Application of GeTe phase-change films in the directly heated two-port switch design

S Qu\textsuperscript{1,2}, J H Zhang\textsuperscript{1,2,3}, L B Gao\textsuperscript{1,2}, H W Chen\textsuperscript{1,2}, X Li\textsuperscript{1,2}, and J M Wang\textsuperscript{1,2}

\textsuperscript{1}State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science & Technology of China, Chengdu, Sichuan 610054, China
\textsuperscript{2}Collaboration Innovation Center of Electric Materials and Devices, University of Electronic Science & Technology of China, Chengdu, Sichuan 610054, China

Email: jhzhang@uestc.edu.cn

Abstract. Phase-change (PC) materials offer the property of thermally induced reversible change and exhibit different resistance values due to the structure changes between crystalline and amorphous phases. In this work, GeTe films with a thickness of 100 nm were deposited on the glass substrates by radio-frequency magnetron sputtering and annealed at different temperatures. The XRD analysis showed diffraction peaks corresponding to the rhombohedral structure of c-GeTe (021), (200), (202), and (220), respectively. Upon annealing at 300 and 340\textdegree C, the rhombohedral structure would transform into a rock salt structure. The Raman analysis revealed that a-Ge-Te covalent bond is the mixed structure of tetrahedron and defective octahedron changing into tetrahedral cells. The resistivity declined sharply from 0.72 to 3.8\times10^{-6}\ \Omega\cdot m, whereas the Hall mobility of holes sharply rose to 300 m\textsuperscript{2}V\cdot s. Based on the above films, a two-port directly heated switch device was designed and fabricated in sandwich structure to verify its phase-change characteristics. Low-resistance state was converted from crystallization with a 20ns 9V voltage pulse, while high-resistance state was by passing a 2\\mu s 2V voltage pulse. The on/off resistance ratio of switch could reach five orders of magnitude, while the switch state remained stable after the process termination. The results obtained strongly suggest that GeTe is a promising material for RF switches.

1. Introduction
Chalcogenide materials, also known as phase-change materials (PCM), including Ge-Te, Ge-Sb-Te, Sb-Se and In-Sb, are widely used in the production of CDs, due to their excellent optical properties. PCMs provide reversible transformation between crystalline (low-resistivity) and amorphous (high-resistivity) states under electric pulse or laser beam [1]. Recently, PCMs were extensively explored and applied to commercial applications, such as rewritable data storage and nonvolatile digital memory [2-4]. In addition, phase-change switches also emerged as state-of-the-art applications. In contrast to radio-frequency micro-electromechanical systems (RFMEMS) and solid-state switches, which require a continuous energy input to keep them in the required state, PCM-based ones require no energy input and, thus, can be used as nonvolatile RF switches. As a member of PCM family, GeTe has a high crystallization temperature (189\textdegree C) and a melting point (700\textdegree C), which means it would be stable at room temperature and hardly fail in normal situation. Moreover, it is noteworthy that the sheet resistance of GeTe films is one order of magnitude lower than that of state-of-the-art FETs, which means a lower switch-on resistance for a similar device geometry [5]. In addition, there still are some fascinating merits:
high dynamic range (106) [6], fast switching speed [7], small size, low parasitic capacitance, and low power consumption. In a word, GeTe is an extremely promising material for high-speed RF switches.

GeTe has generally been considered to be like a degenerate p-type semiconductor in crystalline state [6, 8-9]. However, in amorphous state, the mode of electronic transport has been controversial for a long time, and some models have been proposed [10,11]. For most materials, the short-range order of its amorphous state is similar to its crystalline state. Kolobov et al.[12] studied quantitative characteristics of PCM and reported the existence of long and short Ge-Te covalent bonds in crystalline GeTe. Moreover, once amorphous GeTe turns into crystalline state, long Ge-Te covalent bonds break, and short covalent bonds become stronger, thus, tetrahedral element is formed. However, Akola [13] and Caravati [14] have shown that amorphous PCM are composed of atoms of octahedral and tetrahedral coordination. Authors [6,15] reported that, in amorphous GeTe, electron transport was attributed to the Poole-Frenkel effect. Bahl and Chopra [6] assumed that conduction occurred as two parallel processes, namely (i) the intrinsic excitation across the band gap and (ii) thermal field-assisted hopping from one localized (trapping) state to another.

Ielmini and Zhang revealed the temperature dependence of subthreshold conduction in amorphous chalcogenide materials and reported that the voltage-dependent activation energy could be attributed to trap-limited conduction [16].

For now, there are two main types of phase change switch: directly and indirectly heated ones. El-Hinnawy [17] has fabricated a four-terminal indirect phase-change switch, which demonstrated a 0.08 Ω-mm Ron with an Fconv of 1.0THz and a zero prime power consumption during steady-state operation. Wang [18] has designed a directly heated two-port RF switch and proposed an equivalent circuit model for such a switch, which had an RF signal path and a separate direct heater path to diminish the insertion losses.

