MIT Open Access Articles

Impact of deposition conditions on the crystallization kinetics of amorphous GeTe films

Massachusetts Institute of Technology

1 ***Impact of deposition conditions on the crystallization kinetics of amorphous***
2 ***GeTe films***
3

4 Chee Ying Khoo[1,2] • Hai Liu[1] • Wardhana.A. Sasangka[3] • Riko I Made [3]• Nobu Tamura[4] • Martin Kunz[4]
5 • Arief S. Budiman[5] • Chee Lip Gan[1,2,3, *] • Carl V. Thompson[2,3,6, #]
6

7 **Abstract** The speed at which phase change memory devices can operate depends strongly on the crystallization

8 kinetics of the amorphous phase. To better understand factors that affect the crystallization rate, we have

9 investigated crystallization of GeTe films as a function of their deposition temperatures and deposition rates,

10 using X-ray synchrotron radiation and Raman spectroscopy. As-deposited films were found to be fully

11 amorphous under all conditions, even though films deposited at higher temperatures and lower rates

12 experienced lower effective quench rates. Non-isothermal transformation curves show that the apparent

13 crystallization temperature of GeTe films decreases with increasing deposition temperature and decreasing

14 deposition rate. It was found that this correlates with a decrease in the activation energy for nucleation

15 (calculated using Kissinger's analysis), while the activation energy for crystal growth remained unaffected.

16 From Raman spectroscopy measurements, it was found that increasing the deposition temperature or decreasing

17 the deposition rate, and therefore the effective quench rate, reduces the number of homopolar Te-Te bonds and

18 thereby reduces the barrier to crystal nucleation.

19 *Chee Lip Gan
20 clgan@ntu.edu.sg
21
22 #Carl V. Thompson
23 cthomp@mit.edu
24
25 [1] School of Materials, Science and Engineering, Nanyang Technological University, Singapore 639798
26
27 [2] Advance Materials for Micro- and Nano-Systems, Singapore-MIT Alliance, Singapore 117576
28
29 [3] Low Energy Electronic Systems, Singapore-MIT Alliance for Research and Technology, Singapore
30 138602
31
32 [4] Advance Light Source, Lawrence Berkeley National Lab, Berkeley, California 94720, USA
33
34 [5] Engineering Products Development (EPD) Pillars, Singapore University of Technology and Design,
35 Singapore 138682
36
37 [6] Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge,
38 Massachusetts 02139, USA
39
40

41

42

43

Introduction

In the mid-1960s, S.R. Ovshinsky proposed the idea of phase change recording [1]. Phase change materials (e.g. $Ge_2Sb_2Te_5$ and GeTe) undergo a reversible transformation between crystalline and amorphous states when subjected to laser-induced or current-induced heating and quenching [2,3]. The attractiveness of phase change materials lies in their very large changes in electrical resistivity and optical reflectivity when switching between these two states [4-6]. This phenomenon is currently used in optical information storage and is under wide-spread investigation for use in electrical information storage devices [7,8]. The operation of these devices strongly depends on the crystallization temperatures and crystallization rates of the materials, and therefore a detailed understanding of factors that influence the kinetics of crystallization is critical. Studies of amorphous $Ge_2Sb_2Te_5$ and GeTe films prepared using different methods, such as sputtering, melt-quenching and ion-irradiation have been carried out [9,10]. The local order of these amorphous films has been examined using Raman spectroscopy and was found to be significantly different [9,10]. These differences were found to correlate with differences in crystallization temperatures [9,10].

In this work, we report studies of the crystallization kinetics of amorphous GeTe as a function of deposition temperature and deposition rate. The crystallization temperature is determined using x-ray synchrotron radiation during in-situ annealing. Effective activation energies for the crystallization process were determined using Kissinger's analysis [11]. The local order of the as-deposited amorphous GeTe films was analyzed using micro-Raman spectroscopy.

Experimental Procedures

1 μm-thick GeTe films were deposited by RF-magnetron sputtering from stoichiometric targets onto Si substrates coated with thin layers of native SiO_2. The background pressure before sputtering was maintained at $\sim 10^{-6}$ Torr. With the presence of argon gas during sputtering, the pressure was maintained at 10^{-3} Torr. A first set of samples was deposited on substrates at room temperature, 60 ^{o}C, 80 ^{o}C and 100 ^{o}C, with a deposition rate of 8 nm/min. For a second set of samples, films were deposited at room temperature using different rates, 7.1 nm/min, 8.8 nm/min and 10.3 nm/min, by varying the argon gas pressure. For both sets of experiments, real-time synchrotron x-ray diffraction with a 2D detector and monochromatic beam (energy = 10 keV, $\lambda = 0.124$ nm) at beamline 12.3.2 of the Advanced Light Source in the Lawrence Berkeley National Laboratory was used to monitor the crystallization. Each exposure time was set to be 60 seconds. The synchrotron X-ray beam has a final focus size of 2 μm (v) x 8 μm (h) (FWHM). The diffraction patterns were collected with a DECTRIS

74 Pilatus 1 M pixel area detector (active area of 179 mm x 169 mm), which was placed at a distance of

75 approximately 140 mm from the sample. More detailed information on the set up at this beamline can be

76 obtained elsewhere [12,13].

77 All samples were annealed at a constant rate of 2 $^{\circ}$C/min, 5 $^{\circ}$C/min or 10 $^{\circ}$C/min from room temperature to

78 230 $^{\circ}$C, a temperature at which they were fully crystalline. Transformation curves at different heating rates were

79 obtained by determining the fraction of the film that had transformed as a function of temperature. The

80 microstructures of the GeTe films were characterized using energy dispersive x-ray spectroscopy (EDX) and

81 transmission electron microscopy (TEM). A focused ion beam (FIB) system with dual-beam capability was used

82 to prepare the TEM samples and a JEOL TEM 2100F with an accelerating voltage of 200 kV was used to

83 examine the as-deposited films. EDX was used to determine the composition of the films used in this

84 experiment.

85 All the as-deposited amorphous GeTe thin films were also analyzed by means of micro-Raman

86 spectroscopy. The samples were excited with a He-Ne laser (λ = 633 nm) and the incident laser power was

87 adjusted to 0.5 mW in order to minimize heating effects in the illuminated sample region of interest [9,14]. The

88 Raman spectra were recorded at an interval of 0.4 cm^{-1}. Accumulation times of 3 minutes were sufficient to

89 obtain a satisfactory signal-to-noise ratio.

90

91 **Results and discussion**

92

93 *Effect of deposition temperatures*

94

95 Figure 1 shows bright field TEM images of GeTe films deposited at room temperature and 100 $^{\circ}$C. Cross-

96 sectional TEM images reveal that all as-deposited films were fully amorphous, but with columnar structures and

97 nano-scale voids. The latter is not uncommon in amorphous films deposited using sputter deposition [15,16].

98 The inset electron diffraction patterns confirm that the films were amorphous as deposited, which was also

99 supported by x-ray diffraction (XRD) analysis. From EDX, the composition of the films was determined to be

100 $Ge_{43}Te_{57}$ ($\pm$ 1% error), which is Te-rich.

