Epitaxial Growth of High Quality ZnS Films on Sapphire and Silicon by Pulsed Laser Deposition

Zhi-Jun Xin, Richard J Peaty, Harvey N Rutt and Robert W Eason

Optoelectronics Research Centre,

University of Southampton, Highfield, Southampton SO17 1BJ, UK

Abstract

In this letter we report for the first time epitaxial growth of high quality ZnS films on sapphire and silicon substrates, using pulsed laser deposition. X-ray diffraction results show that at all growth temperatures from 200 °C to 680 °C, epitaxial wurtzite (002) ZnS films have been successfully grown on $(10\bar{1}2)$ sapphire and (001) silicon substrates. X-ray diffraction data yields full width at half maximum 2θ values of 0.13° for as-grown samples, compared with 2θ values of 0.09° and 0.08° for the sapphire and silicon substrates respectively.

Zinc sulphide (ZnS) has a wide bandgap of 3.7 eV at room temperature and excellent luminescent properties from the near ultraviolet to mid-infrared spectral regions. High quality amorphous ZnS films have long been widely used in optical component coating and flat-screen solid state displays. More recently crystalline ZnS has aroused enormous interest because of its use in electroluminescent devices, blue or ultraviolet light emitting diodes, laser diodes, tunable mid-infrared lasers [1, 2] and second harmonic generation devices [3].

ZnS thin films can be prepared either by conventional deposition techniques such as evaporation and sputtering, or by epitaxial growth via the techniques of liquid or vapour phase epitaxy, including metalorganic vapour phase epitaxy (MOVPE) and molecular beam epitaxy (MBE). While all these methods can produce optical quality films, crystalline films which are specially useful for optoelectronic applications, require epitaxial growth techniques.

Crystalline ZnS has two crystallographic phases, zinc blende (cubic) and wurtzite (hexagonal): wurtzite transforms to a zinc blende structure at 1020 °C [4]. Wurtzite ZnS also has large non-linear optical coefficients [4]. Because bulk single crystalline ZnS is not available in reasonable size and quality, epitaxial thin films are of particular interest. Problems arise however from lattice matching between crystalline ZnS and commonly available substrates, for example Si [5, 6], GaAs [7, 8], sapphire [9, 10], GaP [11] and Ge.

Table 1 lists the physical parameters [4] of several of the most commonly used substrates for ZnS epitaxial growth, where α represents the wurtzite crystalline structure, β the zinc blende crystalline structure and n the refractive index. As can be seen, in terms of polarity, lattice constant and thermal expansion, none of these substrates provides an ideal match. This limitation has been the major factor affecting ZnS film quality, resulting in the current difficulty in obtaining high quality ZnS epitaxial films. If we

add the further waveguiding condition that the refractive index of substrates must be lower than that of ZnS at the target lasing wavelength of 2.2 μm [1, 2], it appears that sapphire is the only choice, despite a 11.8% and 24.8% lattice mismatch to β and α phase ZnS respectively.

Due to the low growth temperature and low kinetic energy of the transporting molecules in conventional vapour phase epitaxy, single crystalline ZnS grown on various substrates is normally of zinc blende structure [6, 8, 10, 11]. This is also the case for laser ablative growth on (001) and (111) GaAs substrates [7, 12], although polycrystalline ZnS can be obtained on sapphire [9], silicon [13] and glass [14]. However for applications requiring non-linear optical effects [3], single crystal wurtzite ZnS films are required. In this paper we report for the first time high quality wurtzite ZnS films deposited on sapphire using pulsed laser deposition (PLD).

Compared to other epitaxial methods, PLD has advantages [7, 12, 14, 15] in the following aspects. Firstly, it is a carbon-free and purely physical transport process. Secondly, the high power density ($\sim 10^8$ W/cm^2) of pulsed excimer lasers results in the target material ablating in nanoseconds and forming a high flux plasma plume with very high kinetic energy [12]. This is particularly helpful for the vapour phase epitaxial growth of stoichiometric ZnS films on substrates. Furthermore, the depositing molecules with high kinetic energy have high mobilities on the substrates, which allow them to form high quality films at correspondingly lower substrate temperatures than required in alternative deposition techniques. This subsequently results in that the growth is less dependent on the substrate temperature [15]. This is important as in MOVPE or MBE the defect complexes produced at high growth temperatures and premature reaction and nucleation at low growth temperatures are in conflict.

