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Study on the crystallization by an electrical resistance measurement in $Ge_2Sb_2Te_5$ and N-doped $Ge_2Sb_2Te_5$ films

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An electric resistance measurement was used to study the crystallization process of $Ge_2Sb_2Te_5$ (GST) and N-doped $Ge_2Sb_2Te_5$ (N-GST) films. The relation between conductivity and annealing time was investigated and the crystallization parameters were determined directly by resistance measurement during isothermal crystallization process in the amorphous GST and the N-GST films. The results show that the crystallization processes in both GST and N-GST films are layer by layer. Their conductivities satisfy the equation $\sigma=\sigma_c-(\sigma_c-\sigma_a)\exp(-kt^n)$, at $t>\tau$, where τ is a temperature-dependent time in the process of crystallization. The activation energy for crystallization of amorphous GST films was 2.11 ± 0.18 eV and the Avrami coefficient was between 2 to 4, in close agreement with previous studies using different techniques. After N doping the Avrami coefficient decreased, while the activation energy increased. The formation of a strain induced by the distortion of unit cell after N doping was used to explain the observed results.
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INTRODUCTION

Recently, phase-change materials such as GeSbTe alloys have receiving intensive attention for their potential application to phase-change random access memories (PCRAMs). It is based on the high difference in electrical properties between the amorphous and crystalline phases of this chalcogenide alloy films. Rapid phase changes used for writing and erasing of data are induced by fast electric current pulses. In PCRAM, the performance of a memory cell is largely determined by the crystallization. Therefore, a considerable number of studies for the kinetics of amorphous-crystalline transformation in phase-change media have been done.[1–17] Oshima,[1] Jeong *et al.*,[2] Weidenhof *et al.*,[3] Ruitenberg *et al.*,[4] and Laine *et al.*,[5] reported that the crystallization behaviors of the GeSbTe films in isothermal condition satisfy the Johnson-Mehl-Avrami-Kolmogrov (JMAK) equation $f=1-\exp(-kt^n)$, where f is crystallinity, n is the Avrami coefficient, and k is an effective rate constant describing both the nucleation and growth. The JMAK parameters such as Avrami coefficient, activation energy, etc. have been investigated mainly through microscope observation[10–14] or the optical measurement.[1–4] The resistivity measurement was also used to get information about the crystallization processes.[6,9,16,17] The crystallization temperature and the effective activation energy of GeSbTe were obtained through this method. However, for PCRAM, there are still some problems. (1) How to obtain all JMAK parameters directly by resistance measurement. To our knowledge, using the resistance measurement, people only obtained the effective activation energy of crystallization.[6,9] The other JMAK parameters including the Avrami coefficient n and the effective rate constant k are never got by this method. (2) It is known that the resistance of phase-change media would be decreased due to crystallization, but what is the relation between resistance and annealing time in detail. For the application and simulation of PCRAM, an understanding for the variety of resistance in detail is desired. In this paper, we determined the relation between the conductivities and the isothermal annealing time firstly, and then a method for getting the JMAK parameters directly by resistance measurement was demonstrated. The pure $Ge_2Sb_2Te_5$ (GST) and nitrogen-doped $Ge_2Sb_2Te_5$ (N-GST) were investigated, which can enhance the cell endurance and reduce the writing current for PCRAM than GST.[7,16,17] Then, the results for the GST and the N-GST have been compared to obtain how the nitrogen doping affects the crystallization parameter of GST.

BASIC THEORY

As early as 1935, Bruggeman presented an overview to describe how to calculate the electrical conductivity σ as function of the dopant and the host material properties for various types of composite materials.[18,19] If the amorphous film is crystallized layer by layer and the layers are oriented parallel to the direction of the electrical current, the conductivity σ is given by

$$\sigma=(1-f)\sigma_a+f\sigma_c, \tag{1}$$

where f represents crystallinity (the volume fraction of crystalline clusters) and σ_a and σ_c are the conductivities for the amorphous and crystalline phases, respectively.