101

102
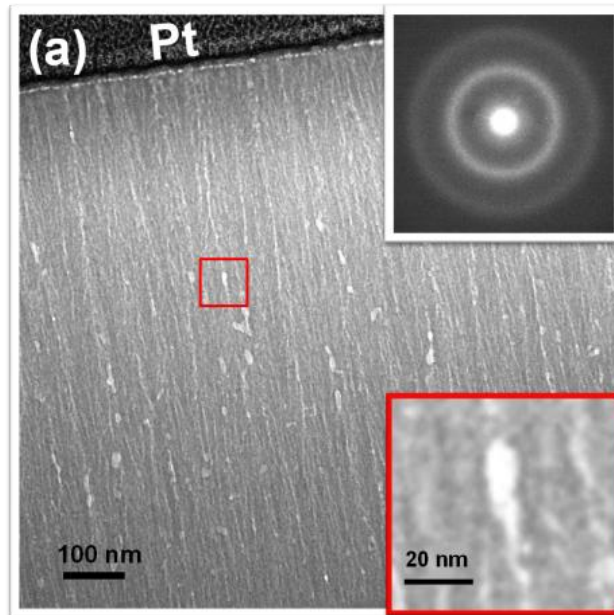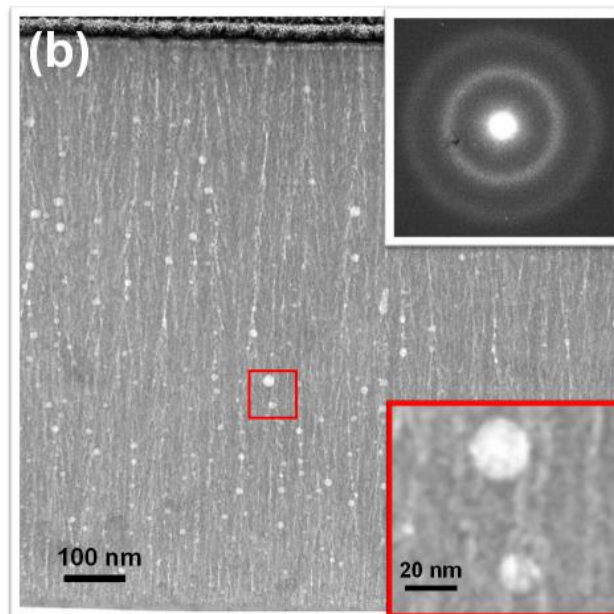
Fig. 1 Bright field TEM images of cross-sections of GeTe films deposited at (**a**) room temperature and (**b**) 100 °C on Si substrates coated with thin layers of native oxide. Top right insets show electron diffraction patterns and bottom right insets show high magnification views of nano-scale voids within the film. Pt layers on top of the films act as protective layers during FIB sample preparation.

Debye-Scherrer rings were generated based on diffraction intensities from the 2D detector integrated in the azimuthal direction. Figure 2 shows XRD results obtained by transforming 2D synchrotron data using XMAS, a software developed in-house at beamline 12.3.2 [17]. The as-deposited films were amorphous at all deposition temperatures, as shown in figure 2a. After annealing to 230 °C, the films were found to be fully crystallized, as shown in figure 2b. Regardless of the deposition temperatures, the GeTe films were composed of the same

phase, with the expected trigonal symmetry [18]. Weak Te peaks were also observed due to the Te-rich composition of the films.
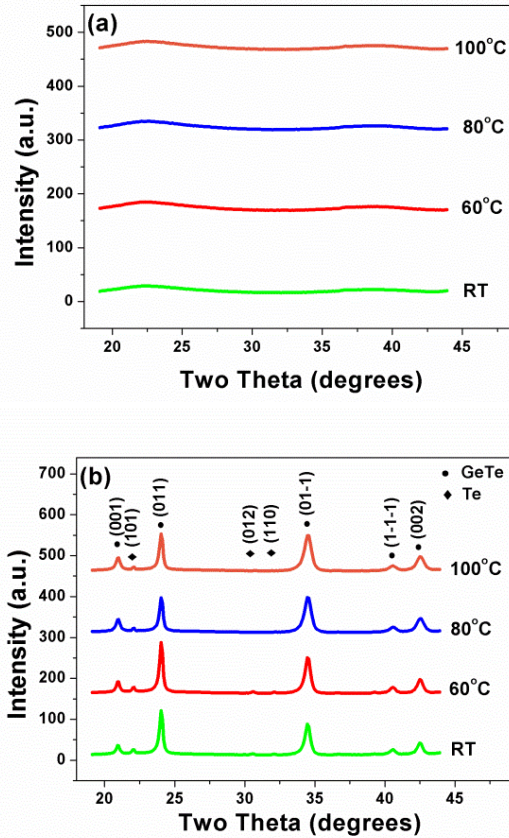
**Fig. 2** XRD results for GeTe films (**a**) as-deposited and (**b**) fully crystallized at 230 $^{\circ}$C, for films deposited at different substrate temperatures (room temperature, 60 $^{\circ}$C, 80 $^{\circ}$C and 100 $^{\circ}$C).

Figure 3a shows transformation curves for crystallization of GeTe, based on the maximum intensity of the (011) peak normalized by the maximum intensity of this peak after full transformation at 230 $^{\circ}$C. The sample was heated at a rate of 2 $^{\circ}$C/min from room temperature to 230 $^{\circ}$C. The apparent crystallization temperature was defined as the temperature at which half of the sample was crystallized [19]. The apparent crystallization temperatures observed in this study are higher than values reported by others, as determined from optical reflectivity measurements [20,21]. This is expected as all the films here are Te-rich in composition. From the transformation curves, it is clearly seen that the apparent crystallization temperatures decrease with increasing deposition temperature. Figure 3b shows transformation curves for GeTe films deposited at room temperature and heated at different rates: 2 $^{\circ}$C/min, 5 $^{\circ}$C/min and 10 $^{\circ}$C/min. As expected, the apparent crystallization temperature increases with increasing heating rate [22,23].

5

128

129
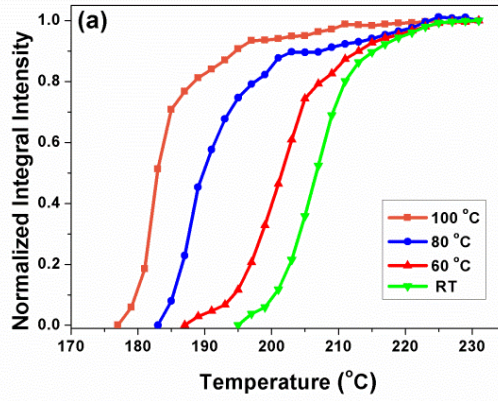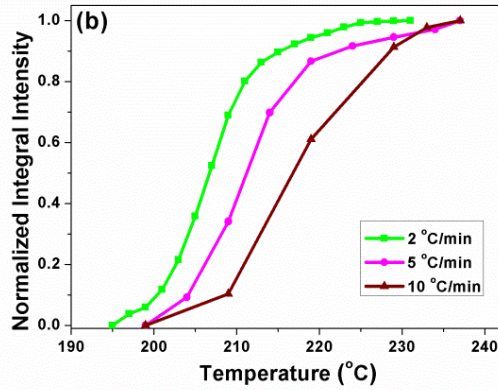
Fig. 3 (**a**) Transformation curves for GeTe films deposited at different temperatures, based on normalized magnitudes of the (011) peak observed at 230 $^{\circ}$C. The heating rate was 2 $^{\circ}$C/min. (**b**) Transformation curves for GeTe films deposited at room temperature and heated at different rates.