The growth is carried out in an oil free vacuum chamber with a base pressure of $\sim 10^{-7}$ mbar. A pulsed KrF excimer laser is focused to an oval spot (1 mm by 2.5 mm) on a rotating ZnS disc target, made from high purity

polycrystalline ZnS. The distance from the target to the substrate is 5 cm. Because the ablated ZnS plume is highly directional, in order to deposit uniform films over a large area, the substrate is scanned in two dimensions, relative to the target: the heated substrate oscillates vertically, while the ZnS disc target rotation is offset. The excimer laser was operated at a 10 Hz repetition rate, in constant energy mode, with an energy density on the target of ~ 20 J/cm^2. The substrate temperature was varied between room temperature and ~ 800 °C. Substrates were cleaned using solvents followed by H_2SO_4:H_2O_2 = 4:1 solution in a standard cleaning process.

Growth was performed from room temperature up to 680 °C on (001) silicon and $(10\bar{1}2)$ r-plane sapphire substrates, as well as on glass microscope slides. Film thicknesses from 105 nm to 3500 nm have been obtained. Figure 1 shows the measured temperature dependence of growth rates for silicon and sapphire substrates. Growth is easily controlled and optimised by adjusting the laser energy, pulse repetition rate, substrate to target distance and substrate temperature. As can be seen in Figure 1, the dependence of growth rates on substrate temperature from room temperature to 680 °C is not particularly strong and the growth is relatively fast, in comparison with other epitaxial techniques [5, 13, 16]. As we mentioned earlier, this seems attributable to the fact that in PLD the kinetic energy of transporting ZnS molecules is much higher than the substrate thermal energy. The reduction in growth rate near 600 °C suggests an increase of re-sublimation of ZnS from the heated substrates. The errors bars here arise from the thickness change across the samples. This has been greatly improved in the most recent growth runs by realigning the target.

A Siemens D-5000 diffractometer was used to perform x-ray diffraction characterization, using Cu K_{α_1} radiation. The samples used were as-grown on $(10\bar{1}2)$ sapphire or (001) silicon substrates. As can be seen in figure 2, which plots full width at half maximum (FWHM) 2θ values as a function of growth temperature, the ZnS film samples demonstrate crystalline

diffraction peaks with FWHM values varying from 0.13° to 0.20° for sapphire substrates at $T \geq 400$ °C and for silicon at $T \geq 500$ °C. These values are to be compared with those obtained for sapphire and silicon substrates alone, of 0.09° and 0.08° respectively. In contrast, ZnS deposited on glass substrates shows an absence of any discernible diffraction peaks, implying uniform amorphous film growth. The results for ZnS on silicon obtained here can be compared with previously published values. Table 2 compares published results for ZnS films grown by a range of methods with that from this work. We see that our experimental 2θ values are very low, particularly for these as-grown, unannealed films. Our results were further comfirmed by the analysis made at Cranfield University. It used a "texture" camera mapping the two dimentional distribution of X-ray diffractive intensity, rather than a single angular dependence as a conventional X-ray diffractometer does. This can give distinguishable information on crystalline structures.

UV absorption spectra have also been recorded for those samples with sapphire substrates at room temperature. The results are shown in Figure 3. The cut-off wavelength shows a systematic variation with growth temperature. However the exact causes of the shift of the cut-off are not very clear. It is interesting to notice the derivative changes of the absorption coefficients with respect to wavelength at the cut-off against different growth temperatures, as shown in Figure 3. With growth temperature increase, the cut-off edge becomes steeper. This change could result from the nonuniformitity and microscopic defects related to low temperature growth, which is improved at higher temperature. The FWHM plateau appearing temperature of $\sim$ 400 °C in Figure 2 is consistent with that in the inset of Figure 3 which indicates that the growth temperature 400 °C is a turn over point for ZnS crystalline quality in this experiment.

