Pulsed Laser Deposition of Chromium-Doped Zinc Selenide Thin Films for Mid-Infrared Applications

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Abstract

We have grown Cr doped ZnSe thin films by pulsed laser deposition on GaAs, sapphire and Si substrates through KrF excimer laser ablation of hot-pressed targets containing appropriate stoichiometric mixtures of Zn, Se, and Cr species and hot-pressed ceramic targets made of ZnSe and CrSe powders in vacuum and He background environment (10^{-4} Torr). Deposited films were analyzed using X-ray diffraction to determine quality of crystalline structure and energy dispersive X-ray fluorescence to confirm Cr incorporation into the films. Photoluminescence measurements on the films show intracenter Cr^{2+} emission in the technologically important 2-2.6 μm spectral range.

II-VI semiconductor materials doped with transition metal ions (TM^{2+}:II-VI materials) have been widely investigated recently for affordable laser operation in the mid-infrared (mid-IR), a spectral range in demand for many laser spectroscopic applications [1,2]. In this study we focus on chromium doped zinc selenide (Cr:ZnSe) semiconductor films that have shown promising tunable laser operation at wavelengths between 2 and 3 μm. Electronic structure calculations performed in the mid 1980s have established that Cr^{2+} ions incorporated in ZnSe host crystals feature intracenter mid-IR transitions between crystal-field-split ground $^5T_2$ and first excited ^5E states [3]. Previous fabrication efforts of Cr:ZnSe gain media have involved both bulk crystals and thin films. In the case of bulk material, Cr species have been incorporated into the ZnSe lattice by adding Cr metal to the melt in solidification processes [1], by thermal diffusion of Cr in an existing host crystal [4,5,6,7,8], and by hot-pressing powders of ZnSe and CrSe [9]. In thin film form, Cr:ZnSe has recently been grown by molecular beam epitaxy where optically active Cr^{2+} ions in ZnSe (Cr^{2+}:ZnSe) were obtained [10]. In this letter we report the growth of Cr:ZnSe thin films using pulsed laser deposition (PLD), which enables sufficient flexibility in the exploration and optimization of multiple dopant concentrations by the appropriate choice of ablation target and fabrication conditions [11].

Our focus has been on the growth of Cr:ZnSe film on GaAs (100) substrates featuring low lattice mismatch with ZnSe (0.27%). In addition, films deposited on sapphire (0001) and Si (100) substrates at various temperatures in vacuum and in He background have also been investigated. The grown films were characterized by X-ray diffraction (XRD). Energy dispersive X-ray fluorescence (EDX) was used to confirm the

incorporation of Cr in the films and photoluminescence measurements were used to verify whether Cr was incorporated as optically active Cr^{2+} ions.

Two different types of targets were used in our experiments in an attempt to maximize the likelihood of fabricating films of sufficient optical quality and adequate doping. The first type was a commercially available metallic pellet produced by hot pressing mixtures of Zn, Se, and Cr powders of 99.99% purity. The weight fraction of Cr in these mixtures was varied from 0.01 to 0.5% to provide the desired variation of Cr concentration for our studies. A second type of target had a ceramic constitution having been produced by mixing powders of pure ZnSe and CrSe. In this case a single concentration of 0.1 mol % of CrSe was used to produce the ceramic targets. The mixture was hot-pressed at 30-35 MPa at 1500 K using a combination of resistive and current heating which produced a red-colored transparent material that was cut and polished prior to PLD [9]. Pulsed laser deposition using these targets was carried out employing a KrF excimer laser (248 nm, ~20 ns pulse width). The various factors that affect the quality of films deposited in PLD, including laser energy density, ambient gas, target to substrate distance, laser repetition rate, and substrate surface state were chosen in accordance with previous PLD studies of pure ZnSe [12]. Briefly, the 10-Hz repetition rate laser radiation was focused to a spot of approximately 0.025 cm^2 onto the rotating target leading to a laser energy density on the target in the range of 2.5-4.5 J/cm^2. The substrates were cleaned with trichloroethylene, acetone and methanol in an ultrasonic cleaner for about 5 minutes before insertion into the stainless steel high vacuum PLD chamber. The substrate was placed on a heated rotating platform about 5 cm from the target within the chamber and evacuated to a base pressure below 10^{-7} Torr. Films were grown under He ambient at

10^{-4} Torr on GaAs (400-475°C) and under vacuum on GaAs (510°C), sapphire (510-610°C) and Si (510-610°C). The crystalline structures of the films deposited were determined using XRD with Cu Kα radiation of 1.5418 Å wavelength. The thickness of the films was measured by reflectance spectrometry. Photoluminescence measurements in the mid-IR range were performed by optical excitation using an excitation wavelength of 1.56 μm from a continuous wave Er-fiber laser incident at Brewster angle on the film and using an InSb photodetector held at liquid nitrogen temperature for mid-IR fluorescence measurement.

