Epitaxial Growth of Metal Fluoride Thin Films by Pulsed-Laser Deposition

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ABSTRACT

We have investigated the growth of $GdLiF_4$ thin films for optical waveguide applications using pulsed-laser deposition (PLD). Epitaxial, c-axis oriented $GdLiF_4$ films have been grown from undoped $GdLiF_4$ targets in an on-axis PLD geometry on (100) CaF_2. These films exhibit a high density of particulates on the surface which are ejected from the target in the ablation process. Growth from Nd-doped polycrystalline $GdLiF_4$ ablation targets results in relatively smooth films with lower particulate densities, as Nd doping significantly increases the optical absorption of $GdLiF_4$ at the ablation laser wavelength of 193 nm and permits efficient pulsed-laser deposition. Optical emission spectra of the ablation pume reveals the presence of atomic fluorine, gadolinium, and lithium, indicating the dissociation of the metal-fluorine bonds in the ablation process. In addition, we find that the residual background oxygen pressure must be sufficiently reduced to avoid the formation of $Gd_4O_3F_6$ as an impurity oxy-fluoride phase in the films.

INTRODUCTION

Metal fluorides are important materials for both active and passive optical components. Their low refractive index, wide optical transmission range, and low nonradiative decay rate make them attractive for numerous optical applications. The epitaxial growth of metal-fluoride films for waveguide device structures in of interest for several material systems. Most of the effort in growing epitaxial metal fluorides has focused on binary compounds, such as CaF_2, SrF_2, and BaF_2, using a variety of techniques such as molecular beam epitaxy and chemical vapor deposition.[1-6] These efforts have included the epitaxial growth of rare-earth doped binary fluoride films, as rare-earth doped metal fluoride bulk crystals are among the most actively studied solid-state laser materials. However, little attention as been given to the epitaxial growth of more complex metal fluorides, despite promising properties observed in bulk single crystals. One such metal fluoride material is $GdLiF_4$, which is optically transparent over a large spectral region and is a promising laser host crystal when doped with optically-active rare earth ions.[7] Potential optical waveguide devices utilizing rare earth-doped $GdLiF_4$ thin films include compact, solid state upconversion lasers for display and data-storage applications, and 1.3 and 1.55 μm wavelength optical amplifiers in optic fiber communication systems. Unfortunately, no film growth technique has been shown effective in obtaining epitaxial $GdLiF_4$ films suitable for these waveguide structures. In this paper, we report on the growth of $GdLiF_4$ thin films using pulsed-laser deposition.

EXPERIMENTAL

The $(Gd,Nd)LiF_4$ films were grown using conventional pulsed-laser deposition. An ArF excimer laser beam (~140 mJ, 193 nm, 38ns full-width half-maximum (FWHM) pulse duration, 3.3 Hz) was focused to a horizontal line on ~25 mm diameter stoichiometric $GdLiF_4$ and $Gd_{0.95}Nd_{0.05}LiF_4$ rotating targets. The ablation targets were prepared from high-purity GdF_3, LiF, and NdF_3 powders and sintered in flowing argon at 600°C. The focused laser energy density was 1.5–3.0 J/cm^2, and the heated substrates were placed ~4.5 cm from the sintered

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target. The substrates were heated to 350–450°C with film growth carried out in either vacuum or 100 mTorr argon. Typical growth parameters yielded a film growth rate of ~20 Å/min. Substrates used in this effort included (100)-oriented CaF_2 and (012) Al_2O_3 (sapphire).

