Effects of the amorphous structure on the electrical conductivity and the crystallization kinetics of GeTe thin films

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ABSTRACT

By employing room temperature deposition, ion irradiation and laser irradiation we have formed amorphous GeTe films characterized by different resistance values and activation energy for conduction. The crystallization kinetics as a function of the amorphous structure have been investigated. The effect of low temperature pre-annealing treatments has been also studied.
Key words: amorphous stability, electrical conductivity, crystallization

Phase change memories (PCM) are based on the transition from the amorphous to the crystalline phase of chalcogenide materials. In these materials, such as GeTe or GeSbTe alloys, the amorphous phase commonly exhibits resistance variations upon time [1,2]. Defects annihilation model and stress relaxation have been proposed to explain the origin of the observed resistance drift towards higher value [3]. The phenomenon generating the resistance drift is not yet fully understood but it is an important issue for the development of multi-level PCM cells and has also an impact on the device reliability. It is also known that the amorphous phase of chalcogenide materials can be obtained either by deposition at room temperature or by melt quenching, applying a laser or electric pulse to a crystalline material, with intensity and duration so that the material is melted and rapidly quenched into the amorphous phase. A further method to obtain an amorphous film is by heavy ions low energy irradiation. Amorphous films obtained in different ways usually exhibit different characteristics. The study of the stability of different amorphous film may give important insights on the role of the amorphous structure and on the electrical properties and on the crystallization kinetics. In this paper we have studied the electrical properties of GeTe amorphous films obtained by using different methods: deposition, implantation and laser irradiation. The impact of the variation of the electrical properties of the amorphous material on the crystallization has been studied.

Amorphous GeTe films, 35 nm thick, were deposited at room temperature on thermally grown 85nm SiO_2 layers by DC Sputtering. These films were used for preparation of melt quenched and ion irradiated amorphous materials. Melt quenched films were obtained by irradiation with a pulsed (30 ns) Lambda Physik LPX 205 XeCl excimer laser (λ = 308 nm) at an energy density of 110 mJ/cm^2. The laser was equipped with a beam homogenizer, forming a 6x6 mm^2 spot on the sample. Ion irradiation was performed at room temperature using 130 keV Ge^+ ions at fluence of $1x10^{14}$ ions/cm^2 and 20 keV Ge+ ions at fluence of $8x10^{13}$ ions/cm^2. Double implantation at these low and high energies ensures a nearly uniform nuclear energy loss across the layer thickness. The dose and the beam energy were chosen in such a way to reduce the effect of sputtering and then to avoid any appreciable change in the stoichiometry of the film.

Some samples were annealed in furnace at temperatures in the range 80-120°C, at which no crystallization occurs even under annealing up to several hours. The electrical properties of the different amorphous films (as prepared and after pre-annealing) have been studied by resistance measurements as a function of temperature in the range 30-80°C, using a four point probe configuration. From such measurements the activation energy for conduction in the amorphous materials has been evaluated.

Amorphous samples prepared in different ways were then annealed at 150°C or 160 °C in order to convert the film into the crystalline phase. The crystallization process was followed by in situ time resolved reflectivity (TRR) using a 15 mW He-Ne laser probe during annealing, measuring the crystallization time, experimentally defined as the maximum in the first derivative of the reflectivity vs time.

Figure 1 shows the conductivity as a function of reciprocal temperature for all the investigated amorphous materials. Solid symbols represent as prepared samples while open symbols refer to pre-annealed samples. As deposited films are characterized by the lowest conductivity while the highest conduction is observed for the melt quenched amorphous. After the pre-annealing the material is still amorphous, as indicated by reflectivity measurements, and the conductivity is lower for all the amorphous structures, i.e. all the amorphous are not stable and evolves toward a more resistive material. All of the samples exhibit an activated temperature dependence with an activation energy for conduction that can be obtained by linear fit to data shown in fig. 1. The activation energy spans from 0.32 eV, measured in the melt quenched amorphous material, to 0.41 eV (as deposited + pre-annealing at 120°C). These values imply a change in the mobility gap from 0.64 to 0.82 eV, in agreement with optical bandgap measurements as a function of drift [4].

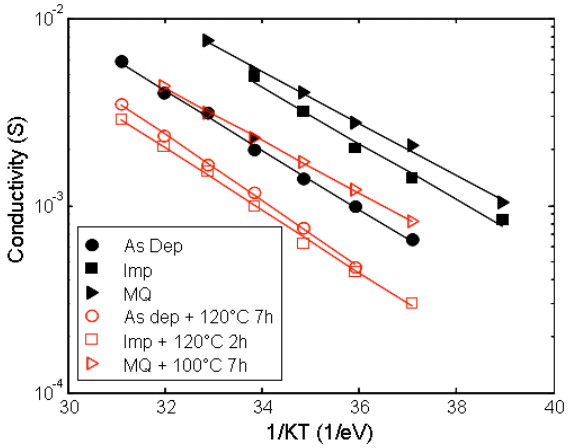

Figure 1: Conductivity as a function of reciprocal temperature for different kinds of amorphous GeTe films. Solid symbols have been obtained in as prepared samples, open symbols are after pre-annealing.