Figure 4a shows the local effective activation energy E_c as a function of the fraction transformed α. E_c was determined using the Kissinger method for various values of α for data obtained at different heating rates shown in Figure 3b [11]. The Kissinger equation can be written as follows,

$$\ln\left(\frac{\beta}{T_c^2}\right) = -\frac{E_c}{kT_c} + const \,, \tag{1}$$

where β is the heating rate, k is Boltzmann's constant, E_c is the activation energy at a particular transformed fraction α and T_c is the temperature at which the transformed fraction α is reached.

The dependence of E_c on the fraction transformed is affected by changes in the nucleation and growth behavior during the crystallization process [24-26]. The local activation energy $E_c(\alpha)$ is composed of two parts, the activation energy of nucleation (E_n) and the activation energy of growth (E_g) [27-29]. E_c at a given α can be written as,

$$E_\alpha = aE_n + bE_g \ (I \geq 0, U \geq 0), \tag{2}$$

6

144   where I and U are the steady state nucleation rate and growth velocity respectively, with a and b are two

145   variables related to the Avrami parameter, having values $0 \leq a, b \leq 1$ and $a + b = 1$ [28,29]. In the early stage of

146   transformation, with lower values of α, crystallization is dominated by nucleation whereas at later stages, higher

147   values of α, crystallization is dominated by growth. Fitting the plot in Figure 4a using a non-linear regression

148   method (shown using dotted lines), we estimated the value of the activation energies for nucleation and growth,

149     $E_c(\alpha=0) = E_n$ and growth $E_c(\alpha=1) = E_g$, respectively. The fitting was carried out under the assumption that the

150   values of a and b at a particular value of α are the same for all deposition temperatures. Figure 4b shows values

151   of the activation energies for nucleation and growth obtained from Figure 4a. It is seen that the activation energy

152   for nucleation decreases significantly with increasing deposition temperature, from 4.0 eV to 2.6 eV. In contrast,

153   the activation energy for growth remains relatively constant at 2.0 eV. Thus, the decrease in the effective

154   activation energy for crystallization of GeTe observed for increasing deposition temperatures is primarily due to

155   a reduction in the activation energy for nucleation. Similar activation energies for nucleation and growth of

156   films deposited at room temperature have been reported elsewhere using a different technique [10,30]. Films

157   deposited at room temperature experience a higher effective quench rate as compared to films deposited at

158   higher temperatures [31]. We postulate that this results in fewer clusters that can act as precursors of crystalline

159   nuclei, thus making nucleation more difficult. That the activation energy for growth is unaffected by the

160   deposition conditions may explain why it has been found in other studies that samples having the same

161   composition but made under different conditions have the same temperature dependence for crystallization,

162   while differences in the crystallization rate are still observed due to differences in the nucleation rates [32,33].
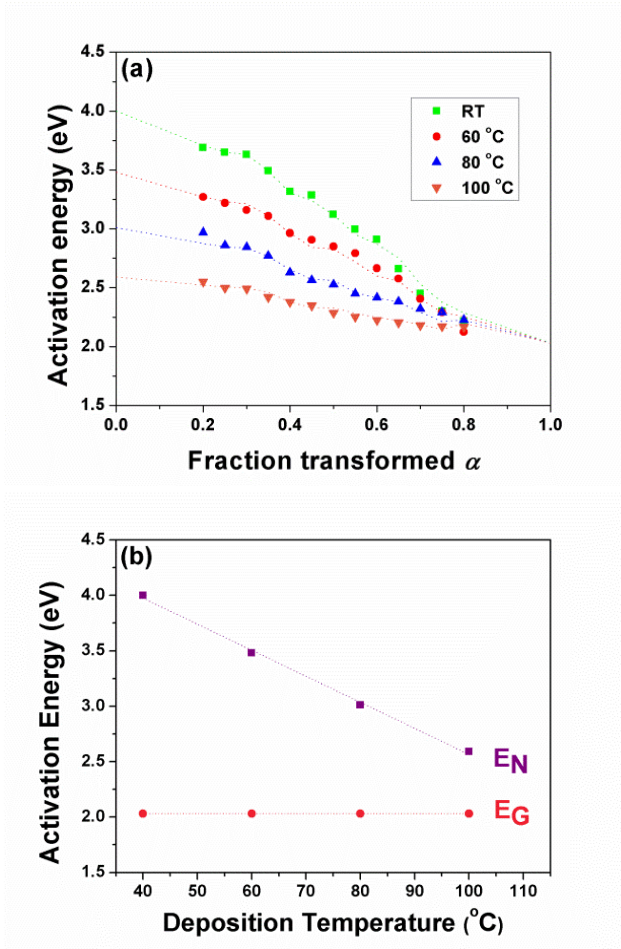
Fig. 4 (**a**) The local effective activation energy E_α as a function of the fraction transformed α for films prepared at various deposition temperatures and (**b**) activation energies for nucleation and growth as a function of the deposition temperature.

Figure 5 shows Raman spectra for GeTe films deposited at different temperatures. For all the Raman spectra, there are peaks found at 88 cm^{-1}, 120 cm^{-1}, 139 cm^{-1} and 160 cm^{-1}. The broad peaks found at 88 cm^{-1} and 160 cm^{-1} are contributed by Ge-Te vibration modes [14,34,35]. Two distinct peaks were also observed at 120 cm^{-1} and 139 cm^{-1}, and their intensity decreased with increasing deposition temperature. It is know that crystalline Tellurium has strongest peaks at 120.4 $\pm$ 0.5 cm^{-1} and 140.7 $\pm$ 0.5 cm^{-1} [36]. The close proximity of the observed peaks suggests the presence of homopolar Te-Te bonds in the as-deposited state. It is known that homopolar Te-Te bonds are forbidden in the crystalline structure [10]. It has therefore been suggested that the presence of these homopolar Te-Te bonds might retard the crystallization process [9]. Our results suggest that the specific effect of Te-Te homopolar bonds is to raise the barrier for nucleation of the crystalline phase, rather than to impede crystal growth.
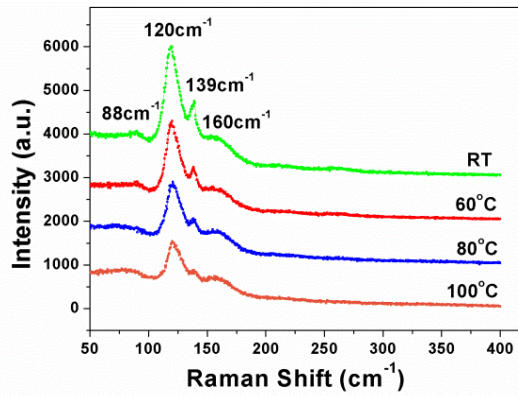
178

179 **Fig. 5** Raman spectra for amorphous GeTe films prepared at various deposition temperatures.

