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Abstract — **In this work a scheme for fabricating a conductive bridge non-volatile memory arrays, using ion bombardment through a mask, is demonstrated. Blanket films and devices have been created to study the structural changes, surface roughness and device performance. Ar^+ ions interaction on thin films of Ge_xSe_{1-x} system have been studied using Raman Spectroscopy, Atomic Force Microscopy (AFM) and Energy Dispersive X-Ray Spectroscopy (EDS). The performance of the memory devices has been analyzed based on the formation of vias and damage accumulation due to Ar^+ ion interactions with Ge_xSe_{1-x} (x=0.25, 0.3 and 0.4) thin films of chalcogenide glasses (ChG). This method of devices/arrays fabrication provides a unique alternative to conventional photolithography for prototyping redox conductive bridge memory without involving any wet chemistry.**

Keywords—Redox conductive bridge memory; chalcogenide glass; film and device characterization

I. INTRODUCTION

An imminent scaling limit of Si-based flash memories accelerated the search for new memory technology [1]. Due to this search a number of alternate memory technologies are being explored. The conductive bridge non-volatile memory technology is an emerging way to replace the traditional charge based memory devices for future neural networks and configurable logic applications. These devices are based on electrically switchable resistance by the formation or dissolution of conductive bridge caused by redox reaction at respective electrodes [2], known as redox conductive bridge (RCBM). These devices exhibit high speed access, fast switching, high density and low power consumption [3]. By integrating the RCBM cells into a system, they can fulfill the essential role of memory with high storage density, precision, and access speed [4]. The array structure also provides powerful capability in information processing [5], synapse creation for neuromorphic systems [6], arithmetic computation [7], pattern comparison [8], and reconfigurable field programmable gate arrays (FPGA) [9]. RCBM devices have a simple capacitor like Metal insulator Metal (MIM) structure. The device switches between high resistance state (HRS) and low resistance state (LRS) due to the formation or dissolution of a conductive molecular bridge between the two metal electrodes by the application of either Write or Erase voltage. In addition, the Write and Erase voltages do not need to be applied continuously to maintain the state, thus making RCBM a non-volatile memory.

In this work, a method is demonstrated for creating Ge_xSe_{1-x} (x=0.25, 0.3 and 0.4) chalcogenide based RCBM arrays by directly forming the vias in the Ge-Se film, by bombarding it with Ar^+ ions through a mask. The openings in the mask thus defined the devices size. Formation of array relies on the high resistivity of the Ge-Se film which expands in the range of hundreds of giga-ohms. In this manner the non-sputtered regions act as isolation between the adjacent cells in the array. The arrival of the energetic ions causes the surface atoms to be removed from the material. As a consequence vias are created in the Ge-Se layer, forming the devices. The high energy particles cause surface roughness, compositional variations, and structural alterations in the irradiated layer [10] which are investigated in this work. The viability of this method is demonstrated by electrical testing of the fabricated RRAM arrays, formed by capping the vias with silver (Ag) electrode.

II. EXPERIMENTAL DETAILS

Arrays of RCBM devices were created on a Ge_xSe_{1-x} /W/SiO_2/Si stack. On a Si <100> substrate, a 200nm of SiO_2 was thermally grown followed by 100nm of sputtered W (Tungsten), and 1µm of thermally evaporated Ge-Se ChG thin films. Devices array was created by bombarding the Ge-Se layer with Ar^+ ions using an INA-X (SPECS, Berlin) Secondary Neutral Mass Spectrometer (SNMS) [11] by placing a 50µm×50µm nickel mesh over the sample. In contrast to most ion beam tools where ion energy has a Gaussian distribution, the current is highly uniform within the SNMS machine over the entire bombarded region. This resulted in uniform depth profiles in the Ge-Se layer for all the cells in an array. A copper holder was placed on top of the nickel mesh to keep it in place and protect part of the sample from ion bombardment for analysis of ion-induced effects. Surface bombardment was performed with low pressure Electron Cyclotron Wave Resonance (ECWR) Ar^+ plasma. The resulting configuration can be seen in Fig. 1. SNMS depth profile data were used to determine the sputtering rate, and bombardment times, for creating 100nm and 200nm of Ge-Se layer at the base of the vias to form the array. Each ion bombardment was performed at 100 kHz frequency with 80% duty cycle applied to the sample. Using a DC magnetron

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sputtering system, 50 nm of Ag was deposited at $5x10^{-3}$mbar on top of the formed vias.

