

Novel ultraviolet photoluminescence of ZnO/ZnGa₂O₄ composite layers

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Abstract

ZnO/ZnGa₂O₄ composite layers were synthesized by simple thermal oxidation of ZnS substrates with gallium in the air.

The continuous-wave and time-resolved photoluminescence measurements for the composites were performed at room

temperature. It is found that the visible deep level emission from ZnO in ZnO/ZnGa₂O₄ composite layer was almost

suppressed. In addition, the UV emission with long lifetime was also observed in comparison with that of pure ZnO layer

without ZnGa₂O₄.

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1. Introduction

ZnO has a wide direct band-gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, which is recognized as one of the promising semiconductors for optoelectronic device applications in the ultraviolet (UV) region, such as UV light-emitting diode (LED) and laser diode (LD) [1,2]. To date, much effort has been carried out to decrease the visible emission and improve the emission efficiency in the UV region [3-7]. In this letter, we report the simple synthesis of ZnO/ZnGa₂O₄ composites, which exhibit a UV photoluminescence (PL) with long lifetime.

2. Experimental

The ZnO/ZnGa₂O₄ composite layer was synthesized by the thermal oxidation of ZnS substrates with molten gallium in the air. Gallium was melted around 35-40 °C, then manually applied to the surface of ZnS substrates with ~1 cm size and 1 mm thickness. The ZnS substrates with molten gallium were loaded into a quartz tube which is open to the air. The oxide growth was performed at a temperature of 800 °C for 5 h. On the other hand, pure ZnO layer was synthesized by the thermal oxidation of ZnS substrates without gallium under the same growth conditions.

Structural and morphological properties of the as-synthesized oxides were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM) and scanning TEM (STEM) with energy dispersive X-ray spectroscopy (EDS). PL properties were examined at room temperature. Continuous-wave PL spectra were obtained under excitation of 325 nm He-Cd laser with 5 mW power. Time-resolved PL spectra were obtained under excitation of 266 nm Ti-sapphire laser with 1 mW power.

3. Results and Discussion

Figure 1 shows XRD spectra of the as-synthesized pure ZnO layer and ZnO/ZnGa₂O₄ composite layer. As shown in Fig. 1(a), hexagonal ZnO were synthesized by the thermal oxidation of ZnS substrates. On the other hand, after the thermal oxidation of ZnS with molten gallium, additional diffraction peaks corresponding to the cubic ZnGa₂O₄ appeared, as shown in Fig. 1(b). It means that ZnO/ZnGa₂O₄ composites were formed by oxidation of the surface of ZnS substrates.

Figures 2(a) and (b) show surface SEM images of the as-synthesized pure ZnO layer and ZnO/ZnGa₂O₄ composite layer, respectively. Cross-sectional SEM image of ZnO/ZnGa₂O₄ composite layer is shown in Fig. 2(c). The pure ZnO layer consists of particle like ZnO grains. As revealed in the inset in Fig.2(a), the average grain size of ZnO is about 300 nm. By contrast, the surface of ZnO/ZnGa₂O₄ composite layer became smooth. As shown in Fig. 2(d), the lattice fringe with a spacing of about 0.52 nm was observed near the surface region of ZnO/ZnGa₂O₄ composite layer, which corresponds to the (0001) plane of hexagonal ZnO. In addition, HRTEM image of the ZnO/ZnGa₂O₄ composite layer, taken at the substrate side of the ZnO region in ZnO/ZnGa₂O₄ composite layer as shown in Fig.2(e), confirms the formation of ZnO and ZnGa₂O₄, which are adjoining with each other at the interface of ZnO/ZnGa₂O₄ composite layer. Fig.2(f) shows STEM image of ZnO/ZnGa₂O₄ composite layer with corresponding EDS mappings in Fig.2(g) and (h). As indicated by the arrow shown in Fig.2(f), the ZnO domain with diameter of about 200 nm in ZnO/ZnGa₂O₄ composite layer can be clearly distinguished. It is noted that the ZnO/ZnGa₂O₄ composite layer (Fig2.(c)) is covered by thin ZnO layer (Fig.2(d)) or domains (Fig.2(f-g)).