DISCUSSION

Figure 1 shows x-ray diffraction patterns obtained from a $GdLiF_4$ thin film deposited on (100) CaF_2. The film was grown at 450°C in vacuum with a base pressure of 6×10^{-7} Torr. The diffraction pattern indicates strong (002)and (004) $GdLiF_4$ peaks very close to the (00ℓ) peaks from the CaF_2 substrate, as well as weaker peaks attributed either to polycrystalline $GdLiF_4$ or an oxy-fluoride impurity phase. A ϕ-scan through the $GdLiF_4$ (105) indicates that the c-axis oriented material is in-plane aligned with lattice parameters of a=5.21Å and c=10.98Å. The polycrystalline $GdLiF_4$ observed in the diffraction pattern appears to originate from a significant density of randomly-oriented $GdLiF_4$ particulates on the film surface. Particulates are often observed in films grown by on-axis PLD, particularly when the ablated material has a relatively low optical absorption coefficient at the ablation wavelength. Under these conditions, the ablation laser pulse interacts with a relatively large volume of the target material. While some of the ablated material is vaporized in the ablation process, a significant fraction is ejected from the target as particulates. The high density of $GdLiF_4$ particulates in these films reflects the low optical absorption coefficient of the target at 193 nm.

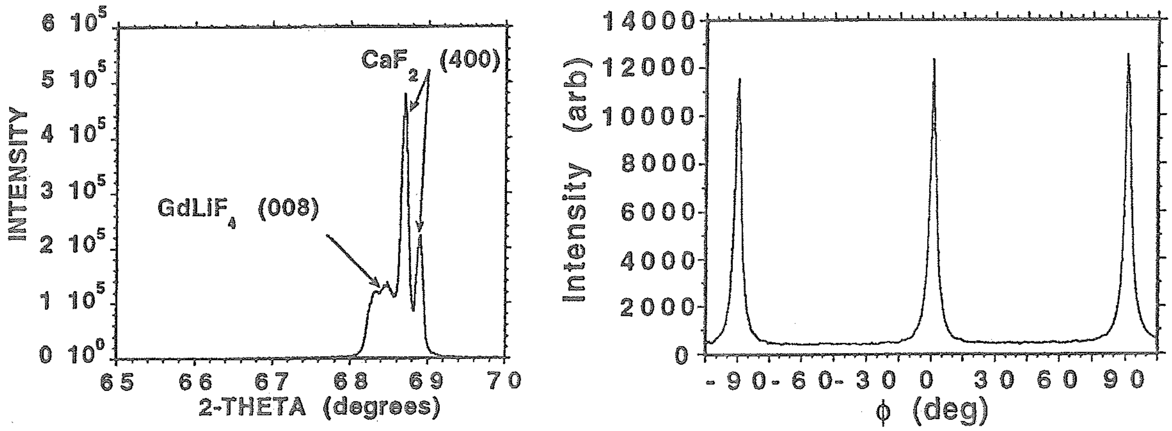

Fig. 1 Four-circle x-ray diffraction patterns from a (a) $\theta-2\theta$ scan and (b) ϕ-scan through the $GdLiF_4$ (105) peak for a $GdLiF_4$ film grown on (100) CaF_2 by pulsed-laser deposition.

For waveguide applications, surface roughness is a significant issue, as it leads to optical losses. In an attempt to reduce the density of particulates in these films, we investigated the laser ablation growth of Nd-doped $GdLiF_4$ films, where Nd was added to increase the optical absorption coefficient of the ablation target at 193 nm and permit more efficient laser ablation using an ArF excimer laser. Nd is also an interesting active rare-earth dopant with a high solubility in $GdLiF_4$. Several of the absorption lines of Nd^{+3} ions overlap the emission lines of GaAs-GaAlAs lasers, making Nd-doped thin-film structures suitable for use in GaAs-based optoelectronic systems.[8] Using pulsed-laser deposition, we were able to grow c-axis oriented $Gd_{0.95}Nd_{0.05}LiF_4$ films on a variety of substrates, including (100) CaF_2 and Al_2O_3. Figure 2 shows the x-ray diffraction pattern for a 500 nm-thick, c-axis oriented $Gd_{0.95}Nd_{0.05}LiF_4$ film grown on single crystal Al_2O_3 at 350°C. Similar results were observed on (100) CaF_2

