Enhanced ultraviolet photoconductivity in semiconducting $ZnGa_2O_4$ thin films

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We have investigated the conductivity and photoconductivity response of undoped and Li-doped $ZnGa_2O_4$ epitaxial films grown using pulsed-laser deposition. A significant enhancement of the ultraviolet (UV) photoresponse is observed with Li doping that also correlates with an enhanced luminescent intensity. The wavelength dependence observed for creation of free carriers under UV excitation suggests that the transition is either band-to-band or involves a defect level near the band edge. Moderate *n*-type dark conductivity is observed for undoped films processed under reducing conditions. With Li doping, dark conductivity is reduced, suggesting that lithium ions in the zinc gallate lattice serve as deep acceptors. In addition, Li doping effectively eliminates persistent photoconductivity that is commonly observed in undoped films, suggesting the possible use of Li-doped $ZnGa_2O_4$ as a visible wavelength blind UV photodetector. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1396829]

I. INTRODUCTION

$ZnGa_2O_4$ is an interesting wide band-gap oxide possessing the spinel crystal structure. It is an attractive phosphor host candidate material for flat panel displays because of its favorable photo-(PL) and cathodoluminescence (CL) properties and excellent mechanical and thermal stability. $ZnGa_2O_4$ exhibits an intense green emission when doped with Mn^{2+} ions; blue luminescence is realized in undoped material via a transition involving a self-activated center.[1–3] With a band gap of 4.4–5.0 eV, semiconducting $ZnGa_2O_4$ is potentially useful as a transparent conducting oxide, particularly if transparency through the violet to near UV spectrum is desired. Room temperature resistivity on the order of 30 mΩ cm has been reported for polycrystalline bulk $ZnGa_2O_4$.[4] Other semiconducting spinel oxides that have been investigated for their electroconductive properties include $CdGa_2O_4$ ($E_g = 3.1$ eV) and $MgIn_2O_4$ ($E_g = 3.4$ eV).[5,6] Of these spinel structures, semiconducting $ZnGa_2O_4$ is unique in providing transparency into the UV. Despite promise as a transparent electronic material, relatively little work has been done to elucidate the effects of processing and doping on the transport properties of semiconducting $ZnGa_2O_4$ materials, particularly as thin films.

In this article, we report on the properties of semiconducting $ZnGa_2O_4$ films grown by pulsed-laser deposition. In particular, we have investigated the transport and photoconductivity properties of Li-doped and undoped epitaxial films. The use of epitaxial $ZnGa_2O_4$ films eliminates spurious effects that may result due to grain boundaries. The photoconductivity response of $ZnGa_2O_4$, both doped and undoped, was measured at wavelengths sufficiently short for band-gap excitation. For undoped films, photoconductivity is relatively weak. However, we observed a significant enhancement of the ultraviolet photoconductivity for epitaxial Li-doped $ZnGa_2O_4$ films. The photoconductivity correlates with an enhanced photoluminescence intensity. In all cases, the films remained relatively transparent to visible light.

II. EXPERIMENTAL DESCRIPTION

Epitaxial $ZnGa_2O_4$ thin films with different amounts of lithium were grown on (001) MgO using pulsed-laser deposition. Polycrystalline 1 in. diam $ZnGa_2O_4$, $Li_{0.05}Zn_{0.95}Ga_2O_4$, and $Li_{0.25}Zn_{0.5}Ga_{2.25}O_4$ targets were prepared by mixing and pressing Li_2O [Alfa, 99.99%], ZnO [Alfa, 99.999%], and Ga_2O_3 [Alfa, 99.9995%] powders, followed by sintering in air at 1250 °C for 24 h. Mosaic targets were required in order to provide excess Zn flux necessary to compensate for Zn loss due to its high vapor pressure at the growth temperature.[1] Approximately 2-μm-thick films were grown using an excimer KrF laser with a wavelength of 248 nm. The laser fluence was approximately 3.5 J/cm^2. Single crystal (100) MgO substrates were used, providing a 1% lattice mismatch with $ZnGa_2O_4$. The films were grown at 730 °C under oxygen partial pressure [$P(O_2)$] of 100 mTorr. Crystal structure was investigated using four-circle x-ray dif-