All films grown at substrate temperatures $\geq$ 200 °C have a mirror-like surface finish, even under scanning electronic microscope examination at $\times$15000 magnification. For temperatures $<$ 200 °C however, the surface is

slightly rough. The curve on the top in Figure 4 shows the surface roughness of a ZnS sample grown on a sapphire substrate at 200 °C along a line of 50 μm obtained from an atomic force microscope scan. It is compared with the lower curve representing the roughness from a sapphire substrate used in this work which has epitaxial surface quality. Figure 5 shows mode coupling spectra for two films obtained using a commercial prism coupling set-up (Metricon 2010, USA), for TE modes at an excitation wavelength of 633 nm. The sharp modes show that high optical quality films have been achieved. The refractive index value was measured as 2.35, which agrees well with the bulk literature value of 2.35 (the index of the zinc blende and wurtzite phases are almost the same at 633 nm).

In conclusion, we have epitaxially grown high quality ZnS films on sapphire and silicon substrates. The films are of wurtzite and (002) orientation on the substrates at all temperatures. The temperature dependencies of 2θ x-ray diffraction and absorption coefficient derivative show that high quality films can be obtained at $T > 400$ °C, but are optimized between $500 < T < 600$ °C so as to avoid low growth rate and defects formed at high temperature. A 2θ x-ray diffraction FWHM of 0.13° has been achieved for as-grown films. This is better than or comparable to previous results deposited on various substrates using different growth methods, even on GaAs substrates using MBE or MOVPE.

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Table 1: Crystal characteristics of ZnS and a few other materials used as ZnS substrates for epitaxial growth.

Material	Structure	Lattice Constant	Lattice Mismatch	Thermal Expension	n $\lambda = 2\ \mu$m
ZnS	β	5.4093 Å	0%	6.36×10^{-6}/K	2.26
	α	3.8230 Å			
Si	β	5.43089 Å	0.40%	2.49×10^{-6}/K	3.4
GaAs	β	5.6533 Å	4.51%	5.4×10^{-6}/K	3.34
GaP	β	5.4512 Å	0.78%	5.3×10^{-6}/K	3.45
Ge	β	5.65754 Å	4.59%	6.1×10^{-6}/K	4.1
Al_2O_3	α	4.77 Å	11.82%	5.8×10^{-6}/K	1.75

Table 2: Crystalinity of ZnS films deposited on different substrates via various growth techniques. The values of $0.3 \sim 0.4°$ in the last row are from x-ray rocking curves.

Substrates	Crystalinity	Techniques & References
Silicon	polycrystalline	MOVPE [13] and MBE [17]
Sapphire	polycrystalline	MOVPE [9] and MBE [10]
GaAs	$0.12° \; 2\theta$	MBE [16]
GaAs	$0.3° \sim 0.4°$	PLD [7, 12]

Figure 1, Z. XIN, APL

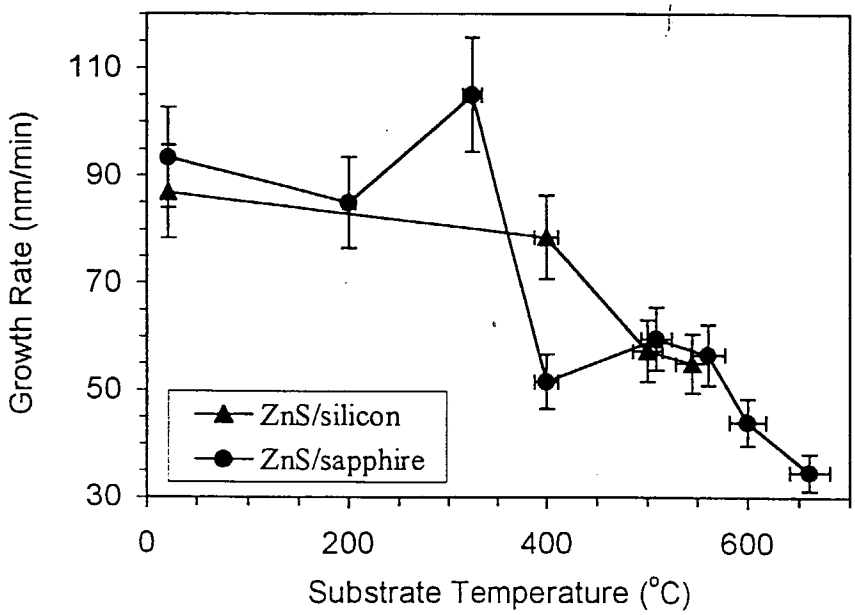

Figure 1: The temperature dependence of growth rates for films on sapphire and silicon substrates.