Figure 1 shows XRD patterns for Cr:ZnSe films (thickness 1 – 8 μm) grown on GaAs(100), sapphire (0001) and Si (100) substrates at various temperatures. All measurements show polycrystalline films of ZnSe in the cubic phase. The results shown in Fig. 1(a) are from films grown on GaAs in a He background of 10^{-4} Torr using the metallic targets described above (i.e., from Zn, Se, and Cr powders). The films seem to have a preferential orientation with the (111) direction of the cubic structure oriented perpendicularly to the substrate. Increasing substrate temperature seems to favor this preferred orientation as reflections originating from (111) planes become more intense. This tendency toward the formation of polycrystalline ZnSe with grains preferentially oriented along the (111) direction during PLD has been reported previously for the case of pure ZnSe grown on GaAs [13]. For relatively low temperatures the dynamic deposition conditions of PLD supersede the driving force of the substrate toward epitaxy. At high enough temperatures, this tendency is reversed and epitaxial films grow on GaAs in the (400) direction. Since in our studies our primary intention was to investigate polycrystalline films, no effort was made to remove any amorphous oxide layer on the

surface of the substrate during substrate cleaning. Hence, our films are expected to be polycrystalline even at higher temperatures.

Figure 1(b) and 1(c) show XRD patterns of Cr:ZnSe films grown on sapphire (0001) and Si (100) in vacuum at 10^{-6} Torr using the same metallic targets as in Fig. 1(a). Films grown on both substrates are polycrystalline as was expected due to large lattice mismatch between ZnSe with sapphire and Si. Shown in Fig. 1(b), the XRD pattern of the film grown at higher temperature (610°C) at first glance seems to be a cubic single crystal oriented in the {111} direction. However, other crystal orientations leading to reflections with intensities significantly lower than the (111) peak, are also present. They become more prominent as the temperature is lowered to 550°C. This indicates that the crystal grains are preferentially oriented along the {111} direction at higher temperature. The FWHM for the (111) peak at 550°C and 610°C were 0.538° and 0.433° showing that 610°C offers higher quality film growth. From Fig. 1(c), the films grown on Si are polycrystalline with the {111} direction of the ZnSe cubic structure preferentially oriented along the substrate normal. Measured values for FWHM were 0.511° and 0.344° at 550°C and 610°C, respectively. Compared to other peaks in the pattern, the relative intensity for the (111) peak is much greater at 610°C than at 550°C showing, similarly to films grown on sapphire, that at 610°C films are of improved quality.

Figure 2 shows XRD measurements of films (thickness ~ 8 μm) grown on GaAs, sapphire and Si at 510°C using the ceramic target made from hot-pressed ZnSe and CrSe powders. These films on all three substrates were also polycrystalline with essentially the same general crystallographic characteristics observed in the films produced with the metallic target. Photoluminescence measurements however, indicate that films produced

with the metallic targets are not optically active in the mid-IR. All films produced with the ceramic target, on the other hand, exhibit PL at room temperature. Absence of Cr^{2+} PL signal from the films grown from metallic target demonstrates that the quality of the ablation target highly affects whether the Cr^{2+} doping is adequate.

Figure 3 shows the room temperature PL spectra of Cr:ZnSe films grown on (a) GaAs, (b) Si and (c) sapphire. Figure 3(d) also shows the room temperature PL spectrum of a bulk sample made from hot-pressed polished ceramic of ZnSe and CrSe powders made with the same concentration of Cr (0.1 mol %) as the films. The PL emission of films grown on all substrates is observed over the 2 – 2.6 μm range with a peak emission around 2.1 μm; slightly red shifted from the bulk peak emission (2.2 μm). The PL spectra obtained from thin films exhibited significantly lower signal-to-noise ratio than the bulk material over the entire spectral range. Nevertheless these spectra show that Cr has been incorporated into ZnSe as optically active Cr^{2+} ions (Cr^{2+}:ZnSe) within the films with observable emission in the mid-IR range.

In this study we showed that PLD can be used to grow Cr^{2+}:ZnSe films for mid-IR applications providing an alternative route to molecular beam epitaxy in the fabrication of thin film TM^{2+}:II-VI mid-IR gain materials. The obtained result represents an important step to accelerate research in the development of mid-IR laser materials that can be integrated into waveguide structures for optimized optical performance in the 2–3 μm range.

