Characterization of interface between amorphous $Ge_2Sb_2Te_5$ and TiN by x-ray photoelectron spectroscopy

Doo Seok Jeong,[1*] Suyoun Lee,[1] Jeung-hyun Jeong,[1] Byung-ki Cheong,[1] and Cheol Seong Hwang[2]

[1]Thin Film Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea,
dsjeong@kist.re.kr
[2]Department of Materials Science and Engineering and Inter-university Semiconductor Research Center,
Seoul National University, Seoul 151-744, Republic of Korea

ABSTRACT

We investigated interface between $Ge_2Sb_2Te_5$ (GST) and a very thin and discontinuous TiN film by analyzing the electron band structure near the Fermi energy using x-ray photoelectron spectroscopy (XPS). The intensity of photoelectrons (PEs) from GST covered with TiN was formulated in a form of the convolution integration. Using this formula the deviation of the PE intensity of the covered GST from that of the uncovered could be evaluated. Three different calculated spectra, one was from the uncovered GST, another from the covered GST, and the other from TiN were fitted to the XPS spectrum of TiN/GST in the vicinity of the Fermi energy. From the fitting, a shift of the valence band spectrum of the covered GST due to Fermi energy alignment after the junction formation was observed. The shift was explained in terms of the formation of an interfacial dipole layer at the TiN/GST interface and space charges in GST attributed to the valence-alternation-pair formation.

Key words: chalcogenice, x-ray photoelectron spectroscopy, interfacial dipole layer.

1. INTRODUCTION

After Ovshinsky's having initiated research on nonvolatile resistive switching in chalcogenide materials[1], great attention for their applications to phase change random access memory (PRAM) devices triggered active research on these materials.[2,3,4] Despite vigorous studies on chacogenides nowadays, fundamental physics behind their many interesting properties has been hardly clarified so that further study on chalcogenides is required for a better understanding. Especially, interface between electrode and chalcogenide materials needs to be vigorously investigated because of its importance in the phase change behavior. The Joule heat generated at the interface might play a very important role in the phase change. The Joule heat is regarded to be influenced by the electric field and potential distribution in the vicinity of the interface. That is, the band structure at the interface might strongly affect the phase change behavior.

For the calculation of the band structure near electrode/chacogenide interface, space charge density in chalcogenide should be evaluated. Unlike general semiconductor, positively- and negatively-charged centers in chalcogenide are likely to be related to each other by means of conversion between them by alternating their bonding states.[5] This conversion should be taken into account when one evaluates space charge density in chalcogenide. In this study, we deal with interface between GST and TiN. TiN is a promising material as electrode and heater in PRAM devices, due to its compatibility with complementary-metal-oxide-semiconductor processes and a proper electrical resistivity for heat generation. It is therefore meaningful to look into TiN/GST interface for both scientific and technological purposes. We obtain the photoelectron spectra of GST films covered with very thin TiN films using x-ray photoelectron spectroscopy (XPS) analysis. Comparison between each spectrum is conducted to check shifts of the valence band due to the TiN films on GST. In general, valence band shifts of many crystalline materials with insulating or semiconducting properties have been determined from shifts of core level peaks.[6,7] However, it should be noted that majority space charges in these crystalline materials, resulting in the shifts of the valence band, are attributed to impurities, namely, extrinsic atoms. In this case, the impurities barely affect the chemical states of the intrinsic elements so that the shifts of the core level peaks can be good evidences of the valence band shift. For

describing valence band shifts of amorphous chalcogenide materials this method is unlikely to be available. Intrinsic defects such as chalcogens with different bonding numbers and the number of bound electrons are probably in charge of space charge formation.[8] This implies the space charges leading to a valence band shift are related to a change in the chemical states of the intrinsic elements. Therefore, the shift of the valence band of chacogenide materials cannot be easily judged by the core level peak shift. Instead, we focus on the valence band spectra of the GST films in order to determine shifts of the valence band due to the TiN films on GST. The shifts are explained in terms of an interfacial dipole layer (IDL) at the TiN/GST interface and space charge in GST.

2. EXPERIMENTS

100 nm thick amorphous GST films were formed on thermally-oxidized Si substrates using RF sputtering at room temperature. Very thin and discontinuous TiN films were deposited using in-situ sputtering on the GST films at room temperature for three different sputtering times (5, 20, and 30 sec.) to vary the thickness of TiN. Let us name them TG1, TG2, and TG3, respectively. XPS analysis for TG1, TG2, and TG3 as well as GST without TiN was performed in order to obtain the valence band spectra of the samples. In order to obtain the band spectrum near the Fermi energy of TiN, 100 nm thick TiN film was formed directly on an oxidized Si substrate and analyzed by XPS as well.