180

181 *Effect of deposition rates*

182

183 Figure 6 shows bright field TEM images of GeTe films deposited at deposition rates of 7.1 nm/min and 10.3

184 nm/min. The observed structures are similar to those of the films deposited at different temperatures (Fig. 1).

185 The inset electron diffraction patterns confirm that the films are amorphous as deposited, which was also

186 supported by XRD analysis. Using EDX, the composition of the films was determined to be $Ge_{47}Te_{53}$ ($\pm$ 1%),

187 independent of the Ar pressure and sputtering rate.

188
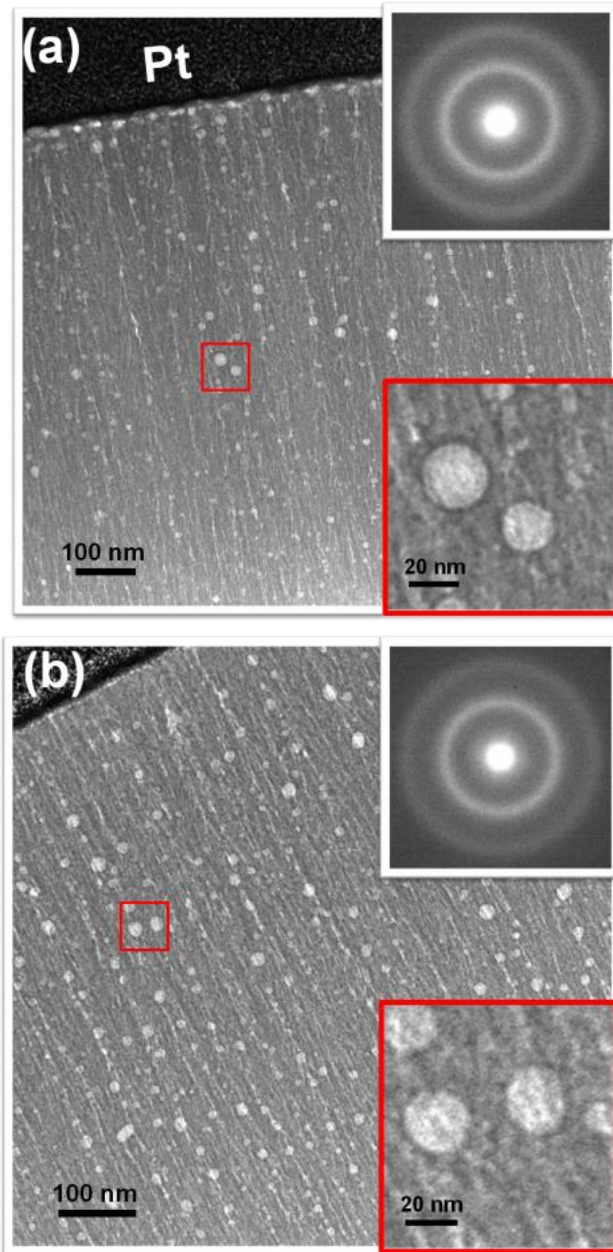
189

190 **Fig. 6** Bright field TEM images of cross sections of GeTe films deposited at deposition rates of (**a**) 7.1 nm/min

191 and (**b**) 10.3 nm/min, on Si substrates coated with thin layers of native oxide. Top right insets show electron

192 diffraction patterns and bottom right insets show high magnification views of nano-scale voids within the film.

193 Pt layers on top of the films act as protective layers during FIB sample preparation.

194   Figure 7 shows XRD results for these films deposited at different sputtering rates. The as-deposited films

195 were amorphous at all deposition rates, as shown in figure 7a. After annealing to 235 $^{\circ}$C, the films were found to

196 be fully crystallized, as shown in figure 7b. Regardless of the deposition rate, weak Te peaks were also observed

197 due to the Te-rich composition of the films.

198

199
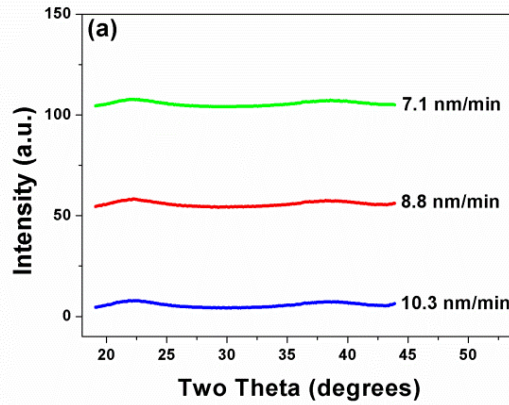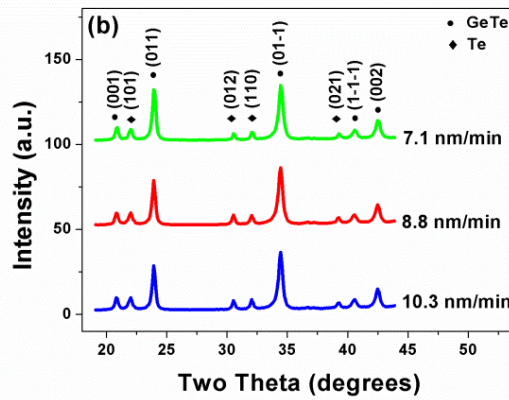
Fig. 7 XRD results for GeTe films (**a**) as-deposited and (**b**) fully crystallized at 235 $^{\circ}$C, for films deposited at different deposition rates.

Figure 8a shows transformation curves for crystallization of GeTe, based on the maximum intensity of the (011) peak normalized by the magnitude of this peak after full transformation at 235 $^{\circ}$C. . The samples were heated at a rate of 2 $^{\circ}$C/min from room temperature to 235 $^{\circ}$C. From the transformation curves, it is clearly seen that the apparent crystallization temperatures increase with increasing deposition rate. Figure 8b shows transformation curves for GeTe films deposited at a deposition rate of 7.1 nm/min and heated at different rates: 2 $^{\circ}$C/min, 5 $^{\circ}$C/min and 10 $^{\circ}$C/min.