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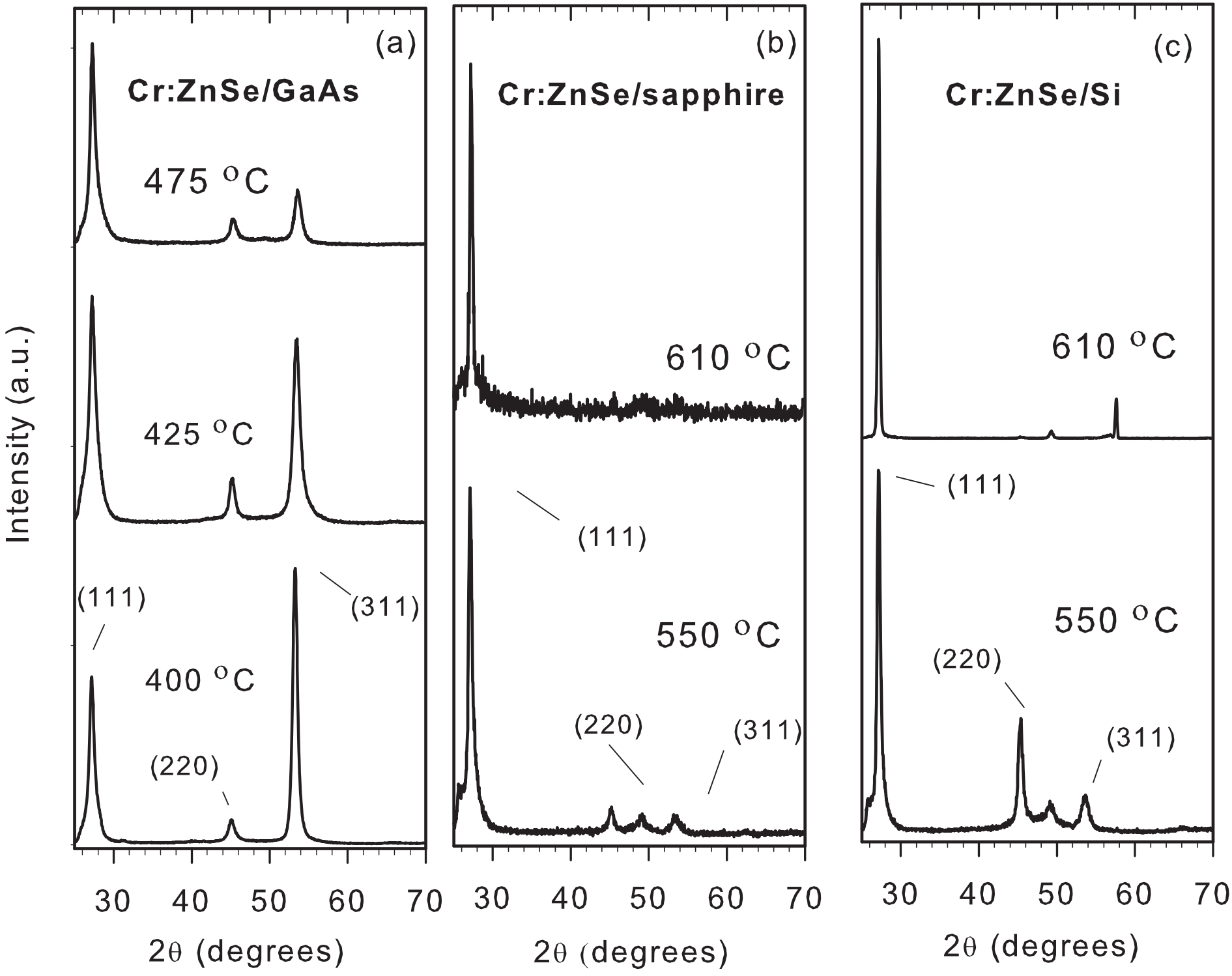
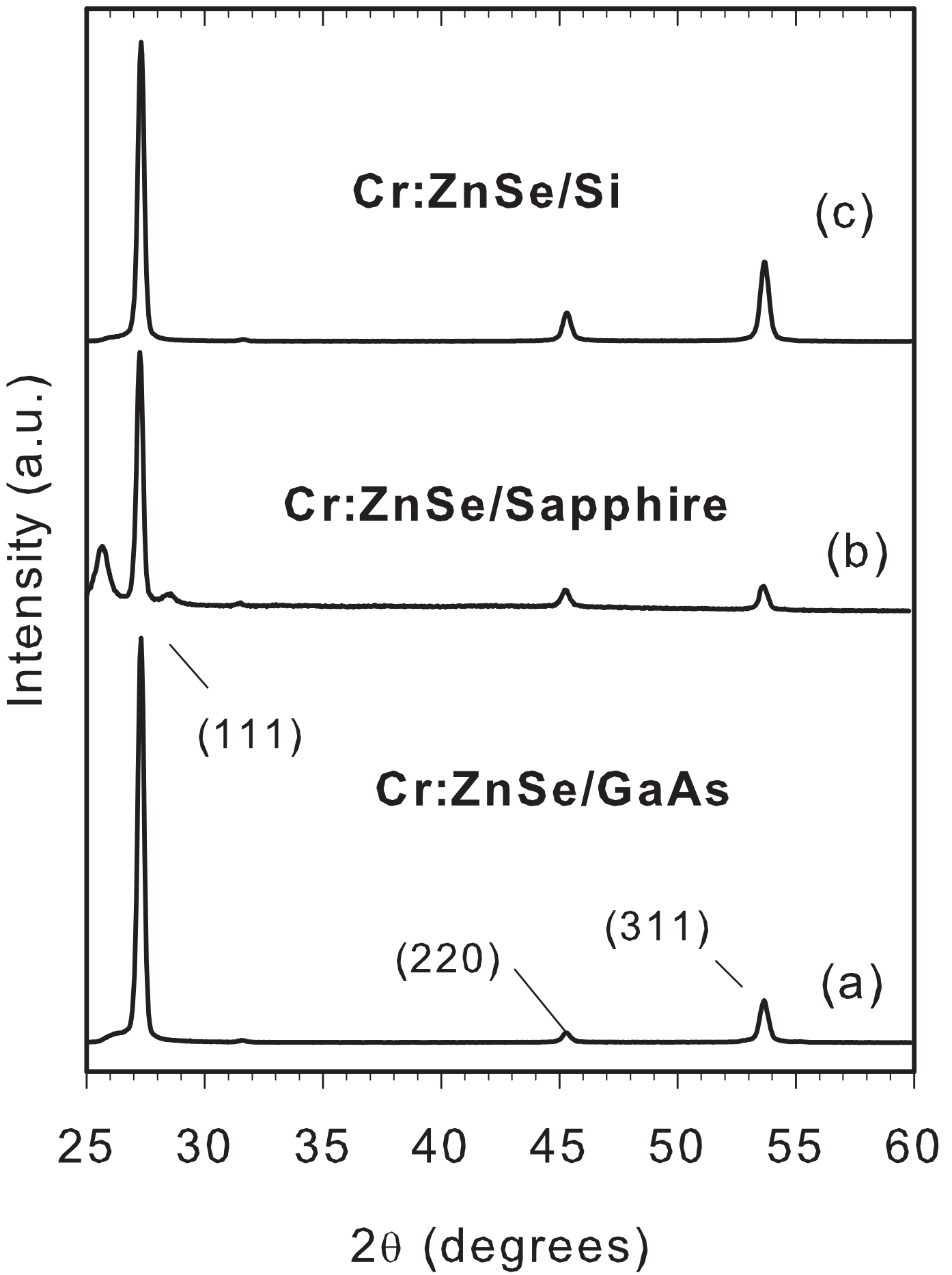
Figure Captions

