Size-dependent nucleation rate of $Ge_2Sb_2Te_5$ nanowires in the amorphous phase and crystallization activation energy

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ABSTRACT

Simple and unified models have been established for size-dependent crystallization activation energy and nucleation rate of $Ge_2Sb_2Te_5$ nanowires in the amorphous phase based on size-dependent melting temperature of low dimensional materials. The models are free of any adjustable parameters and predict a decreasing trend of crystallization activation energy and an increasing trend of nucleation rate in the amorphous phase with the size dropping of nanocrystals. Both the phenomena attribute to the increasing surface to volume ratio with the size dropping and surface atoms plays an important role. The model predictions agree well with available experimental results of $Ge_2Sb_2Te_5$ wires, which supply an easy way to understand crystallization behavior of phase change memory nanomaterials.

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1. Introduction

Recently, there is a strong demand on high speed, high density, low-power, and non-volatile memory to save data without a battery [1]. PCM (phase change memory) is one of the most promising candidates for the next generation non-volatile memory in terms of device speed, scalability, and long-term durability [2–14]. The information in PCM is stored as amorphous phases and exploiting the appreciable voltage pulse can induce change in electrical resistance accompanying the rapid and reversible phase transformations between crystalline and amorphous states, which enable repeated recording information.

Since these phenomena are strongly related to the crystallization behavior of PCM, a careful analysis of it's crystallization kinetics in the amorphous phase is important [15]. Some experimental results show that crystallization activation energy ($E_a(D)$) decreases [9,15] and nucleation rate ($N(D)$) in the amorphous phase increases [5,9] with the size dropping, namely $E_a(D) < E_a(\infty)$ and $N(D) > N(\infty)$, where D denotes the diameter of nanoparticles and nanowires or the thickness of thin films and ∞ denotes the bulk size. In spite of its technological significance, not much is known about the underlying mechanism of crystallization from the amorphous phase [9] and it is heavily dependent on the definition of crystallization temperature (T_c), which is often quite arbitrary [15].

Many potential candidate PCM materials have been proposed such as In_2Se_3 [7], GeTe [13,14], Ge–Sb–Te [1,3–6,8–12,15] and $Ge_2Sb_2Te_5$ is considered as a promising PCM material [3,4,9,11,15]. In this contribution, simple analytical equations are developed for $E_a(D)$ and $N(D)$ functions of PCM nanomaterials without any free parameters. The model predicts a decreasing trend of $E_a(D)$ and an increasing trend of $N(D)$ with size dropping. In this case, this model not only enables us to reproduce a number of experimental results of PCM nanomaterials in the full size ranges, but also supplies an easy way to understand crystallization behavior of PCM nanomaterials.

2. Model

The crystallization process of $Ge_2Sb_2Te_5$ in the amorphous phase is nucleation-dominant [9] and according to heterogeneous nucleation theory, the nucleation rate can be expressed as following,

$$N = wC\exp(-E_a/kT) \tag{1}$$

Where w and C are the frequency factor and concentration of atoms occupying heterogeneous sites respectively, and k is the Boltzman constant. w depends on the degree of undercooling and is assumed to be size-independence under identical conditions [9], namely $w(D) = w(\infty)$. Generalizing this relationship into nanometer size range, it can be read as $N(D) = w(D)C(D)\exp(-E_a(D)/kT)$ and the relative nucleation rate with respect to a reference size can be expressed as,

$$\frac{N(D)}{N^r} = \frac{C(D)}{C^r} \exp\left(\frac{E_a^r - E_a(D)}{kT}\right) \tag{2}$$

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where the superscript r denotes the reference size. $C(D)/C^r$ represents the ratio of the concentrations of atoms present on heterogeneous nucleation sites (surfaces) and it is approximately equal to the relative surface to volume ratio (A/V) (namely $C(D)/C^r = D^r/D$) [9]. Thus, the Eq. (2) can be rewritten as,

$$\frac{N(D)}{N^r} = \frac{D^r}{D} \exp\left(\frac{E_a^r - E_a(D)}{kT}\right) \tag{3}$$

