# High Quality Crystalline ZnS Films Grown on Sapphire and Silicon Using Pulsed Laser Deposition

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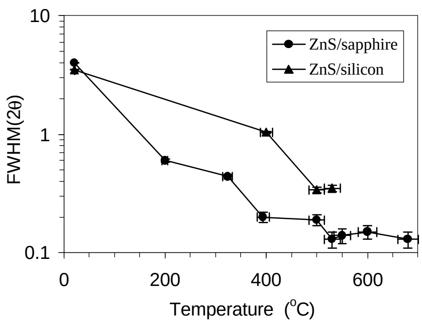
Crystalline Zinc sulphide (ZnS) is widely applied in electroluminescent devices, blue or ultraviolet light emitting diodes, laser diodes and tuneable mid-infrared lasers and second harmonic generation devices.

Crystalline ZnS has two crystallographic phases, zinc blende (cubic) and wurtzite (hexagonal): wurtzite has strong nonlinear optical effects and it transforms to the zinc blende structure at 1020 °C. Problems arise however from lattice, polarity and thermal parameter matches in using commonly available substrates Si, GaAs, sapphire, GaP and Ge for epi-growth of crystalline ZnS.

Crystalline ZnS thin films can be prepared by conventional deposition techniques such as liquid or vapour phase epitaxy. Due to low growth temperature and low kinetic energy of the transporting molecules in conventional epitaxy, crystalline ZnS grown on various substrates is normally of zinc blende structure and poor crystalline quality. Pulsed laser deposition (PLD) on the other hand is a carbon-free and physical transport process. The ablative target material has very high kinetic energy and forms a high flux plasma plume. This is particularly helpful for the vapour phase epitaxial growth of stoichiometric ZnS films.

The growth is carried out in an oil free vacuum chamber with a base pressure of $10^{-7}$ mbar. A pulsed KrF excimer laser is focused to an oval spot (1 mm by 2.5 mm) on a rotating ZnS target. 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 700 °C. Growth was performed on (001) silicon and (10 2) r-plane sapphire substrates, as well as on glass microscope slides. Film thicknesses from 105 nm to 3500 nm have been obtained. Growth is easily controlled and optimised by adjusting the laser energy, pulse repetition rate, substrate to target distance and substrate temperature.



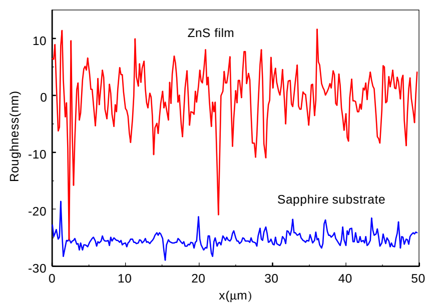




Figure 1 (left) shows the variation of FWHM (full width at half maximum) of the x-ray diffraction peaks of ZnS as a function of growth temperature, obtained from the as-grown samples on sapphire or silicon substrates. The FWHM values of the ZnS films vary from 0.13° to 0.20° for sapphire substrates at $T \geq 400$ °C and for silicon at $T \geq 500$ °C respectively. These values are to be compared with those obtained for sapphire and silicon substrates alone, of 0.09° and 0.08° respectively. All films grown at substrate temperatures ≥ 200 °C have a mirror-like surface. Figure 2 (right) shows the roughness measured by an atomic force microscope. The lower curve, which represents the roughness from a sapphire substrate used in this work with epitaxial surface quality, is compared with the sample surface.

In conclusion, we have, for the first time, epitaxially grown high quality wurtzite ZnS films on sapphire and silicon substrates. Experiment shows that high quality films are obtained at T > 400 °C and are optimized between 500 < T < 600 °C. An FWHM of 0.13° for as-grown films suggests that the film quality is better than or comparable to previous results deposited on various substrates using different growth methods, even on GaAs substrates using MBE or MOVPE.