3. RESULTS & DISCUSSION

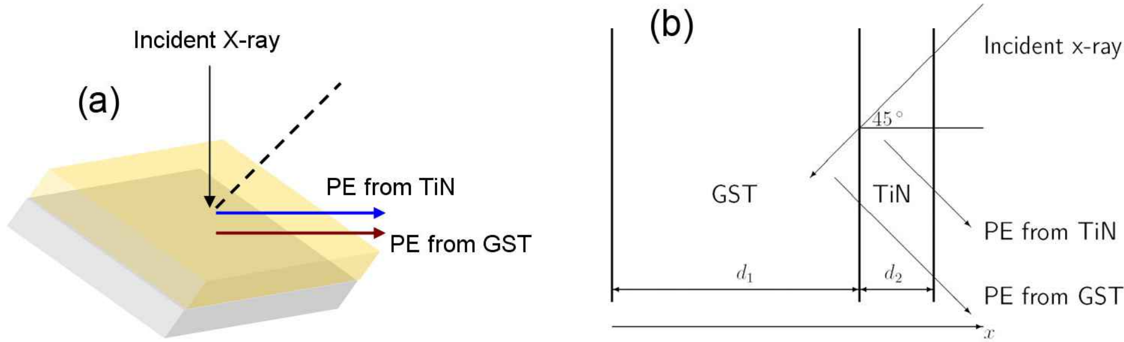

Figure 1. (a) Configurational schematic of xps analysis. (b) Configuration of a TiN/GST sample, incident x-ray, and PE.

A GST film covered with a thin TiN film will show a less photoelectron (PE) intensity than an uncovered one because of the attenuation of incident x-ray intensity in the TiN film and a finite mean free path of PEs. PE intensity at a certain spatial point in GST can be described in a form of the convolution integration. For the configuration of TiN/GST as shown in Fig. 1(b) the intensity of PEs at a particular binding energy from GST at x where $0 < x < d_1$ is expressed as

$$I_{GST}(x) = A_1 \int_0^x i(u) I^{in}(x-u)\,du \,, \tag{1}$$

where A_1 denotes the coefficient including the density of states at a given binding energy. i is the intensity of PE generated at $u\,(\le x)$ and is given by $i(u) = i_0 e^{-\sqrt{2}(x-u)/\lambda}$ with a finite mean free path of λ and an incident x-ray angle of $\pi/4$. i_0 means the intensity at $u = x$. I^{in} denotes the intensity of incident x-ray, which is given by $I^{in}(x-u) = I^{in}_{d_1+d_2} e^{-\sqrt{2}\alpha_2 d_2} e^{-\sqrt{2}\alpha_1 (x-u)}$ where $I^{in}_{d_1+d_2}$ means the intensity of the incident x-ray at the surface. α_1 and α_2 denote the absorption coefficients of GST and TiN, respectively. With a simple calculation, Eq. 1 can be rewritten as

$$I_{GST}(x) = \frac{k_1 \lambda}{\sqrt{2}(1+\alpha_1 \lambda)} e^{-\sqrt{2}(\alpha_1 x + \alpha_2 d_2)} \times \left(e^{\sqrt{2}\alpha_1 x} - e^{-\sqrt{2}x/\lambda}\right). \tag{2}$$

k_1 is the product of all the coefficients, A_1, i_0, and $I^{in}_{d_1+d_2}$. Assuming negligible collisions of PEs in vacuum between the TiN surface and the PE detector in an XPS apparatus, PE intensity at the detector is almost equal to one at the TiN surface placed at $x = d_1 + d_2$. The intensity of PEs from GST at $x = d_1 + d_2$ is given by

$$I_{GST}(d_1 + d_2) = I_{GST}(d_1) e^{-\sqrt{2}d_2/\lambda}, \tag{3}$$

where $I_{GST}(d_1)$ is the intensity of PEs at $x = d_1$. Similarly, the PE intensity of TiN at $x = d_1 + d_2$ is obtained as follows.

$$I_{TiN}(d_1 + d_2) = \frac{k_2 \lambda}{\sqrt{2}(1+\alpha_2 \lambda)} \left[1 - e^{\sqrt{2}(\alpha_2 + 1/\lambda)d_2}\right], \tag{4}$$

where k_2 is the product of the coefficients for TiN as k_1 for GST. Electron mean free path λ is well-known to satisfy a universal law.[9] Since now, we regard the PEs of GST and TiN to follow the universal law. There might be a deviation from the universal law depending on materials where PEs are placed. However, the deviation is unlikely to affect our results because the TiN thickness is very thin. Furthermore, because of the very thin TiN film α_2 also has negligible influence on the intensity of PEs.

