INFLUENCE OF DEPOSITION PARAMETERS ON COMPOSITION AND REFRACTIVE INDEX OF FEMTOSECOND AND NANOSECOND PULSED LASER DEPOSITED GALLIUM LANTHANUM OXYSULPHIDE

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Abstract

The influence of the deposition parameters on femtosecond and nanosecond pulsed laser deposited gallium lanthanum oxysulphide (GLSO) glass has been investigated. A systematic comparison between films deposited by femtosecond and nanosecond pulsed laser deposition (PLD) shows that the compositional range of each regime varies significantly; in particular femtosecond PLD shows a unique potential for selective fabrication of films with high lanthanum content well outside the conventional glass melting region. We demonstrate how manipulation of PLD parameters can influence the stoichiometric transfer of the PLD process, leading to thin films with compositions significantly different from the GLSO target material, and reveal how refractive index of the as-deposited films is dependent upon the composition (and hence deposition parameters). We also briefly discuss the thermal properties of GLSO material for various compositions for applications in data storage device applications

Introduction

Amorphous chalcogenide glass is of great interest for many applications in photonics [1]. Since their initial discovery over 30 years ago [2], gallium lanthanum sulphide (GLS) has provided an attractive non-toxic alternative to As- and Ge-based chalcogenides. The optical and electronic properties of GLS are greatly influenced by the specific elemental composition of the material and the effect of depositions conditions has been shown to influence the optical properties of the deposited films [3]. For many of applications it is necessary to prepare the material in a thin film form. There are many methods that can be used for this, for example spin coating, evaporation of material at low pressures and high temperatures in vacuum, ionic and magnetron sputtering and CVD methods. Many of these methods, in particular sputtering, generally produce films with a stoichiometry that is very close to that of the target and any large deviations are generally not possible [4]. It is essential, therefore, that fundamental studies be carried out to investigate methods of fabricating a range of compositions within the GLSO basic system, so that the properties of interest can be optimised for both current and potential novel applications.

Pulsed laser deposition (PLD) has been used to deposit GLS films for more than a decade [5-7]. Rapid quenching from a molten state is a viable way of synthesising these glasses, and the equivalent fast-quenching of each deposited layer inherent in the PLD technique, induces the film to assume an amorphous phase, which can potentially lead to new amorphous compositions far from the conventional glass-formation region [8].

Sulphide-based phase-change materials have shown potential as the active medium for data storage and devices using a number of physical mechanisms. These include storage of charges within deep levels in the semiconductor bandgap [9], sulphurization of metallic elements in the film [10] and structural phase transitions [11]. GLS materials have proven to be switchable between their crystalline and amorphous phases [12]. The covalent bond strengths of chalcogen atoms is greatest for sulphur and is reduced through selenium and lowest for

tellurium [13], thus allowing a corresponding reduction in the material's glass transition temperature. Electrical phase-change data storage is reliant on the switching ability of the active film, thus the material must be stable in its crystalline form and also have good glass-forming abilities. Historically telluride materials are chosen [14] since they were first used to demonstrate threshold switching in the late 1960's. In addition they are good glass formers and have a lower glass transition temperature than sulphides and selenides [13]. However, as one moves down the periodic table from sulphur to tellurium, the atomic bonds become more metallic and isotropic, the energy gap decreases and electro-negativities decrease resulting in a material with higher electrical conductivity. Phase-change materials with lower electrical resistivity in their crystalline phase are desirable since the electrical current required to joule heat can be lower. This becomes increasingly important as the device dimensions are reduced, since the size of transistors used to address the phase change RAM (PCRAM) cell is also reduced and limits the maximum current that can be supplied to the cell. Hence, the high characteristic temperatures (glass transition temperature, T_g, peak crystallisation temperature, T_p, and melting temperature, T_m) of sulphide and selenide chalcogenides results in comparatively higher joule heating efficiency, and is therefore a drawback for small (<1μm) data storage cells. Since cell dimensions are now sub 100nm in size, such high temperatures are achievable and novel line-type cell designs limit interface reactions and increase the quench rate [15]. With this in mind, GLS material is proposed as a promising phase change material.

We present compositional analysis of the $(GaLaS)_xO_{1-x}$ system for both nanosecond and femtosecond PLD regimes, and show that the elemental ratios of Ga, La and S can be controlled by the careful selection of the deposition parameters. We discuss the effect of the Ga:La ratio on the thermal properties of bulk GLSO and show that the choice of deposition method (femtosecond PLD or nanosecond PLD) can play an important role in affecting the compositions of the deposited films.