If the amorphous film is crystallized by a random formation of spherical crystalline clusters, the conductivity σ is given by

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$$\sigma = [2\sigma_p - \sigma_p{}' + \sqrt{(2\sigma_p - \sigma_p{}')^2 + 8\sigma_a\sigma_c}]/4, \tag{2}$$

with $\sigma_p = (1-f)\sigma_a + f\sigma_c$ and $\sigma_p{}' = f\sigma_a + (1-f)\sigma_c$. Equation (2) is generally referred to as the Bruggeman-type effective medium approximation.[18,19]

With the JMAK equation, Eqs. (1) and (2), respectively, give

$$\sigma = \sigma_c - (\sigma_c - \sigma_a)\exp(-kt^n), \tag{3}$$

and

$$2\sigma - \sigma_a\sigma_c/\sigma = (2\sigma_c - \sigma_a) - 3(\sigma_c - \sigma_a)\exp(-kt^n). \tag{4}$$

Therefore, if the rate constant k is independent of time and the film is crystallized layer by layer, the plot of $\ln\{-\ln[(\sigma_c-\sigma)/(\sigma_c-\sigma_a)]\}$ as a function of $\ln(t)$ should be in a straight line with slope n and intercept $\ln(K)$. But the plot of $\ln(-\ln\{[\sigma_a\sigma_c+\sigma(2\sigma_c-\sigma_a)-2\sigma^2]/[3\sigma(\sigma_c-\sigma_a)]\})$ as a function of $\ln(t)$ gets n and $\ln(K)$ for the amorphous film crystallized by a random formation. From the discussion above, we can get the values of n and k through electrical resistance measurement.

EXPERIMENT

Pure and N-doped $Ge_2Sb_2Te_5$ films were deposited on Si (100) substrates by pulse laser deposition at room temperature. The power of laser was 160 mJ/pulse. The background pressure was 5×10^{-4} Pa. The protective atmosphere was Ar for undoped GST, but for N-doped $Ge_2Sb_2Te_5$ (N-GST), it was N_2 and Ar gas mixture and the flow ratio of N_2/Ar gas was 0.1. The pressures of both the Ar and N_2/Ar mixture were 0.6 Pa. The chemical compositions of the films were determined by x-ray photoelectron spectroscopy (ESCALab, MK-II). The dopant concentration was about 2.4%. The thickness of all films for electric measurement was about 120 nm. The crystallization of amorphous films has been completed in the ranges of 135–155 °C for undoped GST and 155–175 °C for N-GST. The higher temperature used for N-GST is due to increasing of the crystallization temperature for GST after N doping.[7,16,17]

RESULT AND DISCUSSION

Figure 1 shows the resistance as a function of time measured at 140 °C in an undoped GST film. The as-deposited sample was amorphous. Its sheet resistance was about 10^6 Ω/sq. The sheet resistance decreases continuously before time τ, at which a sudden drop of resistance occurs. The sudden drop of the resistance can be correlated with the transition from amorphous to crystalline phase structure and it is confirmed by XRD measurements (not show here). The time τ depends on the annealing temperature.[3,4,9,12] After time τ_c the resistance reduces slightly, which implies that the crystallization has accomplished.

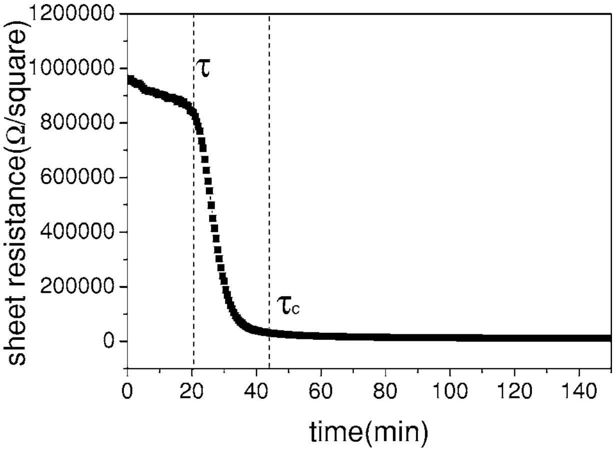

FIG. 1. The resistance as a function of annealing time measured at 140 °C for undoped GST.