It is well known that the activation energy is proportional to crystallization temperature, namely, $E_a = AT_c$, where A is a size-independent coefficient [16] and extending it to nanoscale range, it can be expressed as $E_a(D)/E_a(\infty) = T_c(D)/T_c(\infty)$. For nanocrystals, $T_c(D)$ decreases with decreasing size and the suppression of $T_c(D)$ is attributed to softening of lattice vibrations due to the increasing of A/V [9,17]. The melting temperature (T_m) presents the temperatures required for the activation of lattice vibrations and the relation between T_c and T_m can be expressed as $T_c(D)/T_c(\infty) = T_m(D)/T_m(\infty)$ [17]. The size-dependent melting temperature has been established by Jiang et al. [18] that,

$$\frac{T_m(D)}{T_m(\infty)} = \exp\left(-\frac{2S_{vib}(\infty)}{3R}\frac{1}{(D/D_0 - 1)}\right) \tag{4}$$

Where $S_{vib}(\infty)$ is the bulk vibrational melting entropy and R is the ideal gas constant. D_0 is a critical radius at which almost all atoms of the particle are located on its surface. For low dimensional crystals, D_0 is dependent on the dimension of crystals d, namely $D_0 = 2(3-d)h$, where h is atomic distance and $d=0$ for nanoparticles, $d=1$ for nanowires and $d=2$ for nanofilms. For a nanoparticle, D has an usual meaning of diameter. For a nanowire, D is taken as its diameter. For a thin film, D denotes its thickness [19]. According to the above consideration, the size-dependent activation energy with respect to bulk and a reference size can be expressed as,

$$\frac{E_a(D)}{E_a(\infty)} = \exp\left(-\frac{2S_{vib}(\infty)}{3R}\frac{1}{(D/D_0 - 1)}\right) \tag{5-1}$$

$$\frac{E_a(D)}{E_a^r} = \exp\left\{\frac{-2S_{vib}(\infty)}{3R}\left[\frac{1}{(D/D_0 - 1)} - \frac{1}{(D^r/D_0 - 1)}\right]\right\} \tag{5-2}$$

Combining Eq. (5-2) with Eq. (3), the complete expression of $N(D)$ can then be written as,

$$\frac{N(D)}{N^r} = \frac{D^r}{D} \exp\left(\frac{E_a^r - E_a^r \exp\left\{\frac{-2S_{vib}(\infty)}{3R}\left[\frac{1}{(D/D_0-1)} - \frac{1}{(D^r/D_0-1)}\right]\right\}}{kT}\right) \tag{6}$$

3. Results and discussion

Fig. 1 shows the comparisons between the model prediction in terms of Eq. (5-2) and experimental results for the $E_a(D)$ of Ge$_2$Sb$_2$Te$_5$ nanowires. As shown in Fig. 1, $E_a(D)$ decreases with a corresponding decrease in size and a dramatic increase in $E_a(D)$ is observed for the size range of $D < 50$ nm. Beyond $D > 50$ nm, $E_a(D)$ increases rather gently until it approaches to the value of reference size for larger D. This can be expected as the increased number of atoms on surface or larger surface/volume ratio when D is reduced. Thus the contribution of surface atoms to materials properties becomes prominent, due to their distinct physical characteristics comparing with that of interior atoms. According to the classical nucleation theory, the activation energy is proportional to interface energy (γ) and $\gamma(D)$ decreases with the size dropping [20]. It is reported that $\gamma(D) \propto E_c(D)$, where $E_c(D)$ denotes the cohesive energy [20]. For nanomaterials, although the single bond energy is strengthened, the lower coordination number of surface atoms results in the decreasing cohesive
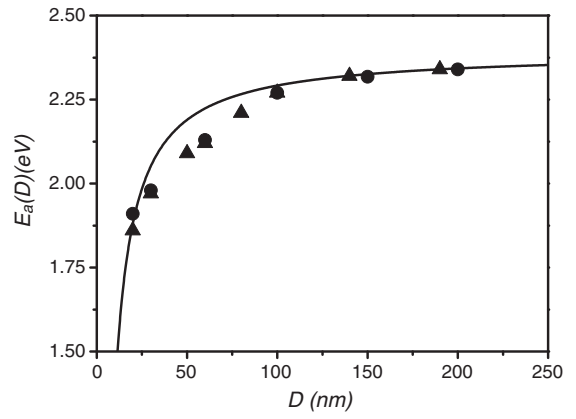

