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Switching Studies on $Ge_{15}In_5Te_{56}Ag_{24}$ Thin Films

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***Abstract*—**Germanium Telluride based quaternary thin film switching devices with composition $Ge_{15}In_5Te_{56}Ag_{24}$, have been deposited in sandwich geometry on glass substrate with aluminum as top and bottom electrodes. The bulk glassy form of the said composition is prepared by melt quenching technique. In this technique, appropriate quantity of elements with high purity are taken in a quartz ampoule and sealed under a vacuum of 10^{-5} mbar. Then, it is allowed to rotate in a horizontal rotary furnace for 36 hours to ensure homogeneity of the melt. After that, the ampoule is quenched into a mixture of ice - water and NaOH to get the bulk ingot of the sample. The sample is then coated on a glass substrate using flash evaporation technique at a vacuum level of 10^{-6} mbar. The XRD report reveals the amorphous nature of the thin film sample and Energy - Dispersive X-ray Analysis (EDAX) confirms that the film retains the same chemical composition as that of the base sample. Electrical switching behavior of the device is studied with the help of Keithley (2410^c) source-measure unit interfaced with Lab VIEW 7 (National Instruments). Switching studies, mainly SET (changing the state of the material from amorphous to crystalline) operation is conducted on the thin film form of the sample. This device is found to manifest memory switching as the device remains 'ON' even after the removal of the electric field. Also it is found that amorphous $Ge_{15}In_5Te_{56}Ag_{24}$ thin film unveils clean memory type of electrical switching behavior which can be justified by the absence of fluctuation in the I-V characteristics. The I-V characteristic also reveals that the switching is faster in this sample as no data points could be seen in the negative resistance region during the transition to on state and this leads to the conclusion of fast phase change during SET process. Scanning Electron Microscopy (SEM) studies are performed on the chosen sample to study the structural changes at the time of switching. SEM studies on the switched $Ge_{15}In_5Te_{56}Ag_{24}$ sample has shown some morphological changes at the place of switching wherein it can be explained that a conducting crystalline channel is formed in the device when the device switches from high resistance to low resistance state. From these studies it can be concluded that the material may find its application in fast switching Non-Volatile Phase Change Memory (PCM) Devices.

***Keywords*—**Chalcogenides, vapor deposition, electrical switching, PCM.

I. Introduction

AGGRESSIVE downscaling of Flash memory, which has been the sole player for the last 20 years in the field of non-volatile memory technology, impacts data retention performance and electrostatic interactions issues between adjacent cells for NAND, which in turn leads to threshold voltage instabilities and reading errors. Phase change random access memory (PCRAM), with a potential of reversible phase transformation and concocted from chalcogenides, stands as a strong alternative to flash memory because of advantages like better scalability, fast programming time, an ameliorated endurance [1], [2]. In this short span of time, semiconducting chalcogenides have gained wide popularity as it is being used immensely in infrared optical fibers [3], solar cells [4], optoelectronics [5], optical recording systems [6], phase change memories etc.

PCRAM being capable of reversible phase change has two states of existence:

1) One being the amorphous state where the resistance is high and so is considered as 'OFF' or 'logic zero' state [7], [8].
2) The other is the crystalline state where the resistance is low and is termed as 'ON' or 'logic one' state. [7], [8].

The work of S.R. Ovshinsky brought expansive light in electrical switching behavior of amorphous semiconductors [7]. Electrical switching in chalcogenides is a rapid process which occurs at about 10^{-10} sec at a critical voltage known as threshold voltage or switching voltage and the material instantly changes from low conducting state to high conducting state. There are two types of switching phenomenon in chalcogenide glasses:

1) Threshold switching in which the material reverts back to OFF state once the electric field is removed.
2) Memory switching where the material gets latched to low resistance ON state.

