Growth of alternating $\langle 100\rangle/\langle 111\rangle$-oriented II-VI regions for quasi-phase-matched nonlinear optical devices on GaAs substrates

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(Received 20 December 1993; accepted for publication 5 April 1994)

We present a technique for fabricating laterally patterned $\langle 111\rangle$ and $\langle 100\rangle$-oriented regions of CdTe on GaAs by metalorganic chemical vapor deposition. Patterning of the crystal orientation is important for quasi-phase-matched nonlinear optical frequency conversion in semiconductor waveguides. Scanning electron micrographs and x-ray diffraction analysis are used to confirm the presence of $\langle 111\rangle/\langle 100\rangle$ grating structures. The CdTe layer is shown to be a suitable template to pattern the orientation of subsequently grown wide-band-gap films of ZnSe and ZnTe.

Nonlinear optical frequency conversion in waveguides has been widely studied as a means of generating coherent visible and mid-infrared radiation from near-infrared pump lasers.[1,2] The majority of these devices are currently based on periodically poled oxide ferroelectrics such as lithium niobate and potassium titanyl phosphate. Efficient operation is possible at input powers below 100 mW, levels readily available from commercial semiconductor diode lasers.[3,4] A significant difficulty in practical application of this technology results from the strict alignment tolerances for the hybrid coupling between the diode laser and the waveguide. Monolithic integration of the nonlinear waveguide with the pump laser would eliminate this problem. One approach to such integration requires fabrication of an appropriate waveguiding nonlinear film on a III-V substrate, and means for accomplishing phase matching in the film. In this letter we describe growth of wide-band-gap II-VI films on GaAs substrates, and patterning of the orientation of these films for quasi-phase-matched (QPM) nonlinear interactions.

II-VI semiconductors, with transparency from the far infrared to the visible, and large nonlinear susceptibilities, have potential for efficient waveguide nonlinear devices. II-VI materials in the zincblende structure are optically isotropic, and hence cannot be used for birefringently phasematched interactions.[5] A powerful alternative technique, QPM, requires periodic patterning of the sign or magnitude of the nonlinear susceptibility on a micron spatial scale.[2] In ferroelectrics this modulation can be accomplished by periodically reversing the orientation of the ferroelectric domains, which changes the sign of the effective nonlinear coefficient in adjacent domains.

An alternative method, suitable for nonferroelectric media such as the II-VI semiconductors, is to laterally pattern the crystal orientation of the nonlinear film during growth. Ideal QPM could be accomplished in zincblende crystals by creating a $[111]/[\bar{1}\bar{1}\bar{1}]$ pattern, in which the nonlinear coefficient d_{eff} varies as $\pm 2d_{14}/\sqrt{3}$. The combination of $[111]/[001]$ orientations, utilized in this work, results in an amplitude modulation of d_{eff} between $2d_{14}/\sqrt{3}$ and 0, which is one fourth as efficient as the ideal case. The nonlinear susceptibility of II-VI compounds is relatively large, ranging from d_{14} values of 27 pm/V in ZnS to 90 pm/V in ZnTe, compared to d_{33} in $LiNbO_3$ of approximately -34 pm/V.[6] Using the formalism of Ref. 2, for a structure with a ZnSe core, an input power of 100 mW, a waveguide length of 0.5 cm, an effective area of 10 μm^2, and doubling to a wavelength of 532 nm, the theoretical conversion efficiency for ideal first order QPM is 12.5%, which is roughly half the theoretical value for $LiNbO_3$.[2]

A possible II-VI frequency doubler, shown schematically in Fig. 1, consists of a waveguide with laterally patterned crystal orientation for QPM. The desired crystal orientations are established in a template layer which lies below the waveguide. One way to order the template is to use a CdTe layer on a $\langle 100\rangle$ GaAs substrate. Patterning is achieved by introduction of a thin interlayer, such as ZnTe, in those regions which will be $\langle 100\rangle$ oriented.[7] A variety of materials may be used for the core and cladding layers of the waveguide pictured in Fig. 1. We will use a ZnTe core and ZnSe cladding layer for a proof of principle device doubling from a wavelength of 1.5–0.75 μm. Lower absorption of visible second harmonic wavelengths could be achieved by the use of wider band-gap layers such as ZnSe, ZnS, and ZnS_xSe_{1-x}.

