Upconverting Tm-doped $BaYYbF_8$ optical waveguides epitaxially grown on GaAs

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TM-doped $BaYYbF_8$ films were epitaxially grown on both (100) and (111) GaAs substrates using CaF_2 or LiF as intermediate layers. The $BaYYbF_8$ phase was found to be a previously unreported cubic phase with a lattice constant of 0.5711 nm, which is different from a monoclinic phase reported for bulk crystals. The films produced UV and visible radiation with wavelengths at 360 nm (UV), 450–480 nm (blue), and 500–550 nm (green) when pumped by laser radiation at 647 nm.

Upconversion lasers represent a class of optically pumped lasers that oscillate at frequencies higher than those used for pumping. The upconversion lasers produce output at wavelengths from violet to red spectral regions using infrared pump wavelengths accessible with III–V semiconductor lasers. These compact light sources are important in optical data storage, high-speed laser printers, large-screen displays, and undersea communications. Materials commonly used for upconversion lasers include rare-earth metal-doped BaY_2F_8[1,2] and $YLiF_4$[3,4] in single crystal or glass-fiber form. Chwalek and Paz-Pujalt reported on both amorphous and crystalline films of Tm-doped $BaYYbF_8$ (hereafter referred to as $BaYYbF_8$) on a quartz substrate producing upconversion excitation.[5] Still, it would be desirable to grow epitaxial films on GaAs, so that diode lasers, upconverting waveguides, light detectors, and electronics can be integrated on the same chip. Epitaxial films of Er-doped PbF_2 were recently reported to grow on (100) GaAs with an intervening SrF_2 cladding layer,[6] but no data are available on epitaxial growth of $BaYYbF_8$ on GaAs.

There are significant obstacles for the growth of epitaxial films of $BaYYbF_8$ on GaAs in waveguide form, because of the following reasons: (a) GaAs has the zinc-blende structure with the lattice parameter 0.5673 nm, while $BaYYbF_8$ is structurally almost identical to BaY_2F_8, which has the monoclinic structure with $a=0.6972$ nm, $b=1.050$ nm, $c=0.4260$ nm, and $\beta=99.70°$[7,8] and (b) the refractive indices of BaY_2F_8 are known to be ~ 1.5,[9] so that very few fluorides can be selected as cladding layers, which have lower refractive indices and lattice matched structures.

In this letter, we report a heteroepitaxial multilayer structure with a $BaYYbF_8$ film epitaxially grown on GaAs and forming a waveguide with its underlying buffer layer of CaF_2 or LiF.

$(NH_4)_2S_x$-treated (100) and (111) GaAs wafers were used as substrates for epitaxial growth of fluoride films. After a conventional cleaning in organic solvents, the wafers were etched in a solution with $H_2SO_4:H_2O_2:H_2O=1:8:500$ for 30 s, followed by a deionized water rinse. Prior to being loaded in an evaporator, the samples were placed in a saturated $(NH_4)_2S_x$ solution for 3–5 min. Following this soak, the ammonium sulfide solution was diluted with deionized water and the samples were immersed in the diluted solution for 3–5 min before being dried under a stream of nitrogen. This method has been used to grow nonlinear optical waveguides on GaAs without *in situ* thermal etching or sputter cleaning.[10]

Either CaF_2 or LiF was deposited directly on GaAs by electron-beam evaporation. The deposition process was carried out at 1×10^{-7} Torr, and the substrate was heated by a radiative heater consisting of tantalum wires. The growth temperature was 400–550 °C and monitored by an infrared pyrometer using published emissivity values. The deposition rate was 0.1–0.4 nm/s and the thickness of the CaF_2 or LiF films was about 300–500 nm.[11]

The source used for $BaYYbF_8$ was prepared from powders using electronic grade BaF_2, YF_3, YbF_3, and TmF_3 having a mole ratio of 1:1:1.1:0.01. The mixed powders were pelletized under a pressure of 5000 psi. $BaYYbF_8$ films were deposited on CaF_2 or LiF-covered GaAs by *e*-beam evaporation. The deposition was carried out at a rate of 0.1–0.4 nm/s at temperatures of 400–550 °C, and the thickness of the $BaYYbF_8$ films was about 300–500 nm.

The composition of the resulting fluoride films was determined with Rutherford backscattering spectrometry (RBS) and the structural properties were characterized by x-ray diffraction (XRD) and ion channeling.

RBS measurements showed the evaporated fluoride film on GaAs having nominal composition $BaY(Yb+Tm)_{0.95}F_8$. To determine the ratio of Tm to Yb is not possible because their signals overlap on the spectrum. The successful deposition of the fluoride films using a single electron beam is attributed to the similar vapor pressures of the constituent fluorides.