Figure 3 shows continuous-wave PL spectra of the as-synthesized pure ZnO layer and ZnO/ZnGa₂O₄ composite layer. The PL spectrum of the pure ZnO layer shows a sharp UV emission band at 385 nm and a wide visible emission band at 500 nm. It is commonly believed that the UV emission is attributed to the near-band-edge transition, and the visible

emission is originated from the zinc or oxygen vacancy defect-related deep level. For the ZnO/ZnGa₂O₄ composite layer, the peak position of the UV emission is blue shifted to 378 nm, and the intensity is reduced. Moreover, the visible emission is almost suppressed. It is well known that ZnGa₂O₄ has a band-gap of 4.4 eV, which is significantly higher than that of ZnO. And due to the self-activated optical centers of ZnGa₂O₄, the excitation spectra of ZnGa₂O₄ and ZnO emissions are expected to differ significantly [8,9], which indicates the UV emission from ZnO.

Figure 4 shows time-resolved PL spectra of the as-synthesized pure ZnO layer and ZnO/ZnGa₂O₄ composite layer detected at 380±10 nm. The relaxation process of the UV emission can be described by single-exponential decay fitting of 90% to 10% of the UV peak intensity. The PL decay times for the pure ZnO layer and ZnO/ZnGa₂O₄ composite layer from the fittings are 10.7 ps and 16.3 ps, respectively. Compared with the ZnO layer, the ZnO/ZnGa₂O₄ composite layer shows a slower relaxation process.

The enthalpy of formation of Ga₂O₃ (51.8 kcal/g-atom) is higher than that of ZnO (41.9 kcal/g-atom) [10], the Ga-O bonding would be preferably formed, the Ga atoms could be easily incorporated into ZnO host crystals, and thus improved the crystalline quality in the surface regions of the ZnO by occupying the zinc vacancies and suppressing the oxygen vacancies, which is expected to decrease the visible emission of the ZnO significantly [6,7].

In addition, Ga would act as a charged donor in ZnO. The excess carriers supplied by the Ga impurity to the conduction band increase the electrical conductivity of ZnO. And due to the low density of states of ZnO near the conduction band minimum, the conduction band edge is filled by excessive optical band-to-band transitions, which is known as the

band-filling effect (Burstein-Moss shift). Besides the band filling effect, grain size effect is another reason to induce blue shift of UV emission. However, for this case here, the grain size of ZnO in the ZnO/ZnGa₂O₄ composite layer is almost as same as that in the pure ZnO layer. Therefore, it is considered that the grain size effect is not likely for the blue shift of UV emission.

On the other hand, the excess gallium remaining on the surface of ZnS substrates could be oxidized to form Ga₂O₃, which then was consumed to form ZnGa₂O₄, while existing with ZnO [11,12]. Thus the ZnO and ZnGa₂O₄ would contact with each other closely, which provides a possibility for the charge carriers transport through the interface between ZnO and ZnGa₂O₄. Although the relative energy levels between ZnO and ZnGa₂O₄ are not clear presently, the excited electrons and holes may migrate between ZnO and ZnGa₂O₄ due to their band-gap discontinuity. It is considered that such an interfacial charge transfer brings down the direct transition probability from conduction band to valence band in ZnO, which decreases the UV emission intensity. Moreover, the large extent of ZnGa₂O₄ means that electrons and holes can diffuse far away from the interfaces and then delay the recombination time, which results in the slow relaxation of UV emission.

4. Conclusions

We synthesized ZnO/ZnGa₂O₄ composite layers by the thermal oxidation of ZnS substrates with gallium in the air. The visible emission from ZnO in ZnO/ZnGa₂O₄ composite layer was almost suppressed, and the UV emission with long lifetime was observed. The ZnO/ZnGa₂O₄ composite layer can be a promising phosphor for UV emission applications.

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Figure Captions

Fig. 1 XRD spectra of (a) ZnO layer and (b) ZnO/ZnGa₂O₄ composite layer.