Figure 2, Z. XIN, APL

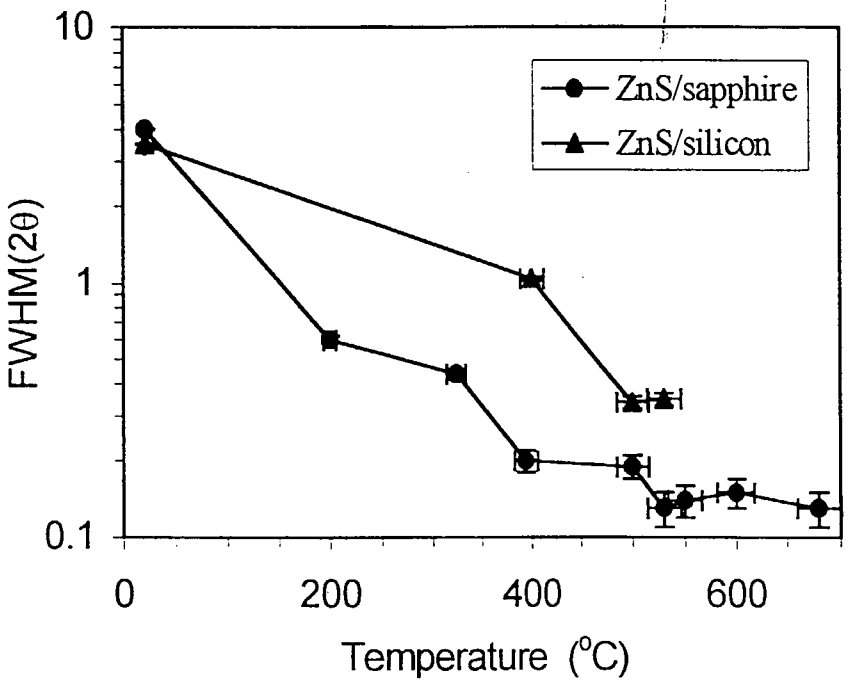

Figure 2: The temperature dependence of 2θ FWHM of x-ray diffraction

Figure 3, Z. XIN, APL

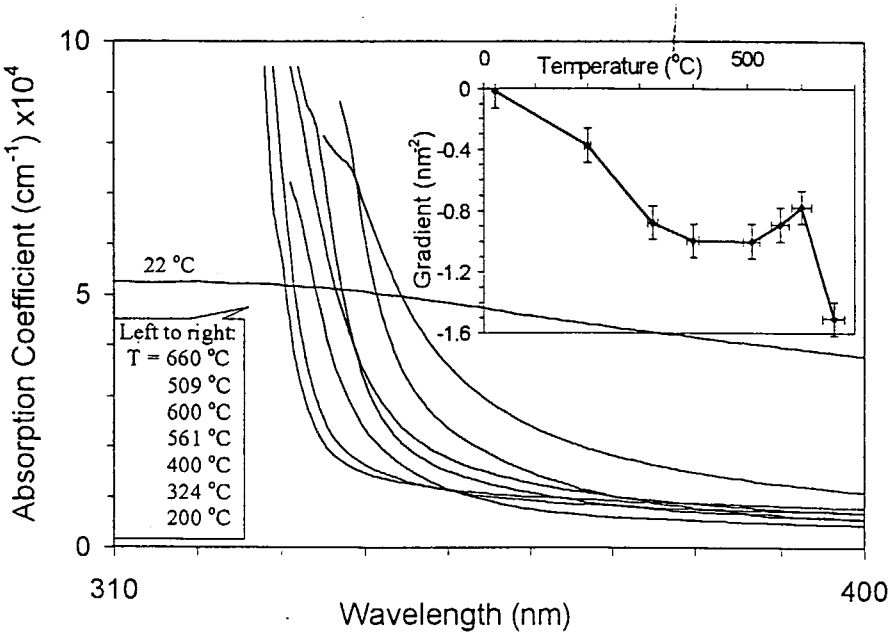

Figure 3: The spectra of absorption coefficient around the cut-off for the samples grown on sapphire substrates at various growth temperatures. The inset shows the derivative changes of the absorption coefficients with respect to wavelength at the band edge cut-off for different growth temperatures.