Experimental

Both nanosecond and femtosecond PLD experiments were conducted in the same vacuum chamber with an argon ambient gas pressure ranging between $2x10^{-4}$mbar and $2x10^{-1}$mbar. The target was rotated spirographically in order to increase the usable target area during a deposition run. For the femtosecond PLD experiments, a Ti:sapphire laser was used to ablate the target material with 130 fs pulses at a wavelength of 800nm operating at a repetition rate of 1kHz. The fluence was varied by adjusting the position of a focussing lens to alter the incident spot-size on the target's surface. The spot-size itself was measured using the knife-edge technique. All depositions were conducted for a duration of 5 minutes and all films were deposited at room temperature. The nanosecond PLD experiments were conducted in the same vacuum chamber using a frequency-quadrupled Nd:YAG laser (λ = 266 nm) with a repetition rate of 10 Hz. GLSO was deposited on silicon, CaF_2 and quartz substrates under both regimes. To investigate the effect of off-axis deposition on the stoichiometry of the film, a larger Si substrate (~8 cm x 1 cm) was used.

The target material was made using a high purity $GaS_{1.4}$ precursor material, which was synthesized by flowing H_2S gas over a gallium metal (9N purity) at 965 °C for 36 hours. To synthesize the La_2S_3, LaF of 4N purity was heated to 1250 °C to remove water molecules from the crystal structure before sulphurization in a flowing H_2S atmosphere at 1150 °C. The precursor materials $72.5GaS_{1.4}$ - $21.5La_2S_3$ - $6La_2O_3$ (molar %) were batched into vitreous carbon crucibles under nitrogen. Each glassy target was formed by melting the load inside the crucibles at 1150 °C in a flowing argon atmosphere for 24 hours and then quenching in a water-cooled jacket. In order to remove stresses from the targets, the resultant glass was then annealed for 6 hours at 550 °C before cutting and polishing to an optically flat surface.

The compositions of the samples were determined by a scanning electron microscope (LEO 1455VP SEM) to which an energy dispersive X-ray analyser (EDAX) was attached (Oxford

Inca 300). Compositional measurements for each sample were taken at the centre of the film. For analysis of off-axis deposition, measurements were taken over a range of distances along the surface of the film up to 2 cm away from the centre. An X-ray diffractometer (Siemens D5000) was used to investigate the crystallinity of the films. Film thicknesses were determined using a surface profiler (KLA Tencor P-16).

Results and discussion

A. Crystallisation properties of GLSO for various compositions of bulk glass studied

Figure 1 shows the measured glass transition temperature, T_g, peak crystallisation temperature, T_p, and melting temperature, T_m as a function of the Ga:La ratio. One should notice that the melting temperature is largely insensitive to any composition change, unlike the glass transition and crystallisation temperatures. Increasing the proportion of gallium reduces (T_m-T_p) and reduces T_g. A small separation of T_m and T_p is indicative of a material which crystallises with a low viscosity [16]. This is confirmed by figure 2, which shows the viscosity of the material as a function of Ga:La ratio at 640 °C (this temperature is approximately halfway between the T_g and T_p for most of the compositions studied). One should notice that viscosity is extremely sensitive to the Ga:La concentration and increasing the ratio from 1.5:1 to 3:1 reduces the viscosity by roughly two orders of magnitude. The crystallization temperature dependence on heating rate was measured and Kissinger analysis [17] was performed to make an estimation of the crystallization activation energy. For a bulk material of $65GaS_{1.4}$, $29La_2S_3$ and $6La_2O_3$ (atomic percentages) the activation energy was 2.74 eV. As expected this is slightly higher than telluride based films, and as such the materials show promise of higher stability and lifetime The crystal growth rate is clearly of great importance in phase-change data storage since it can dictate the time taken to crystallise a previously written data bit and hence could limit the data transfer rate. The crystal growth rate is dependant on the atomic mobility and has an indirect dependence on $1/\eta$, hence materials which have a high concentration of gallium are of interest for fast crystallising phase-change materials [18]. In contrast to high crystallisation rate at elevated temperatures,

the material's crystallisation rate at operating temperatures should ideally be zero. The glass transition temperature can be considered the minimum temperature at which crystallisation can occur [13], and therefore materials with a high T_g are also sought. Figure 1 shows that the highest T_g compositions also have the highest lanthanum content. However, since the glass transition temperature of these materials is very high in comparison to other well-known data storage materials [13], the materials are expected to have superior archival properties.