Fig. 2 (a) Surface SEM image of pure ZnO layer with high magnification in the inset. (b) Surface and (c) Cross-sectional SEM images of ZnO/ZnGa₂O₄ composite layer. (d) TEM image of the surface region of ZnO/ZnGa₂O₄ composite layer. (e) HRTEM image of the interface of between ZnO and ZnGa₂O₄ in ZnO/ZnGa₂O₄ composite layer. (f) STEM image of ZnO/ZnGa₂O₄ composite layer with corresponding EDS mappings of (g) Zn and (h) Ga.

Fig. 3 Continuous-wave PL spectra of ZnO layer and ZnO/ZnGa₂O₄ composite layer.

Fig. 4 Time-resolved PL spectra of ZnO layer and ZnO/ZnGa₂O₄ composite layer detected at 380±10 nm.

Figure1
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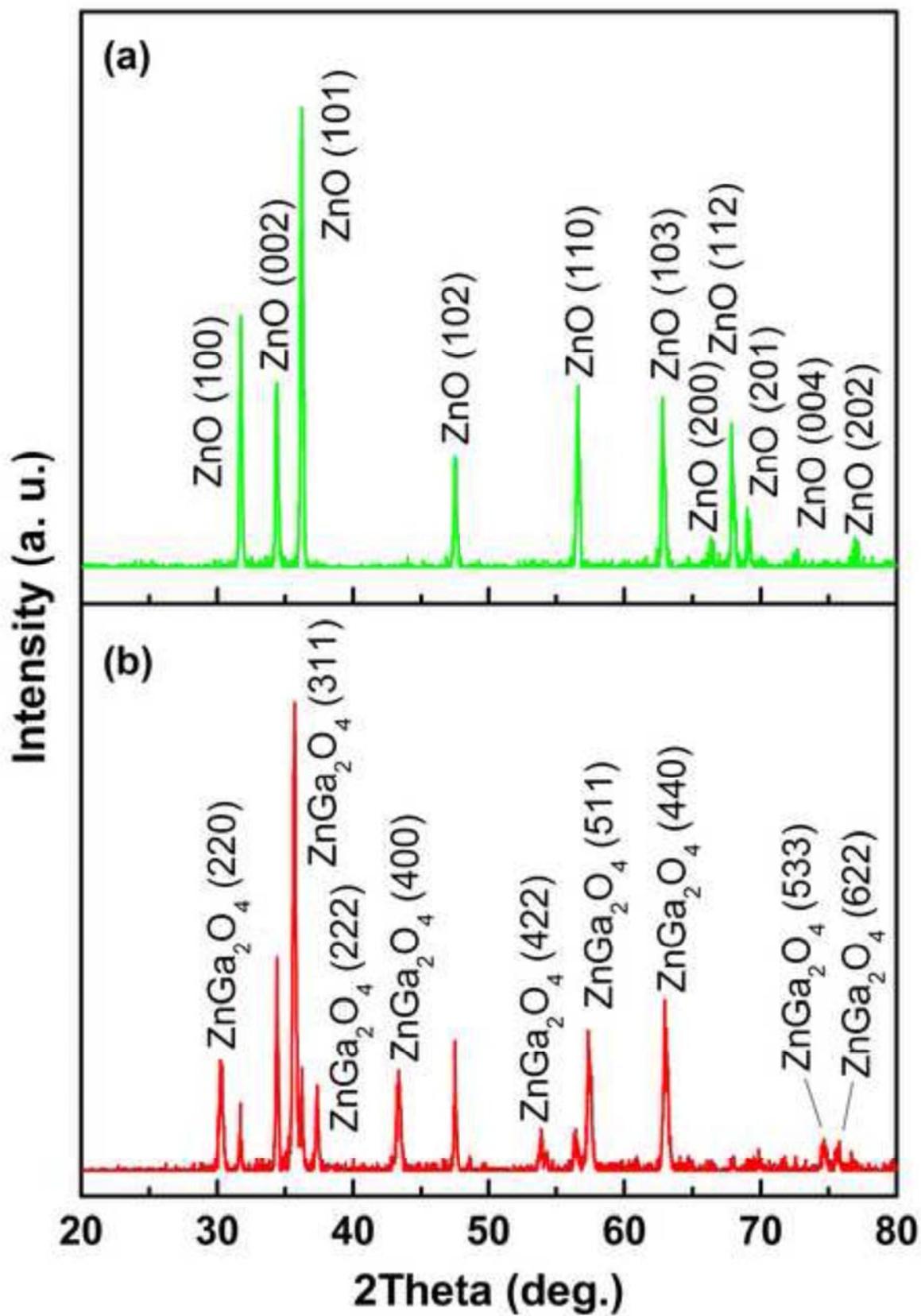