Although there is great interest in GeTe, the data on its electrical properties are still lacking. In the past few years, studies on its electrical properties were mostly focused on the threshold voltage [19] and resistance ratio [20]. However, there are only few detailed reports on GeTe material-to-switch process, for example, the material selection and preparation prior to device fabrication.

In this paper, X-ray diffraction was used to analyze the structure of GeTe films annealed at different temperature. The Raman spectroscopy was used to study the vibration modes of GeTe films. The mobility and the concentration of holes were measured by the Hall-effect device at different temperatures. A simple directly heated two-port switch has been designed, fabricated, and tested to verify phase-change transition. The systematic analysis of electrical performance and structure transformation with temperature is instrumental in the further applications of radio-frequency phase-change switches.

2. Experimental

GeTe films were prepared on glass substrates by the magnetron sputtering (JGP450 of SKY Technology Development) at room temperature. Prior to sputtering, the chamber base pressure was at a high degree of vacuum of 5×10^{-4} Pa and pressure during sputtering was fixed at 0.6 Pa. Ar was the sputtering gas, and the flow rate is constant at 50sccm. With these conditions above, the sputtering rate is about 0.3 nm/s. To make GeTe crystalline, the deposited GeTe film was annealed by placing it in a tube full of flowing Ar at a constant temperature of 240°C, 300°C, 340°C for 3 hours. 50nm Si3N4 dielectric barrier material is then deposited plasma enhanced CVD (PECVD) by TRION TECHNOLOGY, INC, MINLOCK-ORION III. The structure of films has been characterized by X-ray diffraction (XRD) using CuKa radiation with k = 0.1540 nm using a PANalytical B.V. The Raman scattering spectra was recorded using a 514 nm Ar ion laser of a Renishaw InVia Raman spectrometer. The Raman shift was in the range from 100 to 250 cm\(^{-1}\), and the spectral resolution was 1 cm\(^{-1}\). The Hall test was carried out using a Larkshore 8404 system with a heated probe to heat up from 50 to 200°C. An Si3N4 dielectric barrier material was then deposited via plasma-enhanced CVD (PECVD) by TRION TECHNOLOGY, INC, MINLOCK-ORION III. Voltage pulse was triggered by RIGOL DG1022U function generator, and the resistance measurement was detected using an Agilent Keithley 2400 digital source meter.
3. Results and discussion

Figure 1 shows the XRD measurements of the newly deposited GeTe films and those annealed at 240, 300, and 340°C, respectively. The diffraction peaks are not observed in as-deposited films, while diffraction peaks of 2θ = 26, 30, 43, and 52° appear in the annealed film at 240°C. The diffraction peaks correspond to the rhombohedral structure of GeTe (021), (200), (220) and (042), respectively. This indicates that GeTe changes from amorphous to crystalline state by annealing. Upon annealing at 300 and 340°C, new phase peaks appeared. In [21], higher temperatures transform the rhombohedral structure into the rock salt one. Therefore, new peaks in XRD pattern of films annealed at 300 and 340°C correspond to the rock salt structure.

![Figure 1. XRD patterns of GeTe films annealed at different temperatures.](image1)

Figure 2 shows the Raman spectra of the GeTe film annealed at different temperature. In the amorphous GeTe, four major peaks appear in the wave numbers in the range of 50-250 cm\(^{-1}\) at 70 cm\(^{-1}\) (A), 124 cm\(^{-1}\) (B), 160 cm\(^{-1}\) (C), 220 cm\(^{-1}\) (D), respectively. In the crystalline GeTe, the two major peaks are located at 80 and 120 cm\(^{-1}\), respectively. Peaks of 124 and 160 cm\(^{-1}\) are red-shifted about 40 cm\(^{-1}\), as compared to c-GeTe. As in [10], the bond energy and frequency are related as follows: \(E(d^2)=0.635E(d^1)\). Hence, the energy in amorphous-to-crystalline transition decreases as the bond dilates. It would cause the peak appearance at 124 cm\(^{-1}\) in the amorphous state and at 80 cm\(^{-1}\) in the crystal state.

![Figure 2. The Raman spectra of GeTe films annealed at different temperatures.](image2)
Figure 3 is the Gaussian line fit of the Raman spectra on a-GeTe. There are four main bands: A, B, C, and D, which represent different vibration modes listed in table 1. Bands A and D are related to the symmetric and antisymmetric bending modes, respectively, for $F_2$ of the GeTe$_4$ tetrahedra [22]. The peak D is attributed to the unipolar Ge-Ge broadband because it appears only in the germanium-rich system [22,23]. As compared to the Raman spectrum of c-GeTe, the low intensity peak D in a-GeTe becomes weaker, which means that the number of Ge-Ge covalent bonds was diminished.

