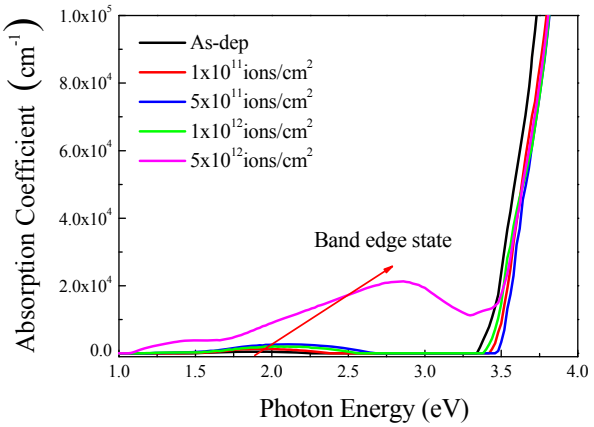

Fig. 5. (Color online) Absorption coefficient of the as-deposited and irradiated TiO_{2-x} films as a function of Au ion irradiation dose.

of the spherically symmetric s-orbital compared to the directional d orbital.[26] These combination of molecular orbital ordering for 3d and 4sp orbitals are strongly correlated to the dramatic modulation of electrical mobility as a function of Au ion irradiation dose.

Figure 5 shows the sub-band edge states below the conduction band examined by SE measurement. The orbital band gap of various irradiated films represented no changes near ~3.5 eV. However, the sub-band edge states below the conduction band were drastically increased in the irradiated film above the Au ion dose of 5×10^{12} ions/cm^2. The sub-band edge states are regarded as electrical defect states because those can trap and scatter the charge by the unoccupied states in the electronic structure, which induces the degradation of electrical charge transport. XAS and SE results suggest that the modulation of electrical mobility depending on the Au irradiation dose, is caused by the modification of electronic structure in the conduction band and of sub-band edge states below the conduction band.

4. Conclusions

Electrical mobility of radio frequency sputtered TiO_{2-x} films were investigated as a function of swift heavy Au

ion irradiation dose from 1×10^{11} to 5×10^{12} ions/cm^2 at room temperature. In irradiation dose of 1×10^{12} ions/cm^2, the mobility of irradiated TiO_{2-x} films was enhanced to 3.07×10^2 cm^2 V^{-1} s^{-1} without the modification of physical properties. This remarkable change of mobility of TiO_{2-x} films is strongly associated to the changes of electronic structure in the conduction band, and sub-band edge states below the conduction band. Noticeable crystal-field splitting and ordering of Ti 3d orbital hybridization, and dominance of orbital mixture of Ti 3d and 4sp in the conduction band enhance the charge transfer within the conduction band as a function of Au ion irradiation dose. In addition, the increase of sub-band edge state below the conduction band are strongly correlated with the decrease of electrical mobility.

Acknowledgment

This work was supported by the National Research Foundation (NRF) Grant (2013M2A8A1035822, 2015M2A8A1045181, 2015K2A2A7056357, and 2016R1A4A1012950) from the Ministry of Science, ICT and Future Planning (MSIP) of Korea.

1) K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, Nature **432**, 488 (2004).
2) H. Q. Chiang, J. F. Wager, R. L. Hoffman, J. Jeong, and D. A. Keszler, Appl. Phys. Lett. **86**, 013503 (2005).
3) K. Nomura, T. Aoki, K. Nakamura, T. Kamiya, T. Nakanishi, T. Hasegawa, M. Kimura, T. Kawase, M. Hirano, and H. Hosono, Appl. Phys. Lett. **96**, 263509 (2010).
4) M. J. Lee, S. J. Kang, J. Y. Baik, K.-J. Kim, H.-D. Kim, H.-J. Shin, J. Chung, J. Lee, and J. Lee, J. Appl. Phys. **108**, 024507 (2010).
5) E. Fortunato, P. Barquinha, A. Pimentel, L. Pereira, G. Goncalves, and R. Martins, Phys. Status Solidi: Rapid Res. Lett. **1**, R34 (2007).
6) B.-J. Kim, H.-J. Kim, T.-S. Yoon, Y.-S. Kim, and H. H. Lee, Electrochem. Solid-State Lett. **13**, H419 (2010).
7) E. Tokumitsu, M. Senoo, and T. Miyasako, Microelectron. Eng. **80**, 305 (2005).
8) J. Park, K.-C. Ok, B. D. Ahn, J. H. Lee, J.-W. Park, K.-B. Chung, and J.-S. Park, Appl. Phys. Lett. **99**, 142104 (2011).
9) M. Katayama, S. Ikesaka, J. Kuwano, Y. Yamamoto, H. Koinuma, and Y. Matsumoto, Appl. Phys. Lett. **89**, 242103 (2006).
10) K.-H. Choi and H.-K. Kim, Electrochem. Solid-State Lett. **14**, H314 (2011).
11) S. K. Kim, W.-D. Kim, K.-M. Kim, C. S. Hwang, and J. H. Jeong, Appl. Phys. Lett. **85**, 4112 (2004).
12) J. N. Hart, R. Cervini, Y.-B. Cheng, G. P. Simon, and L. Spicci, Sol. Energy Mater. Sol. Cells **84**, 135 (2004).
13) H. Köstlin, G. Frank, G. Hebbinghaus, H. Auding, and K. Denissen, J. Non-Cryst. Solids **218**, 347 (1997).
14) K. Hashimoto, H. Irie, and A. Fujishima, Jpn. J. Appl. Phys. **44**, 8269 (2005).
15) K. C. Ok, Y. Park, K. B. Chung, and J. S. Park, Appl. Phys. Lett. **103**, 213501 (2013).
16) B. D. Ahn, K.-C. Ok, J.-S. Park, and K.-B. Chung, J. Vac. Sci. Technol. B **31**, 021204 (2013).
17) C. S. Yeo, K. B. Chung, J. H. Song, K. H. Chae, J. S. Park, J.-H. Song, S. H. Park, and M. H. Cho, J. Korean Phys. Soc. **62**, 781 (2013).
18) B. D. Ahn, J. S. Park, and K. B. Chung, Appl. Phys. Lett. **105**, 163505 (2014).
19) R. L. Fleischer, P. B. Price, and R. M. Walker, J. Appl. Phys. **36**, 3645 (1965).
20) A. E. Volkov and V. A. Borodin, Nucl. Instrum. Methods Phys. Res., Sect. B **146**, 137 (1998).
21) Z. G. Wang, C. Dufour, E. Paumier, and M. Toulemonde, J. Phys.: Condens. Matter **6**, 6733 (1994).
22) P. A. Cox, *Transition Metal Oxides* (Oxford University Press, Oxford, U.K., 1992).
23) M. Sacerdoti, M. C. Dalconi, C. Carotta, B. Cavicchi, M. Ferroni, S. Colonna, and M. L. Di Vona, J. Solid State Chem. **177**, 1781 (2004).
24) K. B. Chung, J. P. Long, H. Seo, G. Lucovsky, and D. Nordlung, J. Appl. Phys. **106**, 074102 (2009).
25) K. H. Choi, K. B. Chung, and H. K. Kim, Appl. Phys. Lett. **102**, 153511 (2013).
26) H. W. Park, M. J. Choi, J. H. Song, K. H. Chae, B. H. Jun, B. D. Ahn, J. M. Huh, H. D. Kim, and K. B. Chung, J. Korean Phys. Soc. **68**, 190 (2016).