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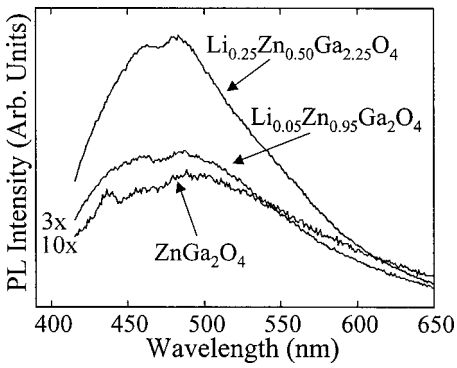

FIG. 1. PL spectra for blue thin-film phosphors deposited using mosaic targets of $ZnGa_2O_4$/ZnO, $Li_{0.05}Zn_{0.95}Ga_2O_4$/ZnO, and $Li_{0.25}Zn_{0.5}Ga_{2.25}O_4$/ZnO.

fraction (XRD) with Cu $K\alpha$ radiation (0.154 06 nm wavelength). Photoluminescence spectra were measured at room temperature using a broadband incoherent UV light excitation source with a dominant excitation wavelength of 254 nm. Conductivity was measured using van der Pauw measurements. Photoconductivity of the films was determined via four-point conductivity measurements at room temperature. For contacts, Cr(1.5 nm)/Au(100 nm) dots were deposited on the films using electron beam evaporation.

III. RESULTS AND DISCUSSION

The as-deposited films were epitaxial with good out-of-plane and in-plane alignment. X-ray diffraction provided no evidence for the formation of lithium-related impurity phases.[2] Earlier efforts showed that mixtures of $ZnGa_2O_4$ and $LiGa_5O_8$ exhibit considerable enhancement in luminescent intensities as compared to undoped $ZnGa_2O_4$. This has led to continued efforts in developing highly efficient $LiGa_5O_8$–$ZnGa_2O_4$ and Li_2O–$ZnGa_2O_4$ phosphor materials for display applications. Recently, we reported on the effect of Li doping on the CL properties of undoped and Mn-doped epitaxial $ZnGa_2O_4$ films grown by pulsed-laser deposition. Our results showed that the addition of Li to $ZnGa_2O_4$ considerably enhances the low voltage CL efficiencies. As-deposited blue and green lithium zinc gallate thin-film phosphors exhibited CL efficiencies of 0.21 and 0.29 lm/W at 1 kV and 2.26 μA/cm^2, respectively.[2] Figure 1 shows the PL spectra for films with different amounts of lithium. A remarkably enhanced PL intensity is observed for the films containing lithium. The peaking wavelength was located at approximately 483 nm. The films containing lithium also exhibited a second peak at approximately 455 nm. A similar enhancement with lithium doping is observed in the cathodoluminescence spectra. The mechanism by which Li doping improves luminescent properties in $ZnGa_2O_4$ phosphor materials will be discussed later.

In order to elucidate the effects of Li doping on the semiconducting properties of $ZnGa_2O_4$ we investigated the conductivity and UV photoconductivity response of the epitaxial films. Conductivity in the epitaxial $ZnGa_2O_4$ films via the formation of oxygen vacancies was achieved by post-annealing in ~1 atm 4% H_2/ 96% Ar at 650 °C for 1 h. Stoichiometric $ZnGa_2O_4$ is an insulator with the large band gap, showing *n*-type semiconductor behavior after annealing at high temperature under reducing atmosphere.[3] The dark conductance in $ZnGa_2O_4$ is due to free electrons excited from oxygen vacancies that introduce shallow donor levels below the bottom of the conduction band. Under these processing conditions, semiconducting $ZnGa_2O_4$ films with resistivity $\rho(300\,\mathrm{K}) = 100\,\mathrm{m}\Omega$ cm were realized. This resistivity is slightly higher than that reported for polycrystalline bulk samples, and may reflect the absence of grain boundaries or slight deviations in cation ratios. Hall measurements indicate that the films are *n*-type as expected, although quantitative Hall results were difficult to obtain due to the high resistivity of the samples. With Li doping, the conductivity decreased significantly. For a $Zn_{0.95}Li_{0.05}Ga_2O_4$ film grown and post-annealed under the same conditions as described above, the room temperature resistivity was on the order of 28 Ω cm.