208

209
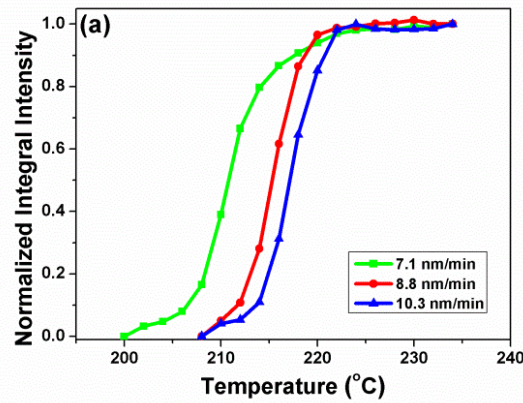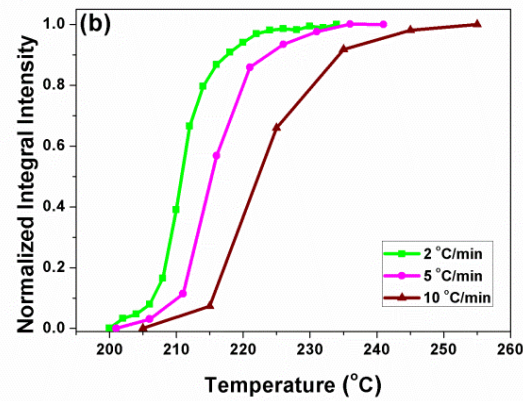
Fig. 8 (**a**) Transformation curves for GeTe films deposited at different deposition rates, normalized by the magnitude of the (011) peak observed at 235 °C, with a heating rate of 2 °C/min and (**b**) transformation curves for GeTe films deposited at deposition rate of 7.1 nm/min and heated at different rates.

The same approach discussed earlier was used to obtain the local effective activation energy E_α as a function of the fraction transformed α as shown in Figure 9a. Figure 9b shows values of the activation energies for nucleation and growth obtained from the data in Figure 9a. It is seen that the activation energy for nucleation increases with increasing deposition rate, from 3.5 eV to 4.0 eV. In contrast, the activation energy for growth remains constant at a value of 1.9 eV. Thus, the increase in the effective activation energy for crystallization of GeTe observed for increasing deposition rates is primarily due to an increase in the activation energy for nucleation. It is expected that films deposited at higher deposition rates experience a higher effective quench rate [31]. This dependence on the effective quench rate is consistent with the results obtained for films deposited as different temperatures.
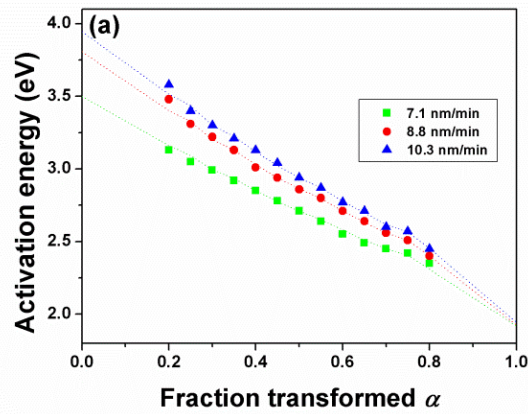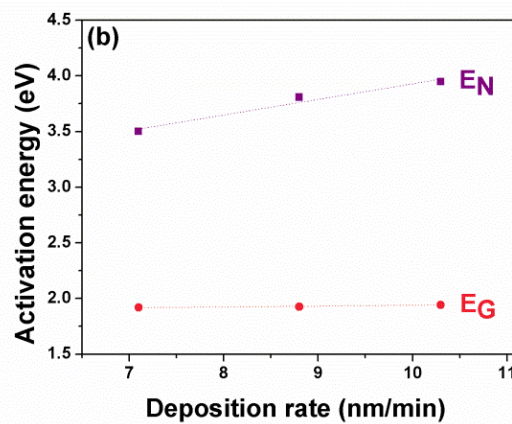
Fig. 9 (**a**) The local effective activation energy E_α as a function of fraction transformed α for films prepared at various deposition rates and (**b**) activation energies for nucleation and growth as a function of the deposition rate.

Figure 10 shows Raman spectra for GeTe films deposited at different deposition rates. Similar to what was found for films deposited at different temperature, two distinct peaks were also observed at 120 cm^{-1} and 139 cm^{-1}, and their intensity increased with increasing deposition rate. This suggests the presence of homopolar Te-Te bonds in all the as-deposited films regardless of the sputtering rate. However, this also shows that the number of Te-Te homopolar bonds increases with increasing deposition rate, which, we suggest, raises the barrier for nucleation of the crystalline phase.
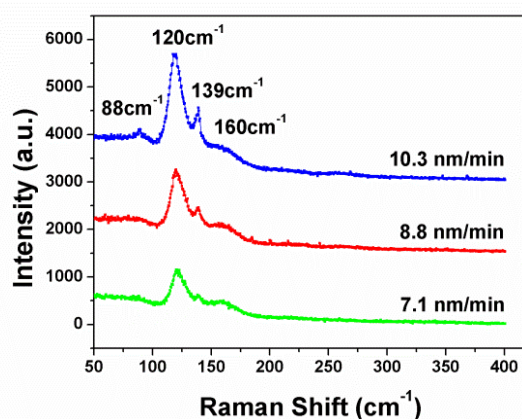
Fig. 10 Raman spectra for amorphous GeTe films prepared at various deposition rates.

Different sputtering targets were used in both set of experiments. It should be noted that the film deposited at room temperature in the first set of experiments exhibits higher activation energies for nucleation as compared to those in the second set of experiments. This is likely due to the higher amount of excess Te in the first set of film, resulting from the use of different sputtering targets for the two sets of films. Work done by Carria *et al.* has shown that increasing amounts of excess Te will lead to a higher activation energy for crystallization [21]. However, this does not affect our interpretation of the data within a single set of samples having a fixed amount of access Te, and the correspondence of the trends observed for both sets. It has been shown through experiments carried out by others that Te-Te homopolar bonds exist even in stoichiometric amorphous GeTe films [37,38]. We have also carried out experiments on stoichiometric $Ge_2Sb_2Te_5$ films deposited at varying substrate temperatures, with the XRD results and Raman spectra shown in Figures S1 and S2 (Online Resource 1). Even with stoichiometric $Ge_2Sb_2Te_5$ samples, the intensity of the 120 cm^{-1} Raman peak changes with the substrate temperature in a way that is analogous to what is seen for GeTe, and there are corresponding analogous changes in the crystallization behavior. This is consistent with other reported observations on stoichiometric GeTe and $Ge_2Sb_2Te_5$ films in which the crystallization rate is observed to decrease with the increased presence of homopolar Te-Te bonds [9,10]. Taken together, these results support our proposition that the Te-Te bond density is the critical factor that affects crystal nucleation in the as-deposited films.

Summary and Conclusions

We have studied the crystallization of amorphous GeTe films prepared by sputter deposition onto substrates held at different temperatures and deposited at different sputtering rates. Through analysis of the crystallization

14

process carried out at different heating rates, it is shown that the deposition temperature and deposition rate have a significant effect on the nucleation of the crystalline phase, but a negligible effect on its growth. The activation energy for crystal nucleation increased with decreasing deposition temperature and with increasing deposition rate. Decreasing the deposition temperature and increasing the deposition rate both increase the effective quench rate. This highlights the influence of the effective quench rate on the crystallization of phase change materials. Raman spectral analysis indicates an increase of the number of homopolar Te-Te bonds with decreasing deposition temperature or increasing deposition rate. Given that homopolar bonds do not exist in the crystalline phase, we suggest that it is clustering of Te atoms in the films deposited at low temperatures and high rates that raises the barrier to nucleation of the crystalline phase.

