Improved Nanometer Resolution XANES Imaging of Individual PC-RAM Devices

Jan H. Richter[1,2], Milos Krbal[1,2], Alexander V. Kolobov[1,2,3], Paul Fons[1,2,3], Xiamoin Wang[1,2], Kirill V. Mitrofanov[1], Robert E. Simpson[1,2], Junji Tominaga[1,2], Hitoshi Osawa[3] and Motohiro Suzuki[3]

[1]Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, 305-8562, Ibaraki, Japan

[2]Collaborative Research Team Green Nanoelectronics Center, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, 305-8562, Ibaraki, Japan

[3]SPring-8, Japan Synchrotron Radiation Institute (JASRI), Kouto 1-1-1, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

e-mail: Jan.Richter@AIST.GO.JP

ABSTRACT

We report a x-ray nanobeam XANES study of single devices of *in situ* switched phase change memory. The devices investigated are of two different types: line cell devices and lance type cells. The deposition of our samples by helicon wave sputtering was carried out at AIST, while pattering was performed in the nanodevice fabrication facilities at NIMS. Line cell samples (see figure 1a) consisted of TiN contact electrodes covered with an additional metal (Au, Pt

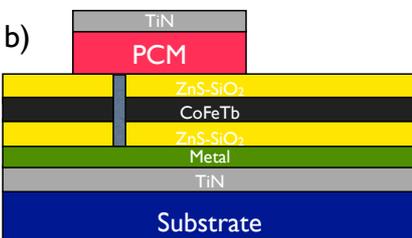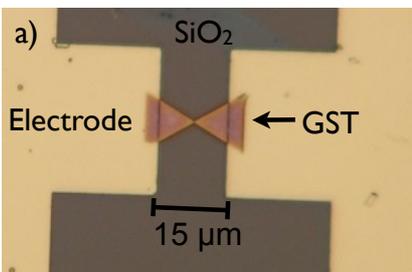or W) for better contact formation and the phase change material $Ge_2Sb_2Te_5$. The $Ge_2Sb_2Te_5$ layer was deposited overlapping the contact electrodes and consisted of two triangular regions facing each other with a 200 nm by 250 nm bridge connecting the triangles forming the active device area. The $Ge_2Sb_2Te_5$ surface was firstly covered by a ZnS-SiO$_2$ layer directly on top and then further protected from atmosphere by a larger SiO$_2$ capping layer. To ensure good contact between the electrodes and the GST and also to render the GST crystalline and conductive the samples were annealed on a hot plate at 200°C for 60 minutes. The lance type cells (figure 1b) consisted of a continuous bottom electrode of TiN/M (M being Au or W) with devices consisting of layers of ZnS-SiO$_2$/CoFeTb/ZnS-SiO$_2$/Ge$_2$Sb$_2$Te$_5$/TiN. The triple layer of ZnS-SiO$_2$/CoFeTb/ZnS-SiO$_2$ served the double function of insulator and current path defining device. To that end a single laser pulse with spot size of about 1 μm and varying pulse duration (10 ms to 1 μs) was fired at each device prior to GST deposition. The samples could be switched *in situ* at the synchrotron using a Keithley 4200 SCS semiconductor characterization system and an Agilent 81160A arbitrary wave generator in conjunction with an Agilent DSO 90254A oscilloscope.

Figure 1: a) Visualization of the line cell device type sample under an optical microscope. b) Schematic of the lance type cell devices.