B. Compositional engineering by deposition parameter manipulation.

Figure 3 shows compositional data points (normalized ratios of gallium, lanthanum and sulphur)) for nanosecond and femtosecond PLD grown films (0.2 μm – 2.5 μm thick), in comparison to elemental ratios for conventional melting (shaded area) [8]. Films were deposited over a broad range of deposition conditions. The results indicate that both femtosecond and nanosecond PLD films have compositions that range well outside the conventional glass-formation region [2]. A notable point here is that the nanosecond PLD films all have a roughly constant gallium percentage, whereas the femtosecond PLD films occupy a broader region of the ternary diagram that includes compositions that are richer in lanthanum.

The Ga:La ratios of the films (0.5 μm – 1.5 μm thick) deposited by nanosecond PLD for various fluences, target-substrate distances and pressures are shown in figure 4. We can see that all the films have a lower Ga:La ratio than the target material (33Ga - 11La - 56S). Of all the parameters we have changed, background pressure has the greatest effect on the films stoichiometry, reducing the pressure by three orders of magnitude results in reduced Ga:La ratio by 44%. The higher pressures resulted in a film stoichiometry that is higher in lanthanum content and lower in sulphur (the fraction of gallium appears to be relatively unaffected by any pressure variation). The effect of target-substrate distance on the film's stoichiometry shows a similar correlation, affecting the composition along a line of roughly constant gallium. At closer target-substrate distances the film composition more closely

follows the target stoichiometry. Composition did not appear to vary significantly (Ga:La ratio varies by <10%) for any of the fluences investigated (0.6 J/cm^2 to 2.4 J/cm^2).

For films deposited by femtosecond PLD, a target with a composition of 20Ga-20La-60S (atomic percentages) was used since it was desirable to deposit films with a high lanthanum content for archival data storage applications (the glass transition temperature has been shown to increase for materials high in lanthanum [16]). The Ga:La ratios of the films (0.2 μm – 2.5 μm thick) deposited by femtosecond PLD for various fluences, target-substrate distances and pressures are shown in figure 5, with normalised compositional ratio data points plotted on a ternary diagram in the inset. The effect of ambient gas pressure was again the most influential parameter on the film's composition, reducing the Ga:La ratio by ~50% when the pressure was reduced from $2x10^{-4}$ to $5x10^{-2}$mbar. Contrary to the nanosecond deposited films, pressure change did not affect the film's composition along a line of constant gallium; instead the lanthanum content was affected to a greater extent, resulting in films higher in lanthanum for films deposited under higher pressure environments. Similar to the nanosecond PLD experiments, closer target-substrate distances resulted in film compositions more closely comparable to the target material.

C. Compositional engineering by off-axis growth geometry PLD.

The effect of off-axis deposition on the composition of the film deposited by femtosecond and nanosecond is shown in figure 6. Measurements were taken along a distance of 11 mm from the centre of the film (corresponding to the centre of the plasma plume incident upon the substrate). These results reveal the differences in the nature of the non-stoichiometric transfer of femtosecond and nanosecond PLD for off-axis deposition geometries. A notable observation here is the atomic percentage of lanthanum at various distances along the substrate. For the femtosecond PLD, the film's gallium content decreases and film material becomes considerably richer in lanthanum at distances further away from the centre of the film. The composition of the femtosecond PLD film is effected along a line of roughly

constant (±2%) sulphur. However, for nanosecond PLD, the film material deposited at higher off-axis geometries is increasingly deficient in sulphur, while the lanthanum and gallium content remains relatively (±5%) constant.

D. Refractive index of GLSO films for various compositions

The refractive index of the films was calculated from the single transmission technique measurements [19]; that is refractive index dispersion can be measured by interpolating along the upper and lower interference fringes which occur due to multiple reflections at the interfaces of transparent media. The refractive index is calculated according to equation 1 [19]. This technique was chosen over ellipsometry due to the film's low absorption in the visible spectrum. Although it is normal to measure transparent films, an accurate measurement of the film depth at the analysis point is required. Since the film's depth profile is non-uniform, the single transmission measurement, which can be performed without the additional knowledge of depth, allows measurement of refractive index free from the introduction of additional error sources.

Equation 1

$$n = \sqrt{N^2 \sqrt{N^2 + s^2}},$$

where $N = 2s\frac{T_M(\lambda) - T_m(\lambda)}{T_M(\lambda)T_m(\lambda)} + \frac{s^2(\lambda)+1}{2}$, $s(\lambda)$ is the refractive index of the substrate and can be calculated according to $s(\lambda) = \frac{1}{T_s^2(\lambda)} + \sqrt{\frac{1}{T_s^2(\lambda)} - 1}$, T_s^2 is the transmission of the substrate, T_M is the maxima interpolated transmission value, T_m is the minima interpolated transmission value. The dispersion accuracy of this method is determined by the

interpolation. If the frequency of peaks is high, the accuracy is also high and is said to be within ± 1 nm. The maximum absolute accuracy of T_M and T_m is ± 0.001.