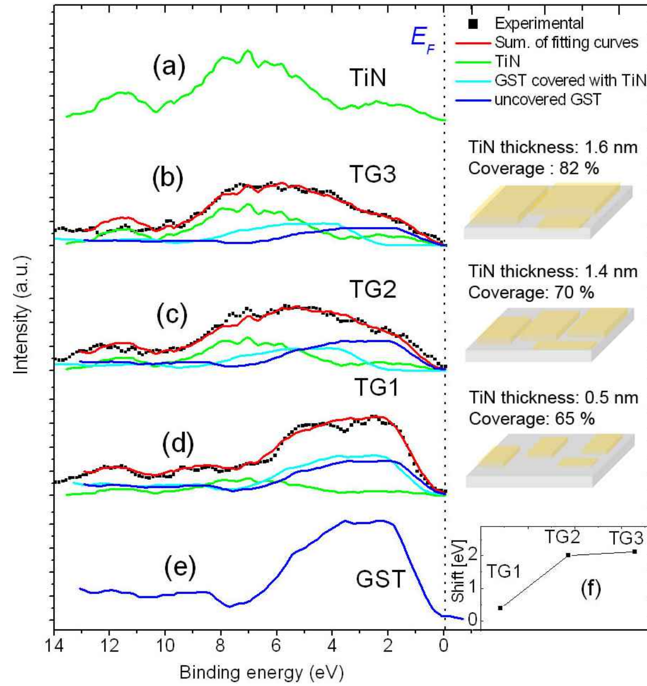

Figure 2. Band spectra of (a) 100 nm thick TiN, (b) TG3, (c) TG2, (d) TG1, and (e) GST. The Fermi energy is taken as the reference energy. (f) A shift of the band spectrum with respect to each sample. The TiN thicknesses and degrees of TiN coverage in the right column were fitting parameters. α_1 and α_2 were set 10^6 m^{-1} and 5×10^6 m^{-1}, respectively.

The valence band spectra of GST covered with TiN can be calculated using Eq. 3 from the measured valence band spectrum of uncovered GST. Since GST without TiN is directly in contact with vacuum, the PE intensity from GST does not undergo attenuation through the vacuum so that k_1 of Eq. 2 at $x = d_1$ can be obtained as a function of binding energy by comparing Eq. 2 with the experimental valence band spectrum. Therefore, if the valence band spectrum of GST along the binding energy axis is known, the valence band spectra of GST with various thicknesses of TiN can be calculated. For the calculation of the intensity of PEs from a very thin TiN film, the same procedure can be applied. From the band spectrum in the vicinity of the Fermi energy of TiN with an enough thickness (> 10 nm) to show saturated PE intensity, k_2 in Eq. 4 can be evaluated as a function of binding energy. Thus, the PE intensity of TiN with various thicknesses can be calculated using Eq. 4.

Regarding the general growth behavior of metal thin films, TG1, TG2, and TG3 samples most probably have discontinuous TiN films. In fact, the average thickness of TiN in TG3 was determined to be at most below 2 nm from the average areal density measured by x-ray fluorescence (XRF). Such thin TiN films are strongly believed to be discontinuous. In fact, the surface conductivity of all the TG1, TG2, and TG3 samples, measured using conductive atomic force microscope, showed almost no difference from the uncovered GST, eventually indicating that TiN films are discontinuous without percolation paths for electric conduction. For the analysis of the valence band spectra of the three samples, we assume that the GST films are partly covered with very thin TiN slabs with three different thicknesses and degrees of coverage of the GST films. Measured valence spectra of GST, TG1, TG2, TG3, and TiN are plotted in Fig. 2. Unless interfacial states between TiN and GST with prominent density are formed, the measured band spectra might correspond to the superposed sum of the three different band spectra for the uncovered and the covered GST, and TiN, respectively. Measured valence band spectra of TG1, TG2, and TG3 were fitted using the three spectra and the results are plotted in Figs. 2(b), (c), and (d). Three critical parameters affecting the fitting results are TiN thickness, the degree of TiN coverage, and a valence band shift of the covered GST due to the alignment of the Fermi energy across the TiN/GST interface. However, the former two parameters are not independent because the product of the thickness and the degree of TiN coverage should be equal to the measured average thickness, which was determined from the XRF analysis as mentioned earlier. Moreover, the parameters are restricted in the sense that TiN thickness must increase with increasing sputtering time, that is, from TG1 to TG3. Therefore, the third parameter is the only unrestricted parameter. The fitting results are in a good agreement with the experimental data, which demonstrates the validity of our hypothesis; the measured spectra are due to the superposition of the three spectra without the formation of remarkable interfacial states.

