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LASER INDUCED PHONONS (LIPS) IN MBE GROWN ZnSe

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TITLE: LASER INDUCED PHONONS (LIPS) IN MBE GROWN ZnSe

AUTHOR: KEVIN WELFORD

DATE: OCTOBER 1991

SUMMARY

Thin film ZnSe, grown by the MBE method, has been examined using the technique of degenerate four wave mixing, DFWM, using laser illumination at 532nm. Laser induced phonons are observed in this thin film material but are not seen in a sample of bulk polycrystalline ZnSe. This observation of laser induced phonons is the first reported in ZnSe.

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INTRODUCTION

Sample of MBE grown ZnSe were prepared at RSRE. Three different samples were made, each onto a glass substrate, and each having a nominal thickness of 5μm. Growth at different substrate temperatures results in different thin film microstructure. The ZnSe grows in columns, orientated with the ‹110› axis perpendicular to the plane of the substrate, but with the crystallographic orientation of the columns randomised. The effect is a 1-D crystal with disorder in the plane, the size of the crystallite being a function of the substrate temperature during growth. At low substrate temperatures the ZnSe grows with crystallites ≈250Å in diameter, whereas at high substrate temperatures the ZnSe grows with larger crystallites, ~1000Å, and has an increase in the density of stacking faults(1). For the work described here the three samples were grown with substrate temperatures of 25°C, 100°C, and 300°C.

The degenerate four wave mixing measurements were performed at CREOL, Florida, USA, using a frequency doubled Nd^+:YAG laser in the green, at 532nm, with a pulse length of 30ps.

LASER INDUCED PHONONS - LIPS

If two optical pulses are arranged to arrive, at an angle to one another, at the surface of a material in temporal and spatial coincidence, an optical intensity interference pattern results. The period of the interference pattern being governed by the optical wavelength and the angle between the two propagation directions. Within the material the optical intensity is spatially modulated. Where the intensity is greatest the material is more strongly excited and where optical interference results in complete cancellation the material is not excited. Generation of electron-hole pairs occurs where the optical intensity is highest. Various energy relaxation routes can follow. Either the carriers can diffuse to regions of low excitation, if the recombination time is sufficiently long, eventually decaying via a radiative or non-radiative route, generating thermal excitation. Under some circumstances the recombination time can be extremely short so that no diffusion of the carriers results. The generation of phonons in a spatially confined region during a temporally short period causes a coherent sequence of phonon pulses to be excited. These phonon pulses are the laser induced phonons or LIPS. This is an extremely unusual situation in solid materials, more usually observed in liquid systems(2).

DETECTING LIPS

Provided the formation of the phonon population is fast compared with their propagation velocity, a pulse of phonons will be generated in the high intensity optical regions. If either the duration of the optical excitation or the lifetime of the carriers is too long a broad phonon creation envelope will result. Although strictly still LIPS they will not be able to manifest themselves in a manner that is necessary for optical detection, and are thus not referred to as LIPS.

The rapid generation of phonons results in a local reduction of material density in the high optical intensity regions, and an increase in local density in the regions of low optical density. A spatial variation in refractive index is thus created which can cause diffraction in a third optical pulse incident upon the refractive index grating. Once the density profile is coherently established in the material, relaxation drives counterpropagating density waves. Because each low density region relaxes in phase, recreation of diffraction grating occurs each time the counterpropagating waves become coincident. This time evolution of the diffraction grating can be monitored by measuring the diffraction efficiency of the third optical pulse.

EXPERIMENTATION

The optical technique of degenerate four wave mixing (DFWM) is well established. A pulse of light is twice split using appropriate beam splitters to produce two equally intense optical pulses and a third much less intense pulse used as the probe pulse. The two excitation pulses are arranged to arrive at the sample in temporal and spatial coincidence. In this particular arrangement the excite pulses are incident on the sample from the same side. An alternative could be for the excite pulses to be counter propagating. If the angle between the two excite pulses is θ the spatial period of the refractive grating generated by the phonons will be;

$$d = \lambda/(2\mathrm{Sin}(\theta/2)) \qquad (1)$$

where λ is the wavelength of the incident light. The third optical pulse, used to probe the dynamics of the grating, arrives from the opposite side of the sample and is diffracted back along one of the excite pulse directions, see Figure 1. Delay of the probe pulse, with respect to the excitation pulses is achieved by mechanically controlling an additional path length. Monitoring the diffraction efficiency as a function of time delay of the probe pulse reveals the temporal properties of the grating and the existence of LIPS.