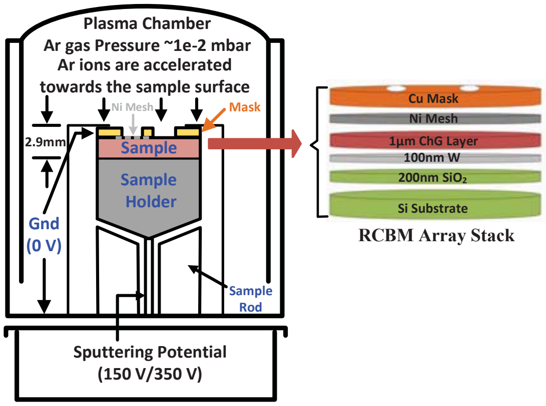


Figure 1. SNMS System configurations with sample stack

Compositional analysis of the ions bombarded films was achieved through application of EDS by a Hitachi S-3400N EDS system. 30kV accelerating voltage, and 10nA beam current were used for EDS measurements. The surface morphologies of Ge-Se films bombarded with Ar^+ ions were studied in tapping mode using an OTESPA probe on a Veeco Dimensions 3100 AFM system equipped with a Nanoscope IV controller. Raman spectra of the irradiated films were performed in a vacuum chamber using a Horiba Jobin Yvon T64000 Raman spectroscopic system in back scattering mode.

Electrical testing on the devices was performed using an Agilent 4155B Semiconductors Parameter Analyzer equipped with triax cables to avoid residual charge build up. W and Ag pads were probed with correct biasing for SET and RESET conditions. Various cells in the array were tested in dual sweep mode with a voltage step size of 6mV and compliance current set to 50nA. Data were analyzed and recorded by Easy Expert Software provided by Agilent. The testing equipment (sample stage holder, triax cables and probes) was placed inside a Faraday cage sharing a common ground to avoid static charge build up.

III. RESULTS

A SEM image of the fabricated 20x20 array is shown in Fig. 2 with Ge-Se film isolating individual cells. Energy Dispersive X-ray Spectroscopy (EDS) was performed in five different cells at five different locations on each sample, so that 25 points were used to determine the uniformity of the film within each composition. The film compositions were measured in the cell vias created by ion bombardment as well as in the planar regions shadowed by the mask and the results are presented in Table 1.

Raman spectra of the as deposited films, ion bombardment areas (vias), mode assignments, and corresponding structural units characteristic for the studies Ge_xSe_{1-x} film compositions are presented in Fig. 3a. The as deposited films are well relaxed since their structure resembles the one of the bulk material with their composition. The spectra show peaks located at $178cm^{-1}$, $195cm^{-1}$ and $219cm^{-1}$, corresponding to ethane-like (ETH), corner-sharing (CS) and edge-shared (ES) structural units respectively [12]. Development of the spectra as a function of increasing Ge concentration shows an increase in the intensity of the peaks relating to the ES and ETH modes. A close observation of ES to CS area ratio demonstrates a change in the area ratio for Ge rich compositions for the ion bombarded regions as shown in Fig. 3b, with the largest change being observed in $Ge_{40}Se_{60}$, as illustrated in Fig. 3c. The surface morphology within the cell vias of the Ge_xSe_{1-x} layer created by Ar+ ion bombardment, were studied by AFM and the results are presented in Fig. 4. AFM scans were performed on virgin (non-bombarded area), cell 1, cell 9, and cell 18 in the 9th row of the array structure on a $25\mu m^2$ area within the device vias. An improvement in the surface smoothness is observed with the increase in the Ge concentration.

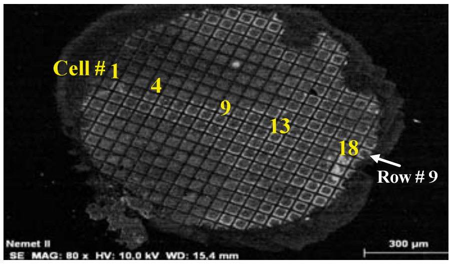


Figure 2. SEM Image of the RCBM Array

Table 1. EDS Results on Planar and Ion Bombarded regions for Ge_xSe_{1-x} Films (where x=0.25, 0.3 & 0.4)

Sr. No.	**Source Composition**	**Planar Region**		**Ion Bombarded Region**		**% Change**
		%Ge	**%Se**	**%Ge**	**%Se**	**Δ**
1	$Ge_{25}Se_{75}$	25.6±0.061	74.4±0.061	24.8±0.51	75.2±0.51	± 0.8
2	$Ge_{30}Se_{70}$	31.2±0.037	68.8±0.037	30.7±0.15	69.3±0.15	± 0.5
3	$Ge_{40}Se_{60}$	39.9±0.19	60.1±0.19	38.8±0.14	61.2±0.14	± 1.1

