Supporting Information

Synthesis and optical characterization of high-quality ZnS substrate available for optoelectronics and UV solar-energy conversion
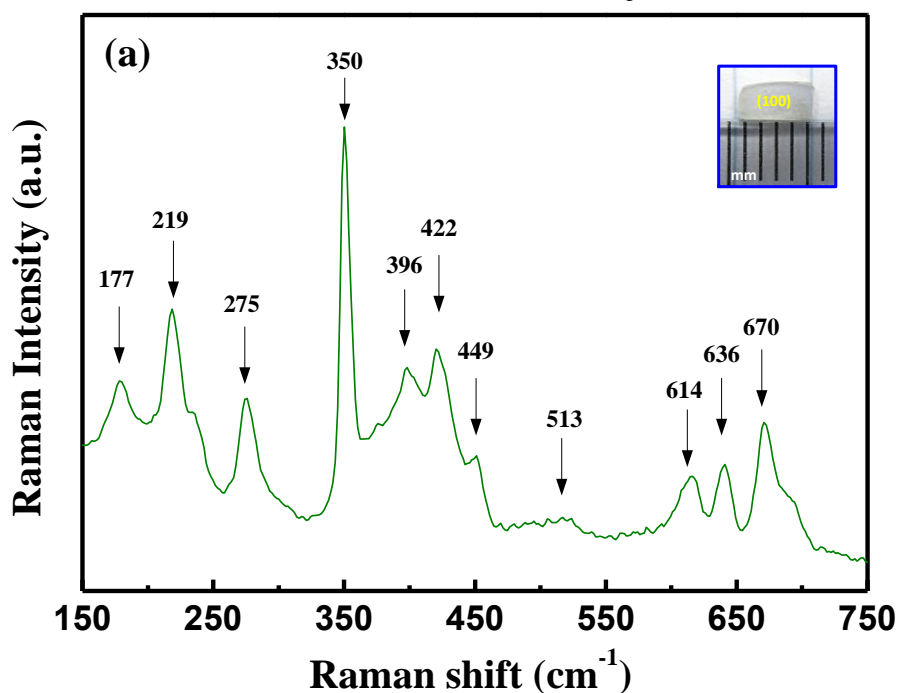
Ching-Hwa Ho [a,b,*] and Min-Han Lin [a]

[a] Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan

[b] Graduate Institute of Electro-Optical Engineering and Department of Electronic and Computer Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan
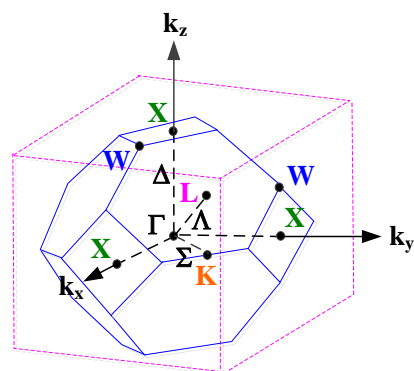
[*]E-mail: chho@mail.ntust.edu.tw

c-ZnS substrate crystal

(a)

Raman Intensity (a.u.) vs Raman shift (cm^{-1})

Peaks labeled: 177, 219, 275, 350, 396, 422, 449, 513, 614, 636, 670

Raman frequency (cm^{-1})	Attribution	BZ points / lines
177	2 (TA)	Γ
219	2 (LA)	X-Γ
275	TO	Γ
350	LO	Γ
396	LO+TA	X
422	TO+LA LO+TA	X L
449	LO+LA	Γ
513	2(0) at W	W
614	2 (TO)	L
636	LO+TO	Γ
670	2 (LO)	Γ

(b)

Zincblende Brillouin Zone (BZ)

(c)

Figure S1. (a) Room-temperature Raman spectrum of *c*-ZnS substrate crystal on the {100} plane. The inset shows the crystal morphology and size of the substrate crystal. (b) Values and assignments of the Raman modes detected in the Raman spectrum. (c) The representative scheme for cubic Brillouin zone of the zinc blende structure in accounting for the Raman phonon bands of the ZnS in (b).

Figure S1(a) shows the Raman spectrum of a *c*-ZnS substrate crystal grown by CVT.

The experiment was done on the {100} *c*-ZnS as the crystal morphology (picture)

shown in the inset. The measurement range is from 150 cm^{-1} to 750 cm^{-1} by using a

A^{+}-ion laser of 514 nm as the excitation source. A lot of peak modes have been

detected in Figure S1(a), which are all indexed to the cubic phase of the ZnS.[32,33] The

attribution and origin of the detected Raman modes are listed in Figure S1(b) together

with a representative scheme of cubic Brillouin zone (BZ) of the zinc blende ZnS is

also included in Figure S1(c) for comparison. As shown in Figure S1(a), the most

prominent peak is the longitudinal-optical phonon mode (LO ~ 350 cm^{-1}) occurred at

the Γ center point of the BZ in Figure S1(c). This prominent LO phonon goes through

the entire bulk *c*-ZnS crystal, and which can be clearly detected by the

low-temperature PL spectra with LO replicas [see Figure 4(a)], and also obtained

from the temperature-dependent analysis of energy shift of the free-exciton emission

in Figure 4(b), i.e. the Θ_B value in the Bose-Einstein fit. As shown in the BZ of Figure

S1(c), the Γ is the zone center, the X point is that of the <100> direction, L point is

<111>, and K point represents that of <110>, respectively. From Γ to X, it must

undergo the *k* vector change of Δ, and from Γ to L it will change the *k* vector along Λ.

From Γ to K, the *k* vector changes along Σ. The 117 cm^{-1} peak in Figure S1(a) is 2

(TA, transverse acoustic) phonon occurred at Γ, and the 219-cm^{-1} mode is 2 (LA)

vibration along the X-Γ in the BZ. The 275 cm^{-1} peak is the TO mode of the *c*-ZnS at

Γ and the 396 cm^{-1} peak responsible for the combination of LO+TA occurred at X

point. The 422 cm^{-1} frequency may contain both of TO+LA at X and LO+TA at L.

The peaks of 449, 513, and 614 cm^{-1} in the Raman spectrum are those of LO+LA at Γ,

2(0) at W, and 2 (TO) at L point, respectively. The LO+TO and 2(LO) modes are

respectively occurred at 636 and 670 cm^{-1} in the zone center of the BZ. All the

structural characterization identifies an excellent *c*-ZnS substrate crystal has been

successfully grown by the CVT method with I$_2$ as the transport agent.

Supporting Information Reference:

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(33) W. G. Nilsen, *Phys.Rev.* 1969, **182**, 838-850.