Figure2
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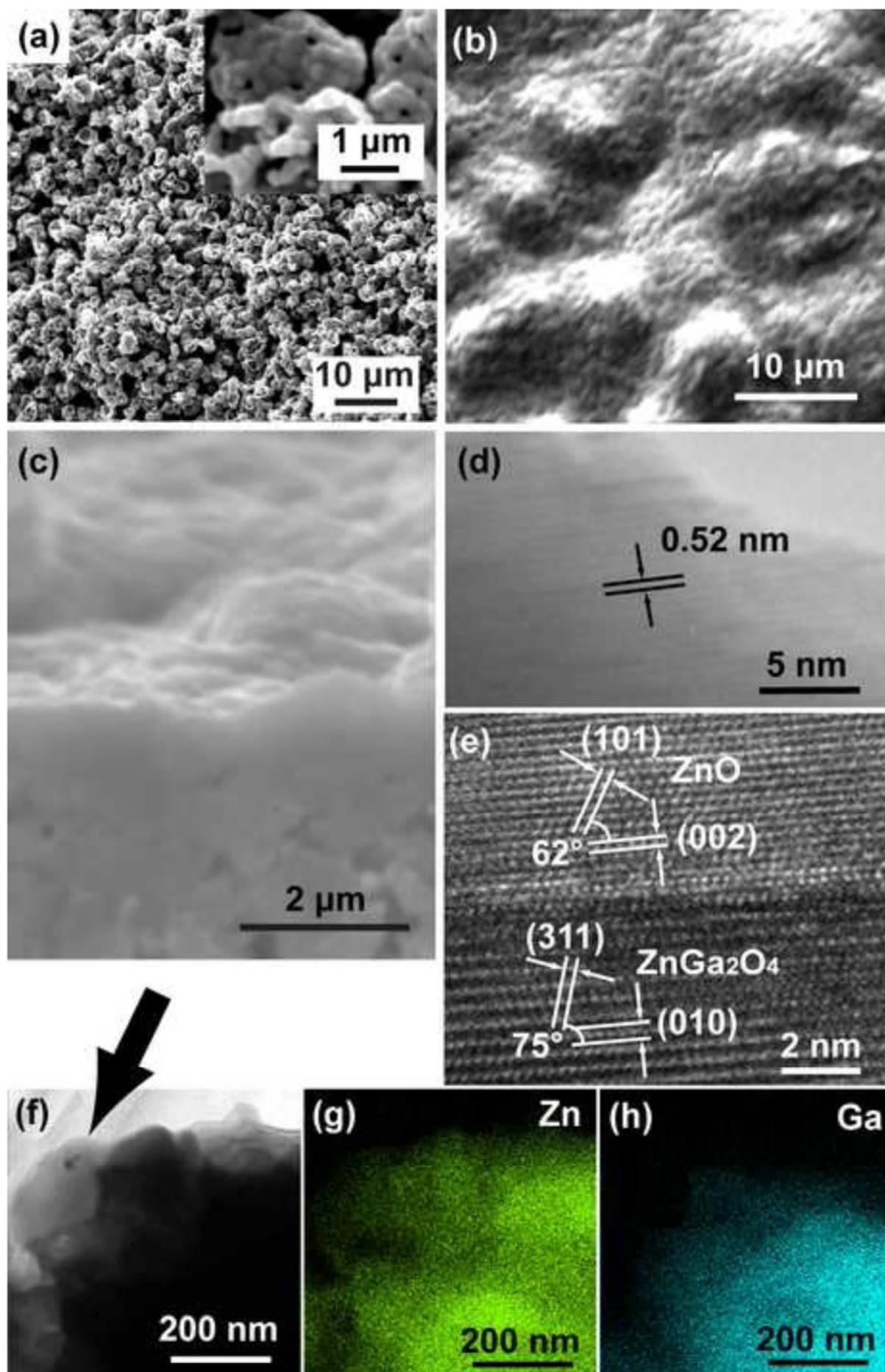


