APPLIED PHYSICS LETTERS VOLUME 80, NUMBER 13 1 APRIL 2002

Reduction of reflection losses in $ZnGeP_2$ using motheye antireflection surface relief structures

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(Received 29 October 2001; accepted for publication 4 February 2002)

We report the reduction of surface reflection losses in zinc germanium phosphide ($ZnGeP_2$, or ZGP) crystals by fabricating an antireflection (AR) structure in the substrate itself using subwavelength motheye surface patterns. The motheye AR patterning works by creating a region of gradually varying effective refractive index between air and the ternary nonlinear crystal. Motheye structures were created using interference lithography and reactive-ion etching in a $SiCl_4$ plasma. The ZGP crystal with motheye patterning on the output surface reached a transmittance of ~67% at a cutoff wavelength of 3.8 μm (close to the theoretical maximum of 73%), with negligible surface contamination from the motheye etching process. The motheye patterning technique could be applied to other nonlinear crystals where surface reflection losses are a concern. [DOI: 10.1063/1.1466519]

Zinc germanium phosphide (ZGP) is a nonlinear optical material used in the generation of mid-IR radiation.[1] In a typical nonlinear process, a ZGP crystal is pumped by a high-energy laser source (e.g., $\lambda_{IN}=2.09$ μm) on one (input) crystal surface and emits longer-wavelength, broadband tunable radiation ($\lambda_{OUT}=3$–6 μm) from the other (output) surface.[2] To increase the transmittance of both surfaces, dielectric antireflection (AR) coatings are usually applied to reduce Fresnel reflection losses. Thin-film dielectric coatings, however, suffer from several fundamental problems, including poor adhesion and thermal mismatch (due to the anisotropic thermal expansion coefficients of ZGP crystals[3]) surface contamination, and catastrophic damage, especially under high-power operating conditions.[4,5] An increase in laser damage threshold (and nonlinear crystal performance) is possible if the AR functionality could be directly "integrated" into the substrate itself. Motheye surface structures are one way to achieve this integration, and pose an alternative to dielectric AR coatings.

The motheye is a periodic subwavelength surface relief structure that can produce nearly zero reflectance over a large range of wavelengths and fields of view.[6] The basic motheye geometry is illustrated in Fig. 1(a): a repeated pattern of tapered features is etched into the surface, with the pattern period Λ designed to be smaller than the smallest wavelength of interest. The result is a "transition" region that continuously grades the effective refractive index n from that of the incident medium (in our case, air, $n_0=1.0$) to that of the nonlinear crystal ($n_{ZGP}=3.17$). Provided the motheye pattern is etched deep enough with optimal profile,[6] light incident on a motheye-patterned substrate should suffer no Fresnel reflection losses. Previously, motheye patterning has been employed to reduce reflection losses in diamond,[7] and diamond-coated Ge.[8] Because the motheye AR structures are patterned in the nonlinear crystal itself, they have the same thermal and physical properties as the bulk crystal, making them interesting for high-power applications where reflection losses are an issue. The specific period, depth, and cross-sectional geometry of the pattern determine the AR proper-

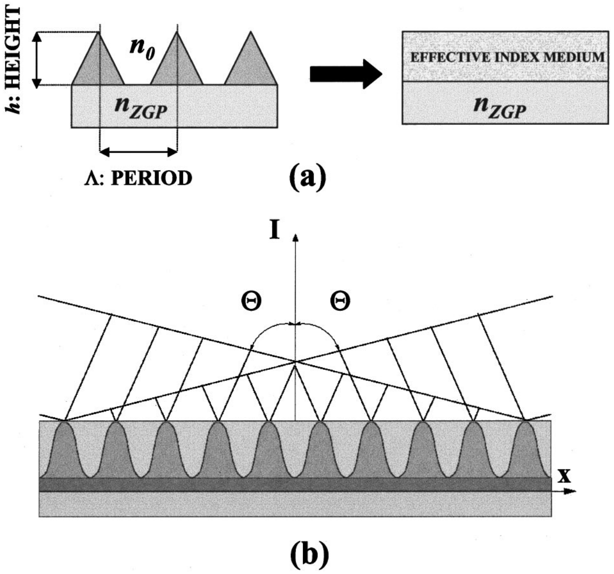

FIG. 1. (a) Schematic diagram of an etched motheye surface relief structure that acts as a region of graded index of refraction between air and the nonlinear optical crystal (in our case, ZGP). (b) Illustration of interference lithography.

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ties of the motheye, as well as the lower and upper cutoff wavelengths of operation. In this letter, we report on the motheye patterning of ZGP crystals, where we realized an increase in the transmission of the output signal at 4.18 μm, with the best result of 67% transmission. This can be compared with the theoretical maximum of 73% for the single surface transmission.[9] The etching process leaves negligible surface contamination and the procedure should be applicable to motheye patterning in other nonlinear crystals.

