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Diffusion Bonding of GaAs Wafers for Nonlinear Optics Applications

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ABSTRACT

Diffusion-bonded stacked periodic structures represent a new family of optical materials with spatially patterned nonlinear properties. The bonding process preserves both the optical and mechanical properties of the bulk materials. GaAs devices up to 20 layers were diffusion bonded and characterized. Optical loss was from interfacial voids and gaps at shorter wavelengths and from processing-induced p-type free carrier absorption at longer wavelengths.

Introduction

High-power laser sources in the mid-infrared (MIR) spectral range (between 1 and 10 μm) have wide applications in remote sensing and military countermeasures. However, currently available high-power lasers have output wavelengths around 1 μm (rare earth doped crystals) and 10 μm (CO_2 laser). One way to generate high-power laser radiation at MIR wavelengths is to convert the output of currently available lasers to the desired wavelengths by nonlinear optical frequency conversion. Unfortunately, existing MIR nonlinear optical crystals are difficult to grow, have poor thermal properties and low optical damage thresholds, and are expensive.

Single-crystal GaAs has a large nonlinear coefficient, good optical transmission between 1 and 12 μm, and a high optical damage threshold. It has good chemical stability, good mechanical properties, and a well-developed growth technology. However, optically isotropic crystals like GaAs cannot be used directly for nonlinear frequency conversion, because the interacting waves cannot be phasematched, *i.e.*, there is no way to compensate for the wavelength dependence of the refractive indexes (dispersion). Figure 1a shows second harmonic power as a function of interaction length for a nonphasematched situation. Since refractive indexes determine phase velocities of the waves, the fundamental wave has a different phase velocity than the second harmonic wave. As the two interacting waves propagate through the crystal, the phase difference increases and the conversion efficiency decreases. One coherence length into the crystal, the two waves are out of phase by π radians, and the power in the second harmonic wave begins converting back to the fundamental wave.

Changing the sign of the nonlinear optical coefficient every coherence length allows continuous growth of the second harmonic power, as shown in Fig. 1b. For a $\bar{4}3m$ crystal like GaAs with wave propagation normal to the surface, the maximum nonlinear coefficient is obtained with a (110)-oriented wafer. The sign of the nonlinear optical coefficient can be reversed in a (110) wafer by a 180° rotation around [1$\bar{1}$0]; thus, a stack of (110) GaAs plates, each one coherence length thick and alternately rotated about their [1$\bar{1}$0] direction, produces a quasi-phasematching (QPM) structure. Second harmonic generation (SHG) in a QPM structure was first demonstrated in GaAs in 1976.[1,2] Plates were polished to one coherence length (106 μm for SHG of 10.6 μm radiation) and aligned at Brewster's angle. Enhanced conversion efficiency was measured; however, this method has not seen practical application, largely due to alignment difficulties, optical losses and mechanical fragility at air-GaAs interfaces.

QPM in III-V waveguides has been demonstrated earlier by etching gratings in the waveguide surface[3] and by growth of controllably twinned films on template substrates.[4] For high-power applications, a bulk device is preferable to a waveguide structure. Previously, we had

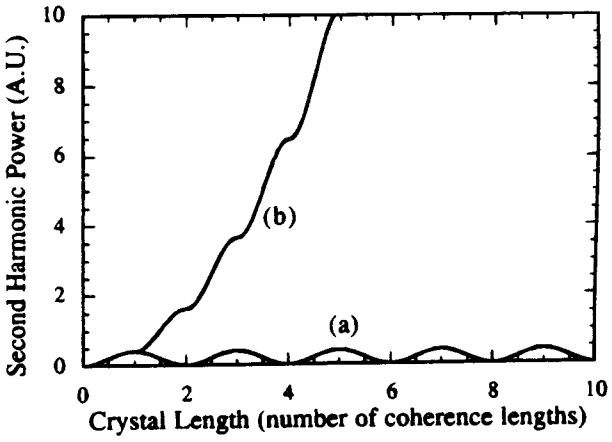

Fig. 1. Theoretical second harmonic power as a function of crystal length: (a) nonphasematched interaction (b) quasi-phasematched interaction.

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diffusion-bonded stacks of GaAs plates for bulk QPM interactions.[1,9] Figure 2 shows a schematic of a diffusion-bonded crystal that can be used for frequency doubling CO_2 laser radiation. We observed the expected improved nonlinear optical properties in our initial bonded stacks: however, the MIR losses were higher than expected. In theory, practical devices will require bonded stacks of 50 or more GaAs plates to achieve a 10% conversion efficiency with 10 MW/cm^2 input intensity. Optical losses introduced by the bonding process must therefore be lower than 0.1% per layer for efficient energy conversion. Here we report the identification of loss mechanisms and reduction of optical loss in diffusion bonded stacked GaAs through refinements in processing parameters.