The materials used in this study were grown by metalorganic chemical vapor deposition (MOCVD) at atmospheric pressure using dimethyl cadmium, di-isopropyl telluride, diethyl zinc, and di-isopropyl selenide in a hydrogen carrier

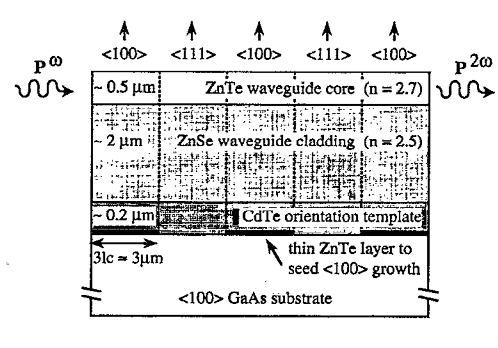

FIG. 1. Device geometry for the proposed II-VI optical frequency doubler on GaAs.

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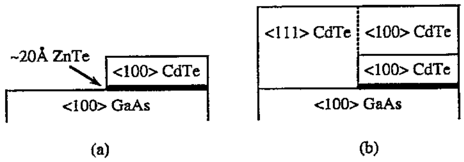

FIG. 2. (a) Etching and (b) regrowth procedures for lateral patterning of CdTe orientation on ⟨100⟩ GaAs.

gas. The reactor includes a horizontal, rectangular quartz reaction chamber and a graphite wafer support, which is heated by incandescent lamps, allowing different layers to be grown in the optimum temperature range for each material.[8] Typical growth temperatures for CdTe, ZnTe, and ZnSe are 330, 350, and 390 °C, respectively.

Our method for growing patterned II-VI films is based on the observation that the orientation of a CdTe film on a GaAs substrate depends on the surface preparation.[9] CdTe grows in the ⟨111⟩ orientation on a very clean ⟨100⟩ GaAs surface, obtained by a wet chemical clean and an *in situ* prebake at 600 °C for 5 min. If the GaAs surface is seeded with a thin (~20 Å) ZnTe layer after the high-temperature prebake, a subsequently grown CdTe film maintains the ⟨100⟩ orientation of the GaAs substrate. It has been suggested that this behavior is related to the nearly 15% lattice mismatch between ⟨100⟩ CdTe and ⟨100⟩ GaAs.[10,11]

The film patterning procedure is illustrated in Fig. 2. First, a ⟨100⟩ CdTe film is grown on a bare GaAs substrate, using a thin ZnTe layer at the interface to achieve the ⟨100⟩ orientation. For this growth, the substrate is cleaned in 1,1,1-trichloroethane and acetone, etched for 5 min in 5:1:1 H_2SO_4:H_2O_2:H_2O, rinsed in water, and spun dry. The wafer is loaded into the reaction chamber and heated to 600 °C in hydrogen for 5 min to desorb the native GaAs oxide. The ZnTe layer is grown at 330 °C by successive 40 s pulses of the Te and Zn precursors. Di-isopropyl telluride is first passed over the wafer at a partial pressure of 1×10^{-4} atm., followed by diethyl zinc at 1.7×10^{-4} atm. The first CdTe layer is grown at 330 °C in the ⟨100⟩ orientation, at a growth rate of approximately 1.5 μm/h.

After the growth of the ⟨100⟩-oriented layer, the wafer is masked with photoresist gratings having 5, 10, and 20 μm periods. The film is etched back to the GaAs substrate using KI:I:HBr, an etch chosen for its high selectivity between CdTe and GaAs.[12] The sample is prepared for regrowth by a solvent clean of 1,1,1-trichloroethane, acetone, and methanol. An *in situ* cleaning process consisting of heating the wafer to 330 °C in an ambient of 1×10^{-4} atm. of di-isopropyl telluride for 2 min allows subsequent growth of high quality ⟨111⟩ CdTe on the bare GaAs regions, while the ⟨100⟩ CdTe stripes remain in place. Following this preparation, CdTe growth is resumed at 330 °C. ⟨100⟩ CdTe grows in the masked regions at approximately 1.5 μm/h, and ⟨111⟩-oriented CdTe grows in the etched areas at nearly 3 μm/h. The length of this second CdTe growth period is timed so that the growth terminates with a flat surface, which may be further smoothed by using a polishing etch. For the samples discussed here, the surface morphology was specular, although the patterned layers exhibit some scattering which is partially due to diffraction by the grating pattern.

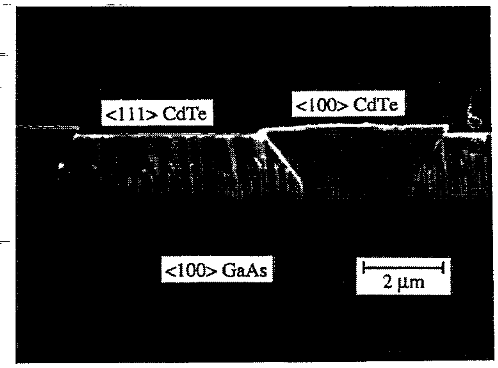

FIG. 3. Scanning electron micrograph showing growth of laterally patterned ⟨111⟩/⟨100⟩ CdTe on GaAs.