Within the spinel structure, it is useful to consider where the Li dopants might reside. Lithium can potentially occupy two different sites in the spinel lattice, as well as interstitial sites. The unit cell for the spinel structure is composed of 8 elementary cells, consisting of 32 oxygen ions, 8 tetrahedral cations, and 16 octahedral cations. In $ZnGa_2O_4$, the Zn cations occupy tetrahedrally coordinated sites; the Ga occupies the octahedral sites. The total numbers of tetrahedral and octahedral vacancies in the unit cell are 64 and 32, respectively. Therefore only 1/8 of the tetrahedral and 1/2 the octahedral sites are filled by cations. With a small ionization potential and suitable ionic size, Li could occupy tetrahedral vacancy sites ($Li_i^{\bullet}$) and be ionized so as to release electrons into the conduction band, and consequently decrease the resistivity of the films.[4] Lithium also possesses a similar ionic radius to that for Zn $[R(Li^+) = 0.059\,\mathrm{nm},\ R(Zn^{2+}) = 0.060\,\mathrm{nm}]$ and may substitute on the tetrahedral zinc sites (Li'_{Zn}). From cation valence arguments one would anticipate that Li (+1) substitution for Zn (+2) introduces an acceptor level. The results for Li-doped $ZnGa_2O_4$ films suggest that Li behaves as a deep acceptor dopant, given the decrease in *n*-type conductivity. This is also consistent with the behavior observed for ZnO, where Li doping introduces a deep acceptor, making ZnO insulating.[7]

In addition to conductivity we also investigated the photoconductivity response of undoped and Li-doped $ZnGa_2O_4$ films. Three wavelength regions were explored for photoconductive response: broadband visible, long wavelength UV (365 nm), and short wavelength UV (254 nm). For both Li-doped and undoped $ZnGa_2O_4$, no photoconductivity response was observed for visible or 365 nm UV excitation, consistent with the reported band gap. However, photoconductivity was observed for irradiation at 254 nm in both doped and undoped material. Most notably, a significant enhancement in photoconductivity was observed for the Li-doped material. Figure 2 shows the variation of dark-and photocurrent response with applied voltages measured at room temperature. For photoconductivity measurements, the UV intensity was approximately 1000 μW/cm^2. First note that the dark conductivity (with no UV excitation) of the undoped $ZnGa_2O_4$ film is lower than that for the Li-doped

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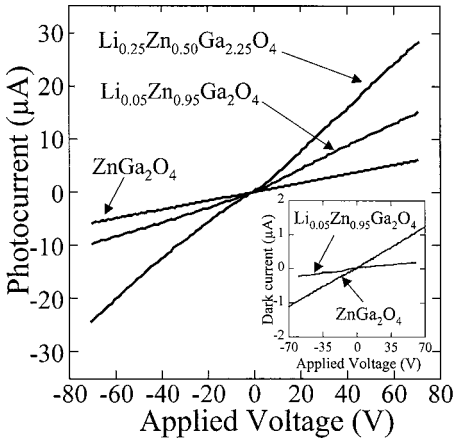

FIG. 2. Variations of photocurrent under UV excitation for films deposited using mosaic targets of $ZnGa_2O_4$/ZnO, $Li_{0.05}Zn_{0.95}Ga_2O_4$/ZnO, and $Li_{0.25}Zn_{0.5}Ga_{2.25}O_4$/ZnO with applied voltages at room temperature. Relationship of dark current vs applied voltage is inserted.

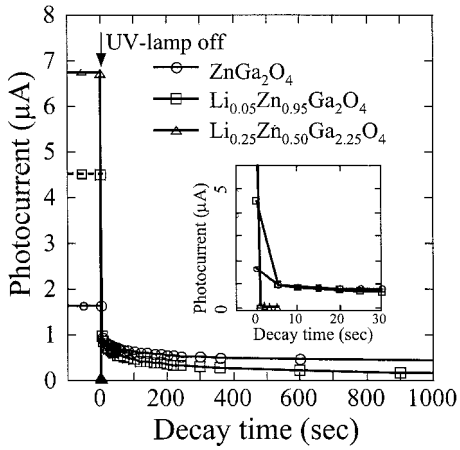

FIG. 3. Decay curves for films deposited using mosaic targets of $ZnGa_2O_4$/ZnO, $Li_{0.05}Zn_{0.95}Ga_2O_4$/ZnO, and $Li_{0.25}Zn_{0.5}Ga_{2.25}O_4$/ZnO at fixed voltages of 20 V and at room temperature. Initial relaxation is inserted.