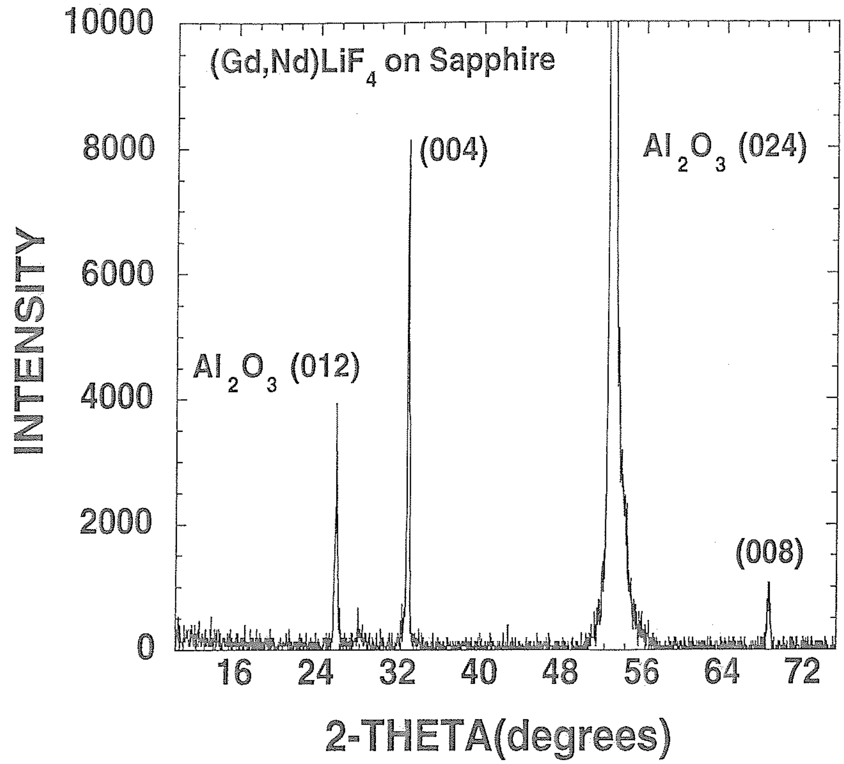

Fig. 2. X-ray diffraction data for c-axis oriented, 0.5 μm thick $Gd_{0.95}Nd_{0.05}LiF_4$ thin film grown on (012) Al_2O_3.

substrates. This film was grown in a background gas of 100 mTorr argon with a base pressure of 2×10^{-7} Torr.

While clearly c-axis textured, four-circle x-ray diffraction revealed no evidence of in-plane alignment of this films, possibly due to the relatively low growth temperature utilized. These films were significantly smoother than films grown from the undoped target. Figure 3(a) shows surface profile scans for films deposited from undoped and Nd-doped $GdLiF_4$ ablation targets using pulsed-laser deposition. From the surface profiles, one can see that the film grown from the Nd-doped target is significantly smoother with a lower density of particulates than the film grown from the undoped target. Figure 3(b) shows a scanning electron micrograph of a film grown from the $Gd_{0.95}Nd_{0.05}LiF_4$ target. From the micrograph, one observes some particles on the surface, although the underlying film appears to be relatively smooth. The presence of these particles in both undoped and Nd-doped films suggests that an alternative PLD geometry, such as off-axis, may be necessary in growing films smooth enough for waveguide applications.