Figure 2(a) is the plot of $\ln\{-\ln[(\sigma_c-\sigma)/(\sigma_c-\sigma_a)]\}$ as a function of $\ln(t)$. A linear relation is only observed after time τ and a similar result was reported in Ref. 3. It is due to that the nucleation rate reaching equilibrium needs a certain time.[3,12] The value of Avrami coefficient strongly depends on the choice for the starting time of transformation.[3] In order to obtain JMAK coefficient, two different analysis methods were used. The first one is to identify the starting time of transformation $t=0$ when the sample reaches the desired temperature.[1,2,4] The second one is to neglect the small amount of crystallized materials before τ and to define τ as the starting time.[3] Following JMAK model, the starting time of the crystallization should be the time as the first nucleus

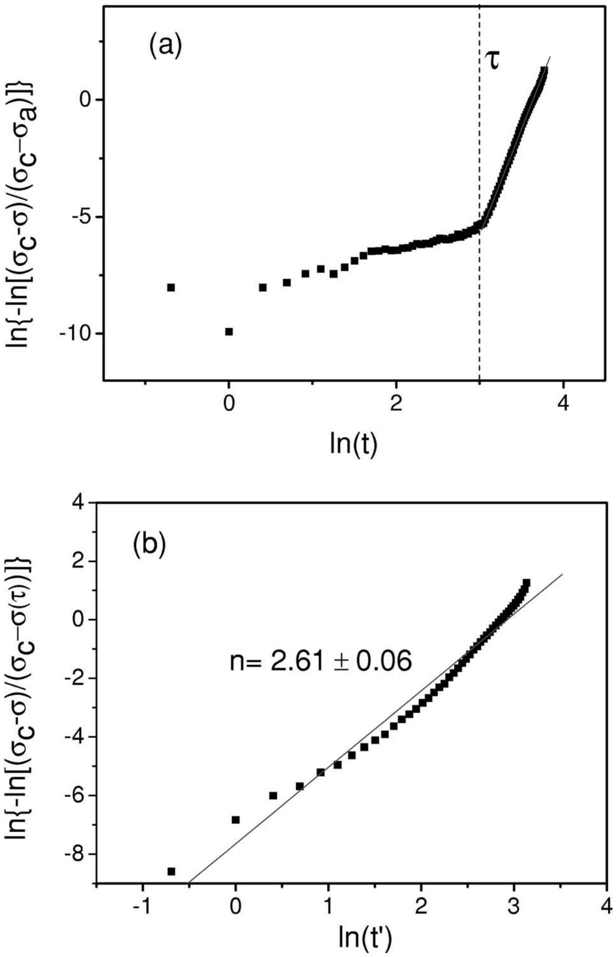

FIG. 2. The result for undoped GST annealed at 140 °C: (a) after time τ, the plot of $\ln\{-\ln[(\sigma_c-\sigma)/(\sigma_c-\sigma_a)]\}$ against $\ln(t)$ shows a linear fit; (b) after rescaled time t, a straight line with slope n=2.61 is fitted to the data points.

TABLE I. Avrami coefficient n as a function of annealing temperature for undoped GST.

Temperature (°C)	135	140	145	150	155
n	2.43±0.07	2.61±0.06	3.26±0.16	2.91±0.10	3.24±0.10

forms. The incubation time (t_{inc}) is the passing time before the first nucleus forms. While one measures JMAK coefficient, the time t should be rescaled to $t' = t - t_{\mathrm{inc}}$. To find out the incubation time is helpful for determining the JMAK coefficient but it is difficulty to obtain the incubation time accurately. When the annealing temperature is high the incubation time would be short. Then it is reasonable to ignore the incubation time and identify the starting time of transformation with the time $t=0$ (the first method). The annealing temperature is low, however, the incubation time will be longer and it cannot be ignored. In this case, identifying $\tau = t_{\mathrm{inc}}$ would be comparative credible (the second method).

On the basis of the discussion above and considering the low annealing temperature in this work, we chose the time τ for the start time of crystallization. A curve of $\ln\{-\ln[(\sigma_c - \sigma)/(\sigma_c - \sigma_a)]\}$ as a function of $\ln(t)$ has been plotted with the substitution $\sigma(\tau)$ for σ_a and $t-\tau$ for t, as shown in Fig. 2(b). A straight line with slope $n=2.61$ was fitted to the data points. The result for different temperatures was shown in Table I. From Table I one can find that the Avrami coefficient n lies between 2 and 4. The result seems to be compatible with the values of 2.6±0.1 reported by Weidenhof *et al.*[3] and 3.4±0.9 reported by Ruitenberg *et al.*[4]

Figure 3 shows a plot of $\ln k$ as function of annealing temperature and a straight line fitted to the data point. Based on the equation $k = \nu \exp[-E_A/(k_B T)]$, the value of E_A can be obtained from the slope of the line. The activation energy was 2.11±0.18 eV, which is in agreement with the results determined by optical (2.0±0.2 eV) (Ref. 3) or differential scanning calorimetry (2.23 eV) (Ref. 15) measurement. Here, it should be noted that the crystallization of PCRAM films is found to be influenced by surface, capping layers, electron beam exposure, etc.[1,13,14,20] And a modified result would be got for different condition.

