Minimizing Artifact Formation in Magnetorheological Finishing of CVD ZnS Flats

Introduction and Motivation

The development of optics for new applications is based on the use of materials that have the appropriate mechanical and optical properties. For infrared (IR) window and dome materials that protect imaging systems against damaging conditions, three main considerations are taken into account: material strength, thermal-shock resistance, and optical characteristics, such as transmission, absorption, scattering, and emissivity. To obtain maximum transmittance, a good IR material should exhibit minimum optical scattering due to a rough surface finish. The synthetic materials that meet the requirements for IR windows could be either single crystals or polycrystalline with cubic crystallographic structure, the latter being usually tougher, which is desired.[1] Polycrystalline ZnS is an excellent candidate for these applications.

The chemical vapor deposition (CVD) process was developed in the 1970s in response to the need for increased volumes of polycrystalline ZnS with improved transparency.[2] The CVD process takes place in a chamber similar to an autoclave at increased temperatures (600°C to 1000°C) and at pressures below 100 Torr. Deposits of solid grains are formed on the inside walls of a graphite mandrel. The size of the grains depends on the deposition temperature and has a dramatic impact on the mechanical properties, such as the erosion rate.[3]

Two types of CVD ZnS are available on the market from domestic sources: regular grade and multispectral grade. The first type has a grain size of about 2 to 8 μm, is yellow-orange in color, and is used in the 3- to 5-μm-wavelength and 8- to 12-μm-wavelength regions. The "multispectral (or 'water clear') grade" ZnS is colorless, exhibits high transmittance over a wider range of wavelengths, and can be used in the 0.5- to 12-μm region of the spectrum. This latter material undergoes a hot isostatic pressing (HIP) process to grow the grain size to 20 to 100 μm, eliminating microscopic voids and other internal defects; however, this refining process leads to a reduction in strength and erosion resistance of the clear material.

The CVD process offers many advantages over conventional techniques for preparing infrared transmitting materials, the most significant being the purity of the material, its minimized IR absorption, and the fact that the process is not size limited. A potential disadvantage of the process is that the CVD ZnS material, though it possesses a fine grain structure, contains a micro- to macroscopic inhomogeneous "nodular" structure, referred to as "hillocks" or "pebbles." Pebbles nucleate from dust and dust-like inclusions on the mandrel where substrate growth initiates. These then grow up from the bottom in the form of expanding "cones" through the bulk of a CVD ZnS puck.[4] They may reach several millimeters in size on the free surface.

The process of surface finishing is of great importance since the final surface quality has an impact on optical properties of a ZnS optic. Single-point diamond turning, a common method for finishing nonspherical surfaces, is especially effective with long-wave infrared materials (LWIR = 8 to 12 μm) like ZnS, ZnSe, and Ge. Magnetorheological finishing (MRF), described elsewhere,[5–7] is a deterministic polishing process that is now widely used in the production of high-precision optics around the world. The extension of MRF to a vast array of materials is possible because of the accommodating nature of this finishing process, which offers a wide range of removal rates required for the surface finishing of glasses, crystals, polycrystalline, and plastic materials. The objective of this work was to determine which aqueous magnetorheological (MR) fluid composition and conditions would provide the best polishing and smoothing performance on CVD ZnS flats that differed in initial surface preparation and source of supply. During this research the emergence of pebbles upon polishing with MRF was revealed. Suppression of these artifacts at the surface was accomplished by changing the composition of the MR fluid.

Experimental Details

MR fluids were prepared with a variety of magnetic and nonmagnetic ingredients. Two types of magnetic carbonyl iron (CI) particles were evaluated. Each type was spherical in shape with an average particle size of ~4 μm. One type was mechanically "hard", and the second was mechanically "soft".[8] Four nonmagnetic polishing abrasives were evaluated: cerium oxide, diamond, alumina, and silica. Table 101.IV lists the attributes of these abrasives. Abrasive size was difficult to ascertain. It depended on milling time during use for those abrasives that were strongly agglomerated. These abrasives were used previously in experiments on MRF of polymers.[9]

CVD ZnS from two manufacturers—"regular grade" from II-VI, Inc.,[10] and "high-quality" material from the Research Institute of Synthetic Crystal, Beijing[11]—were used in the experiments. Samples were provided in the form of 35- to 40-mm-diam pucks that were 8 to 20 mm thick. Surfaces were used as prepared by outside sources or after additional processing in-house.

Spotting and polishing experiments with uniform removal (successive dc polishing runs) were conducted on a Q22Y MRF polishing machine.[12] Peak and volumetric removal rates were calculated using interferometric data obtained on a Zygo GPI phase-shifting interferometer.[13] Polishing performance of the various MR fluids was evaluated by measuring the removal rate, the final surface roughness (p–v and rms), and the visual appearance of the surfaces after polishing runs.

The evolution of surface morphology and texture was determined using a Zygo New View5000 White Light Optical Profilometer.[14] This instrument quantifies microroughness and reveals surface defects. Two types of objectives were used for the analysis: a 20× Mirau (with a 0.26-mm × 0.35-mm image size) and a 2.5× Michelson (with a 2.11-mm × 2.81-mm image size for 1× zoom and 5.38 mm to 7.17 mm for a 0.4× zoom) with no digital filter applied. The higher magnification allowed for the evaluation of areal rms and p–v surface roughness, while the lower magnification was useful for studying the extent and shape of pebble-like surface artifacts.

