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AMORPHOUS/CRYSTALLINE STRUCTURE AND PHASE TRANSFORMATIONS IN METASTABLE SEMICONDUCTING $\text{Ge}_{1-x}\text{Sn}_x$ *

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ABSTRACT

The semiconducting crystalline alloys, $\text{Ge}_{1-x}\text{Sn}_x$, are of interest due to theoretical predictions about their electronic band structures which make them useful in infrared photodetectors. However the composition region where these alloys have the desired properties is greater than the equilibrium solid solubility limit of Sn in Ge ($x \leq 0.01$). We have circumvented the solubility limits and produced thin (2000Å) and thick (4-8µm) films of $\text{Ge}_{1-x}\text{Sn}_x$ ($x \leq 0.31$) by rf sputtering. Differential scanning calorimetry (DSC) measurements were performed to study grain growth and crystallization processes in these highly metastable semiconductors. X-ray and electron diffraction measurements indicated the materials were amorphous, but the fact that some of the films were fine-grained polycrystalline samples only became apparent in their DSC spectra. We present models that describe quantitatively the transformation behavior in both sets of films.

INTRODUCTION

Metastable semiconducting crystalline $\text{Ge}_{1-x}\text{Sn}_x$ alloys have predicted direct electronic energy gaps in the mid to far infrared (IR) wavelength range, for Sn concentrations greater than 20at.%. Present IR photoconductive materials (tellurides) in this wavelength range are very expensive to mass produce due to uncontrollability of the constituent elements during deposition. Crystalline $\text{Ge}_{1-x}\text{Sn}_x$ is an alternative to these conventional materials, except that the solid solubility of Sn in Ge is less than 1at.% and for the desired IR sensitivity more than 20at.% is needed. We have successfully produced such high Sn concentration alloys in what we originally thought was an amorphous form. Isothermal annealing in a differential scanning calorimeter (DSC) produced a signal which decayed with time, contrary to the standard bell shaped signal expected from nucleation and growth of the crystalline phase. We will show here that this decaying signal is due to crystal growth and, together with x-ray diffractometry (XRD), indicates that the as-deposited material was already polycrystalline with an 18Å grain size.

EXPERIMENTAL

By rf sputtering in an Ar atmosphere, we successfully fabricated uniform alloys of $\text{Ge}_{1-x}\text{Sn}_x$ for Sn concentrations ranging from 0 to 31at.%. We report here on two specific concentrations and thickness regimes: 25at.%, 0.2µm thick, and 31at.%, 8µm thick. Electron diffraction was performed on the thinner material and diffuse rings were observed; XRD on the thicker material showed broad diffraction peaks. Both sets of measurements indicated the films were "amorphous". For the desired IR photonic properties, the alloys need to be crystalline. We therefore examined the "crystallization" and subsequent phase separation of Sn in a DSC.

We scanned each material at 10K/min as shown in Fig. 1. The thinner material clearly exhibits two well separated exothermic reactions which we identified with a series of electron diffraction measurements on samples annealed to various temperatures. The first exotherm

corresponded to crystallization and the second to phase separation. Figure 1a also shows a second heating scan of the sample, used for baseline determination, which exhibits an endotherm corresponding to Sn melting resulting from the phase separation process. Figure 1b, on the other hand, shows only one broad exotherm with several "bumps" on it indicating the presence of more than one process occurring in the temperature range of the exotherm.

If such processes have slightly different thermal activation energies, *isothermal* anneals at various temperatures will permit time separation of the processes. With this as our motivation, we ramped the temperature of each sample at 10K/min to isothermal anneal temperatures 10–15K lower than the onset of the first transformation in the scanned data. The thin samples exhibited two, time-separated, bell-shaped exotherms (Fig. 2a), which were identified by high resolution transmission electron microscopy (HRTEM) to be crystallization and phase separation. The crystallization exotherm fits the standard Johnson-Mehl-Avrami nucleation and growth theory with a nucleation constant $n=3.5$.¹ Combining the isothermal DSC data with HRTEM, we found the number of nuclei decreased as a function of time and the crystal growth at all sites was three dimensional.

Fig. 1: (a) 10K/min scan of $0.2\mu\text{m Ge}_{0.75}\text{Sn}_{0.25}$ and (b) 10K/min scan of $8\mu\text{m Ge}_{0.69}\text{Sn}_{0.31}$, with the dotted line in each figure representing the second heating scan of the material.