In Figure 2 the measured activation energy for conduction has been plotted as a function of the resistance measured at room temperature. Higher activation energy is obtained for samples with higher resistivity. Amorphous films characterized by different electrical properties also strongly differ in the crystallization time. Figure 3 (a) and (b) shows the reflectivity versus time as measured during annealing for crystallization in as prepared and pre-annealed samples, respectively.

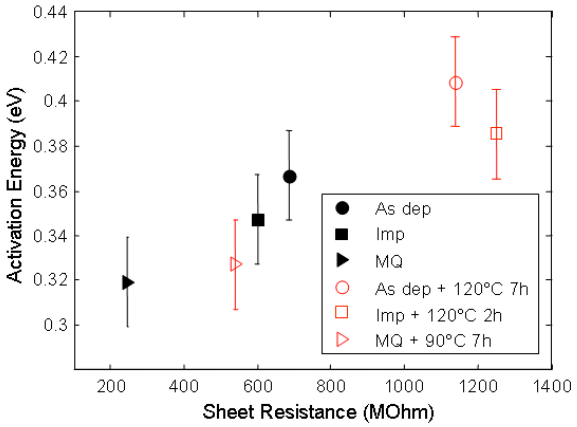

Figure 2: Activation energy for conduction as a function of sheet resistance measured at room temperature in several amorphous GeTe films.

At the same temperature of 160°C in the melt quenched material the crystallization occurs after about 50 s, while the as deposited film is characterized by much longer crystallization time (2500 s). After the pre-annealing all the samples

shows longer crystallization times. In the case of the melt quenched film, the crystallization has been studied at 150°C, in order to have a more reliable measurements, on the scale of thousands of seconds, comparable with the other samples. Therefore in Fig. 3 (b) for the laser irradiated sample the curve at 150°C without pre-annealing in also shown. It is clear from figure 3 that the pre-annealing treatment is effective in improving the stability of the amorphous phase.

On the base of these results we can conclude that the resistance of phase change amorphous materials and its evolution upon temperature and time appears to be determined by two competing processes. One is the drift towards higher resistance value, governed by defects annihilation and characterized by a small driving force. The competing mechanisms is the crystallization, which produces a decrease of the electrical resistivity, and it is instead characterized by a higher driving force and higher activation energy.

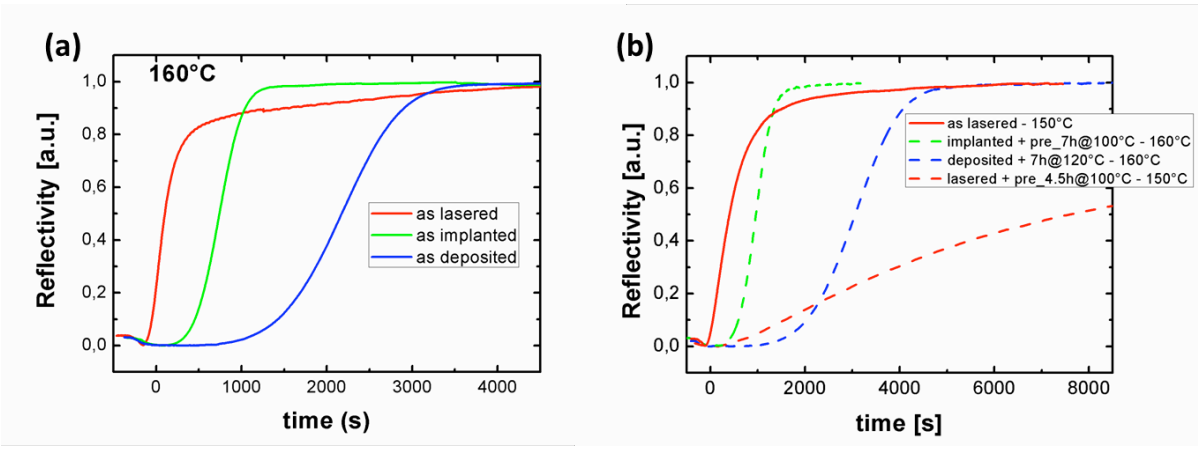

Figure 3: Time resolved reflectivity as a function of time during annealing for crystallization measured in As prepared samples annealed at 160°C (a), and in pre-annealed samples (b). In (b) for the melt quenched material curves obtained at 150°C without and after the pre-annealing are shown.

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Biography

Stefania Privitera received the Master Degree and the Ph.D. degree in Physics from the University of Catania Italy, in 1998 and 2002, respectively.
She was at IMM-CNR and the Physics Department at the University of Catania from 2002 to 2004 as Post Doc, working on phase change materials for non-volatile memories. In 2004 she joined STMicroelectronics, Catania, working in the R&D Department. Since 2011 she is a Staff Research Scientist at the Institute for Microelectronics and Microsystems (IMM) of the National Research Council (CNR), Catania. Her research interests are in the field of the development of semiconductor devices and of electrical and structural characterization of materials for microelectronics. She is author of four international patents and has contributed to 2 book chapters.