Figure3
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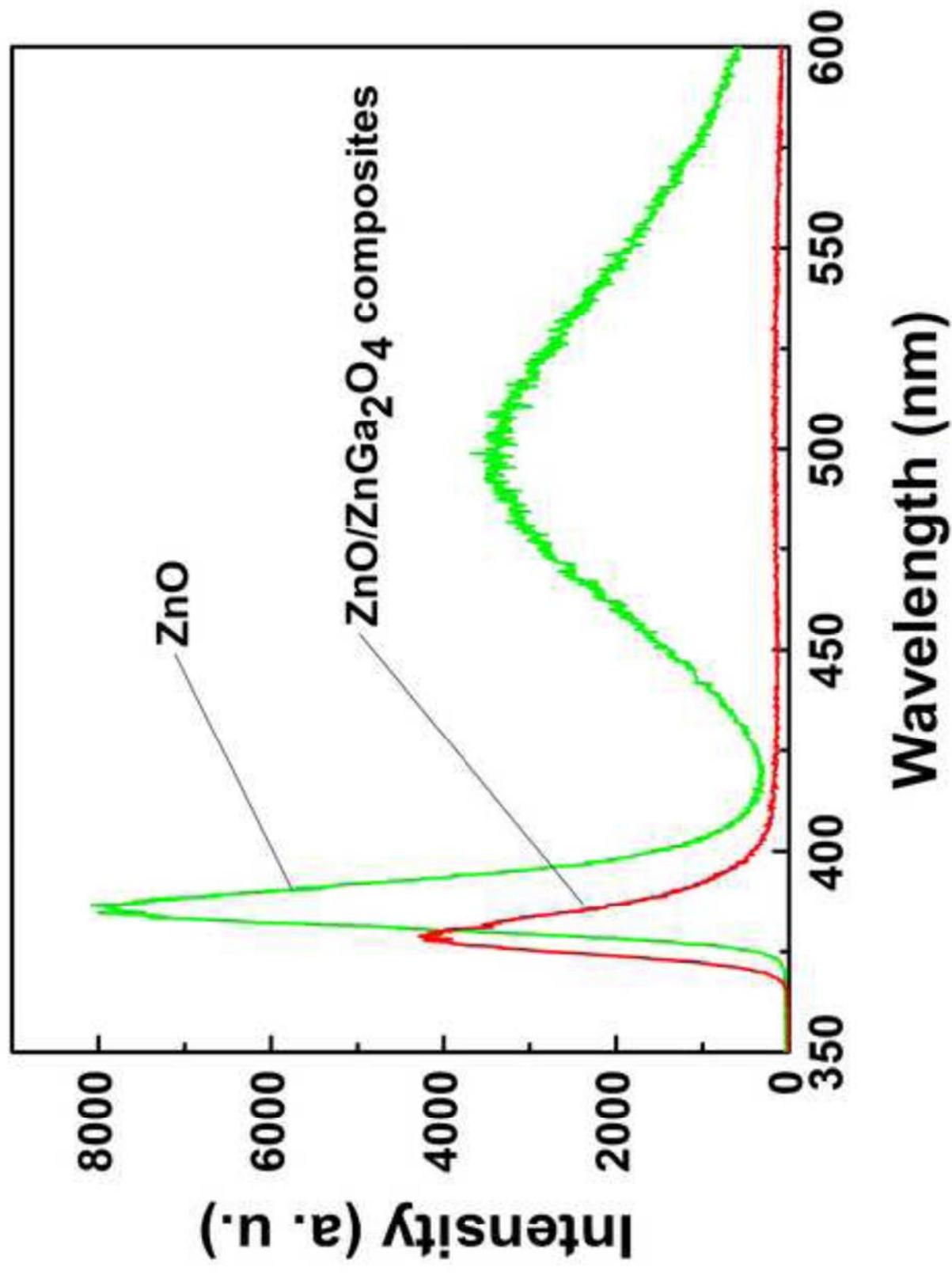