Fig. 1. $E_a(D)$ function of Ge$_2$Sb$_2$Te$_5$ nanowires. The solid line denotes the model predictions in terms of Eq. (5-2). $S_{vib}(\infty) = 22$ J/g-atom-k [21] and $D_0 = 4h = 2.404$ nm with $d=1$ and $h = 0.601$ nm [22] according to $D_0 = 2(3-d)h$. $E_a^r = E_a(190 \text{ nm}) = 2.34$ eV [9]. The symbols ● [5] and ▲ [9] are experimental results.

energy of nanocrystals with the increasing surface atoms and it is reasonable that $E_a(D)$ decreases with the size dropping. Consistency between the model prediction with experimental results confirmed that the model is a valid approach to predict $E_a(D)$ function.

The size effect on $N(D)$ in terms of Eq. (6) is shown in Fig. 2, comparing with experimental evidences. It predicts that $N(D)$ increases with the size dropping and there is an increase of 7 orders of magnitude for a 20 nm comparing to 190 nm nanowires. Calculation performed without including the effect of the increasing A/V (namely ignoring the effect of D^r/D in Eq. (6)) with the size dropping (dash line) predicts the right shift trend but fails to predict the correct values. Calculation combining the effect of A/V (solid line) according to Eq. (6) is well consistent with experimental results, which confirms the significance of the surface atoms for crystallization from the amorphous phase. The analysis indicates that faster crystallization in thinner nanowires results from surface-induced, enhanced heterogeneous nucleation-driven phase-change [9]. The increase of $N(D)$ is related to the suppression of $T_c(D)$ [5] and $T_c(D)$ is proportional to $E_a(D)$ [16]. While $E_a(D)$ decreases with the size dropping according to Eqs. (5-1) and (5-2), the increase of $N(D)$ can be obtained. Considering above analysis, the origin of the increase of $N(D)$ is attributed to the increasing A/V and the decreasing $E_a(D)$ with the size decreasing. The model prediction agrees well with the experimental results, which shows that it not only enables us to reproduce a number of experimental results of PCM nanomaterials in the full size range,
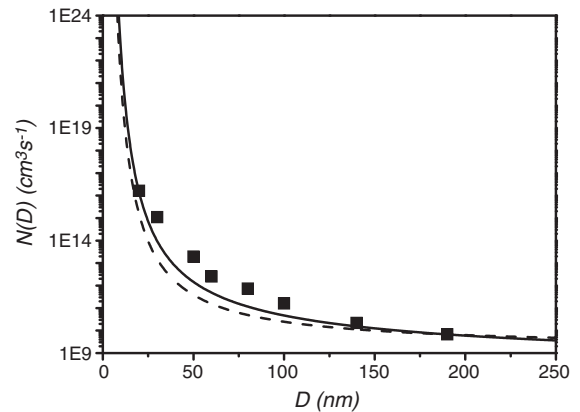

Fig. 2. $N(D)$ function of Ge$_2$Sb$_2$Te$_5$ nanowires. The solid line denotes the model predictions in terms of Eq. (6) and the dash line denotes the predictions ignoring the effect of D^r/D in Eq. (6). $N^r = N(190 \text{ nm}) = 6.77 \times 10^9 (\text{cm}^3\text{s}^{-1})$ and $T = 433$ K [9]. The symbol ■ [9] denotes the experimental results.

but also supplies an easy way to understand crystallization behavior of PCM nanomaterials.

4. Conclusions

In summary, thermodynamically quantitative models have been developed to calculate $E_a(D)$ and $N(D)$ functions of $Ge_2Sb_2Te_5$ nano-wires in the amorphous phase. $E_a(D)$ decreases and $N(D)$ increases with the size decreasing. Both the phenomena attribute to the increasing surface to volume ratio with the size dropping and surface atoms plays an important role. The models can reproduce a number of experimental results of PCM nanomaterials in the full size ranges, which supply an easy way to understand crystallization behavior of PCM nanomaterials.

Acknowledgments

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