References

1. Ovshinsky SR (1968) Reversible electrical switching phenomena in disordered structures. Physical Review Letters 21 (20):1450-1453
2. Kolobov AV, Fons P, Tominaga J (2007) Phase-change optical recording: past, present, future. Thin Solid Films 515 (19):7534-7537
3. Wetnic W, Wuttig M (2008) Reversible switching in phase-change materials. Materials Today 11 (6):20-27. doi:10.1016/S1369-7021(08)70118-4
4. Kolobov AV, Fons P, Frenkel AI, Ankudinov AL, Tominaga J, Uruga T (2004) Understanding the phase-change mechanism of rewritable optical media. Nature Materials 3 (Copyright 2005, IEE):703-708
5. Wuttig M, Yamada N (2007) Phase-change materials for rewriteable data storage. Nature Materials 6 (Compendex):824-832
6. Lencer D, Salinga M, Grabowski B, Hickel T, Neugebauer J, Wuttig M (2008) A map for phase-change materials. Nature Materials 7 (Copyright 2009, The Institution of Engineering and Technology):972-977
7. Raoux S, Wenic W, Lelmini D (2010) Phase change materials and their application to nonvolatile memories. Chemical Reviews 110 (1):240-267. doi:10.1021/cr900040x
8. Lencer D, Salinga M, Wuttig M (2011) Design rules for phase-change materials in data storage applications. Advanced Materials 23 (18):2030-2058. doi:10.1002/adma.201004255

295 9. Carria E, Mio AM, Gibilisco S, Miritello M, d'Acapito F, Grimaldi MG, Rimini E (2011) Polymorphism of
296 Amorphous $Ge_2Sb_2Te_5$ Probed by EXAFS and Raman Spectroscopy. Electrochemical and Solid-State Letters 14
297 (12):480-482. doi:10.1149/2.019112esl
298 10. Mio AM, Carria E, D'Arrigo G, Gibilisco S, Miritello M, Grimaldi MG, Rimini E (2011) Nucleation and
299 grain growth in as deposited and ion implanted GeTe thin films. Journal of Non-Crystalline Solids 357
300 (10):2197-2201. doi:http://dx.doi.org/10.1016/j.jnoncrysol.2011.02.042
301 11. Kissinger HE (1957) Reaction Kinetics in Differential Thermal Analysis. Analytical Chemistry 29
302 (11):1702-1706
303 12. Tamura N, MacDowell AA, Spolenak R, Valek BC, Bravman JC, Brown WL, Celestre RS, Padmore HA,
304 Batterman BW, Patel JR (2003) Scanning X-ray microdiffraction with submicrometer white beam for
305 strain/stress and orientation mapping in thin films. Journal of Synchrotron Radiation 10:137-143.
306 doi:10.1107/S0909049502021362
307 13. Kunz M, Tamura N, Chen K, MacDowell AA, Celestre RS, Church MM, Fakra S, Domning EE, Glossinger
308 JM, Kirschman JL, Morrison GY, Plate DW, Smith BV, Warwick T, Yashchuk VV, Padmore HA, Ustundag E
309 (2009) A dedicated superbend x-ray microdiffraction beamline for materials, geo-, and environmental sciences
310 at the advanced light source. The Review of scientific instruments 80 (3):035108. doi:10.1063/1.3096295
311 14. Andrikopoulos KS, Yannopoulos SN, Voyiatzis GA, Kolobov AV, Ribes M, Tominaga J (2006) Raman
312 scattering study of the a-GeTe structure and possible mechanism for the amorphous to crystal transition. Journal
313 of Physics: Condensed Matter 18 (3):965-979. doi:10.1088/0953-8984/18/3/014
314 15. Bales GS, Zangwill A (1991) Macroscopic model for columnar growth of amorphous films by sputter
315 deposition. Journal of Vacuum Science & Technology A (Vacuum, Surfaces, and Films) 9 (1):145-149.
316 doi:10.1116/1.577116
317 16. Tsukimoto S, Moriyama M, Murakami M (2004) Microstructure of amorphous tantalum nitride thin films.
318 Thin Solid Films 460 (1-2):222-226. doi:10.1016/j.tsf.2004.01.073
319 17. Tamura N (2014) XMAS: a versatile tool for analyzing synchrotron x-ray microdiffraction data, in Strain
320 and Dislocation Gradients from Diffraction: Spatially-Resolved Local Structure and Defects. Imperial College
321 Press, London, United Kingdom
322 18. Matsunaga T, Kojima R, Yamada N, Kifune K, Kubota Y, Tabata Y, Takata M (2006) Single Structure
323 Widely Distributed in a GeTe−Sb_2Te_3 Pseudobinary System: A Rock Salt Structure is Retained by Intrinsically
324 Containing an Enormous Number of Vacancies within its Crystal. Inorganic Chemistry 45 (5):2235-2241.
325 doi:10.1021/ic051677w
326 19. Ghezzi GE, Morel R, Brenac A, Boudet N, Audier M, Fillot F, Maitrejean S, Hippert F (2012)
327 Crystallization of $Ge_2Sb_2Te_5$ nanometric phase change material clusters made by gas-phase condensation.
328 Applied Physics Letters 101 (23):233113-233114
329 20. Gourvest E, Lhostis S, Kreisel J, Armand M, Maitrejean S, Roule A, Vallee C (2009) Evidence of
330 Germanium precipitation in phase-change $Ge_{1-x}Te_x$ thin films by Raman scattering. Applied Physics Letters 95
331 (3):031908 (031903 pp.). doi:10.1063/1.3186077
332 21. Carria E, Mio AM, Gibilisco S, Miritello M, Bongiorno C, Grimaldi MG, Rimini E (2012) Amorphous-
333 crystal phase transitions in Ge_xTe_{1-x} alloys. Journal of the Electrochemical Society 159 (2):H130-H139.
334 doi:10.1149/2.048202jes
335 22. Friedrich I, Weidenhof V, Njoroge W, Franz P, Wuttig M (2000) Structural transformations of $Ge_2Sb_2Te_5$
336 films studied by electrical resistance measurements. Journal of Applied Physics 87 (9):4130-4134
337 23. Choi Y, Jung M, Lee Y-K (2009) Effect of heating rate on the activation energy for crystallization of
338 amorphous $Ge_2Sb_2Te_5$ thin film. Electrochemical and Solid-State Letters 12 (7):F17-F19.
339 doi:10.1149/1.3129137
340 24. Abu El-Oyoun M (2009) Determination of the crystallization kinetic parameters of $Ge_{22.5}Te_{77.5}$ glass using
341 model-free and model-fitting methods. Journal of Alloys and Compounds 486 (1-2):1-8.
342 doi:10.1016/j.jallcom.2009.06.137
343 25. Kasyap S, Patel A, Pratap A (2014) Crystallization kinetics of $Ti_{20}Zr_{20}Cu_{60}$ metallic glass by isoconversional
344 methods using modulated differential scanning calorimetry. J Therm Anal Calorim 116 (3):1325-1336.
345 doi:10.1007/s10973-014-3753-z
346 26. Dohare C, Mehta N (2012) Iso-conversional kinetic study of non-isothermal crystallization in glassy
347 $Se_{98}Ag_2$ alloy. J Therm Anal Calorim 109 (1):247-253. doi:10.1007/s10973-011-1696-1
348 27. Wei L, Biao Y, Wen-hai H (2005) Complex primary crystallization kinetics of amorphous Finemet alloy.
349 Journal of Non-Crystalline Solids 351 (40-42):3320-3324. doi:10.1016/j.jnoncrysol.2005.08.018
350 28. Majhi K, Varma KBR (2009) Crystallization kinetic studies of $CaBi_2B_2O_7$ glasses by non-isothermal
351 methods. Journal of Materials Science 44 (2):385-391. doi:10.1007/s10853-008-3149-1
352 29. Soares RS, Monteiro RCC, Lima MMRA, Sava BA, Elisa M (2014) Phase transformation and
353 microstructural evolution after heat treatment of a terbium-doped lithium-aluminum phosphate glass. Journal of
354 Materials Science 49 (13):4601-4611. doi:10.1007/s10853-014-8162-y