The validity of some fitting parameters was again confirmed by comparing the PE peak intensities of Ti $2p_{1/2}$ for TG1, TG2, and TG3 with the intensities calculated semi-empirically using Eq. 4. This comparison is shown in Fig. 3(a). For TG1 and TG3 it shows an almost perfect agreement, although there is a small deviation from the experimental value for TG2.

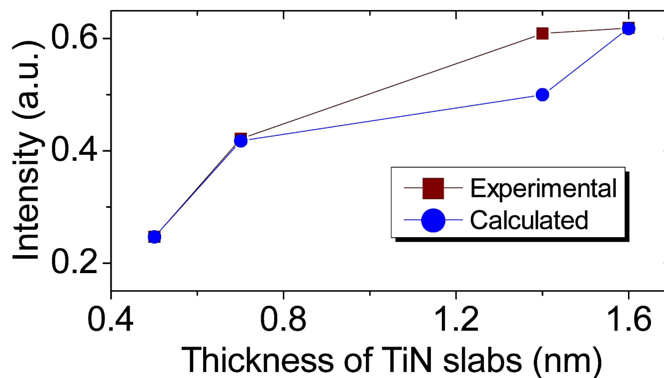

Figure 3. Comparison between the measured intensity of the Ti $2p_{1/2}$ peaks from TG1, TG2, and TG3 and calculated intensity. The same parameters as used for the valence band fitting in Fig. 2 were applied to the intensity calculation.

A shift of the valence band spectra of the covered GST for varying the TiN slab thickness is depicted in Fig. 2(f). It can be noted that the shift is saturated as increasing the slab thickness. The shift may be attributed to either only band bending on the GST side due to space charge formation or the formation of an IDL[10] combined with band bending at the TiN/GST interface. Considering that the strongest PE intensity of GST is from near interface region on the GST side, any model is unlikely to account for the shift of the valence band spectra without taking into account the IDL . Therefore, a voltage drop in the IDL needs to be looked into to describe the nature of the TiN/GST interface. In order to evaluate voltage distribution along the axis running across the TiN/GST interface including an IDL, one should solve the Poisson equation with space charge density in both GST and TiN.

4. CONCLUSION

We investigated TiN/GST interface by means of XPS analysis on valence spectra of TiN/GST junctions. For XPS analysis, a new formula of PE intensity from a GST film underlying a very thin TiN film was introduced. The analysis results suggested that an IDL is formed at the interface. It turned out that a large internal voltage, approximately 2 V, is applied in the IDL.

ACKNOWLEDGEMENT

The authors would like to acknowledge financial support through Institutional Research Program of KIST by Korean Ministry of Education, Science and Technology (MEST) and also one through National Research Program for 0.1 Terabit Non-Volatile Memory Devices sponsored by Korean Ministry of Knowledge Economy (MKE).