Fig. 2: (a) 540K isothermal DSC signal of $0.2\mu\text{m thick Ge}_{0.75}\text{Sn}_{0.25}$; (b) 450K isothermal signal from $8\mu\text{m thick Ge}_{0.69}\text{Sn}_{0.31}$.

The 450K isothermal anneal of the thick material is very different, see Fig. 2b. For approximately the first eight minutes, the rate of enthalpy release decays with time and then the material exhibits a "bumpy" but bell-shaped exotherm. XRD of a sample annealed partially through the decay (4 min.) indicates that no Sn phase separated from the sample. However, XRD of a sample annealed through the bell-shaped exotherm demonstrates that this exotherm is due to Sn phase separation, as was the case for the second exotherm in the thin sample. XRD of the sample annealed through four minutes of the decay also exhibited sharper diffraction peaks than in the as-deposited sample, indicating less disorder in the annealed sample. To determine the thermal response of the process occurring during this short decay, we lowered the isothermal anneal temperature to 410K, see solid line in Fig. 4a, which produced a much longer decay (~80 min. before the signal started to rise indicating the onset of phase separation). XRD of a sample annealed through 70 minutes of the 410K isotherm again displayed sharpened diffraction peaks.

We postulated that this decay in rate of heat release was due to grain growth and will now show that using this model simulations of such a grain growth do indeed describe the experimental observations exceptionally well. Assuming grain growth, the sharpening of the x-ray peaks corresponded to an increase in the average crystallite size from 18Å to 35Å. The following analysis follows that of Chen and Spaepen.² Starting from the standard grain growth power law equation for the evolution of the average grain size, r , as a function of time, t , at temperature T gives

$$r^n(t) = r_0^n + t k(T) \quad (1)$$

where r_0 = the grain size in the as-deposited material and $k(T)$ = rate constant. The time evolution of the interfacial enthalpy, $H(t)$, as the grains grow at a given temperature T , is related to the enthalpic part of the interfacial tension, g_H , the molar volume of the sample, V , and a geometrical factor $g = 1.3 \pm 0.2$ (for equiaxed grains)

$$H_T(t) = g_H V / r_T(t) \quad (2)$$

$$H_T(t) r_T(t) = g_H V = \text{constant} = (H_0)_T (r_0)_T \quad (3)$$

where H_0 = the initial enthalpy of the system. Combining these three equations, the rate at which heat is released from the sample during the grain growth process at temperature T is given by:

$$-\dot{H}_T(t) = \frac{(H_0)_T (r_0)_T}{n} \frac{k(T)}{(r_0^n + k(T)t)^{(n+1)/n}} \quad (4)$$

If a fitting parameter τ is defined such that

$$\tau \equiv \frac{(r_0)_T^n}{k(T)} \quad (5)$$

then the rate at which heat is evolved during grain growth at a given temperature is:

$$-\dot{H}_T(t) = \frac{(H_0)_T}{n\tau} \left(1 + \frac{t}{\tau}\right)^{-(n+1)/n} \quad (6)$$

Using the definition for the time evolution of the enthalpy during grain growth:

$$H_T(t) = (H_0)_T + \int_0^t \dot{H}_T(t) dt \quad (7)$$

$H_T(t)$ can be rewritten in terms of the fitting parameter τ

$$H_T(t) = (H_0)_T \left(\frac{t+\tau}{\tau}\right)^{-1/n} \quad (8)$$

A plot of $\ln H(t)$ versus $\ln(t+\tau)$ should produce a straight line of slope $(-n)$, if we do have grain growth and τ is chosen appropriately. Since both isothermal anneal temperatures were well below the onset of the exotherm observed during the temperature scan of the sample, the total enthalpy of the decaying portion of each isothermal spectrum was taken to be the same as that measured during the lower temperature isotherm (410K) and was 304cal/mol. Figure 3 shows the best fit to our 410K and 450K isothermal anneal data (Figs. 4a and 2b), with $\tau = 3.4$ -3.5min and 4.2-4.8min respectively.

Fig. 3: (a.) dashed line shows fit to 410K isothermal DSC data (solid line) for $\tau = 3.4$ min; slope = -1.77 and (b.) dashed line shows fit to 450K isothermal DSC data (solid line) for $\tau = 4.5$ min, slope = -1.6.

The grain growth constant determined from these plots is $n=1.76 \pm 0.01$ for the 410K isothermal and $n=1.6 \pm 0.1$ for the 450K isothermal. These numbers are within the range of other

experimentally measured values for n (0.5 to 4).³ Theoretically n should be 2. Using these values for n and τ , and the grain growth model discussed above, we simulated the DSC output using equation 6. The results are shown in Fig. 4.