material, as pointed out earlier. For both the doped and undoped $ZnGa_2O_4$ films, the photocurrent observed for 254 nm irradiation, corresponding to a photon energy of 4.88 eV, appears to result from band-to-band electron–hole pair generation, although excitation involving a defect level near the band edge cannot be ruled out. Irradiation by 3.20 eV UV photons did not show appreciable changes in conductivity. The addition of lithium introduces deep acceptor levels in the energy band gap, trapping electrons and subsequently reducing the dark conductivity of the films. The mechanism for enhanced photoconductivity with Li doping can also be related to the deep acceptor level, explained as an excitation of electrons from occupied Li acceptor levels to the conduction band. At the relatively high doping levels used, the Li could conceivably produce an extended impurity band that also participates in conduction when depopulated via UV excitation. More work will be needed in order to determine energy levels associated with Li substitution.

In addition to the enhanced photoconductivity, Li doping also results in a significant reduction of the so-called persistent photoconductivity that is present in undoped $ZnGa_2O_4$ films. In general, persistent photoconductivity indicates the presence of deep-level traps possessing a capture barrier E_c that must be overcome via thermal excitation (at high temperatures) or electron tunneling via multiphonon emission (at low temperatures).[8] It is often observed in ionic semiconductors, including GaN. Photocurrent decay curves measured at a fixed voltage of 20 V are shown in Fig. 3 for $ZnGa_2O_4$ films with different Li doping levels. The undoped zinc gallate film, exhibiting a lower photocurrent under UV excitation, shows a long tail in the decay curve after the cessation of excitation. Persistent photoconductivity in undoped and lightly doped $ZnGa_2O_4$ films display decay times on the order of minutes. In contrast, the film deposited using the target of composition $Li_{0.25}Zn_{0.5}Ga_{2.25}O_4$/ZnO reveals a much higher photocurrent at the voltage of 20 V, and a decay time that is orders of magnitude smaller than that for the undoped film. In fact, for the time resolution achieved in these measurements, the persistent photoconductivity appears to be eliminated by Li doping. Decay times will typically be determined by defect levels in the forbidden energy gap. The reduced relaxation period after the cessation of UV light results from the formation of deep acceptor levels by the lithium ion. Persistent photoconductivity is typically associated with deep traps that have a large activation energy for being occupied. The absence of persistent photoconductivity with Li doping indicates the introduction of a deep level that possesses no effective barrier to trapping, at least at room temperature.

Note that the creation of free carriers during UV excitation in Li-doped $ZnGa_2O_4$ films also correlates with enhanced PL intensity. To address the possible relationship between the PL intensity and photoconductance in the films, one must delineate the mechanism by which blue luminescence in $ZnGa_2O_4$ occurs. It has been suggested that the oxygen vacancies producing free electrons and Ga^+ ions are responsible for blue luminescence in $ZnGa_2O_4$ based on the following observations.[9–12] (1) The excitation spectrum of the blue emission band for selected gallium containing oxides was identified by ligand-field theory as due to a Ga^+ luminescence center. (2) The intensity of blue luminescence in gallium-possessing oxide phosphors is typically enhanced by annealing under a reducing environment. (3) Annealing many gallium-containing phosphors, including Ga_2O_3, Mg–Li gallate, and Mg–Zn gallate, in an atmosphere of pure oxygen decreases luminescence intensity. Based on these arguments it appears that the Ga^{3+} ions in the spinel lattice combine with UV-generated free electrons, giving rise to blue luminescence. The addition of Li, resulting in an increased photogenerated carrier density, directly contributes to the radiative recombination process with Ga^{3+}, leading to enhanced luminescence as seen in Li-doped $ZnGa_2O_4$.

In summary we have investigated the transport properties of semiconducting $ZnGa_2O_4$ films. A decrease in dark current with lithium doping suggests that lithium ions introduce deep acceptor levels. The addition of lithium considerably enhanced PL intensity for the films. This increase in PL and CL correlates with an increase in photoconductivity response under 254 nm irradiation. Generated free carriers un-

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der UV excitation appear to be directly responsible for the enhancement in luminescence properties.

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