355   30. Lu QM, Libera M (1995) Microstructural measurements of amorphous GeTe crystallization by hot-stage
356   optical microscopy. Journal of Applied Physics 77 (2):517-521. doi:http://dx.doi.org/10.1063/1.359034
357   31. Chu JP, Lai YW, Lin TN, Wang SF (2000) Deposition and characterization of TiNi-base thin films by
358   sputtering. Materials Science & Engineering A (Structural Materials: Properties, Microstructure and Processing)
359   A277 (1-2):11-17. doi:10.1016/S0921-5093(99)00560-2
360   32. Jeyasingh R, Fong SW, Lee J, Li Z, Chang K-W, Mantegazza D, Asheghi M, Goodson KE, Wong HSP
361   (2014) Ultrafast characterization of phase-change material crystallization properties in the melt-quenched
362   amorphous phase. Nano Letters 14 (6):3419-3426. doi:10.1021/nl500940z
363   33. Orava J, Hewak DW, Greer AL (2015) Fragile-to-Strong Crossover in Supercooled Liquid Ag-In-Sb-Te
364   Studied   by   Ultrafast   Calorimetry.   Advanced   Functional   Materials   25   (30):4851-4858.
365   doi:10.1002/adfm.201501607
366   34. Andrikopoulos KS, Yannopoulos SN, Kolobov AV, Fons P, Tominaga J (2007) Raman scattering study of
367   GeTe and $Ge_2Sb_2Te_5$ phase-change materials. Journal of Physics and Chemistry of Solids 68 (5-6):1074-1078.
368   doi:10.1016/j.jpcs.2007.02.027
369   35. Mazzarello R, Caravati S, Angioletti-Uberti S, Bernasconi M, Parrinello M (2010) Signature of Tetrahedral
370   Ge in the Raman Spectrum of Amorphous Phase-Change Materials. Physical Review Letters 104 (8):085503
371   36. Pine AS, Dresselhaus G (1971) Raman Spectra and Lattice Dynamics of Tellurium. Physical Review B 4
372   (2):356-371
373   37. G. Fisher, J. Tauc, Verhelle Y (1974) Amorphous and Liquid Semiconductors. vol 2. London
374   38. Hosokawa S, Hari Y, Kouchi T, Ono I, Sato H, Taniguchi M, Hiraya A, Takata Y, Kosugi N, Watanabe M
375   (1998) Electronic structures and local atomic configurations in amorphous GeSe and GeTe. Journal of Physics:
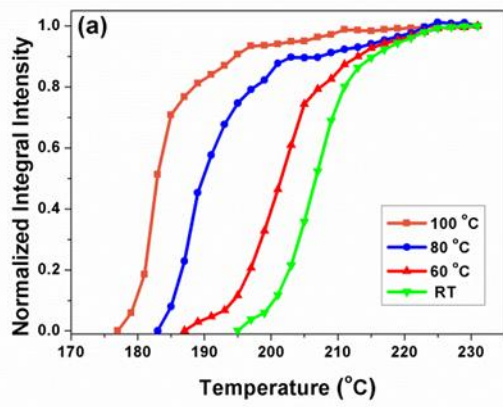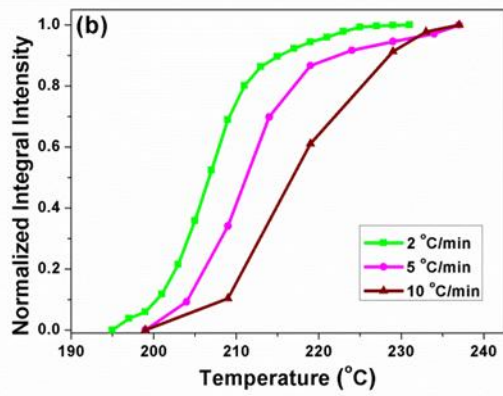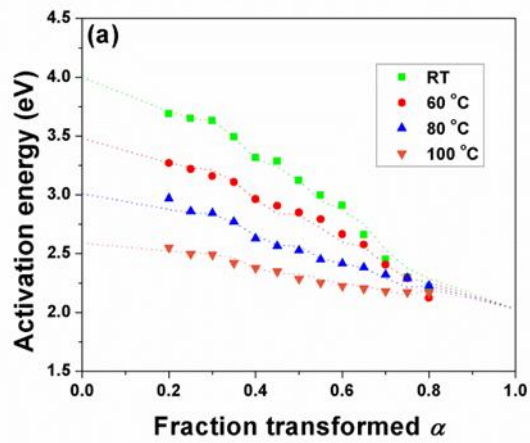376   Condensed Matter 10 (8):1931-1950. doi:10.1088/0953-8984/10/8/024
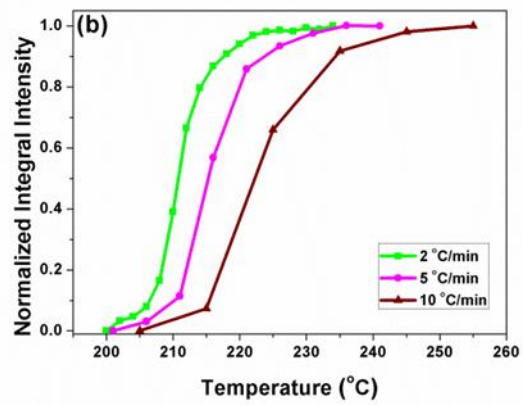
377
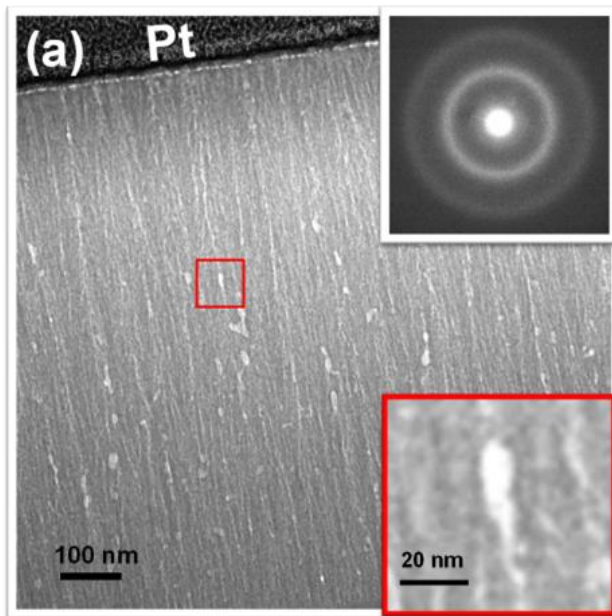
378
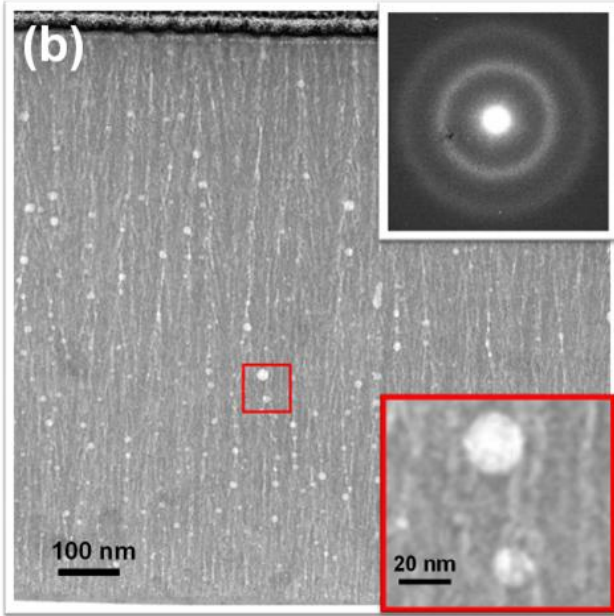
379
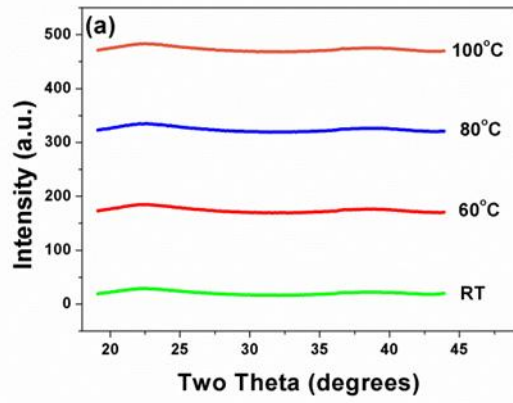
380
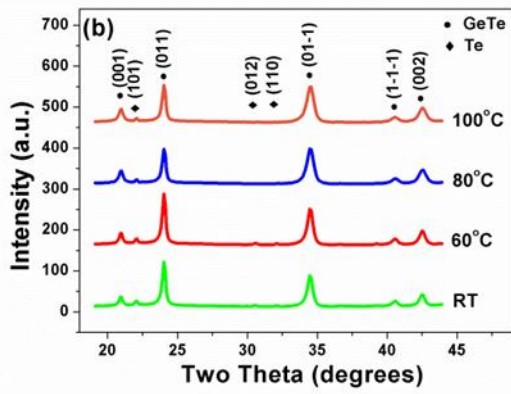
381