RESULT - THE DIFFRACTED SIGNAL

If the LIPS are present the diffraction efficiency will show oscillations in time that correspond to the time it takes for the density wave to propagate across one grating period. By altering the grating period a check can be made that the LIPS are present. The oscillation period should alter by a proportionate amount.

Illustrated in Figure 2 are the diffraction efficiencies for two grating periods, measured in the same ZnSe material. Reducing the angle between the two excitation pulses causes the grating period to extend and hence the expectation is that the oscillation period of the diffraction efficiency should also increase. This is in accord with the experimental results. From equation 1, the phonon propagation velocity can be calculated using the oscillation periods extracted from the DFWM experiment.

$$V(\theta = 4.6) = \frac{d_1}{\tau_1} = \frac{6.77\mu m}{1.65ns} = 4100 ms^{-1}$$

and

$$V(\theta = 11.9) = \frac{d_2}{\tau_2} = \frac{2.57\mu m}{0.6ns} = 4300 ms^{-1}$$

These two measurements strongly indicate the presence of LIPS for two reasons;

(1) Altering the grating period results in the oscillation period of the diffraction efficiency to scale appropriately. The implied velocity remains constant.

(2) The implied velocity is in very good agreement with the phonon velocity for bulk ZnSe.

If the only relaxation process within the material were rapid phonon generation and lattice expansion it might have been expected that the oscillation amplitude of the diffraction efficiency would have been more well defined. From Figure 2 it is clear that even when the density wave is in mid cycle, and hence the refractive index within the material would be expected to be uniform, there is still a substantial diffraction efficiency. There seems to be two processes going on together. One which creates fast phonon generation, resulting in LIPS, and a second that preserves the induced refractive index grating, decaying over a much longer, nanosecond, time scales. This may be related to the thermal properties of the underlying glass substrate, and the decay rate may be indicative of the thermal diffusion properties of the glass. Further work is required.

RESULT - THE EFFECT OF SAMPLE MICROSTRUCTURE

If the microstructure is altered, by growing the thin films at different substrate temperatures, a range of effects on the optical properties might be conjectured.

Once the carriers are excited by the optical pulses their recombination time might be affected by the dimensions of the crystal. Trapping of carriers at grain boundaries could reduce the recombination time over that of the crystalline material. With the crystallites varying in size, depending upon the growth conditions, the recombination time may be affected by the growth condition. These effects, if occurring, will be confined to subpicosecond time scales and will not be directly measurable using the 30ps pulses. Faster recombination may be expected to create a more localised phonon pulse leading to differences in the LIPS signal. Alterations in the oscillation amplitude might result. Measurements performed on three different ZnSe samples, each with different crystallite sizes, do not reveal any significant differences in the LIPS signal. The phonon propagation velocity is preserved as well as the diffraction efficiency oscillation amplitude, see Figure 3. A more detailed investigation of microstructural influence needs to be conducted on shorter time scales.

RESULT - COMPARISON WITH BULK ZnSe

Arranging for the thin film ZnSe to be exchanged for a sample of bulk polycrystalline ZnSe allows a comparison to be made between the two. The difference between the two DFWM signals is notable.

For the bulk ZnSe sample the dissipation of the induced grating is extremely rapid as compared to the thin film sample. Exponential decay of the diffracted signal occurs in as little as 0.15ns, which is roughly two orders of magnitude quicker than for the thin film sample. Consequently, any appearance of LIPS will not be observed. The measurements can be seen in Figure 4. Why the behaviour of these two samples should be so dissimilar is not known, at this stage. One conjecture might be the effect of the glass substrate.

