Фізика напівпровідників, квантова та оптоелектроніка. 1998. Т. 1, № 1. С. 71-74.
Semiconductor Physics, Quantum Electronics & Optoelectronics. 1998. V. 1, N 1. P. 71-74.

PACS 61.72.V; 72.80.E

Crystallization kinetics of $Ge_{22}Sb_{22}Te_{56}$ doped with Se and Ni

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Abstract. Effects of Ni and Se incorporation on the crystallization kinetics of Ge:Sb:Te alloys have been studied. Both elements were found to increase the stability of the amorphous structure. The kinetics of crystallization under isothermal treatments indicates that Ni reduces both the barrier for thermal crystallization and the crystallization rate. Crystallization of samples containing Se is also retarded, possibly due to a stronger bonding of this element in comparison with Te.

Keywords: crystallization kinetics, RF-sputtering technique, electrical conductivity.

Paper received 14.07.98; revised manuscript received 20.08.98; accepted for publication 27.10.98.

Introduction

Phase change optical memory technology, in which data are stored in the form of laser-induced structural phase transformations, originated with Ovshinsky more than twenty-five years ago [1]. The general idea is to write data bits as micron-size amorphous regions. These data can be erased by recrystallizing the amorphous regions through heating with the same laser. Therefore, the recrystallization behavior of thin alloy films is fundamental to the technology of phase change optical recording. Recently, ternary alloys based on Ge:Sb:Te have been successfully applied in commercial optical disk based data storage systems [2]. Although the phase change technology has been recognized for the simplicity of recording and reading, its commercial success was predicted due to the capability of direct overwriting.

For direct overwriting, the phase change optical memory technology needed appropriate media, i.e. materials that could be recrystallized at approximately the same duration of laser exposure that was used to make them amorphous. Of course, this requires the crystallization process to be very rapid, without degrading the thermal stability of the film. Thus, sensitivity and stability are two necessary features of viable optical recording media.

Optical memory media based on tellurium films with a stoichiometric composition have been previously shown to exhibit the necessary crystallization speed [2, 3]. Tellurium alloys can be made more stable when a chalcogenide element with stronger bonding, such as selenium, is added in small amounts. It is also known [4, 5] that addition of traces of a transition metal, such as Ni, helps nucleation in these alloys; however, the effect of these elements on the crystallization kinetics is not yet clear.

In this work, we analyze the crystallization kinetics of commercially used optical media $Ge_{22}Sb_{22}Te_{56}$ incorporating and not incorporating small amounts of Se and Ni. We have found that both elements improve the stability of the stoichiometric alloy, but they also increase the crystallization time. It was also found that Ni reduces the thermal barrier for nucleation, but decreases the crystallization rate as well.

Experimental

Ge:Sb:Te films were deposited on unheated fused quartz substrates by the RF-sputtering technique from targets having the same composition that was intended for the films. Samples of the following three compositions were prepared: $Ge_{22}Sb_{22}Te_{56}$, $Ge_{22}Sb_{22}Te_{51}Se_5$, and $Ge_{22}Sb_{22}Te_{51}Se_5$+ +5at. % Ni. The first one of these alloys will be hereafter called the pure alloy. All films were deposited at a rate of about 0.3 nm/sec to a total thickness of 300 nm. The electrical conductivity was measured using the two probe technique. To determine the uniformity of composition, Auger composition depth profiles were measured. The films were heated in nitrogen ambient in a tube furnace at temperatures ranging from 130 to 170°C. The conductivity of these films was measured after various annealing times, i.e., a film an-

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nealed at a temperature T for a period of time t was cooled down to the room temperature for conductivity measurements, and then returned to the furnace for another annealing period at the same temperature. The X-ray diffraction data were obtained with a commercial Rigaku diffractometer employing the K_a radiation line.

Results and Discussion

Figure 1 shows an example of the behavior of the p-type electrical conductivity as a function of the annealing time at 140°C for films of the three compositions studied. In the as-prepared samples, Se reduces and Ni increases the room-temperature conductivity, in comparison to the pure samples. After the thermal treatment, the room-temperature conductivity slightly decreases with annealing time until, at a certain point, it suddenly increases by several orders of magnitude, and then remains approximately constant for longer annealing times. This sudden increase in the conductivity is related to the crystallization of the film. You can see from the figure that undoped $Ge_{22}Sb_{22}Te_{56}$ films crystallize first, followed by those containing 5 at.% Se, while films containing Ni and Se require the longest annealing time to crystallize.