The devices were investigated employing the x-ray nanobeam at bl39XU at SPring-8 which has a beam size of only about 100 nm as confirmed by a kni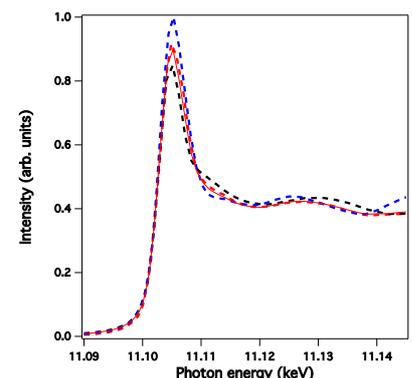fe edge scan [1,2]. We have collected XANES x-ray fluorescence spectra at the germanium K-edge of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ of single devices of phase change memory and could thus compare between the as deposited amorphous, the crystalline and the electrically reamorphized structure as well as with data collected earlier from a study on laser reamorphized material. The germanium K-edge spectra of GST differ dependent on their phase. Figure 2 shows a reference graph displaying data collected from laser modified GST [3]. Here it can be seen that the x-ray response of GST at the Ge K-edge white line (11.105 keV) is reduced by approximately 10% in the amorphous phase compared to the crystalline phase[3,4], while on the high photon energy side the intensity oscillations for the crystalline phase are of higher frequency. It is thus possible to pinpoint the active area of the device and estimate the extent of the phase change region by recording 2D spatial maps at a constant photon energy of the same device area after multiple switching cycles.

Figure 2: reference graph for Ge K-edge XANES data from laser modified Ge$_2$Sb$_2$Te$_5$: blue, red and black dashed lines represent the crystalline, laser re-amorphized and as-deposited amorphous state respectively, the red solid line is a best fit of the laser re-amorphized spectra (see text)

That is we measured a full 2D map of a device switched it multiple times and remeasured a full 2D map after each switching event. Previous studies of this type had been burdened with beamdrift, i.e the position of the sample slightly (in the nm range) changing relative to the beam under the course of the experiment. The improved experimentation reported here provided active correction for beamdrift continuously during data acquisition. To this end an additional 2D piezo stage was attached to the sample stage and the sample was raster scanned after each photon energy. The first method served to reattain the desired position by comparing with a reference Zn signal, while in the second method complete 2D maps of the devices were collected for each photon energy. That is in the second case photon energy dependent 2D maps of the sample were recorded that could later be manually matched in position space.

We have already previously measured single devices of *in situ* switched phase change memory in previous experiments, however with no means to actively compensate for the occurring beamdrift. Additionally the samples investigated at that time suffered from oxidation during measurement, due to ozone generated by the x-ray beam. In these experiments we have demonstrated the feasibility of our method and could to some degree estimate the active phase change region and observe differences between XANES spectra for the different structures.
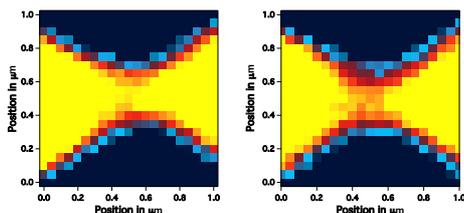

Figure 3: 2D map of the prototype line cell device: crystalline cell (left) and amorphous cell (right) germanium x-ray fluorescence intensity as a function of position recorded at a photon energy of 11.105 keV.

Figure 3 displays 2D maps collected at constant photon energy at the germanium white line photon energy (11.105 keV). On the left hand side of figure 2 a map for the crystalline state of the material is shown, while the right hand image displays the same device measured after it was switched into the amorphous state. Brighter (yellow) colours signify a higher fluorescence intensity while darker colours (red) indicate lower fluorescence response. Firstly it can be observed in the left hand image that the shape of the line cell sample is very clearly resolved by the x-ray imaging with the yellow parts corresponding to crystalline GST and the black parts the substrate region. In the amorphization of this sample performed with the Keithley 4200 SCS the upper measurement limit of the Keithley was exceeded and an increase in resistivity of the device by at least one order of magnitude was observed. In the right hand image we observe a red area of reduced intensity in the center of the device. This intensity reduction of about 10% of the GST signal indicates the presence of amorphous GST. A comparison between the two images reveals that as intended in the device design the majority of the GST remains unaffected by the phase transition and only the material present in the bridge part of the device exhibited a noticeable change. The region of active phase change in this particular sample encompasses the entire device area of about 200 nm by 250 nm. The amorphization appears to be complete, however the convolution of the x-ray beam and the oxidation of the sample should be taken into account, so more study on this subject is warranted.
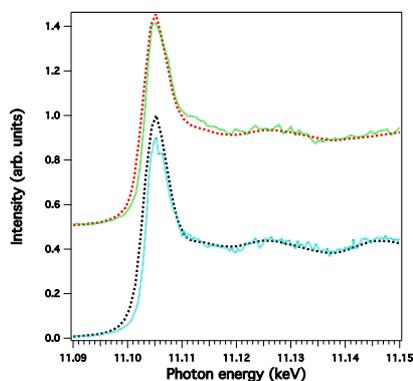