Once the phonon population has been spatially created and the density modulation of the ZnSe lattice established, relaxation along the thin film will be preferred, rather than into the substrate. The density waves counter propagate along the thin film and suffer little decay because the loss of phonons into the substrate is restricted by its inhibited thermal properties. LIPS are thus observed due to the two dimensional nature of the thin film. In the bulk material the situation is different. The generated density fluctuation is now able to relax in three dimensions. The lifetime of the grating is much reduced because the phonons are free to propagate in all directions. What is surprising is that the lifetime should have been reduced

by so much. In a time period of 0.1ns the phonons will only have propagated a distance of 0.4μm and hence it seems surprising that the diffraction efficiency would have reduced by such a distinct amount. This may be evidence for dissimilar relaxation mechanisms in the two types of material.

CONCLUSION

This observation of LIPS is unique in semiconducting materials. A full explanation for why the thin film ZnSe should demonstrate LIPS in this way is incomplete. The technique provides a powerful tool for measuring relaxation processes and phonon properties of thin film ZnSe. These are of potential importance because ZnSe is a favoured material for optical filter fabrication.

ACKNOWLEDGEMENTS

These thin film samples were prepared at RSRE by Prof Lewis, and the measurements were made at CREOL, Florida, USA, with the help of Jiangwei Wang and Profs Miller and Van Stryland.

FIGURE CAPTIONS

Figure 1 Schematic illustration of the arrangement of the three incident optical pulses in the DFWM experiment. The excite pulses generate the interference pattern in the sample and the low intensity probe pulse is temporally delayed and reveals the evolution of the induced refractive grating via its diffraction efficiency.

Figure 2 Diffraction efficiency, normalised signal, from a ZnSe thin film using two different grating periods. The oscillation periods scale to preserve the implied phonon velocity, thus indicating LIPS.

Figure 3 Diffraction efficiency from differently grown ZnSe samples. Evidence for microstructural influence on the optical properties is absent. Each sample appears to behave in a similar manner.

Figure 4 Diffraction efficiency from a thin film and a bulk polycrystalline ZnSe samples. The induced refractive grating decays many times faster in the bulk sample and no evidence of LIPS in seen.

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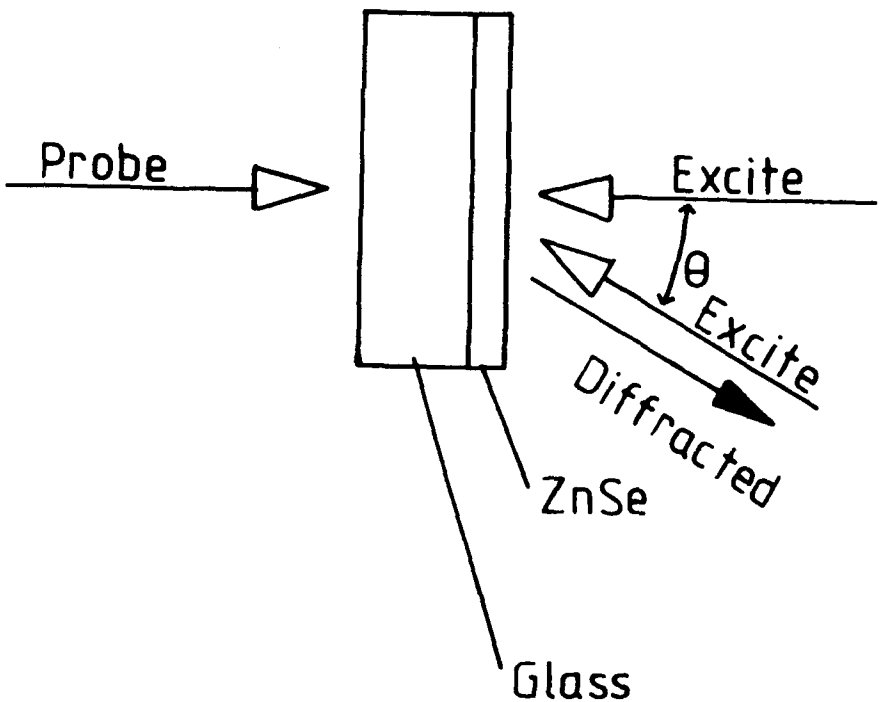