REFERENCES

1. Stanford. R. Ovshinsky: “Reversible electrical switching phenomena in disordered structures”, Phys. Rev. Lett. 21 (1968) 1450
2. M. Wuttig and N. Yamada: “Phase-change materials for rewriteable data storage”, Nature Materials 6(2007) 824
3. K. Kim and G. Jeon: “The prospects of non-volatile phase-change RAM”, Microsyst. Technol. 13 (2007) 145
4. J.-h. Jeong, H. S. Lee, S. Lee, T. S. Lee, W. M. Kim, W. Zhe, S. C. Kim, K. H. Oh, and B. Cheong: “Crystallization and memory programming characteristics of Ge-doped SbTe materials of varying Sb:Te ratio”, J. Phys. D 42 (2009) 035104
5. M. Kastner, D. Adler, and H. Fritzsche: “Valence-alternation model for localized gap states in lone-pair semiconductors”, Phys. Rev. Lett. 37 (1976) 1504
6. M. Copel, J. D. Baniecki, P. R. Duncombe, D. Kotecki, R. Laibowitz, D. A. Neumayer, and T. W. Shaw: ”Compensation doping of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films”, Appl. Phys. Lett. 73 (1998) 1832
7. F. Xu, M. Vos, J. H. Weaver, and H. Cheng: “Interface dipoles, surface work functions, and Schottky-barrier formation at Au/ZnSe(100) interfaces”, Phys. Rev. B 38 (1988) 13418
8. D. Adler and E. J. Yoffa: “Electronic structure of amorphous semiconductors”, Phys. Rev. Lett. 36 (1976) 1197
9. L. C. Feldman and J. W. Mayer: “Fundamentals of Surface and Thin Film Analysis” North-Holland, New York, 1986
10. A. M. Cowley and S. M. Sze: “Surface states and barrier height of metal-semiconductor systems”, J. Appl. Phys. 36 (1965) 3212

Biographies

“Doo Seok Jeong”, Ph.D has been a researcher at KIST since 2008. His research area includes electronic and ionic transport in various chalcogenide materials and nonvolatile resistance switching in them. He received the B.Sc and M.Sc degrees in materials science and engineering from Seoul National University, Seoul, Republic of Korea, in 2002 and 2005, respectively. And he received the Ph.D degree in materials science and engineering from the RWTH Aachen university, Aachen, Germany, in 2008.

“Suyoun Lee”, Ph.D is a senior researcher at KIST. His major area of research has been chalcogenide thin film materials for phase change non-volatile memories, threshold switching devices, and spintronic devices. He received the B.Sc degree in Nuclear Engineering and the M.Sc and Ph.D degrees in School of Physics from Seoul National University, Korea. He spent three and a half years as a senior researcher for developing a phase change random access memory and magnetic random access memory in Samsung Electronics. He has joined KIST in 2006 and has been working in the field of phase change memory.

“Jeung-hyun Jeong”, Ph.D has been a senior researcher at KIST since 2004. His current major area of research includes phase change memory, MEMS sensors specifically employing diamond and PZT films, and mechanical characterization of thin films. He received a B.E., a M.E., and a Ph.D degree in Material Science and Engineering from Seoul National University, Seoul, Korea. He spent two years as a postdoctoral research associate in Department of Mechanical Engineering of Massachusetts Institute of Technology, Massachusetts, U.S.A., doing research on the mechanical assembly of carbon nanotubes and the development of micro energy harvesting device.

“Byung-ki Cheong”, Ph.D has been a senior/principal researcher at KIST since 1994. His major area of research has been chalcogenide thin film materials for phase change optical recording, super-resolution optical storage and non-volatile phase change electrical memory. He received a B.E and a M.E. degree in Metallurgy from Seoul National University, Seoul, Korea and a Ph.D degree in Materials Science and Engineering with a thesis on phase transformation in solids from Carnegie Mellon University, Pittsburgh, U.S.A. He spent two years as a postdoctoral research associate in Data Storage Systems Center (DSSC) of Carnegie Mellon University, doing research on thin film materials for magnetic and magneto-optical information storage until joining KIST in 1994.

“Cheol Seong Hwang” received the M.Sc. degree in 1989 and the Ph.D. degree in 1993 in department of inorganic materials science and engineering, both from Seoul National University-Seoul, South Korea. In 1993 he joined the Materials Science and Engineering Laboratory of National Institute of Standards and Technology, MD USA, as a postdoctoral research fellow. Then, he joined Samsung Electronics as a senior researcher from 1994, made contributions to the fields of semiconductor memory devices with researching on *high*-k dielectrics including $(Ba,Sr)TiO_3$. Since 1998, he has been a professor with department of materials science and engineering in Seoul National University. He has authored or coauthored more than 250 papers in international peer-reviewed scientific journals, which are cited more than 3500 times, has given 40 invited presentations in international conferences. He is a recipient of Alexander von Humboldt fellowship award, which made him to stay in Forschungzentrum Juelich, Germany as a Humboldt fellow in 2004, and the 7th presidential young scientist award of Korean government. His current interests include high-k gate oxide, DRAM capacitors, new memory devices including RRAM/PRAM, ferroelectric materials and devices, and thin film transistors.