![Figure 3. Gaussian line fit of Raman spectra on a-GeTe.](image)

**Table 1. Vibration modes of a-GeTe.**

| Band | Vibration mode |
|------|----------------|
| A    | Bending modes  |
| (A$_1$,A$_2$) | $v_2$(E),$v_4$(F$_2$) of tetrahedral |
| B    | $v_1$ Vibrational bands of corner-sharing tetrahedral units |
| C    | Edge-sharing tetrahedral |
| (C$_1$,C$_2$) | |
| D    | $v_3$(F$_2$) Antisymmetric stretching mode |

Bands B and C correspond to the symmetric stretching mode, A$_1$ (n = 1, 2 corner sharing) and (n = 0 edge sharing) of the different vibrations of GeTe$_4$ tetrahedra, respectively. From the point of view of the peak corresponding to the base unit, bands B and C represent the vibrational modes of the octahedral Ge sites. A complex local structure of a-GeTe$_4$, which contained various types of twisted octahedral elements and tetrahedral elements, has been reported elsewhere [24, 25]. Noteworthy is that high-intensity peaks C were located in similar positions in both states, which meant that the local structure of Te-Te bonds was hardly changed by crystallization, which ensured a rapid transformation [25, 26]. According to the umbrella-flip theory proposed by Kolobov et al. [26], it can be assumed that during the transformation from a-GeTe to c-GeTe, Ge-Te covalent bonds of the mixed structure of tetrahedron and
defective octahedron changed into rhombohedral cells. A “flip” of Ge atoms can achieve a fast switching between two states of GeTe.

Figure 4. (a) Temperature-dependent resistivity measurements for a-GeTe film; (b) Temperature-dependent carrier concentration and Hall mobility measurement for a-GeTe film.

Figure 4 (a) and (b) show the resistivity, mobility, and carrier concentration of a-GeTe at different temperatures. As seen in figure 4 (a), the resistivity of the material decreases slowly as the temperature increases until 70°C is reached. However, at temperatures exceeding 170°C, the resistivity has a sharp decline. The maximum resistivity is 24Ω·m, and the minimum one is 3.8×10^4Ω·m, achieving a dynamic range of 10^6. As shown in figure 4 (b), when the temperature rose from 170 to 210°C, the sample mobility increased rapidly from 0.24 to 295 m^2/V·s, as its carrier concentration rose from 2.80×10^22 to 3.00×10^22 1/m^2.

The rapid increase in mobility is the main cause of resistance changes in a-GeTe. Transport in amorphous chalcogenide alloys is characterized by highly disordered state comprising of a large number of traps or localized states, so that the low mobility in amorphous films may be trap-limited [16]. When the GeTe film is in an amorphous state, the flow of carriers in the film is frequently scattered because the arrangement of the internal octahedron and tetrahedral elements are disordered and messy and there are numerous traps to capture carriers. Thus, the migration of carriers is strongly hindered, which eventually leads to a relatively high p. While the temperature is enough to crystallize GeTe, the lattice will be periodic and the scatter is lower, so that carriers are more likely to flow in the film, resulting in low resistivity.

In this study, we fabricated a simple directly heated two-port phase-change switch. Figure 5 is the cross-sectional diagram of the switch structure. Firstly, a 300 nm Ti/Pt layer was deposited and patterned as bottom electrode above a clean glass substrate. Then, a 100 nm amorphous GeTe film was deposited by the RF magnetron sputtering and crystallized by annealing in Ar for 3h at 240°C. The dielectric layer Si₃N₄ was produced by the PECVD technology. The top electrode was deposited similarly. All these layers were patterned.

Figure 5. Cross-section of two-port directly heated phase change switch

Different voltage pulses were applied to four samples to achieve the amorphous-to-crystalline transition. As shown in figure 6, the device was successfully switched back and forth. The resistance
varied from 50 to 1 mln ohm. The on-to-off state resistance ratio could reach the value of $10^5$. Pulses applied are listed in table 2. As shown in table 2, the pulse applied to sample 3 could ensure its good performance, as the state in the middle area (between on and off states) was the least among the four samples. Although other samples also switched from low to high resistance back and forth, there were too many confusing states in the middle area. Therefore, a 9V-20ns pulse is considered to be the optimal choice to activate GeTe as a phase-change switch.