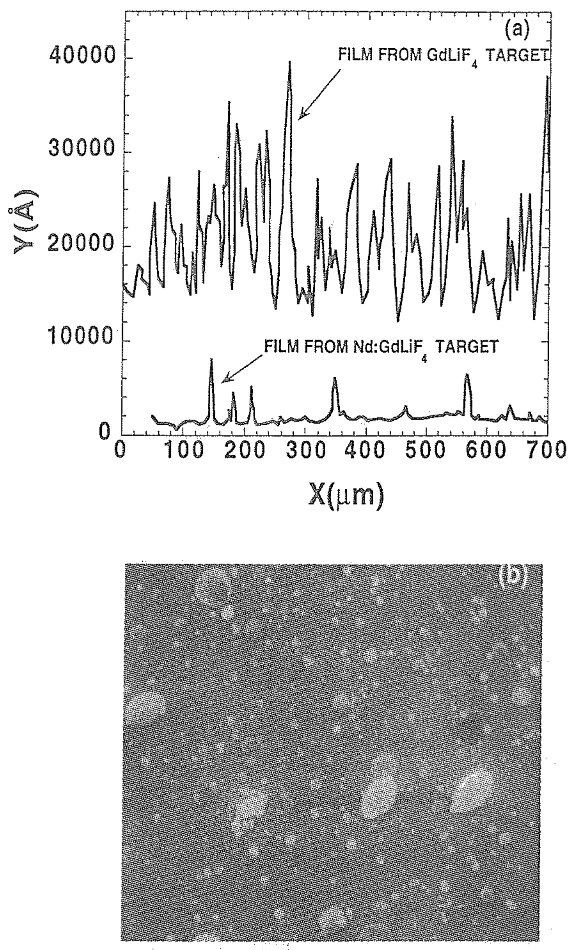

Fig. 3 (a) Surface profile scans of films grown from undoped and Nd-doped $GdLiF_4$ targets showing a high particulate density for films grown from undoped targets. Also shown is a scanning electron micrograph (b) of a 0.5 μm thick $Gd_{0.95}Nd_{0.05}LiF_4$ film grown from a Nd-doped $GdLiF_4$ target. Micrograph dimensions are 28×36 μm^2.

In films that were grown with only moderately low vacuum base pressures, we often observed epitaxial $Gd_4O_3F_6$ as an oxy-fluoride impurity phase. The importance of achieving a low base pressure and eliminating residual sources of oxygen can be seen in x-ray diffraction patterns shown in Fig. 4. These patterns were obtained from two films grown with the same $Gd_{0.95}Nd_{0.05}LiF_4$ ablation target at base pressures of 1.5×10^{-6} Torr and 2.0×10^{-7} Torr. The figure shows that the film grown with a base pressure of 2.0×10^{-7} Torr is c-axis oriented (Gd,Nd)LiF_4. However, pulsed-laser deposition from the same target at a higher base pressure of 1.5×10^{-6} Torr yields the oxy-fluoride $Gd_4O_3F_6$ with virtully no evidence for (Gd,Nd)LiF_4. In fact, we found that with (Gd,Nd)LiF_4 targets, epitaxial $Gd_4O_3F_6$ could easily be grown by pulsed-laser deposition on a variety of substrates. Clearly, the formation of $GdLiF_4$ without the presence of this oxy-fluoride impurity phase requires near-UHV base pressures in the film growth system.

In addition to characterizing the film properties, we also investigated the emission spectra of the ablation plume. Figure 5 shows the emission spectrum of an ablation plume from a $Gd_{0.95}Nd_{0.05}LiF_4$ target irradiated with a focus 193 nm ArF excimer beam. The laser energy density used to obtain this ablation spectrum was 1.7 J/cm^2 with a beam spot size of 1.6×0.7 mm^2. The spectrum was taken 1 cm above the ablation target surface 1 μs after the laser pulse in a base pressure was 10^{-6} Torr. The spectrum shows the presence of atomic fluorine, gadolinium, and lithium in the plume indicating dissociation of the metal-fluorine bonds in the ablation process. Note that this differs from what is typically observed in thermal evaporation sources of metal fluorides in which the metal-fluorine bonds remain intact in the evaporant flux. Atomic metal species in the ablation flux will be quite vulnerable to reacting with any background impurity gases as is observed with the formation of oxy-fluorides.

CONCLUSION

In summary, we have investigated the growth of $GdLiF_4$ thin films for optical waveguide applications using pulsed-laser deposition. Epitaxial, c-axis oriented $GdLiF_4$ films which are in-plane aligned have been grown on (100) CaF_2 substrates. Films grown from undoped $GdLiF_4$ targets in an on-axis PLD geometry exhibit a high density of particulates on the surface which are ejected from the ablation target.