It is also seen in fig. 1 that introduction of Se does not change the shape of the conductivity curve, it only shifts this curve along both axes. This effect could be attributed to a stronger bonding of Se atoms in comparison to Te. Thus, it required a larger thermal energy for nucleation. The stronger bonding of Se can also explain the decrease in conductivity, because stronger bonding means higher ionization energy of acceptor levels for hole conduction.

Incorporation of Ni increases the conductivity of the as-prepared samples and those treated at temperatures before the onset of crystallization. In other words, it increases the conductivity of samples in the amorphous state. After the full crystallization, the conductivity saturates up to a value which is lower than that observed in the fully crystallized pure alloy. This saturation of conductivity is not shown in fig. 1 for the sample containing Ni, because it requires quite long annealing times; however, this behavior is observed for all measurements at higher annealing temperatures. A higher conductivity of the samples in the amorphous state probably indicates that Ni substitutes Ge. If this is indeed the case, Ni atom with a smaller number of valence electrons produces extra holes increasing the p-type conductivity of the amorphous material. During the crystallization, weakly bonded Ni atoms leave the substitutional lattice sites to sit in the interstitial sites where now they can act as donor impurities compensating the acceptor levels and therefore reducing the p-type conductivity. The hole left by Ni probably acts as a nucleation site, because at high temperatures the surrounding bonds would prefer to go into the more stable crystalline phase. As will be discussed later, the number of interstitial atoms is evidently only a small fraction of the total amount incorporated. The remaining atoms are probably responsible for the lower crystallization rate observed in the nickel-doped alloy.

Fig. 2 shows the X-ray data for a $Ge_{22}Sb_{22}Te_{56}$ film before (a) and after (b) thermal crystallization. The pattern corresponding to the as-prepared sample (a) shows broad diffraction lines centered at about 28 and 47 degrees in the 2[theta] scale. This demonstrates the amorphous nature of the as-prepared films. In the pattern (b), the position and relative intensities of the sharper diffraction lines indicate a randomly distributed face centered cubic structure of the crystallized films.

From curves like those in Fig. 1, the crystallization time, t_c, is defined as the annealing time till the onset of crystallization. It was found to depend both on the film composition and on the annealing temperature. As crystallization pro-

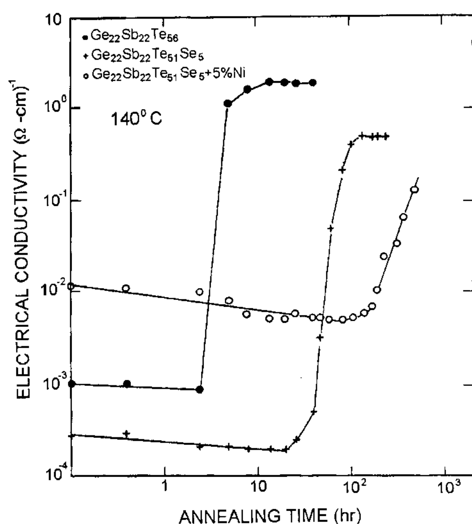

Fig. 1. Electrical conductivity versus annealing time at 140°C for samples of various composition.

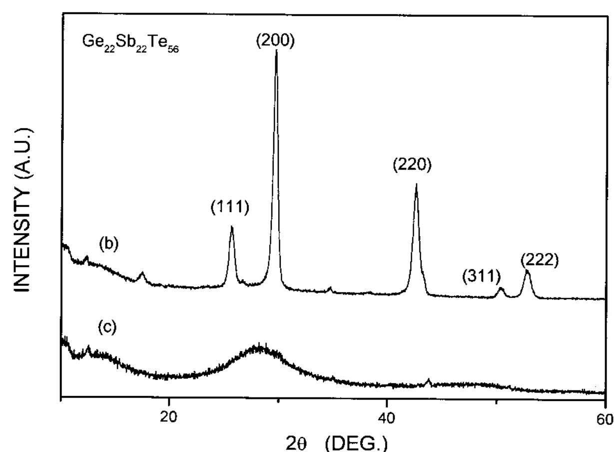

Fig. 2. X-ray diffraction patterns for a $Ge_{22}Sb_{22}Te_{56}$ film: before (a) and after (b) thermal crystallization.