In order to determine the type of crystallization for N-doped $Ge_2Sb_2Te_5$, a sample about 400 nm thick was annealed for 25 min at 170 °C. Two layers with different brightnesses were observed in a cross-sectional image of scanning electron microscopy (not show here). It indicated that N-GST was also crystallized layer by layer and it is in agreement with observation on ion-implanted N-doped sample.[16] By resistance measurement and an analysis procedure similar to GST, we also got the JMAK parameters of N-GST. Figure 4 is the result of the sample annealed at

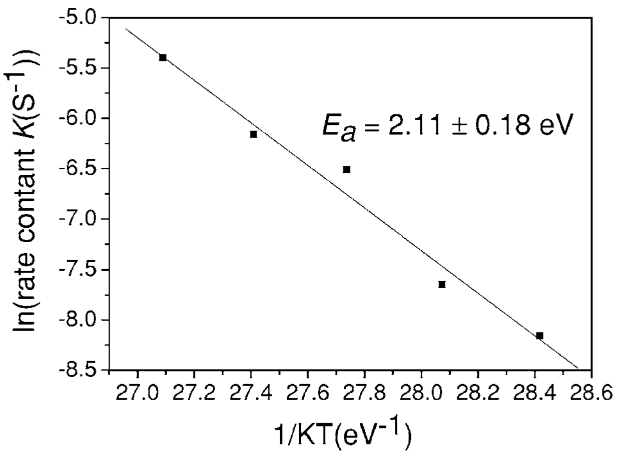

FIG. 3. $\ln k$ as function of annealing temperature for undoped GST.

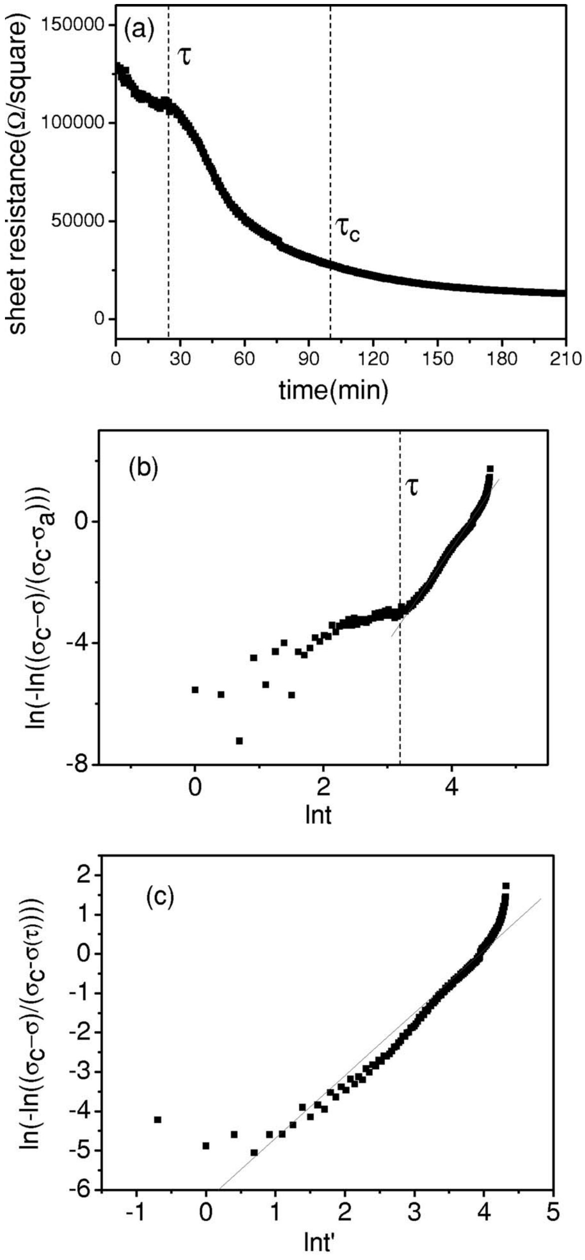

FIG. 4. The result for N-GST annealed at 165 °C: (a) the resistance as a function of annealing time; (b) after time τ, the plot of $\ln\{-\ln[(\sigma_c - \sigma)/(\sigma_c - \sigma_a)]\}$ against $\ln(t)$ shows a linear fit; (c) after rescaled time t, a straight line with slope $n=1.59$ is fitted to the data points.