The refractive index of the films at 1.5 μm has been mapped against corresponding EDX composition measurements and the resultant ternary plot is given in figure 7. The measurements show a gradual increase in refractive index with decreasing lanthanum content. Refractive index measurements GLS glass films deposited by PLD have show that the refractive index, n, increases as fluence is increased [3].

Conclusions

Pulsed laser deposition has shown itself to be a particularly useful deposition method for the fabrication of gallium lanthanum sulphide films with a wide range of compositions. The influence of the deposition parameters on the composition of deposited films is a useful means for engineering film compositions to a tailored application. Femtosecond PLD has shown itself to be a highly non-stoichiometric deposition method, with film compositions containing over three times more lanthanum (normalised elemental ratio) than the target material. We can conclude that for fabrication of films with high lanthanum content, off-axis geometries by femtosecond PLD is preferred. We have also shown how the refractive indices of the as-deposited GLSO films is dependent on the composition (and hence deposition parameters). This opens up the possibly of engineering the refractive index of GLSO film material for a desired applications. Also, crystallisation studies of bulk GLS material have shown how the thermal properties are dependent on the composition, which leads to the potential of fabricating compositions of GLSO film material that is optimum for data storage applications. The compositions we have engineered are well-away from the conventional glass-formation region for GLSO [8], and as such, we believe are previously unexplored for optical or data storage devices. Further analysis of the thermal and optical properties of these films may reveal them to hold superior properties for a range of applications.

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Figures

Figure 1: Measurements of glass transition (T_g) peak crystallization (T_p) and melting temperatures (T_m) as a function of Ga:La ratio.

Figure 2: Viscosity of bulk GLSO as a function of Ga:La ratio.

Figure 3: Composition of films fabricated by femtosecond PLD (cross), nanosecond PLD (diamond). The target composition is also shown (circle). The nanosecond PLD films were deposited with a range of pressures (10^{-1} – 10^{-4}mbar), target-substrate distances (2 – 6 cm) and fluences (2.4 – 0.6 J/cm^2). Femtosecond films where deposited under a range a pressures only ($5x10^{-1}$ – $5x10^{-4}$ mbar).

Figure 4: Effect of varying a) fluence with constant pressure ($2x10^{-4}$ mbar) and distance (4 cm), b) target-substrate distance with constant pressure ($4x10^{-4}$ mbar) and fluence (1.8 J/cm^2) and c) pressure with constant fluence (1.8 J/cm^2) and distance (4cm) on Ga:La ratio of the films deposition by nanosecond PLD with the elemental ratios of Ga, La and S plotted on a ternary diagram (inset).

Figure 5: Effect of varying a) fluence for constant pressure ($5x10^{-4}$ mbar) and distance (3 cm), b) target-substrate distance for constant pressure ($5x10^{-4}$ mbar) and fluence (1.5 J/cm^2) and c) pressure for constant fluence (1.5 J/cm^2) and distance (3cm) on composition of the films deposited by femtosecond PLD with the elemental ratios of Ga, La and S plotted on a ternary diagram (inset).

Figure 6: The elemental percentages of Ga, La and S as a function of distance along the substrate from the centre of the film as measured by EDAX for a) femtosecond PLD and b) nanosecond PLD, and elemental percentages for a) femtosecond and b) nanosecond PLD

plotted on a ternary diagram, with deposition parameters: pressure $5x10^{-4}$ mbar, target-substrate distance 2.5 cm, fluence 2.0 J/cm^2 (femtosecond PLD) and 1.8J/cm^2 (nanosecond PLD).