Since the performance of RCBM devices depends on formation of a conductive filament, it is important to have a smooth surface within the via for reliable device performance. EDS and AFM results suggested that amongst the studied Ge-Se compositions in this work, $Ge_{40}Se_{60}$ is the most suitable for RCBM array fabrication using ion bombardment method as it offers the smoothest surface. RCBM arrays were fabricated and tested with an active $Ge_{40}Se_{60}$ film, having thicknesses of 100nm and 200nm at the base of the vias. The current-voltage (IV) curves of different cells from fabricated arrays with different thickness of $Ge_{40}Se_{60}$ layer in the via is shown in Fig. 5. Multiple IV sweeps under the same conditions were performed to ensure good endurance of the cells within the array. The devices were swept from -0.5V to 2V for each sweep. At first the current is very low (cell resistance: high) until a threshold voltage of ~0.9 V is exceeded. At that moment a conductive connection is formed between the top and bottom electrodes causing a steep increase in the current until it reaches the compliance current, limited to 50nA (cell resistance: low). The device performance was evaluated with 100nm and 200nm thick $Ge_{40}Se_{60}$ films at the base of the via. Analysis of these results shows that the better repeatability and uniformity of the devices is achieved with a 100nm thick $Ge_{40}Se_{60}$ layer left in the device active area after sputtering, which also show lower threshold voltage (~0.8V). The two resistive states i.e. LRS and HRS are presented in Fig. 6 which shows three orders of magnitude difference between the ON and OFF state for both films thickness.

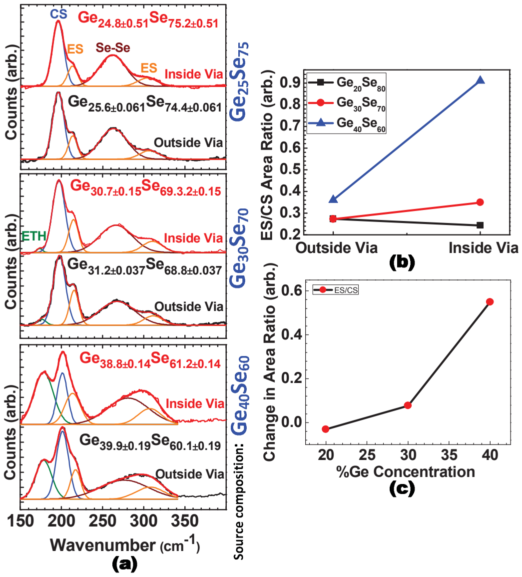
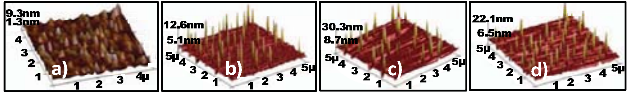


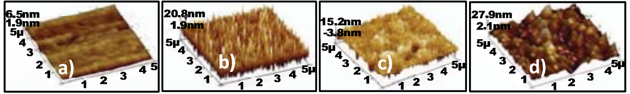
Figure 3. *(a) Raman data and the corresponding mode assignment (b) Area Ratios b/w ES and CS modes (c) Change in area ratio with different Ge concentrations*

$Ge_{25}Se_{75}$ Film within array cell



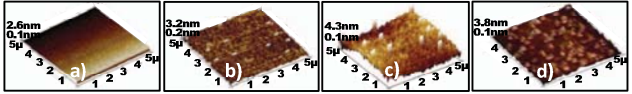
25µm² area scan of (a) Virgin and vias formed in $Ge_{25}Se_{75}$ by ion bombardment in (b) 1st cell of Array (c) 9th cell of Array (d) 18th cell of Array

$Ge_{30}Se_{70}$ Film within array cell



25µm² area scan of (a) Virgin and vias formed in $Ge_{30}Se_{70}$ by ion bombardment in (b) 1st cell of Array (c) 9th cell of Array (d) 18th cell of Array

$Ge_{40}Se_{60}$ Film within array cell



25µm² area scan of (a) Virgin and vias formed in $Ge_{40}Se_{60}$ by ion bombardment in (b) 1st cell of Array (c) 9th cell of Array (d) 18th cell of Array

Figure 4. *Surface morphology of Ge_xSe_{1-x} on a 25µm² area*

IV. DISCUSSION

The accelerated Ar^+ ions used to form the vias in the Ge_xSe_{1-x} film alter the film composition, which causes structural changes and eventually affects the device performance. The two processes of compositional and structural changes taking place by ion bombardment, are imperative for understanding thin films stability and hence device performance. The former is elucidated through EDS analysis of the bare and ion bombarded regions, and the latter is investigated by studying Raman Spectroscopy.