The standard θ-2θ x-ray diffraction pattern in Fig. 1, obtained from a sample comprised of (100) GaAs/CaF_2/$BaYYbF_8$, reveals two diffraction peaks centered at $2\theta=31.3°$ and 65.2° due to the $BaYYbF_8$ phase, in addition to the peaks corresponding to GaAs and (100)-oriented CaF_2. The two $BaYYbF_8$ peaks can be indexed as the (220) and (440) reflections of the well-known monoclinic phase, however, these peaks were not observed to be present for

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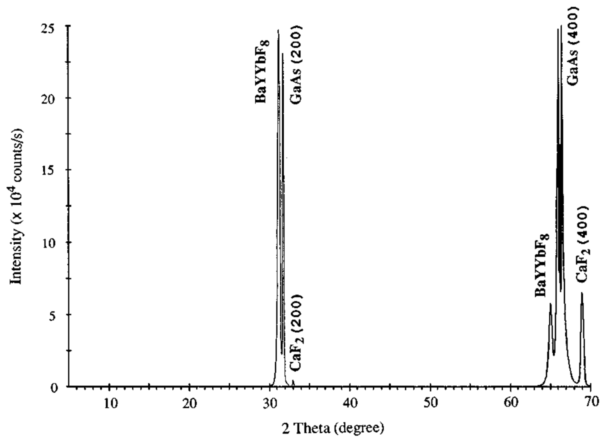

FIG. 1. X-ray diffraction pattern of a Tm-doped $BaYYbF_8$ film grown on (100) GaAs with an interposed CaF_2 layer.

powders.[7] They can also be assigned as the (200) and (400) reflections for a cubic phase with a lattice constant of 0.574 nm. The full width of the rocking curves at half maximum (FWHM) was determined to be about 0.2° for GaAs, 0.5° for CaF_2, and 0.9° for $BaYYbF_8$. The highly oriented $BaYYbF_8$ film was further verified by ion channeling measurements. Figure 2 shows backscattering spectra with He ions at both a random and a [100]-oriented incidence. No interactions between GaAs and fluorides were revealed. The minimum channeling yield, which is defined as the ratio of the aligned yield to the random yield, was determined to be about 0.24. This value is substantially lower than one, indicating good crystal quality.

A highly oriented $BaYYbF_8$ film has also been grown on a (111) GaAs substrate with a (111)-oriented CaF_2 buffer layer. X-ray analysis showed two peaks centered at $2\theta = 27.0°$ and 55.5° other than the (111) reflections of GaAs and CaF_2. Neither of the two peaks can be assigned to the monoclinic phase, however, they can be readily identified as the (111) and (222) reflections of the cubic phase.

In-plane alignment of the $BaYYbF_8$ films grown on

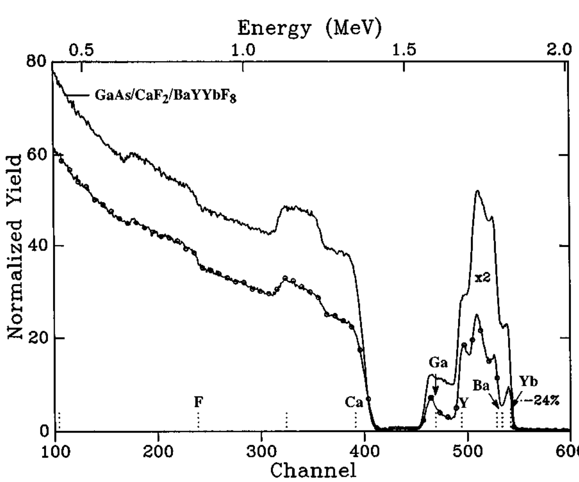

FIG. 2. 2.0 MeV $^4He^{++}$ random and channeling spectra of a (100) GaAs/CaF_2/Tm-doped $BaYYbF_8$ sample.

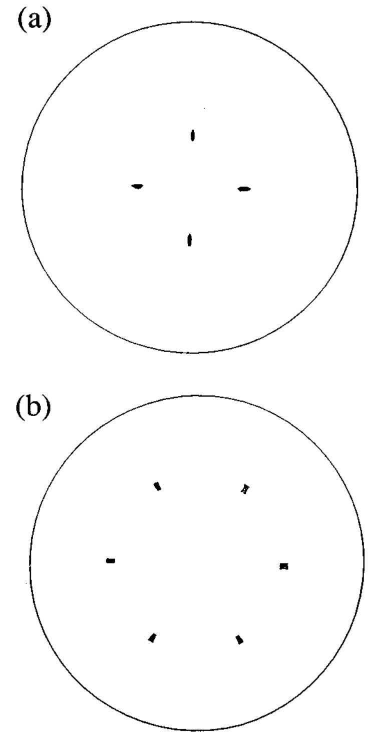

FIG. 3. X-ray pole figures taken from (a) the (220) peak of a Tm-doped $BaYYbF_8$ overlayer grown on (100) GaAs and (b) the (100) peak of a Tm-doped $BaYYbF_8$ overlayer grown on (111) GaAs with a CaF_2 buffer layer.