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Figure 1

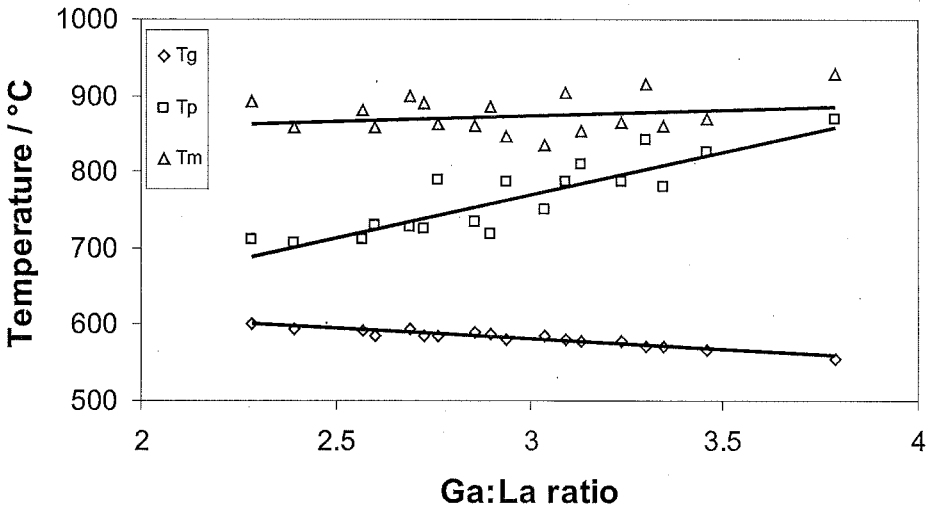

1000
900
800
700
600
500
Temperature / °C
Tg
Tp
Tm
2
2.5
3
3.5
4
Ga:La ratio

Figure 2

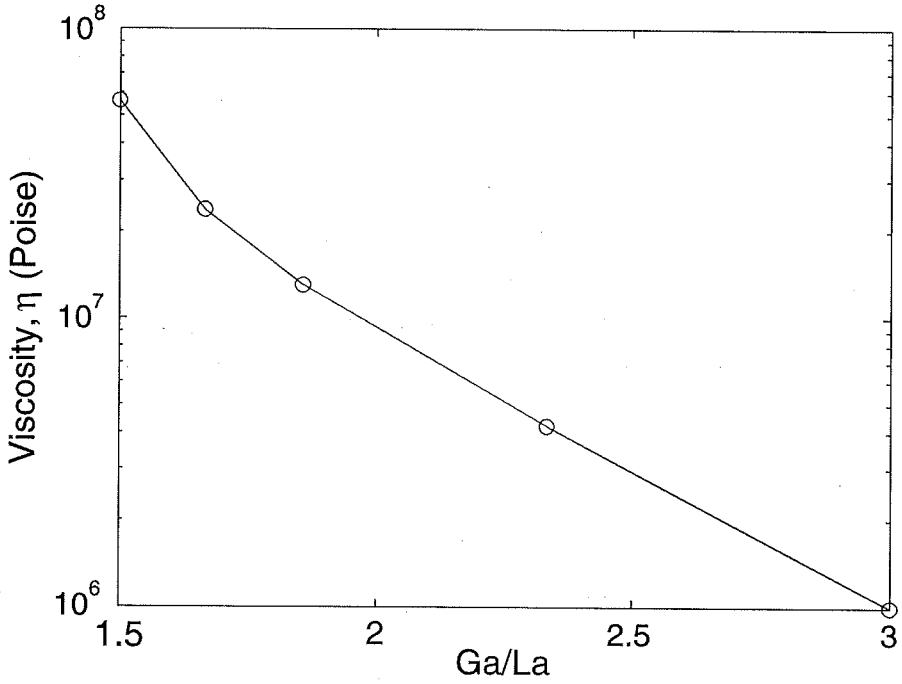


Figure 3
Click here to download high resolution image

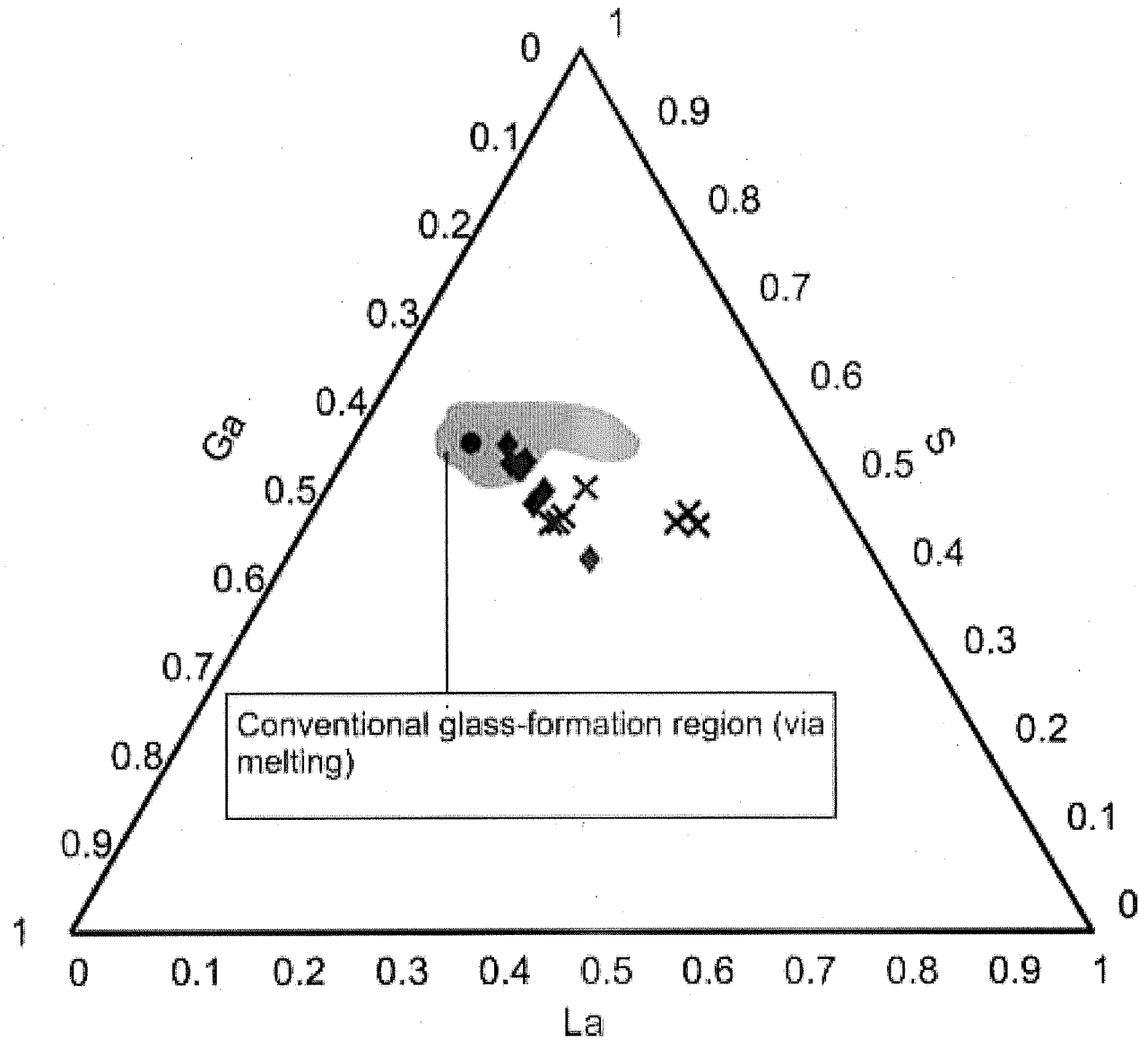


Figure 4

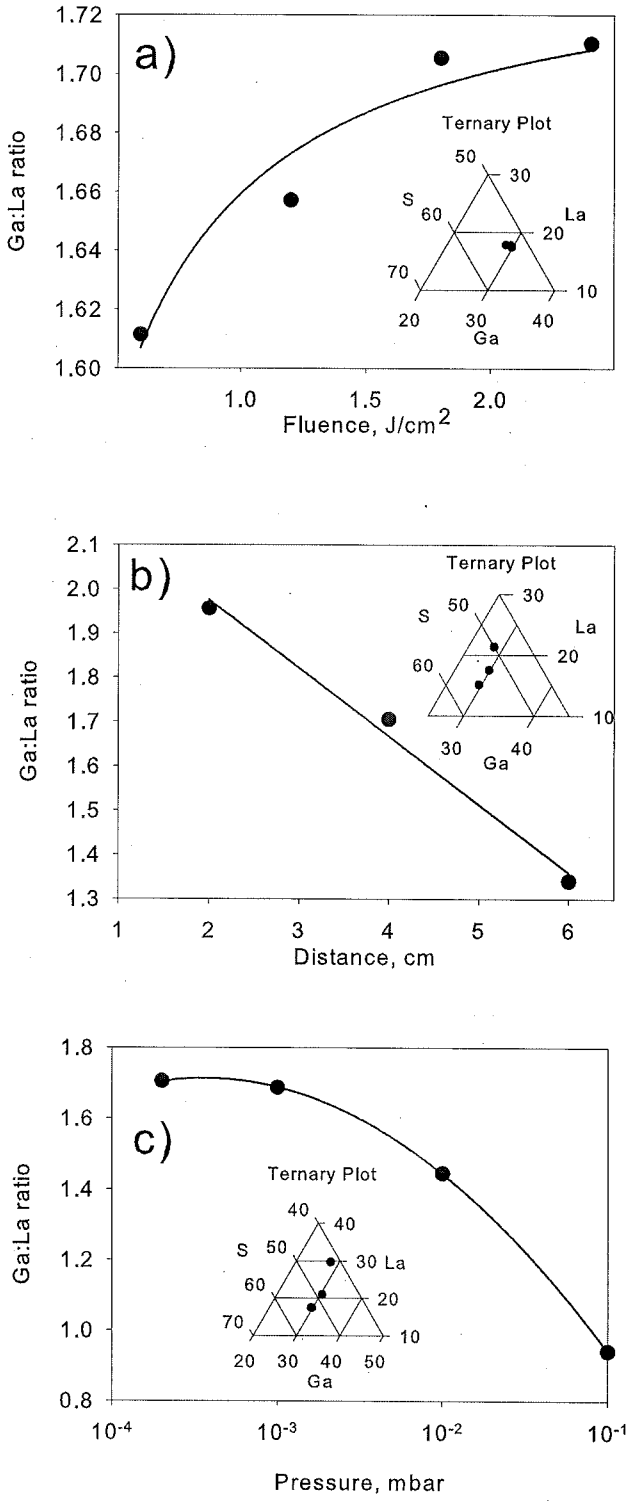

a)
Ga:La ratio
1.72
1.70
1.68
1.66
1.64
1.62
1.60
1.0
1.5
2.0
Fluence, J/cm2
Ternary Plot
50
30
S
60
La
20
70
10
20
30
40
Ga
b)
Ga:La ratio
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1
2
3
4
5
6
Distance, cm
Ternary Plot
S
50
30
La
60
20
10
30
40
Ga
c)
Ga:La ratio
1.8
1.6
1.4
1.2
1.0
0.8
10-4
10-3
10-2
10-1
Pressure, mbar
Ternary Plot
40
40
S
50
30 La
60
20
70
10
20
30
40
50
Ga