Fig. 4: (a.) (above) 410K simulation (dashed line) of the isothermal DSC data (solid line) using $\tau = 3.4$ min and $n = 1.76$; (b.) (top right) shows the 450K simulation (dashed line, $\tau = 4.5$, $n = 1.6$) of the data (solid line); and (c.) (lower right) shows an expanded view of the decay portion and simulation of the 450K isotherm.

The remarkable agreement between the experimental data and the simulation shows that we are indeed justified in hypothesizing that grain growth occurs during the decay observed in the isothermal DSC data.

With this value for the grain growth parameter, n , we can estimate the activation energy for this process by assuming an Arrhenius temperature dependence for the rate constant

$$k(T) = k_0 \exp(-Q/k_B T) \quad (9)$$

Strictly speaking, one should assume an Arrhenius dependence for the jump frequency instead of the rate constant, but the activation energies calculated either way are so close as to be within experimental error of each other and thus the difference can be ignored. If we let $t_{1/2}$ be the time at which the total enthalpy of the system has decreased to half its initial value and combining equations (1), (3), and (9), we find:

$$t_{1/2} H_0^n k_0 \exp(-Q/k_B T) = \text{constant} \quad (10)$$

Thus a plot of $\ln(t_{1/2} H_0^n)$ versus $1/T$ should be a straight line with slope Q/k_B . Such a plot for our data, which was inevitably a straight line since we performed only two different isothermal temperature anneals, produced an activation energy for grain growth of $0.5 \text{ eV} \pm 0.2 \text{ eV}$. A more

accurate determination of this energy requires a minimum of three isothermal temperature anneals. Even so, our activation energy is reasonable in comparison with the activation energy for growth of CoSi_2 from an amorphous matrix (0.97-1.17eV) measured by other methods⁴ and the 2.2eV that Chen and Spaepen determined for grain growth of the icosohedral phase of $\text{Al}_{0.83}\text{Mn}_{0.17}$ from an analysis similar to that presented here.⁵

The enthalpic part of the interfacial tension was also calculated using equation (3) with $g=1.3$, $r_0=18\text{\AA}$, and $H_0=304\text{cal/mol}$. The molar volume was determined assuming 8 atoms per unit cell and a lattice constant of 5.918 $\text{\AA}$, found from the angular position of the (111) peak in the XRD pattern. The enthalpic part of the interfacial tension was 113mJ/m^2 , within the range of 140mJ/m^2 found by Chen and Spaepen for their $\text{Al}_{0.83}\text{Mn}_{0.17}$ samples. It is interesting to note that the grain boundary energy for Sn is 164mJ/m^2 ,⁶ not too different than the 113mJ/m^2 determined for our $\text{Ge}_{0.69}\text{Sn}_{0.31}$ alloys.

SUMMARY

We have demonstrated a very powerful method for distinguishing between truly amorphous samples and very fine grained, 1nm-2nm, polycrystalline ones. X-ray diffraction indicated that both samples were amorphous, yet isothermal DSC measurements were markedly different. The amorphous sample exhibited a bell-shaped crystallization exotherm which, when analyzed using the standard Johnson-Mehl-Avrami formalization, produced an Avrami $n=3.5$ and indicated that the nucleation rate of the crystalline state decreased with increasing time while the grains grew three dimensionally at all nucleation sites. The other $\text{Ge}_{0.69}\text{Sn}_{0.31}$ sample exhibited a decay in the rate of heat released during the beginning portion of the isothermal anneal and subsequently a bell-shaped curve, corresponding to phase separation of Sn from the alloy. Analysis of the decay, using the standard grain growth model of Burke, Turnbull, and others⁷, gave a grain growth exponent of 1.7 ± 0.1 , in reasonable agreement with $n=2$ of the models used; an estimated thermal activation energy for grain growth of 0.5eV; and an interfacial grain boundary energy of 113mJ/m^2 , within the range of the grain boundary energy for Sn, 164mJ/m^2 . These numbers together with a fitting parameter were used to simulate the rate at which heat would be released during an isothermal anneal assuming that the only process occurring during the anneal was grain growth of pre-existing grains. Comparison of these simulations with the experimental isothermal DSC data showed a remarkable agreement between the two. This indicated that indeed only grain growth occurred during the decay portion of the isotherms, despite the indication from XRD that the materials were amorphous and therefore should have undergone nucleation of the crystalline phase first before grain growth occurred. Thus, isothermal DSC measurements are a very powerful tool in identifying nanometer sized polycrystalline grains from amorphous, random networks of atoms.

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