382

383

384
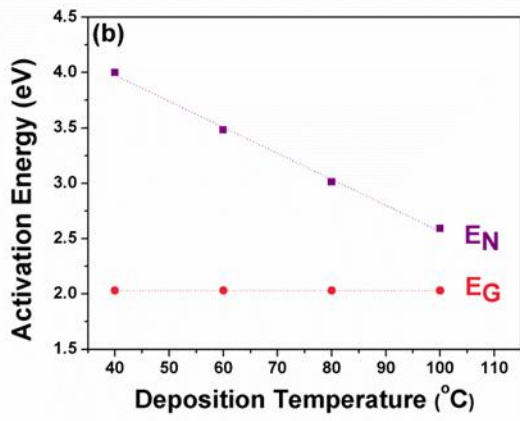
385
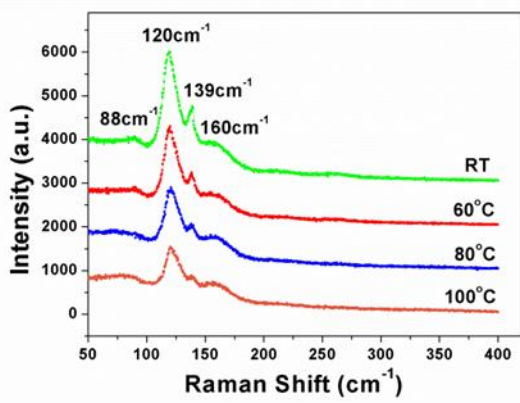
386
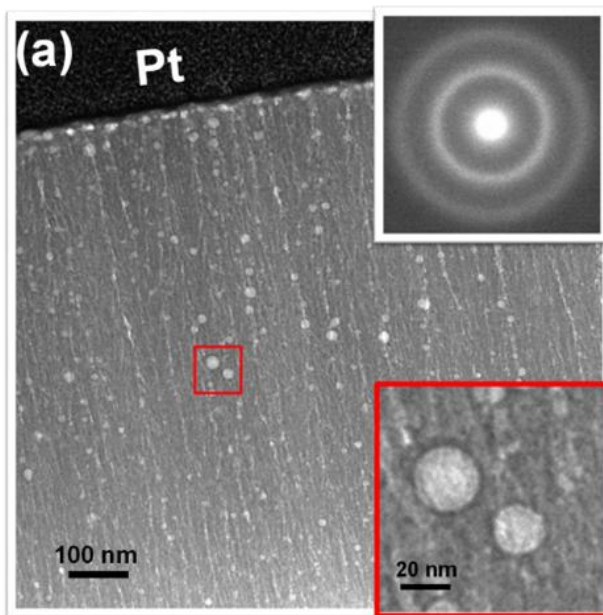
387
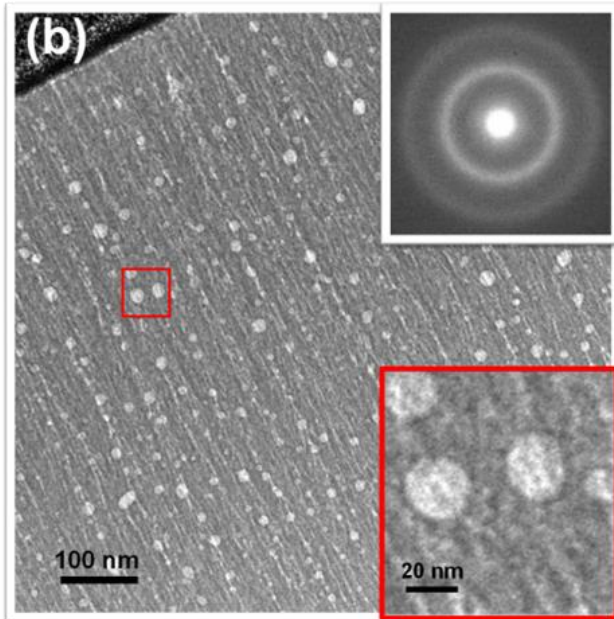
388

389

390

391

392

393

394

22

395