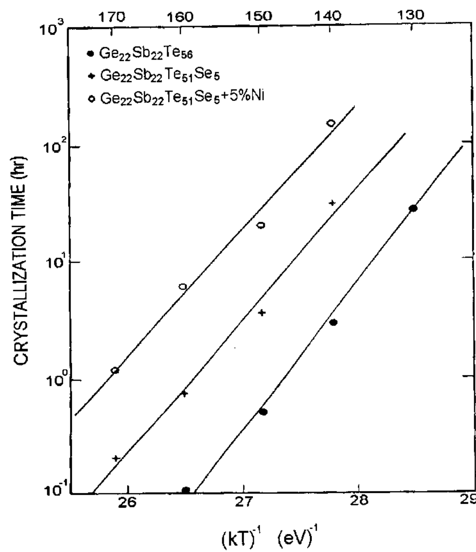

Fig. 3. Arrhenius plot for samples of three different compositions annealed at temperatures ranging from 130 to 170°C.

ceeds through nucleation and growth, its kinetics should be described by the Johnson-Meht-Avrami equation [6]:

$$V_c = 1 - \exp(-kt^n) \tag{1}$$

where

$$k = k_o \exp(-E_a/KT). \tag{2}$$

In eq. (1), V_c is the volume fraction of the crystalline material transformed from the amorphous state at the time t. In eq. (2), k_o is a constant, K – the Boltzmann constant, E_a – the activation energy for the crystallization process, and n is the Avrami exponent related to the time dependence of nucleation and to the dimensionality of growth. For a three-dimensional growth, the expected value for the exponent is between 3 and 5 [6], and values close to 4 have been reported for Ge_xTe_{1-x} alloys [7]. According to eq. (l), the value of n can be derived from the slope of the straight line in the plot of $(\ln(-\ln(I - V_c)))$ vs. $\ln t$. Assuming that V_c is proportional to the conductivity in the range of crystallinity percolation, we have found that the value of n in our samples is close to 4 and does not strongly depend on the composition and annealing temperature.

In fig. 3, the values of t_c for the samples of three compositions annealed at various temperatures are plotted as a function of $(kT)^{-1}$ (Arrhenius plot). The activation energies for each composition calculated by the slopes of the straight lines were as follows: 2.97, 2.65 and 2.43 eV for the $Ge_{22}Sb_{22}Te_{56}$, $Ge_{22}Sb_{22}Te_{51}Se_5$ and $Ge_{22}Sb_{22}Te_{51}Se_5$ + + 5 at. % Ni films, respectively.

These values of the activation energy are close to the bond energies in the same compounds. The activation energy is smallest for the samples containing Ni, which agrees with earlier data indicating that Ni promotes nucleation [5, 8]. A possible mechanism of nucleation has been described in the previous sections of this paper. The fact that the crystallization time is much longer for samples doped with Ni is probably associated with to two factors: first, as mentioned before, Ni incorporated in the substitutional sites of the amorphous lattice is ejected to the interstitial sites, and then most of it diffuses to the crystalline grain interfaces. Atomic diffusion retards the process of crystallization, because it is slow in comparison to the crystallization of amorphous alloys with a stoichiometric composition (in the latter case, the growth after the nucleation is controlled by the attachment of atoms to the growing crystal, which is certainly a quick process). In summary, Ni reduces the thermal barrier for crystallization, thus enhancing nucleation, but due to the slow atomic diffusion mechanism, it slows down the rate of crystallization. The effect of selenium is similar, though less pronounced. In this case, since selenium substitutes tellurium in the stoichiometric crystalline lattice, the increase in the crystallization time could be related to the stronger bonding of selenium, and therefore a higher thermal energy is needed to break these bonds to transform the amorphous network into the crystalline compound.

Acknowledgments

One of the authors (E.G.G.) thanks the support of CONACyT of México, and all authors thank Martin Adelaide for his technical assitance.

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КІНЕТИКА КРИСТАЛІЗАЦІІ $Ge_{22}Sb_{22}Te_{56}$, ЛЕГОВАНОГО Se I Ni

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Вивчено вплив Ni и Se на кінетику кристалізації Ge:Sb:Te сплавів. Виявлено, що обидва елементи підвищують стабільність аморфної структури. Кінетика кристалізації при ізотермічній обробці показує, що Ni зменшує як бар'єр термічної кристалізації, так і швидкість кристалізації. Кристалізація зразків, які містять Se також уповільнена, можливо завдяки більш сильній енергії зв'язку цього елементу в порівнянні з Te.

КИНЕТИКА КРИСТАЛЛИЗАЦИИ $Ge_{22}Sb_{22}Te_{56}$, ЛЕГИРОВАННОГО Se И Ni

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Изучено влияние Ni и Se на кинетику кристаллизации Ge:Sb:Te сплавов. Установлено, что оба элемента повышают стабильность аморфной структуры. Кинетика кристаллизации при изотермической обработке показывает, что Ni уменьшает как барьер термической кристаллизации так и скорость кристаллизации. Кристаллизация образцов, содержащих Se также замедленная, возможно благодаря более сильной энергии связи элемента по сравнению с Te.