Figure 5

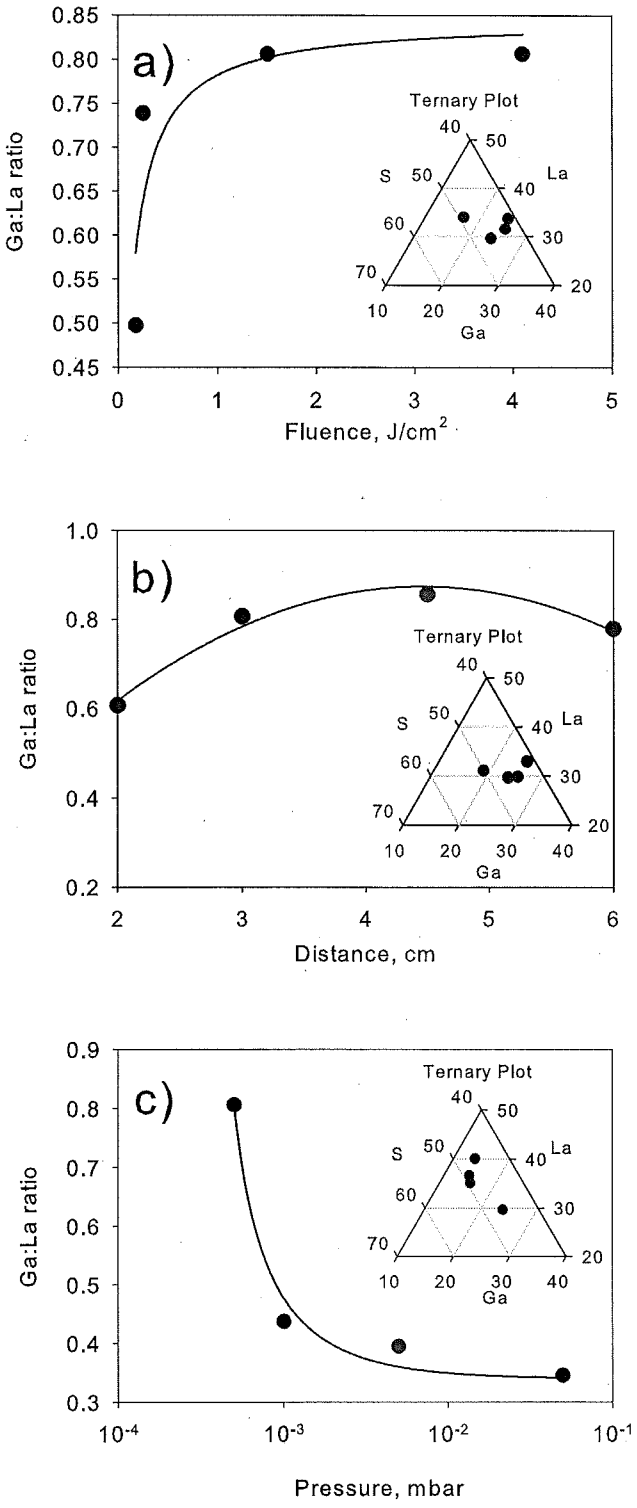
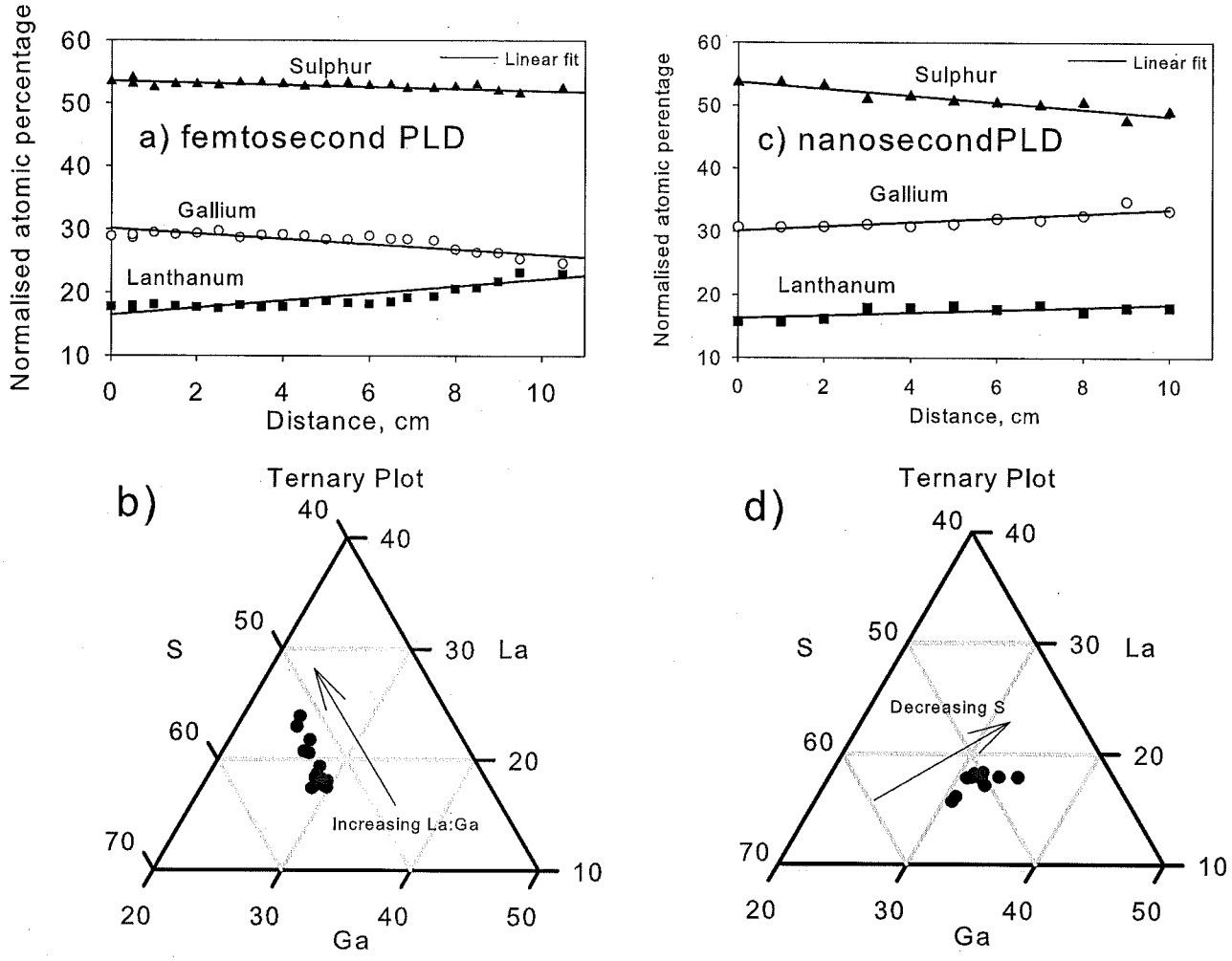

a)
Ga:La ratio
Fluence, J/cm^2
Ternary Plot
S
La
Ga
b)
Ga:La ratio
Distance, cm
Ternary Plot
S
La
Ga
c)
Ga:La ratio
Pressure, mbar
Ternary Plot
S
La
Ga

Figure 6


a) femtosecond PLD
Sulphur
Linear fit
Gallium
Lanthanum
Normalised atomic percentage
Distance, cm
c) nanosecondPLD
Sulphur
Linear fit
Gallium
Lanthanum
Normalised atomic perentage
Distance, cm
b)
Ternary Plot
S
La
Ga
Increasing La:Ga
d)
Ternary Plot
S
La
Ga
Decreasing S