We have also investigated the growth of Nd-doped $GdLiF_4$, where Nd doping of the polycrystalline $GdLiF_4$ ablation targets both increases the optical absorption of $GdLiF_4$ at the ablation laser wavelength of 193 nm as well provides a source of optically-active Nd^{+3} ions in the films. Films grown from Nd-doped $GdLiF_4$ targets by pulsed-laser deposition were significantly smoother with a lower particulate density than films grown from undoped ablation targets, although an off-axis PLD geometry may be necessary in order to achieve waveguide-quality epitaxial films. In addition, we also demonstrated that near-UHV base pressures are required for the deposition of $(Gd,Nd)LiF_4$ films without the formation of impurity oxy-fluorides, such as $Gd_4O_3F_6$.

The authors would like to thank B. C. Chakoumakos for providing the fluoride ablation targets. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Lockheed Martin Energy Systems, Inc.

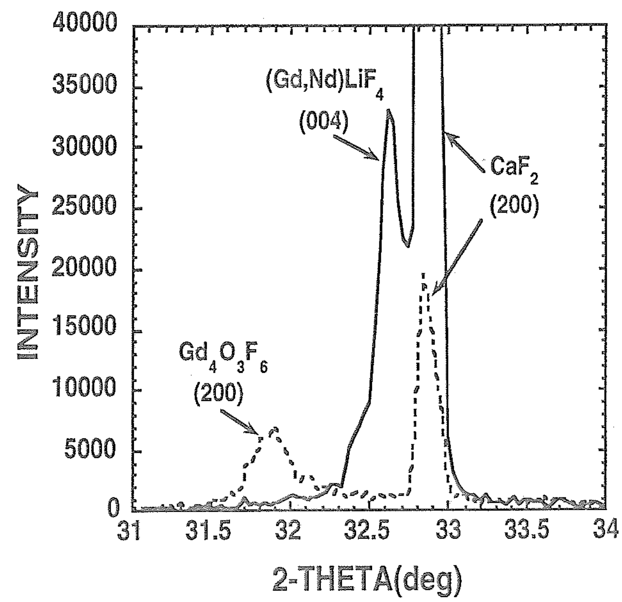

Fig. 4. X-ray diffraction data for $Gd_{0.95}Nd_{0.05}LiF_4$ and $Gd_4O_3F_6$ films obtained from the same target by depositing with different base pressures.

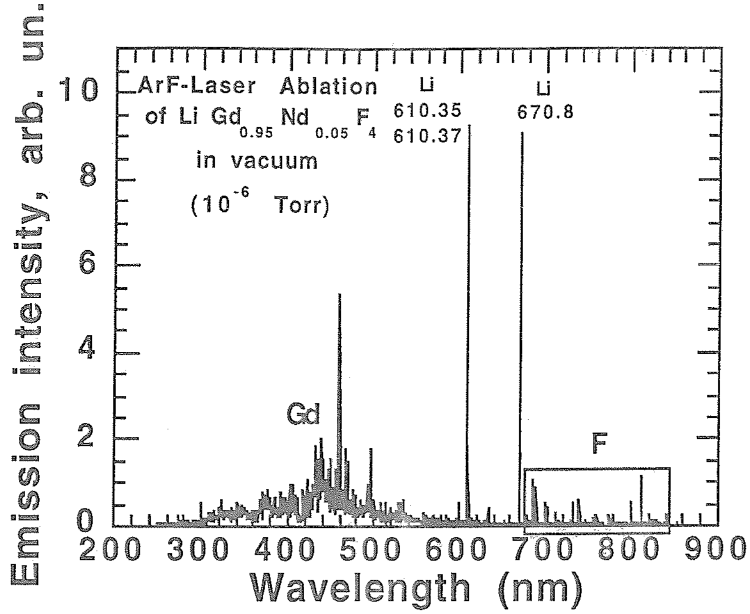

Fig. 5. Emission spectrum of the ablation plume from a $Gd_{0.95}Nd_{0.05}LiF_4$ target showing atomic lines for fluorine, gadolinium, and lithium.

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