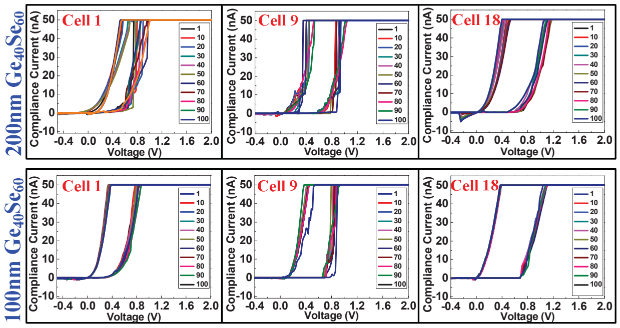


Figure 5. *IV curves in different cells of the 9th row for the fabricated RCBM array*

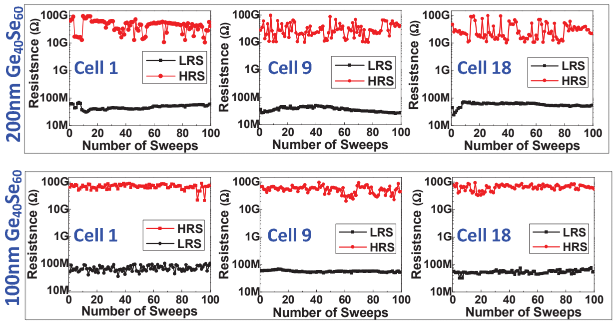


Figure 6. *HRS and LRS plot of $Ge_{40}Se_{60}$ film with different thickness in the via*

EDS data suggest that Ge atoms, having lower atomic mass, sputters out faster than Se atoms. The lowest amount of Ge loss is observed in $Ge_{30}Se_{70}$ which is attributed to the closeness of its composition to the stoichiometric composition where the structure has lowest number of wrong chemical bonds.

Analysis of the Raman spectra using the area ratio between the ES structural units corresponding to the peak located at 218cm^{-1} and CS structural units corresponding to the peak at 202cm^{-1}, demonstrates compositional dependence of the ion beam induced structural changes in the sputtered material. This suggests that the Ar^+ ions mainly affect the bonding sites between Ge-Se atoms. In essence, the loss of Ge atoms should result in increased amount of CS structural units, which is the case in the $Ge_{25}Se_{75}$ samples. The increased areal intensity of the ES structural units could be related to the lower steric energy related to the formation of this structure which keeps its appearance even at reduced amounts of Ge. In the Ge rich samples the availability of ETH structural units includes one more variation for Ge loss. Since the Ge-Ge bond is the weakest, the probability of detaching Ge from this bond is the highest. So the charge distribution and atoms position prefers the formation of ES structural units. At this composition the loss of Ge is the biggest, which we relate to the lower energy that is necessary to expel Ge and from this type of structure. However, the relative intensity of the ETH structural units remains dominant and even remarkably increases after ion bombardment, which suggests that the energy introduced to the films by the bombarding Ar^+ ions contributes to their self-organization and formation of a compact structure. It is realized through clusters formation in which different fractions of ES and ETH units are engaged. The increase of the cluster size leads to formation of ring structures that contain more than the four atoms of the simple ES tetrahedra [13] which relaxes the structure. It is for this reason that the surface roughness, after ion bombardment, is much reduced in $Ge_{40}Se_{60}$ films.

Relating the films characterization data to devices performance, we suggest that there are two main reasons for the poor performance of the $Ge_{25}Se_{75}$ and $Ge_{30}Se_{70}$ films (data not presented due to space limitation); higher surface roughness, which is the reason for uncontrolled growth of the conductive bridge and the fact that, after ion bombardment, these compositions keep a structure characteristic for Se rich films, which results in development of heterogeneous structure [14] when Ag is introduced in them, due to the formation of Ag clusters, causing variable distribution within the ChG matrix. However, in case of Ge rich binary glasses, due to the better surface smoothness the bridge formation is stable over the entire ChG and electrodes interface. The presence of ETH units despite the Ge loss categorizes these films as Ge rich. Therefore, they form homogeneous material with Ag introduced in them [14] which stabilizes the switching characteristics of the devices.

The better performance of the 100nm thick devices compared to the 200nm devices is attributed to the formation of fewer defects in the limited volume of the 100nm devices. Reduction of the devices thickness and lateral dimensions is our further research goal, which we hope will contribute to improvement of the devices and hence arrays reliability.

V. CONCLUSION

In this work, we studied the effect of the Ar^+ ions on the Ge-Se system. Our results demonstrate that ion bombardment causes compositional changes by which the element with smallest mass is sputtered faster, resulting in structural transformations occurring in the films. The structural transformation is also related to direct interaction of Ar+ ions with Ge-Se films that cause major effects in the Ge rich films. We successfully demonstrated the fabrication of a lithography free RCBM array with individual cell addressing and tested the electrical performance of the cells within the RCBM array based on different thicknesses of Ge-Se film in the active region. It was found that the Ge rich film offered the least surface roughness and homogenous distribution of Ag, which contribute to a more stable and repeatable device performance.

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