PCRAM exhibits non-reversible (memory type) switching phenomenon. Electrical switching in chalcogenides makes them the suitable material for phase change memories (PCM). The factors viz. on-state current, local structure, thermal stability, thermal diffusivity, composition of the constituents etc. determines the type of switching (threshold or memory) manifested by the chalcogenide glasses [9]. Both the type of switching is electronic in nature and are initiated by the field induced charge carriers which fill the valence alternation pairs present in the glass and thus intensifying carrier mobility. In memory switching, thermal effects can be seen as crystalline channel gets formed due to inflated current flow [10].

Memory type of switching is exhibited by a wide number of amorphous semiconductors ranging from tellurium based binary glasses like Ge-Te, Si-Te, As-Te, In-Te, Ga-Te [11]-[16] and tellurium based ternary glasses such as Ge-Te-Ag, Ge-Te-Cu, Ge-As-Te [17], [18] to tellurium based quaternary glasses [19].

Blending Silver in chalcogenide glasses is found to have a number of advantages like increase in phase transformation

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rate and electrical conductivity by several orders of magnitude [20]. Metallic impurities like silver immensely impact the switching voltages [21]-[23]. In this work, preparation of thin film of germanium based material- $Ge_{15}In_5Te_{56}Ag_{24}$ is endeavored which has been deposited by flash evaporation technique. An elaborative switching study with a focus on SET operation is carried out. Further SEM and EDAX have been done to study the morphological change that might have occurred during the switching and chemical composition respectively. To support the amorphous nature XRD is done on the sample.

II. Experimental Details

The source material for the thin film is prepared by melt quenching technique. The quartz ampoule inserted in the furnace is loaded with ±0.1 mg accurate and measured proportions of 99.999% pure elements and sealed under 10-5 mbar vacuum level. This sealed ampoule is placed in a high temperature rotary furnace where the temperature is increased by 1000C every hour until it reaches a temperature above the melting points of the constituent elements, i.e. 1100 oC. The ampoule is maintained at this temperature and rotated continuously for 24 hours at 10 rpm to maintain homogeneity of the melt, after which the ampoule is quenched in a mixture of ice water and sodium hydroxide (NaOH) to obtain bulk glassy sample. To acquire the bulk sample, the ampoule is broken.

The thin film $Ge_{15}In_5Te_{56}Ag_{24}$ sample is coated in sandwich geometry on 25 mm × 75 mm glass substrate which is cleaned initially with detergent solution and acetone. Flash evaporation method with a vacuum level of 10^{-6} mbar has been employed to prepare thin film devices. Aluminum is used as top and bottom electrodes. After coating the bottom electrode on the glass substrate the bulk material is coated on the bottom electrode in rectangular shape (the rectangular shape has been achieved with the help of rectangular mechanical mask). The top electrode is coated on the chalcogenide layer with another mask wrapped on it. The active area of the device is the intermediate film area between the top and bottom electrode. Fig. 1 shows the device geometry of the thin film. Sandwich geometry has been chosen for deposition in this work to achieve lower switching voltages of the devices.

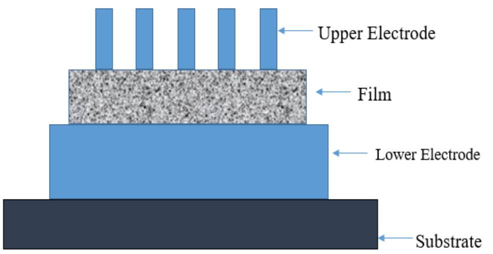

Fig. 1 Schematic diagram of amorphous $Ge_{15}In_5Te_{56}Ag_{24}$ thin film switching device in sandwich geometry

To study the I-V characteristic and the electrical switching behavior, a constant current is passed through the sample and consequently the voltage developed across the device is measured. Keithley (2410c) source-measure unit using LabVIEW 7 is employed to carry out the above process. The source and measure unit is capable of sourcing current in the range of 50 pA to 1.05 A at a maximum compliance voltage of 1100 Volt. The thin film sample is placed in a probe station which is proficient to move in X, Y, Z directions. SEM studies are carried out using VEGA3 TESCAN.