Experimental

Processing.—Two-side polished (110) semi-insulating GaAs wafers 320 μm thick were diced into 1 cm squares. The squares were then etched in NH_4OH for 15 min to remove the native oxide. After rinsing in flowing deionized water for 5 min, they were assembled by stacking in the configuration shown in Fig. 2 while still immersed in deionized water. This process reduced particle contamination at the interfaces.

The wafers were bonded at temperatures ranging from 700 to 975°C in a pure N_2 atmosphere in a vertical bonding furnace shown in Fig. 3. Bonding pressures were varied from 20 to 40 kg/cm^2 and bonding times from 2 to 9 h. The density of optically resolvable voids at the interfaces of cleaved samples was found not to be a strong function of either pressure or time over these ranges.

Characterization.—During commercial polishing, the two sides of the wafer tend to develop slightly different surface qualities. Therefore, during our process development, three "squares" were bonded together each time to test the bonding quality of both surfaces. After bonding, the samples were cleaved and sections of the interfaces observed with an optical microscope and a scanning electron microscope (SEM). Voids at the interfaces were found to be less than 0.5 μm diam. Interfacial gaps about 0.2 μm wide and millimeters long occurred occasionally. Transmission electron microscopic (TEM) analysis indicated that bonding disrupts only a few atomic layers on either side of the interface. Optical transmission was measured from 1 to 14 μm with a Perkin-Elmer Lambda-9 spectrophotometer and a Bio-Rad FTS-40 Fourier transform infrared (FTIR) spectrometer.

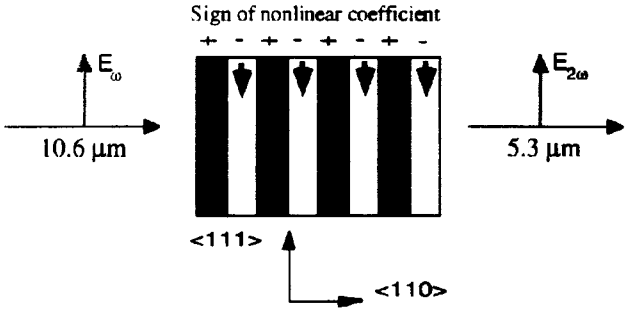

Fig. 2. DBS GaAs for frequency doubling of 10.6 μm CO_2 laser radiation.

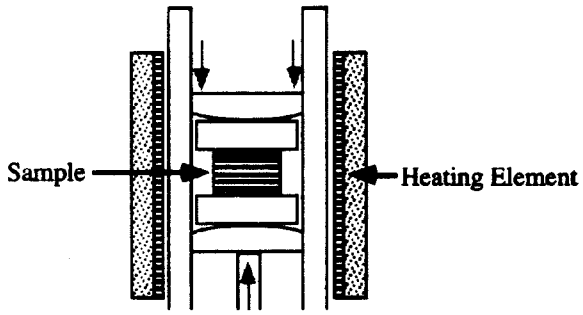

Fig. 3. Schematic of the furnace used for bonding.

Results

To characterize optical loss mechanisms, we bonded 15 to 20 layer stacks of 1 cm GaAs squares which were sufficiently thick to measure the optical loss. The optical transmission spectrum of a 20 layer DBS GaAs (curve a) is compared to that of an unprocessed single GaAs wafer (curve c) in Fig. 4. The near-IR transmission spectrum could be fitted to a theoretical transmission spectrum model which included the effects of scattering and reflections from interfacial voids and gaps.[7] At wavelengths between 1 and 2 μm, the transmission spectrum follows a λ^{-4} behavior similar to that characteristic of Rayleigh scattering, suggesting that the dominant optical loss in this wavelength region results from scattering from subwavelength voids at the interfaces. Between 2 and 3 μm interfacial gaps appear to be the dominant source of the loss, since the transmission spectrum can be fitted to a theoretical model which assumes only interfacial gaps. However, the increase in the losses with increasing wavelength beyond 4 μm cannot be explained by either of these mechanisms.

Figure 5 shows the transmission of a single GaAs wafer annealed at temperatures between 700 and 834°C. Loss at long wavelengths increased as a function of both wavelength and annealing temperature. The observed wavelength dependence is similar to that of p-type free carrier

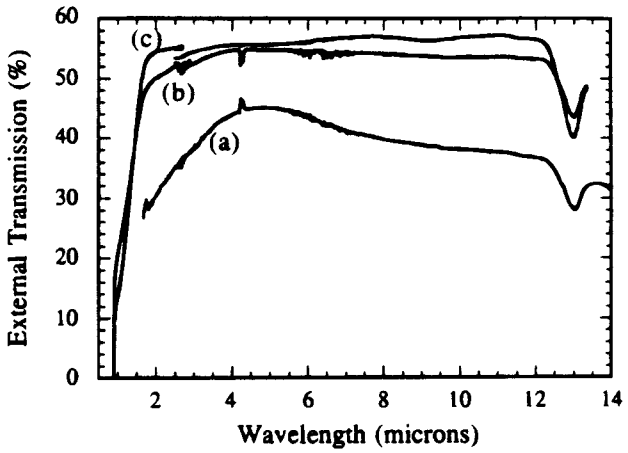

Fig. 4. Transmission spectra of (a) a 20 layer DBS GaAs (6.4 mm long, bonded at 834°C), (b) a 15 layer DBS GaAs (5 mm long, bonded at 700°C), and (c) a single unbonded GaAs wafer for reference.

