

Electrical phase change of Ga:La:S:Cu films

R.E. Simpson, A. Mairaj, R.J. Curry, C.-C. Huang, K. Knight, N. Sessions, M. Hassan and D.W. Hewak

Ga:La:S:Cu films have been prepared by sputter deposition. Amorphous thin films were fabricated with Cu concentrations as high as 66 at.%. The electrical phase change properties of these films have been investigated. The electrical resistivity of these materials is 200 Ωm in the amorphous state and 40 Ωm in the crystalline state. The crystallisation time was measured using an optical pump probe method and confirmed to be 150 ns. The high resistivity of these films in both their crystalline and amorphous states allows low current, Joule, heating and therefore shows potential for the utilisation as the active layer in electrical phase change memory devices.

Introduction: The properties of gallium lanthanum sulphide glasses (Ga:La:S) have been studied for many years owing to their excellent infrared transmission and thermal stability [1, 2]. Initially their low phonon energy has attracted significant interest as a host for near- and mid-infrared emitters with applications in telecommunication and sensing. In addition, their large nonlinear refractive index has also led to investigation of active waveguides, switches and routers [3]. The relative ratios of gallium, lanthanum and sulphur can be controlled to vary the glass transition temperature, crystallisation temperature and viscosity; thus it has been possible to draw optical fibre from this material.

Optical and electrical phase change memories exploit the radical changes in refractive index [4] and electrical resistivity [5] resulting from structural changes in the material. Laser and electrical, Joule, heating in the case of optical and electrical memories, respectively, allow the material to reach the, lower, crystallisation temperature and the, higher, melting temperature. Cooling from these states at a high rate can quench the molten state into an amorphous film or at a slightly slower rate can result in a polycrystalline film. Phase change compositions, which fall along the pseudobinary of Ge_1Te_1 and Sb_2Te_3 , have been applied to rewritable, optical, data storage media [4]. However, the material's applicability to electrical phase change devices is limited by its intrinsically low crystalline resistivity. Thus a large electrical current density is required to switch the material, which has resulted in novel line-type device geometries [6]. In this Letter, for the first time, we report on the phase change properties of Ga:La:S material and discuss its applicability to electrical phase change memories.

Methodology: A high purity $\text{GaS}_{1.4}$ precursor material was synthesised by flowing H_2S gas over a gallium metal (9 N purity) at 965°C for 36 h. To synthesise the La_2S_3 , LaF of 4 N purity was heated to 1250°C to remove water molecules from the crystal structure before sulphurisation in a flowing H_2S atmosphere at 1150°C. The precursor materials $\text{GaS}_{1.4}$ (72.5%), La_2S_3 (21.5%) and La_2O_3 (6%) were melted at 1150°C in a flowing Ar atmosphere for 24 h. The molten mass was then cast in an Ar atmosphere into a 100 mm-diameter circular disc, thus forming a Ga:La:S sputtering target. Cu pieces were attached to the sputtering target to form a Ga:La:S:Cu composite target 100 mm in diameter. An Oxford instruments sputtering system was employed to deposit the films in an argon:oxygen atmosphere with argon:oxygen ratios 10:0, 10:1, 20:1 and 100:1 at a pressure of 5×10^{-3} mbar and an RF power of 100 W. This allowed some degree of oxygen inclusion in the film. The composition of the films was measured by energy dispersive X-ray (EDX) spectroscopy using an Oxford Inca 300 analyser and a JSM 5910 scanning electron microscope.

To test the electrical properties of the material a simple test chip was fabricated on crown glass substrates. The substrate was coated with a 200 nm-thick chromium film. A subsequent coating of photoresist in combination with standard lithographic techniques defined 1 by 1 mm square chromium electrodes. The GLS layer, 200 nm thick, was sputtered on these electrodes before the final 200 nm chromium layer was evaporated. Again, the top layer was outlined by photolithography while a reactive ion beam etch was used to define the top electrode contact area. This dry etch was necessary in order to prevent damage to the chalcogenide layer between the electrodes.

A Keithley 238 electrometer was used to measure the I-V characteristics of the as-deposited Ga:La:S:Cu film in this simple sandwich structure. The film was subjected to 10 ms pulses of increasing voltage and the current was simultaneously monitored.

To measure the crystallisation time of the films, 200 nm-thick films were sputtered onto crown glass substrates. The resultant samples were studied using a dual laser pump probe static tester arrangement [7]. Both pump and probe laser were focused through a 0.65 NA objective onto the films surface. A 658 nm laser diode was electrically modulated by an Avtech pulse generator. The optical power incident on the film was varied between 60 and 130 mW, and the pulse length was controlled between 5 and 400 ns. A second 635 nm diode was used to monitor the optical reflection from the film; the CW power was maintained at 100 μW on the film's surface. The reflected signal was measured using an Si photodetector. Correlated measurements of pulse time, optical power and reflectivity were used to generate a phase transform kinetics (PTK) plot [7].