III. Results And Discussions

A. Electrical Switching of $Ge_{15}In_5Te_{56}Ag_{24}$

To validate the amorphous nature of the as-deposited film, X-Ray diffraction patterns are recorded using Bruker D8 Advance diffractometer. Fig. 2 shows the diffraction pattern of the film confirming amorphous nature. Fig. 3 shows the energy dispersive X-Ray analysis (EDAX) which highlights the composition of different constituent elements in the as-deposited film. The EDAX image of the sample confirms the presence of all base elements.

Fig. 4 shows the I-V characteristics of amorphous $Ge_{15}In_5Te_{56}Ag_{24}$ thin film sample. It can be seen that primarily the amorphous thin film sample is in high resistance state as very small amount of current flows through the device, and denoted as 'OFF state'. As the current is gradually increased, at a voltage known as threshold voltage or switching voltage which is equal to 4.34 V, the device switches from low conducting OFF state to high conducting ON state and current increases abruptly, depicting non-ohmic behavior. The device gets latched to the ON state even after the removal of the electric field and hence manifesting memory type electric switching. The thickness of the $Ge_{15}In_5Te_{56}Ag_{24}$ thin film used in the device is about 10 µm.

Increase in network connectivity, crystallizing ability and electrical conductivity [24], [25] are some of the exciting variations seen in the properties of chalcogenides materials, when the latter is doped with metallic impurities like silver. During switching, with the application of electric field the electrons accelerates thereby increasing the temperature of the material due to joule heating and as a result the material melts and cools to crystalize in between the electrodes and thus manifesting memory switching.

The memory switching exhibited by tellurium based glasses occurs because of two reasons:

a) The presence of long Te chains in the sample leads to effortless occurrence of atomic rearrangement and devitrification.

b) In comparison with sulphides and selenides, glassy tellurides have higher electrical conductance because of which higher joule heating and facile crystallizability occur, leading to memory switching in amorphous tellurium glasses.

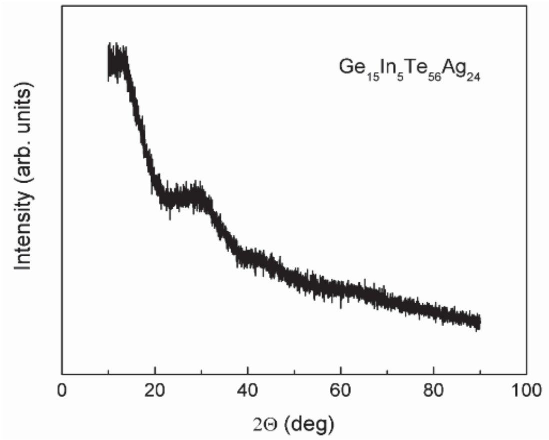

Fig. 2 XRD pattern of $Ge_{15}In_5Te_{56}Ag_{24}$ thin film affirming amorphous nature.

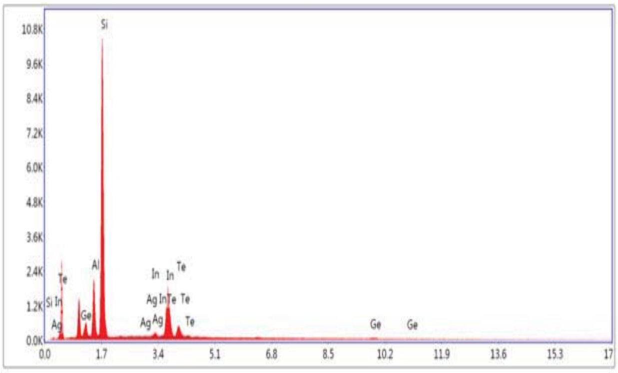

Fig. 3 EDAX analysis of $Ge_{15}In_5Te_{56}Ag_{24}$ thin film

The I-V characteristics also reveal that the switching is faster in this sample as no data points could be seen in the negative resistance region during the transition to on state, which leads to the conclusion that the material exhibits fast phase change during SET process.