Figure 3 shows a scanning electron micrograph of an orientation-patterned CdTe layer in cross section. This sample, approximately 1.5 μm thick, was created by an initial growth of ⟨100⟩ CdTe for 30 min at 330 °C, followed by a 35 min regrowth at the same temperature. The rough cross-section of the ⟨111⟩ regions results from the fact that the crystal is forced to break at the ⟨112⟩ face, which is not a natural cleave plane. The trapezoidal shapes of the crystal domains are believed to be caused by faceting during regrowth: after etching, a ⟨111⟩ surface is exposed at the top edges of the ⟨100⟩ CdTe stripes. This is a very rapid growth direction and grows out to a point bordered by the ⟨100⟩ and ⟨112⟩ faces.

Crystal orientations are confirmed by x-ray diffractometry, in which the grating structure is irradiated by a Cu $K\alpha1$ x-ray source. Figure 4 shows the resulting 2θ scan. The 2θ peak at 56.6° is associated with the (400) CdTe lattice planes, and the 23.7° peak corresponds to (111) CdTe planes. To determine crystal quality, double-crystal rocking curves were acquired using a Philips MRD diffractometer. The full width at half-maximum (FWHM) of the (400) and (111) peaks were found to be 6.5 and 17 arcmin, respectively. The (400) peak is comparable to published values, but the (111) peak is broader than reported.[13,14] Our blanket wafer ⟨111⟩ CdTe exhibits a FWHM of 11 arcmin, implying that the ⟨111⟩ regrowth process requires further optimization.

The dependence of the nonlinear susceptibility on crystal

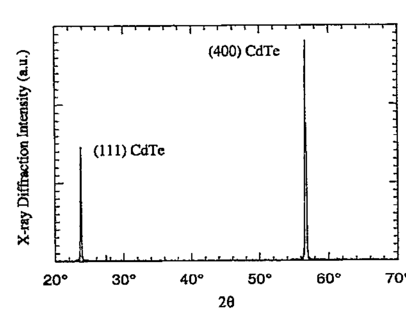

FIG. 4. X-ray diffraction analysis of laterally patterned CdTe, showing ⟨111⟩- and ⟨100⟩-oriented regions.

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orientation has been confirmed optically using reflected second harmonic generation (SHG) measurements.[7] The 1.06 μm s-polarized output of a Q-switched Nd:YAG laser was weakly focused on large (1 cm×1 cm) regions of ⟨111⟩- or ⟨100⟩-oriented material at an incidence angle of 45°. The reflected p-polarized SHG output was measured as the wafer was rotated around the surface normal. The azimuthal dependence of the SHG intensity closely followed the expected fourfold symmetry on ⟨100⟩ films and threefold symmetry on ⟨111⟩ films, with less than 5% deviation in both cases. The strength of the SHG modulation between ⟨110⟩ (ON) and ⟨100⟩ (OFF) polarizations of the input beam was a factor of approximately 750 in the ⟨100⟩-oriented region. This indicates that d_{eff} can be strongly modulated in a II-VI patterned QPM structure.

The patterned CdTe film can now serve as a template for the growth of the remaining layers of the waveguide structure. To verify that the ⟨111⟩ and ⟨100⟩ orientations are maintained in layers grown above this template, ZnSe and ZnTe films were grown on large-area CdTe films of either ⟨111⟩ or ⟨100⟩ orientation. X-ray analysis reveals that these wide-band-gap layers do indeed follow the underlying template orientation, indicating that the orientation established in the CdTe layer can be maintained throughout the structure.

Further steps in fabricating the complete structure shown in Fig. 1 involve the growth of wide-band-gap waveguide layers, and patterning these layers to form channel waveguides. Absorption losses in ZnSe/ZnTe waveguides must be measured, and scatter at ⟨111⟩/⟨100⟩ boundaries characterized.

In summary, alternating ⟨100⟩/⟨111⟩-oriented stripes of CdTe have been grown on GaAs substrates by MOCVD. These structures can serve as a template for the growth of a variety of different materials for quasi-phase-matched waveguide nonlinear optical interactions. Successful implementation of these patterned semiconductor structures will be important both for monolithically integrated visible light sources as well as for the extension of QPM techniques to longer wavelengths beyond the infrared absorption edges of common oxide ferroelectrics.

This work is supported by the Advanced Research Projects Agency through the Optoelectronics Materials Center. M. J. Angell acknowledges fellowship support from the National Science Foundation.

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