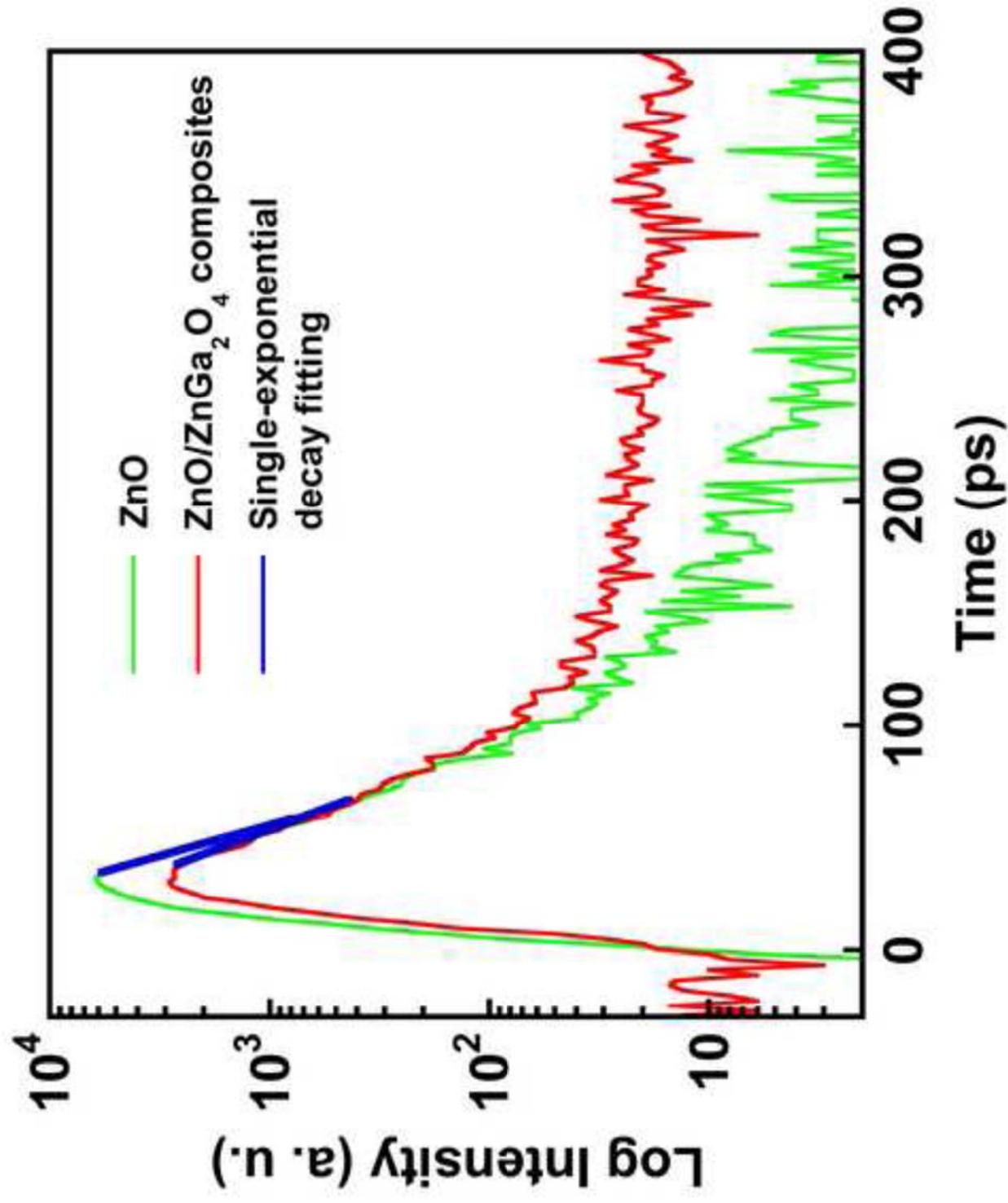


Figure4
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