GaAs was determined by x-ray pole figure analysis. In the analysis, the fluoride phase was first assumed to be cubic with $a = 0.574$ nm, and the assumption was found to be consistent with the following findings. The pole figure of Fig. 3(a), taken from the (220) peak of the $BaYYbF_8$ overlayer grown on (100) GaAs, exhibits four spotlike pole densities, suggesting that the $BaYYbF_8$ film is (100) planar oriented with a fourfold rotation symmetry. The (220) pole figures of $BaYYbF_8$, CaF_2, and GaAs were found to be aligned with the same in-plane orientation, indicating that the $BaYYbF_8$ film is epitaxial. The pole figure of Fig. 3(b), taken from the (100) peak of the $BaYYbF_8$ overlayer grown on (111) GaAs, exhibits six pole figure densities with almost equal intensity. By comparing the pole figure in Fig. 3(b) and that of the underlying CaF_2 and GaAs, one can find a (111) planar oriented $BaYYbF_8$ film grown epitaxially on (111) GaAs. The pole figure of Fig. 3(b) also reveals the presence of high twin density in the epitaxial film $BaYYbF_8$.

The presence of a cubic phase $BaYYbF_8$ was further verified by unit cell evaluation. Under the same deposition conditions mentioned previously, a $BaYYbF_8$ polycrystalline film was prepared on a Si wafer capped with a thermally grown SiO_2 layer. X-ray diffraction analysis showed more than twenty peaks, and all of them can be indexed based on a cubic unit cell with a lattice constant $a = 0.5711$ nm.[12] The intensities of the diffraction peaks suggest that this previously unreported phase is a defective face-centered cubic structure, since some very weak primitive cubic reflections are observed in the diffraction pattern. The difference in the lattice constant between $BaYYbF_8$ deposited on GaAs/CaF_2

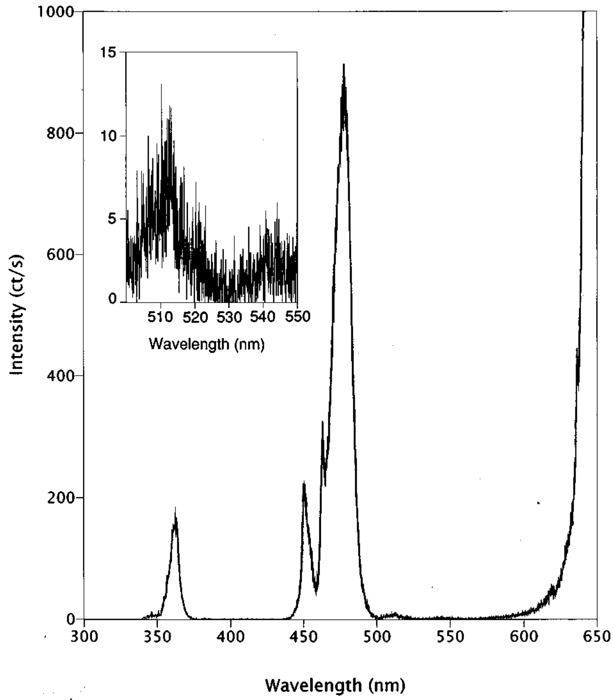

FIG. 4. Spectra of upconverted luminescence for a (100) GaAS/LiF/Tm-doped $BaYYbF_8$ sample pumped by laser radiation at 647 nm.

and that on Si/SiO_2 suggests that one or both films may be strained. The presence of this cubic structure opens up the opportunity of growing $BaYYbF_8$ epitaxial films on GaAs. The investigation of phase stability and phase transformation of the two crystal structures is in progress.

Epitaxial growth of $BaYYbF_8$ film was also achieved on (100) GaAs when using a LiF buffer layer, but it failed on (111) GaAs because the interposed LiF layer exhibited a mixed orientation. Since the refractive index of $BaYYbF_8$ is substantially higher than that of CaF_2 and LiF, one can expect that a waveguide would be formed if the cladding layer is sufficiently thick.

The spectral response of the Tm-doped $BaYYbF_8$ films was assessed by focusing radiation from a laser beam at 647 nm. Figure 4 shows a spectrum of a Tm-doped $BaYYbF_8$ film grown on (100) GaAs with a LiF buffer layer. Similar results were obtained with a CaF_2 interposed layer, although the intensity was lower than that shown in Fig. 4. The films produced UV and visible radiation with wavelengths at 360 nm (UV), 450–480 nm (blue), and 500–550 nm (green). The presence of green upconverted luminescence can be clearly seen in the insert of Fig. 4. Chwalek and Paz-Pujalt[5] reported that the linewidths of upconversion excitation from Tm-doped $BaYYbF_8$ were much broader in an amorphous film grown on a fused silica substrate than that in a bulk single crystal. The broader upconverting luminescence observed in Fig. 4 from epitaxial films is presumably due to high defect densities as suggested by x-ray analysis and/or nonstoichiometric composition as revealed by RBS measurements.

In summary, Tm-doped $BaYYbF_8$ films were grown epitaxially on both (100) and (111) GaAs with CaF_2 or LiF as buffers, providing a desirable structure for monolithic integration of upconverting waveguides and laser diodes. X-ray diffraction indicated that the $BaYYbF_8$ films have a cubic structure with a lattice constant of 0.5711 nm, which is different from the monoclinic structure reported for bulk crystals. To our knowledge, this letter represents the first report on epitaxial growth of $BaYYbF_8$ on GaAs and the presence of an alternative cubic structure of $BaYYbF_8$.

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