We fabricated our motheye patterns by combining interference lithography (IL), capable of producing periodic patterns with submicron period over a large area, with chlorine chemistry reactive-ion etching (RIE) using hardened photoresist as an etch mask. The pattern period Λ can be obtained from the following expression:[6]

$$\Lambda \leqslant \lambda / \{ n_{\mathrm{ZGP}} + n_0 \sin \theta_{\mathrm{MAX}} \}, \tag{1}$$

where n_{ZGP} and n_0 label the ZGP and air indices of refraction, respectively, while θ_{MAX} is the acceptance angle. This expression shows that the periodicity of the surface relief structure must be smaller than the shortest wavelength of operation in order to avoid significant diffraction and surface scatter effects. The sin θ_{MAX} term takes into account the possibility that the incident laser beam may have a finite convergence angle. Because ZGP is a uniaxial birefringent crystal having two refractive indices, $n_o \approx 3.13$ (ordinary) and $n_e \approx 3.17$ (extraordinary) for mid-IR (0.74–12.5 μm) operation,[10] the larger value must be used in Eq. (1). To take into account the finite bandwidth of the pump and signal beams, we included an additional bandwidth margin in the output wavelength specification, e.g., 4.18 ± 0.3 μm, with $\theta_{\mathrm{MAX}} = 10°$. The required height of the motheye structures was taken to be 40% of the longest operating wavelength, i.e., $h \geqslant 0.4 \lambda_{\mathrm{OUT}}$.[6] As a result, for the output $\lambda = 4.18$ μm we obtain $\Lambda = 1.17$ μm and $h = 1.8$ μm.

In order to achieve the necessary repeated features with submicron periodicity, we employed crossed two-beam IL,[11,12] illustrated in Fig. 1(b). For a given motheye periodicity Λ, the IL parameters are easily obtained from the geometry of Fig. 1(b) using the following relation:

$$\Theta = \sin^{-1} (\lambda_{\mathrm{exp}} / 2 n_0 \Lambda), \tag{2}$$

where λ_{exp} is the laser exposure wavelength (457 nm) and Θ is the exposure angle which is to be determined from Eq. (2). The motheye pattern was subsequently transferred into ZGP using a chlorine-chemistry RIE process, with $\mathrm{SiCl_4}$ providing the etching radicals. We established a process that etched ZGP at a rate of 45 nm/min, and an etch selectivity versus photoresist of 1.3:1. The process parameters for our home-built parallel-plate electrode RIE system were: 10 mT pressure, 25 sccm $\mathrm{SiCl_4}$ gas flow, 30 W rf power, and -510 V dc bias.

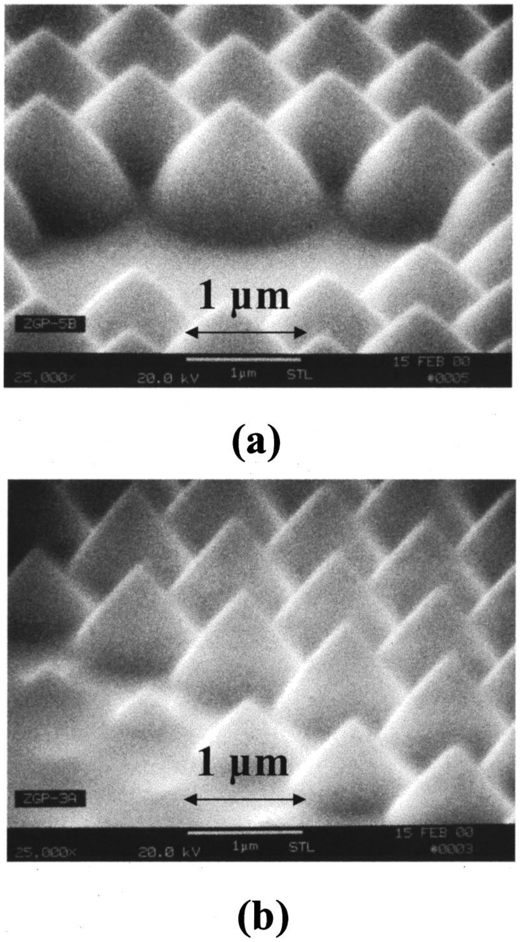

FIG. 2. SEM photographs of the motheye-patterned "output" surfaces of ZGP crystals with (a) convex-tapered and (b) straight-tapered sidewall profiles. The sidewall profile is a function the initial resist mask thickness, the etch anisotropy, and system etching parameters.