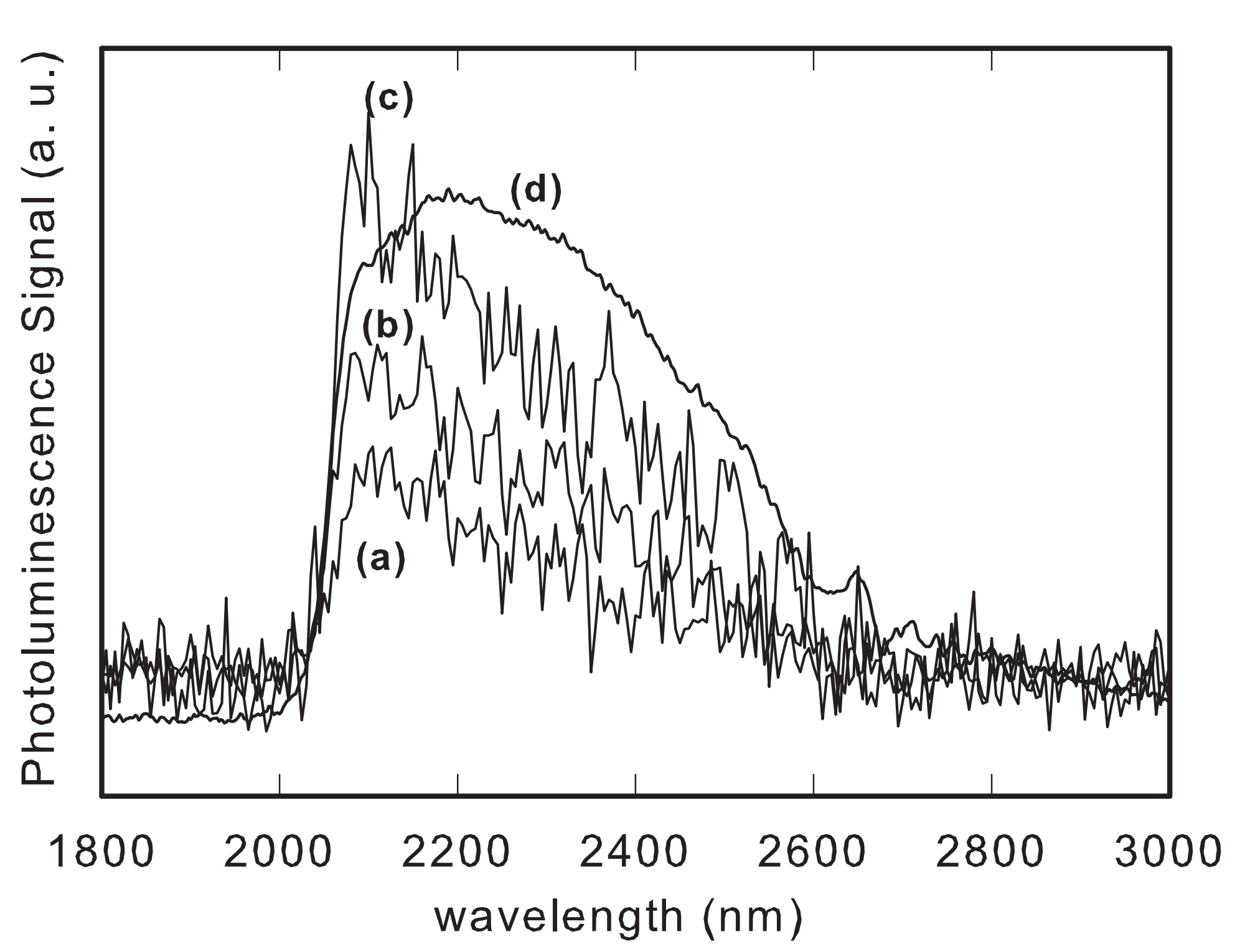
Figure 1: XRD pattern for Cr:ZnSe films grown on (a) GaAs at various temperature in He ambient at 10^{-4} Torr, (b) sapphire (0001) at various temperatures in vacuum at 10^{-6} Torr (c) Si (100) at various temperatures in vacuum at 10^{-6} Torr using ablation target made of Zn, Se, Cr hot-pressed powder