TABLE II. Avrami coefficient n as a function of annealing temperature for N-GST.

Temperature (°C)	155	160	165	170	175
n	1.54±0.02	1.92±0.06	1.59±0.04	1.75±0.07	1.68±0.08

165 °C and the plot of $\ln(-\ln\{(\sigma_c-\sigma)/[\sigma_c-\sigma(\tau)]\})$ as a function of $\ln(t')$ is a straight line with slope of 1.59 [Fig. 4(c)].

Table II shows Avrami coefficient n as a function of annealing temperature for N-GST sample and n is between 1.5 and 2. The result indicated that N doping will reduce Avrami coefficient and the decrease of resistance with time in crystallization process will slow [Eq. (3)]. As we know, the Avrami coefficient, $n=a+md_g$,[4,18] here, a and m are the nucleation and the growth indices, respectively, and d_g is the dimensionality of growth. As reported,[4,21] $a\geqslant 0$ and $m=0.5$ for diffusion-controlled growth, while $m=1$ for interface-controlled growth and the interface-controlled growth for GST has been proved.[10–12] Unfortunately, we cannot determinate whether N doping changes the type of the growth of GeSbTe. But if the type of growth was not changed, the value of m will still be 1. Considering the Avrami coefficient of N-GST $n<2$ and $a\geqslant 0$, the d_g of N-GST could only be 1 (one dimensional growth). Then $a<1$ and the nucleation rate I decreases with time $(I\propto t^{a-1})$.[4,21] Otherwise, if the growth was changed to diffusion controlled, $m=0.5$ and the d_g of N-GST could be 1 or 2. The nucleation rate increases with time when $d_g=1$ and decreases when $d_g=2$. Obtaining concrete value needs further study.

Plot for $\ln(K)$ against $1/T$ shows that the E_A of N-GST is 2.88±0.27 eV (Fig. 5), higher than the value of undoped GST as reported by Jeong *et al.*,[7] Privitera *et al.*,[16] and Kim *et al.*[17] The possible reason is that N cannot substitute Ge, Sb, and Te atoms but locates at the tetrahedral interstitial sites or accumulates in the grain boundaries.[17] The N atoms locating inside the cubic structure contribute to the increase of active energy because the volume of a tetrahedral site is not sufficiently large for a N atom to occupy inside, which results in a distortion of the unit cell and a strain field. Furthermore, the strain effect could account for the higher activation energy.[7,16]

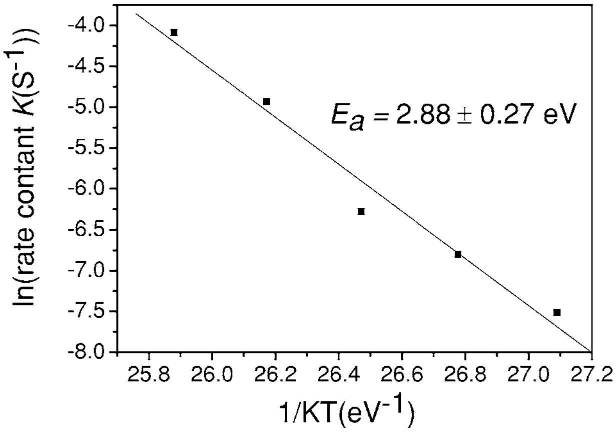

FIG. 5. $\ln k$ as function of annealing temperature for N-GST.

SUMMARY

In conclusion, the crystallization process of GST and N-GST films was studied by electric resistance measurement. The results show that crystallization processes in both GST and N-GST films are layer by layer. After a time τ, their conductivities satisfy the equation $\sigma=\sigma_c-(\sigma_c-\sigma_a)\times\exp(-kt^n)$. Meanwhile, the JMAK parameters were got. A decrease for the Avrami coefficient and an increase for the activation energy were observed after N doping. The formation of a strain induced by the distortion of unit cell after N doping was used to explain the observed results.

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