FIGURE 1

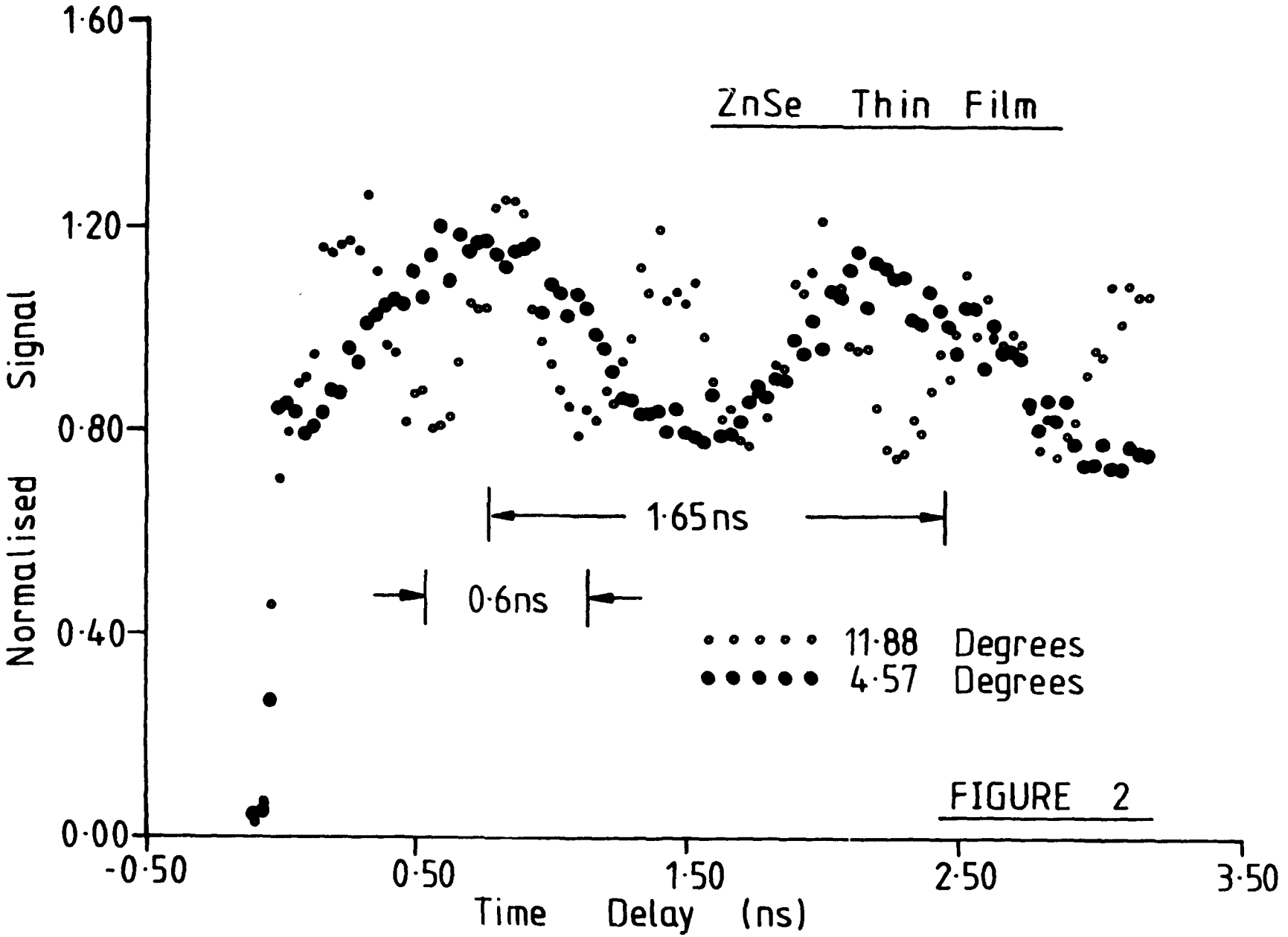

ZnSe Thin Film
1·60
1·20
0·80
0·40
0·00
Normalised Signal
1·65ns
0·6ns
11·88 Degrees
4·57 Degrees
-0·50
0·50
1·50
2·50
3·50
Time Delay (ns)