![Figure 6. Resistance of four samples with voltage pulses applied](image)

| Sample | Crystallizing pulse | Re-amorphous pulse |
|--------|---------------------|-------------------|
| 1      | 7V-20 ns            | 4V-2 us           |
| 2      | 8V-20 ns            | 3V-2 us           |
| 3      | 9V-20 ns            | 2V-2 us           |
| 4      | 10V-20 ns           | 1V-2 us           |

4. Conclusion

GeTe thin films were grown on glass substrates by radio-frequency magnetron sputtering, and as-deposited film is amorphous state. While films annealed at 240°C had crystalline state and rhombohedral structure, in those annealed at higher temperatures, the rhombohedral structure will transform into the rock salt one. The Raman spectra showed that amorphous GeTe has four main vibration modes, and its bond energy drop caused the red-shift about 40cm$^{-1}$ when transforming into the crystal state. GeTe film had a maximum resistivity of 24 $\Omega\cdot$m in amorphous state and a minimum resistivity of 3.8×10$^{-6}$ $\Omega\cdot$m in the crystalline state, reaching a dynamic range of $10^5$. The resistivity of GeTe film decreased rapidly at temperatures above 170°C, while Hall mobility and carrier concentration increased as the crystal structure was regularly arranged and the scatter was diminished. Two-port phase-change switch was successfully switched back and forth with the voltage pulse: 9V 20ns (OFF), 2V 2μs (On). An obvious resistance window was, nd $R_{\text{off}}/R_{\text{on}}$ ratio could reach the value of $10^5$.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grant No. 51602037).

References

[1] Bastard A et al 2011 Appl. Phys. Lett. 99 243103
[2] Nakayama K, Kojima K, Hayakawa F, Imai Y, Kitagawa A and Suzuki M 2000 Jpn. J. Appl. Phys. 39(11) 6157-61
[3] Baker D A, Paesler M A, Lucovsky G, Agarwal S C and Taylor P C 2006 Phys. Rev. Lett. 96(25)
[4] Peng C, Cheng L and Mansuripur M 1997 *J. Appl. Phys.* 82(9) 4183-91

[5] El-Hinnawy N et al 2013 *IEEE Electron Device Lett.* 34(10) 1313-5

[6] Bahl S K and Chopra K L 1970 *J. Appl. Phys.* 41(5) 2196-212

[7] Loke D, Skelton J M, Wang W J, Lee T H, Zhao R, Chong T C and Elliott S R 2014 *PNAS* 111(37) 13272-7

[8] Edwards A H, Pineda A C, Schultz P A, Martin M G, Thompson A P, Hjalmarson H P and Umrigar C J 2005 *Phys. Rev. B.* 73 045210

[9] Fallica R, Volpe F, Longo M, Wiemer C, Salicio O and Abrutis A 2012 *Appl. Phys. Lett.* 101 102105

[10] Andrikopoulos K S, Yannopoulos S N, Kolobov A V, Fons P and Tominaga J 2007 *J. Phys. Chem. Solids.* 68(5-6) 1074-8

[11] Kolobov A V, Fons P, Tominaga J, Ankudinov A L, Yannopoulos S N and Andrikopoulos K S 2004 *J. Phys.- Condens. Matt.* 16(44) S5103-8

[12] Kolobov A V, Fons P, Tominaga J and Ruga T U 2006 *J. Non-Cryst. Solids* 352(9-20) 1612-5

[13] Akola J and Jones R O 2007 *Phys. Rev. B* 76 (23) 235201

[14] Caravati S, Bernasconi M, Kühne T D, Krack M and Parrinello M 2007 *Appl. Phys. Lett.* 91 171906

[15] Beneventi G B, Guarino L, Ferro M and Fantini P 2013 *J. Appl. Phys.* 113 044506

[16] Ielmini D and Zhang Y 2007 *Appl. Phys. Lett.* 90 192102

[17] El-Hinnawy N et al 2013 *IEEE Electron Device Lett.* 34(10) 1313-5

[18] Wang M and Zhang Y 2007 *Appl. Phys. Lett.* 90 192102

[19] Danner B L and R A C Jr 2012 *Procedia Eng.* 47(10) 80-3

[20] Ovshinsky S 1968 *Phys. Rev. Lett.* 21(20) 1450-3

[21] Robe K M and Joannopoulos J D 1987 *Phys. Rev. B* 36(12) 6631-9

[22] Sarkar D, Sanjeev G and Mahesha M G 2015 *Appl. Phys. A* 119(1) 49-54

[23] Andrikopoulos K S, Yannopoulos S N, Voyiatzis G A, Kolobov A V, Ribes M and Tominaga J 2006 *J. Phys.: Condens. Matter* 18(3) 965-79

[24] Kolobov A V, Fons P, Frenkel A I, Ankudinov A L, Tominaga J and Uruga T 2004 *Nature Materials* 3(10) 703-8

[25] Kozyukhin S, Veres M, Nguyen H P, Ingram A, Kudoyarova V 2013 *Phys. Procedia* 44 82-90

[26] Zhou X L, Du Y H, Jitendra K Behera, Liangcai Wu L C, Song Z T and Robert E Simpson 2016 *ACS Appl. Mater. Interfaces* 8(31) 20185-91