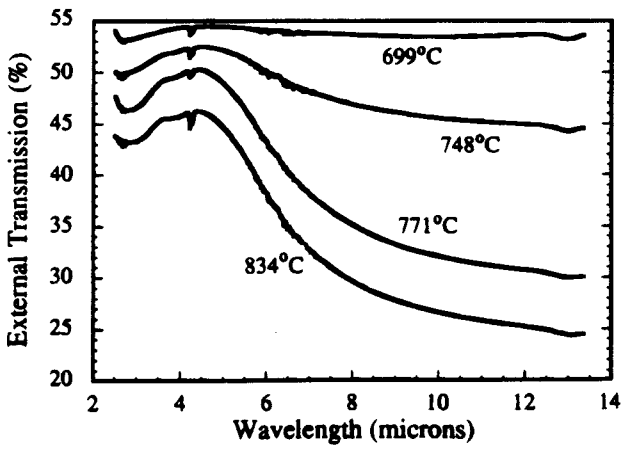

Fig. 5. Transmission of a single GaAs wafer annealed at different temperatures.

absorption.[5] Hall measurements verified that our semi-insulating wafers became p-type after annealing at 834°C, with a carrier concentration around $10^{16}/cm^3$, confirming process-induced bulk absorption.

Semi-insulating to p-type conversion reported previously[9-13] was found to depend on trace doping and the thermal history of the wafers. We found the annealing-induced optical loss could be significantly reduced by bonding at lower temperatures. However, lower bonding temperatures reduced surface mobility, which made it harder to fill interfacial voids. Bonding at 700°C was found to give acceptable bonds without strong p-type conversion; the resulting optical transmission was greatly improved (curve b, Fig. 4).

Summary

In summary, we have bonded multiple GaAs layers with improved optical transmission. Optical losses at shorter wavelengths were due to interfacial voids and gaps, while processing-induced p-type free carrier absorption caused losses at longer wavelengths. Bonding at 700°C minimized the p-type conversion and significantly reduced optical loss.

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Relationship of Processing Parameters to Photoluminescence Intensity and Mechanical Failure in Thick Porous Silicon Layers

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ABSTRACT

The surface passivation of porous silicon has received much attention. While nuclear magnetic resonance may be able to provide insight into the surface passivation of porous silicon, relatively thick (>40 μm) layers are desired. However, mechanically stable layers could only be produced within identifiable ranges of HF concentration, current density, and anodization time. This information allowed sample preparation for ^{29}Si nuclear magnetic resonance characterization of porous silicon. In addition, an inverse correlation between mechanical stability and photoluminescence intensity was observed. In a pairwise comparison, similar porosity and surface passivation were maintained as anodization time increased under otherwise constant conditions. However, at the longer anodization time, photoluminescence intensity and surface area increased. To account for these observations, we hypothesize that the thickness of the silicon wall between pores decreases as electrochemical etching proceeds. Decreasing wall thickness could lead to both mechanical failure and increase the probability of creating regions of quantum confinement. A larger number of quantum confined regions, having the same surface passivation, could account for the observed increased photoluminescence intensity.

Introduction

The discovery of visible light emission by photoluminescence (PL) has renewed interest in porous silicon (PS).[1] The prospect of incorporating optical devices, such as light emitting diodes (LEDs), directly into silicon-integrated circuits would find many applications in very large-scale integrated (VLSI) and display technology. The optoelectronic properties of PS are in sharp contrast to the weak, infrared PL of bulk crystalline silicon, which is a small (1.1 eV), indirect bandgap semiconductor. Many theories have been advanced to account for the PL efficiency (1 to 10%)[2] and the bandgap (~2 to 3 eV) of PS. These include quantum-size effects on the band structure,[3] light emission from localized states such as oxide-related defects,[4-6] and quantum confinement with surface state emission.[7] In addition, temperature dependent PL studies have suggested that the red luminescence from amorphous Si:O:H alloys and from PS may have a similar source.[8] Porous silicon is an inhomogeneous material which displays complex optical behavior.[9] Multiple peaks in the PL spectra have been reported.[10]

Transmission electron microscopy and Raman spectroscopy shows PS contains roughly spherical crystallites with diameters of several nanometers dispersed within a continuous amorphous phase.[11-13] Crystallite dimensions