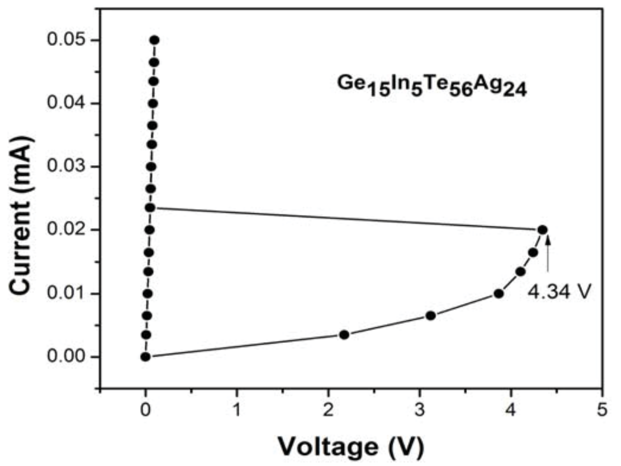

Fig. 4 I-V characteristics of $Ge_{15}In_5Te_{56}Ag_{24}$

B.Morphological Studies

Fig. 5 shows the scanning electron micrograms (SEM) of switched devices of $Ge_{15}In_5Te_{56}Ag_{24}$ thin film sample. The phase change in the electrode region is revealed by the image contrast in the SEM image.

Morphological changes can be seen at the place of switching. These changes could be due to any of the following reasons:

1. Flow of current during switching causes local melting and re-solidification of active material into crystalline state which in turn leads to surface relief causing image contrast.
2. Crystalline phase is denser than amorphous phase, so glass to crystal phase transition amalgamated with local structural change and density densification in the electrode region can show image contrast.
3. With the change in phase from amorphous to crystalline, the resistance also changes drastically by three order of magnitude. The change in conductivity can lead to image contrast.

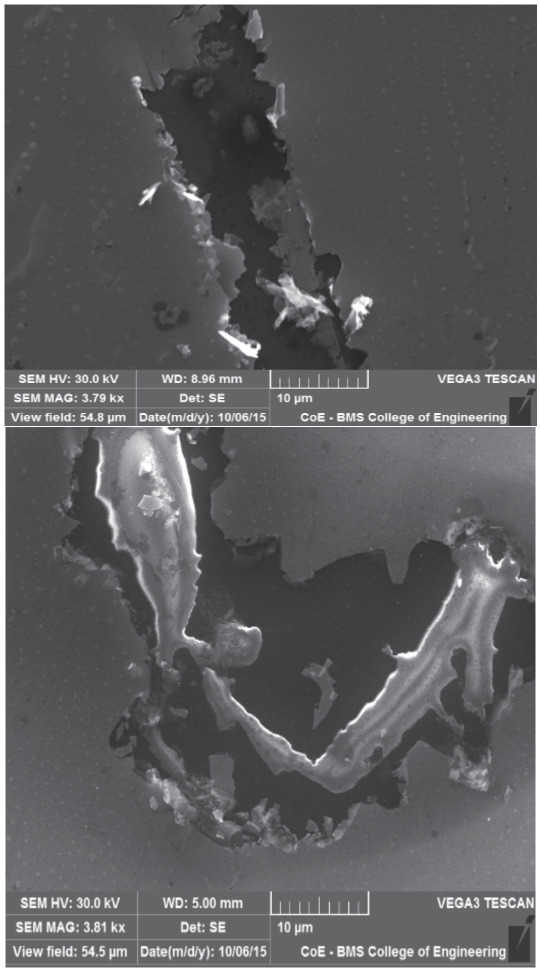

Fig. 5 SEM images of $Ge_{15}In_5Te_{56}Ag_{24}$

IV. Conclusion

Amorphous $Ge_{15}In_5Te_{56}Ag_{24}$ thin film sample coated in sandwich geometry on glass substrate with aluminum as top and bottom electrode with a film thickness of 10 μm is found to exhibit memory type electrical switching having a threshold voltage of 4.34 V. SEM studies on $Ge_{15}In_5Te_{56}Ag_{24}$ specify morphological changes at the place of switching. The phase change in the electrode region is revealed by the image contrast in the SEM image. The present studies reveal that the device can be used for fast switching applications.

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