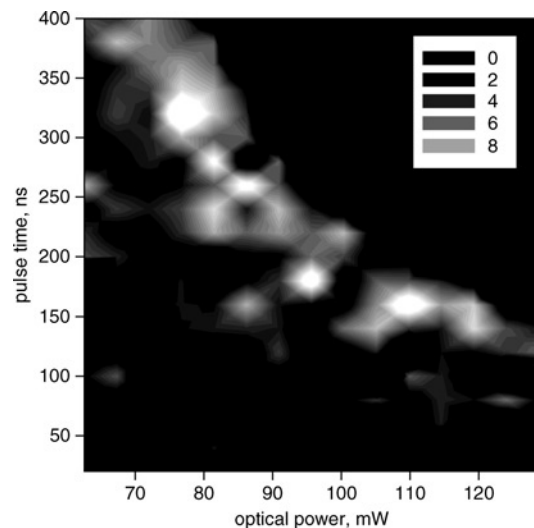


Fig. 1 PTK plot for Ga:La:S:Cu sample

Results and discussion: Ga:La:S:Cu has been successfully sputter deposited as amorphous thin films with Cu concentrations of 66 at.%. An oxygen:argon atmosphere of greater than 1:100 was necessary during deposition in order to achieve amorphous films. Reducing this ratio resulted in polycrystalline films, confirmed by X-ray diffraction. In the case of bulk Ga:La:S glasses it is known that the addition of a small proportion of lanthanum oxide or gallium oxide can act as a network stabiliser and substantially reduce the material susceptibility to crystallisation by increasing the separation of the glass transition and crystallisation temperatures [8]. Similarly in this case, the increased stability against crystallisation during deposition has been attributed to oxygen inclusion into resultant Ga:La:S:Cu film.

Phase change data storage is reliant on the reversible crystalline–amorphous phase transition. It was assumed that the amorphous films deposited in an atmosphere with the lowest concentration of oxygen should be the least stable and therefore have a lower crystallisation activation energy in comparison to films deposited in atmospheres with a greater oxygen content. Fig. 1 shows the PTK plot averaged over three measurements. The x-axis shows optical power incident on the film, the y-axis is the pulse duration and the z-axis shows the reflectivity percentage increase after application of the laser pulse. There is a clear band of crystallisation that extends from 400 ns at 70 mW to below 150 ns at optical powers greater than 110 mW. Reducing the Cu content to 44 at.% increased the minimum crystallisation time to 350 ns. In comparison to the well known optical phase change material $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [4], the powers required are relatively high; this is due to the energy of our pump laser being below the electronic bandgap of the material, and thus the intrinsic absorption is weak. The reflectivity change was measured to be around 8%, which is also small in comparison to that of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, but it is the electrical properties and in particular the Joule heating efficiency that is of interest. These films were found to have a very large electrical resistance in their amorphous state. Fig. 2 shows a typical I–V curve for a film of the same composition sandwiched between two chromium electrodes. The

resistivity of the material in its crystalline state is $40 \Omega\text{m}$ in contrast to the crystalline resistivity of $\text{Ge}_2\text{Sb}_2\text{Te}_5$: $7 \times 10^{-6} \Omega\text{m}$ [6]. The I–V curve in Fig. 2 shows three states of the material: as-deposited, crystallised and melt quenched. The as-deposited material showed a high resistivity until 0.87 V. Increasing the pulsed voltage above this value resulted in a switch to a more conductive state. When the material's I–V measurement is repeated the material displays a low resistivity until 1.25 V, at which point the material switched once again to its high resistivity, initial, state. The changes were stable and could only be altered by application of voltage to the film.

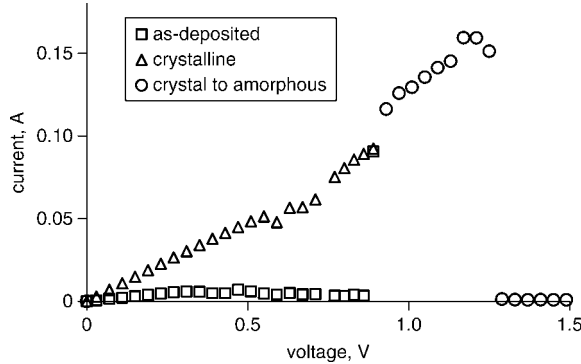


Fig. 2 I–V switching curves for Ga:La:S:Cu sample

Since the crystalline resistivity of Ga:La:S:Cu films is six orders of magnitude greater than that of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, a vast improvement in the heating efficiency of the material is possible. Finite-element modelling (FEM) has revealed that, if such a material was incorporated into a line-type phase change memory device structure, the current required to reset the crystalline volume to amorphous would be around $0.4 \mu\text{A}$: four orders of magnitude improvement on that of a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film. The drive for high data transfer rates means that the 150 ns, intrinsic, crystallisation time of the Ga:La:S:Cu would be the shortest direct overwrite time in such a device. However, this is comparable to the $\text{GeTe-Sb}_2\text{Te}_3$ pseudobinary compositions, which have crystallisation times between 30 and 100 ns [4]. Moreover, the addition of modifiers and dopants provide the potential for reducing the crystallisation time without compromising the low reset currents. The use of such modifiers is the focus of ongoing research.

Conclusions: Ga:La:S:Cu thin films have been successfully sputter deposited and amorphous films with up to 66 at.% Cu are possible by reactive deposition in an oxygen atmosphere. The electrical phase change ability of these films and their application to data storage has

been demonstrated. An optical measurement of the phase transition time has shown that these materials are capable of crystallisation within 150 ns but reducing the Cu content to 44 at.% increased the crystallisation time to 350 ns. The large resistivity and fast crystallisation times of these films make them an ideal choice for low current, electrical, phase change devices.

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