FIGURE 2

FIGURE 3

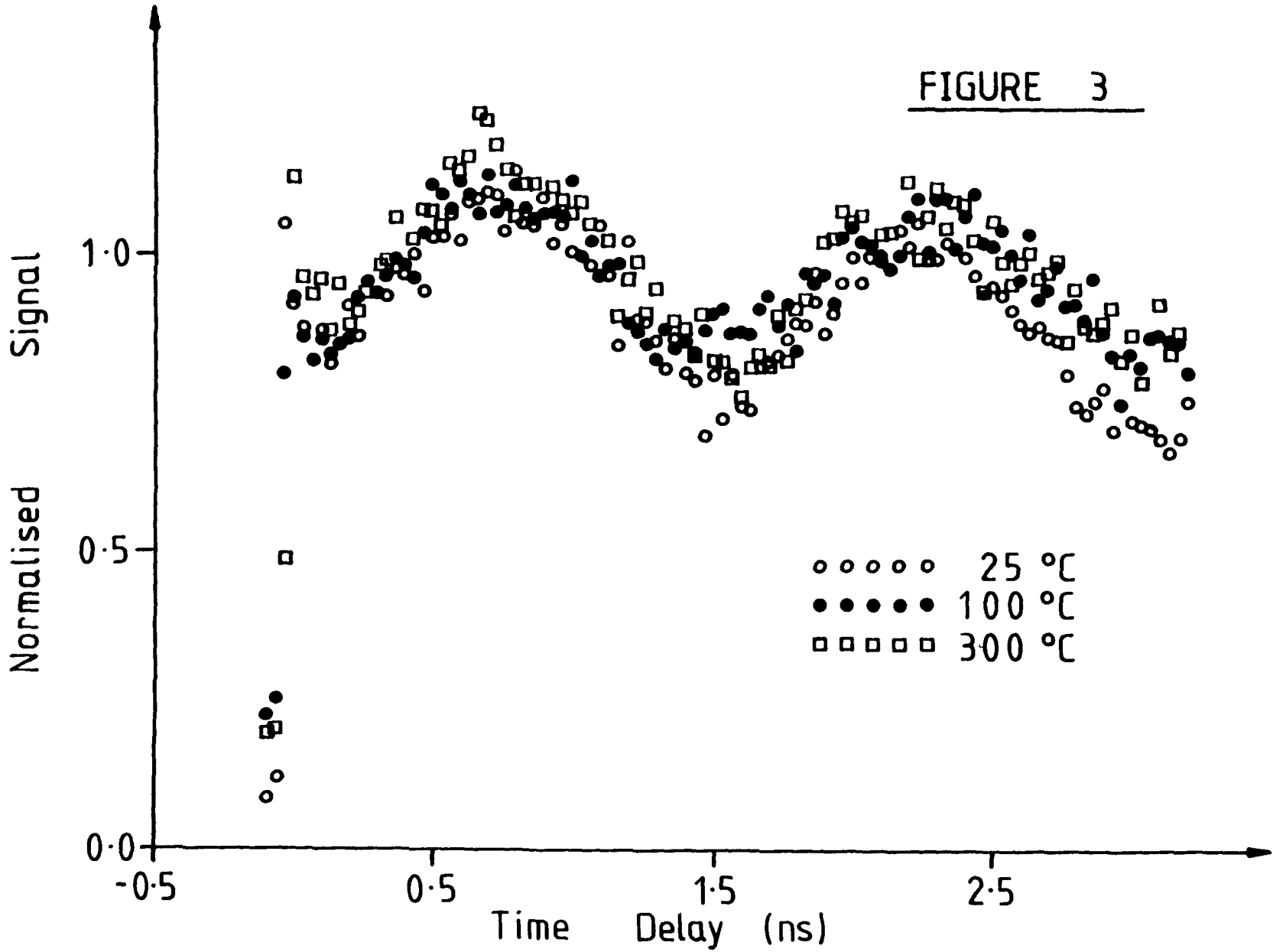
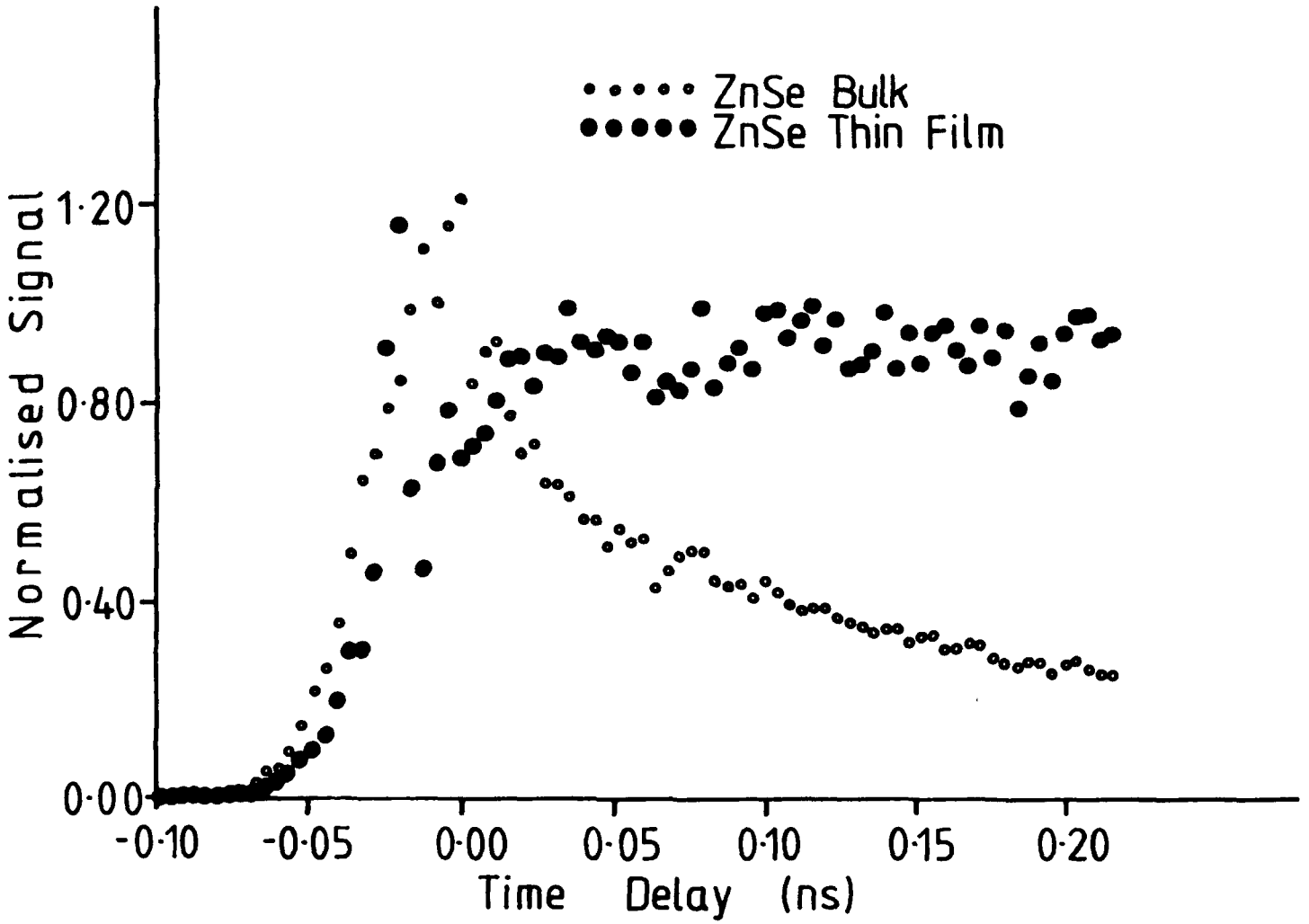

Normalised Signal
1·0
0·5
0·0
-0·5
0·5
1·5
2·5
Time Delay (ns)
25 °C
100 °C
300 °C

FIGURE 4


ZnSe Bulk
ZnSe Thin Film
Normalised Signal
1·20
0·80
0·40
0·00
-0·10
-0·05
0·00
0·05
0·10
0·15
0·20
Time Delay (ns)

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