Figure 2: XRD pattern for films grown on GaAs, sapphire and Si at 510 $^{\circ}$C in vacuum at 10^{-6} Torr using ablation target made from hot-pressed powder of ZnSe and CrSe.

Figure 3: Room temperature PL spectra of Cr:ZnSe film grown on (a) GaAs, (b) sapphire, and (c) Si, in comparison with room temperature PL intensity of (d) bulk polished ceramic made from ZnSe and CrSe hot-pressed powders.


(a)
Cr:ZnSe/GaAs
475 °C
425 °C
400 °C
(111)
(220)
(311)
(b)
Cr:ZnSe/sapphire
610 °C
550 °C
(111)
(220)
(311)
(c)
Cr:ZnSe/Si
610 °C
550 °C
(111)
(220)
(311)
Intensity (a.u.)
30 40 50 60 70
2θ (degrees)
30 40 50 60 70
2θ (degrees)
30 40 50 60 70
2θ (degrees)


Cr:ZnSe/Si
(c)
Cr:ZnSe/Sapphire
(b)
(111)
Cr:ZnSe/GaAs
(220)
(311)
(a)
Intensity (a.u.)
25
30
35
40
45
50
55
60
2θ (degrees)


Photoluminescence Signal (a. u.)
(c)
(d)
(b)
(a)
1800
2000
2200
2400
2600
2800
3000
wavelength (nm)