Figure 4: Ge K-edge XANES spectra: bottom crystalline state reference (black), line cell crystalline state (teal); top: line cell amorphous state (green), best fit (red)

It was attempted to estimate the degree of amorphousness upon reamorphization from the crystalline phase. To that end we assumed the spectra for the electrically reamorphized sample to be a superposition of spectral contributions of the spectra from the laser modified samples (figure 2). The trace for the crystalline sample would correspond to 100% crystallinity while the trace for the as deposited amorphous sample would indicate 100% amorphousness. It is important to keep in mind that the relative intensity differences between the white line region and the higher photon energy regions are dependent on experimental conditions and sample properties, such as thickness of GST and capping layers. Thus these relative intensities can only be compared in identical experiments using identical samples. The comparison thus focuses on the high photon energy oscillations. Figure 4 shows the data collected on the electrically modified sample in comparison to the crystalline trace of the laser modified sample and a best fit for the amorphous phase. In the bottom part of figure 4 a direct comparison between the two traces representing the crystalline material (teal electrical switching, black laser crystallized) reveals the clear similarities between these two methods. The high photon energy oscillations are very well reproduced and the traces can be assumed to indicate identical structure barring the higher statistical noise in the electrically modified sample. In the top of this figure the trace representing the reamorphized electrically switched material (green trace) has been attempted to fit with a convolution of the reference spectra (red trace). The oscillations are quite well reproduced employing a fitting ratio of 25% amorphous and 75% crystalline contribution, yet with some unaccounted intensity in the 11.114 keV region as part of high binding energy shoulder of the main peak. Intensity in this region is usually attributed to GeO, which agrees well with our observation of oxidation of these samples (not shown here). The not full amorphousness of the reamorphized sample might seem

surprising at first, however this behaviour has also been observed in laser reamorphized material. It also does not contradict diffraction data showing no crystalline peaks for reamorphized samples. Here the very local structure is probed and while this retains some crystallinity, long range order can be completely erased.

ACKNOWLEDGEMENTS

REFERENCES

[1] M. Takagaki, M. Suzuki, N. Kawamura, H. Mimura, and T. Ishikawa, Proc. 8th Int. Conf. X-ray Microscopy 7, 267 (2005).
[2] K. Yamauchi, K. Yamamura, H. Mimura, Y. Sano, A. Saito, K. Endo, A. Souvorov, M. Yabashi, K. Tamasaku, T. Ishikawa, et al., Jpn. J. Appl. Phys. 42, 7129 (2003).
[3] P. Fons, H. Osawa, A. V. Kolobov, T. Fukaya, M. Suzuki, T. Uruga, N. Kawamura, H. Tanida, and J. Tominaga, Phys. Rev. B 82, 041203 (2010).
[4] A. Kolobov, P. Fons, A. Frenkel, A. Ankudinov, J. Tominaga, and T. Uruga, Nature Mater. 3, 703 (2004).

Key words: Phase change memory, XANES, nanobeam

Biography

2002-2006 Ph.D. at Uppsala University, Sweden with Hans Siegbahn
Thesis: "Electronic Properties of Metal Oxide Films Studied by Core Level Spectroscopy"
Surface science and synchrotron radiation based electron spectroscopy investigation of modification of metal oxide thin film systems.

2006-2008 Research Scientist at Ilika Technologies, Southampton, England
Contract based combinatorial, high throughput sample growth and analysis in the field of phase change memory materials. Construction of experimental equipment, such as static tester and lab maintenance.

2008-2010 Post Doc at Victoria University of Wellington, New Zealand
Growth and investigation of rare-earth nitrides with regard to magnetic properties as potential spintronics materials.

2010- Research Scientist at AIST, Tsukuba, Japan
Investigation of novel design phase change memory structures. Nanobeam investigation of single devices of phase change memory.