Figure 4, Z. XIN, APL

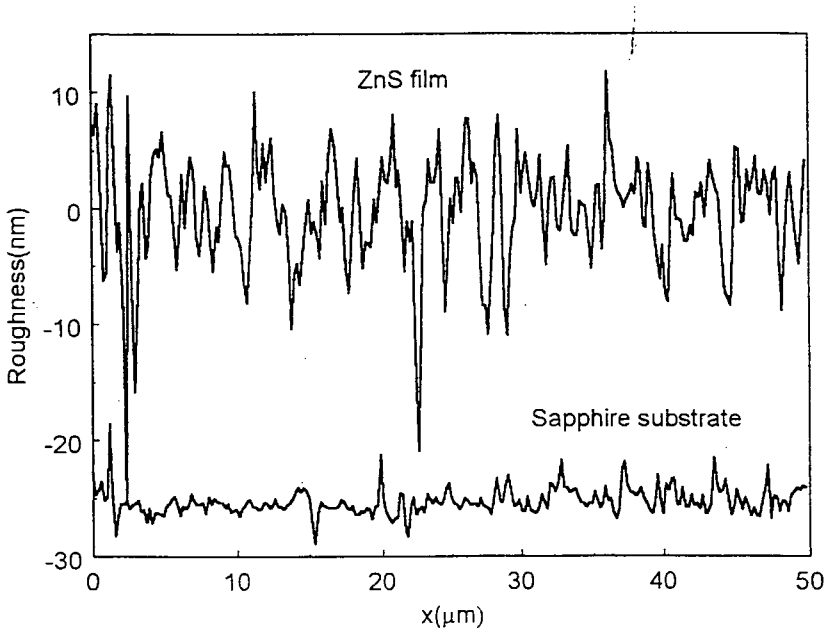

Figure 4: ZnS film roughness (top) scanned by atomic force microscope. It is comparable with the sapphire substrate roughness (lower trace).

Figure 5, Z. XIN, APL

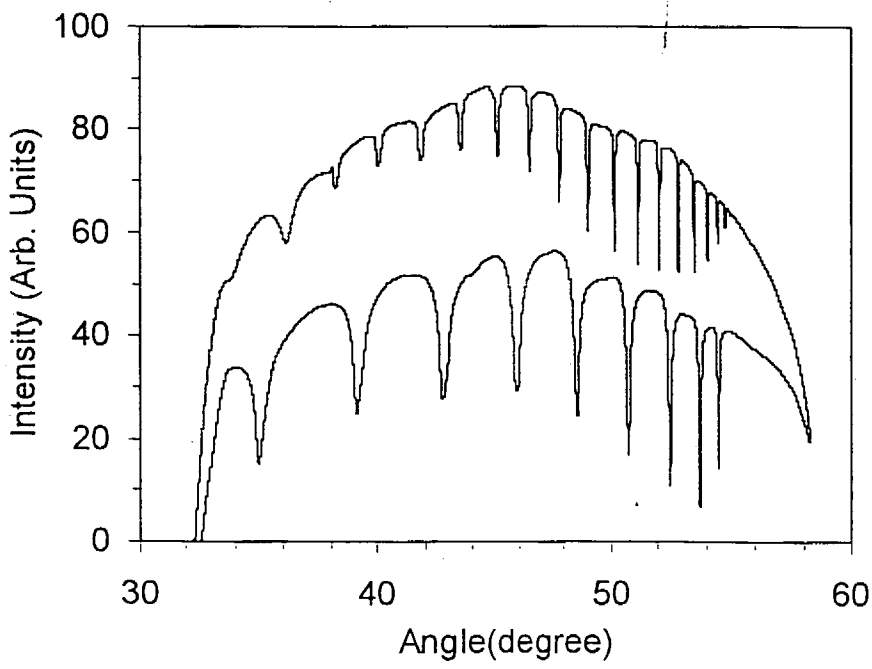

Figure 5: Coupling TE modes found in two samples with prism coupling at $\lambda = 633$ nm. The curve for the sample on silicon is shifted down.