The final relevant issue for motheye patterning is the sidewall profile, which serves to grade the effective index of refraction. The ideal index profile is a function of the bulk substrate index, with a fifth-order-polynomial (quintic) dependence on depth.[9] The actual etched sidewall profile depends on the initial resist thickness and specific plasma etch parameters. Two etched sidewall profiles corresponding to the $\Lambda = 1.17$ μm motheye are shown in the scanning electron microscope (SEM) photographs of Fig. 2. While the etch parameters for both samples were identical, the differences in the sidewall profiles are attributed to the different exposure parameters during IL: [30 mJ in Fig. 2(a) versus 32 mJ in Fig. 2(b)]. We have obtained sidewalls ranging from "convex tapered," as in Fig. 2(a), to "straight tapered," as in Fig. 2(b). While the shape of Fig. 2(b) is closer to the ideal, "concave-tapered" profile for a bulk substrate index of $n_{\mathrm{ZGP}} = 3.17$,[9] the samples did not achieve the targeted etch depth, etching to only ~ 1 μm (versus the intended 1.8 μm). This indicates that the initial resist layer had a suitable profile but insufficient thickness, and hence, etched faster than expected. Even so, these motheye-patterned output surfaces (in crystals with uncoated input surfaces) showed a significant increase in transmission over uncoated crystals, as shown in Fig. 3. In the case of motheye with a straight-tapered sidewall [Fig. 2(b)], the overall transmission reached a maximum of 67% near the cutoff wavelength of 3.8 μm (Fig. 3), instead of the targeted 4.18 μm, which can be attributed to the etch depth. We note that the largest theoretically achievable transmission for a ZGP crystal with only one single patterned surface is 73%. Patterning both the input and output faces with motheye could result in a further reduction of Fresnel reflection losses even without taking into account further process optimization that would ideally

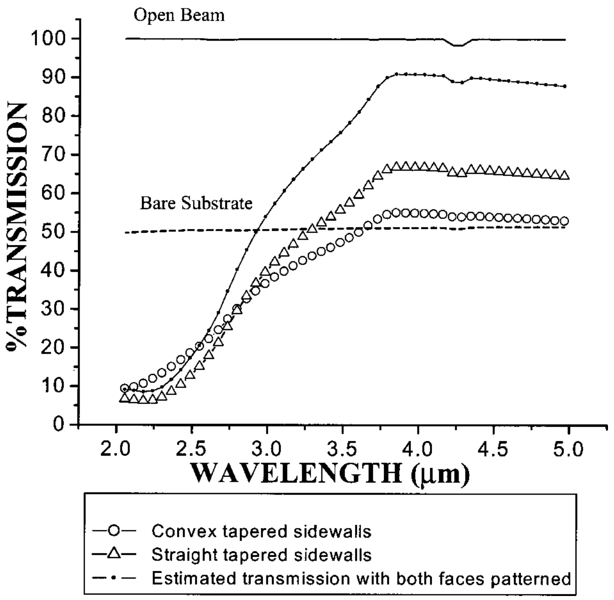

FIG. 3. Comparison of Fourier transform infrared transmission spectra of ZGP crystals with output faces motheye patterned with convex- and straight-tapered protuberances versus unpatterned ZGP crystal. Pointed line shows the estimated transmission spectrum for ZGP with motheye patterning on both input and output faces based on the single surface transmission efficiency (67%) of the straight-tapered sidewall profile.

produce a deeper motheye. The estimated transmission curve for a ZGP crystal patterned on both surfaces using our current process is shown by a dashed line in Fig. 3. The patterning of the input face ($\lambda_{\mathrm{IN}}=2.09$ μm) in that case would, from Eq. (1), require $\Lambda=607$ nm and $h=856$ nm (from $h \geqslant 0.4\lambda_{\mathrm{IN}}$), parameters achievable with the present IL and RIE techniques. Also from Fig. 3, we find that the broadband transmission is nearly constant above the 3.8 μm cutoff wavelength, but drops off dramatically for $\lambda<3.8$ μm due to scattering effects. Other rounds of etching tests provided evidence that etching parameters and results are very reproducible. While intra-valence-band *p*-type optical absorption, due to native Zn vacancies in ZnGeP_2,[13] is a shortcoming (observed in samples etched for 30 min), it can be overcome using a variety of techniques, including annealing.[14] Furthermore, in testing for surface contamination by analyzing the Auger spectra and the time-evolution spectra of Cl, Si, C, O, F, and Al signals, we found that the contaminants are confined to within ~1 ML at the surface, with no other contamination or significant damage extending into the crystal.

In conclusion, we demonstrated that motheye surface relief structures of the proper period patterned on the output surface can be etched into ZGP crystals for mid-IR operation. It was shown that these structures effectively achieve AR functionality by increasing single surface transmittance. Our motheye etching study revealed that: (1) the required surface periodicity can be achieved with the resist geometry formed by a crossed two-beam exposure, but improved etch selectivity of ZGP versus photoresist is required to achieve the desired motheye etch depth; (2) even though our motheye patterns were shallower than ideal and had less than an optimal etch depth, they still significantly reduced reflection losses; and (3) there is negligible surface contamination from the etching process. Future work will include motheye patterning of both crystal surfaces, deeper etching using either a greater lithographic contrast in the photoresist (e.g., with three-beam IL) or other masking materials (e.g., oxide or metal), and determination of the laser damage threshold in motheye-patterned ZGP crystals as compared to those with dielectric AR coatings.[4,5] Clearly, the motheye-patterning technique could also be extended to other ternary nonlinear optical crystals where Fresnel losses are an issue.

This work was funded by the U.S. Air Force through STTR Contract No. F33615-99-C-5428. The processing facilities at Brown University are supported by the Brown MRSEC Center (Grant No. DMR-0079964).

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