Five initial surface states were investigated: deterministically microground, single-point diamond turned, and after pitch-polishing in-house (for ZnS from II-VI); "as received" and after pitch-polishing in-house (for ZnS from China). Pitch-polished surfaces were prepared in-house in a four-step process: controlled loose-abrasive grinding (40 μm of alumina on cast iron, 20 μm of alumina on glass, and 9 μm of alumina on glass) followed by polishing on a beeswax/Gugolz73 lap (10%/90%) with a 50/50 acidic mixture of 0.3 μm of alumina/colloidal silica. Resulting surfaces were flat to better than 0.5 μm p–v, with areal surface roughnesses as good as 10 nm p–v and 0.5-nm rms.[15]

The deterministically microground surfaces were prepared in-house using a three-step protocol consisting of computer numerically controlled removal with three diamond ring tools: rough (220 μm in bronze), medium (15 μm in bronze), and fine (3 μm in resin). Surface-roughness levels after grinding were ~400 nm p–v and ~20-nm rms.

Table 101.IV: Abrasive particles used in MR fluids for CVD ZnS polishing.

Dry Abrasive	pH in DI Water	Primary Particle Size$^{(b)}$	Median Size$^{(c)}$	Comments
CeO_2	—	40 nm	96 nm	$^{(b)}$Provided as 20.9-wt.% solids in pH7.4 solution
Diamond$^{(a)}$	2.5	4 nm	1.4 μm	Milling in an MRF machine increased vol % of particles <0.6 μm from 0.5 to 21 in 7 days
Al_2O_3 γ phase	4.7	33 nm	93 nm	Milling in an MRF machine increased vol % of particles <225 nm from 0 to 75 in 24 h
SiO_2	4.7	40 nm	—	$^{(b)}$Amorphous, fumed, hydrophilic

(a)Standard MR fluid constituent; (b)information supplied by vendor; (c)powder dispersed in DI water with a surfactant and intensively sonicated prior to sizing.

Samples of CVD ZnS from II-VI were single-point diamond turned (SPDT) by an outside vendor;[16] surface-roughness levels after SPDT were 33±6 nm p–v and 6.4±1.0-nm rms.[15] A typical lineout of an SPDT surface is shown in Fig. 101.40. Over a distance of 300 μm one can see the fine diamond-turning marks (spatial periodicity of ~8 μm), superimposed on undulations with large amplitudes and periods of over 100 μm. Power spectral density (PSD) analyses were conducted on these surfaces before and after MRF to track the evolution of these features (described later).

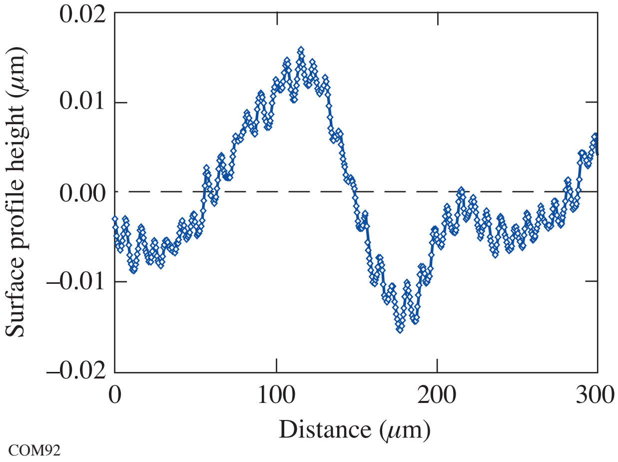

Figure 101.40
The initial surface profile of an SPDT surface on CVD ZnS used in this work.

Some of the CVD ZnS parts manufactured in Beijing were used as received from China (specular surfaces with an areal surface roughness of 300±155 nm p–v and 8.8±0.5-nm rms).[15] Others were used after polishing in-house on pitch (areal-surface roughness of 10±3 nm p–v and 0.8±0.0-nm rms).[15]

No discussion has been found in the literature regarding the relevance of pebble-like structures on CVD ZnS used in IR applications. Since the CVD process imposes rather different growing conditions as the growth surface extends out from the mandrel, care was taken to keep track of CVD ZnS surfaces. The sides of the ZnS pucks that were in contact with the growth mandrel were designated S1 (more yellow coloration), and the sides farthest away from the mandrel were designated S2 (more orange in color).

The work described here consisted of three phases: Experiments were first conducted on the in-house pitch-polished surfaces of CVD ZnS from II-VI. The immediate goal was to identify the optimal nonmagnetic abrasive from the four types of powders in tests with hard CI. S1/S2 side-related effects were studied on 20-mm-thick flats. Secondly, magnetic-particle type and MR fluid chemistry were further altered to make additional improvements in the final surface roughness. Finally, the polishing performance of the altered fluid was evaluated on the four types of surfaces previously described, for both the domestic and foreign-made ZnS materials.

Nonmagnetic Abrasive Study (Phase 1)

MR fluids using hard CI were prepared with each of the four nano-abrasives from Table 101.IV, which differ in particle hardness (from soft silica particles to hard diamond ones), as well as in the particle surface chemistry. This latter characteristic affects fluid rheology, thus setting individual limits for the maximum abrasive content that can be used. MRF trials with each of these abrasives were conducted on the same part and surface (S2). The part was repolished on pitch before each successive trial.

The results of these experiments are presented in Figs. 101.41 and 101.42. Figure 101.41 tracks the evolution of surface microroughness as a function of material removed. Figure 101.42 shows the peak removal rate achieved for a given abrasive concentration and the level of p–v surface roughness after removing 1 μm of material.

The highest removal rate along with the least degradation to surface roughness was provided by the hard CI-based MR fluid with >1.0 vol% of alumina; the removal rate observed for the fluid with nanodiamond was quite similar to that for

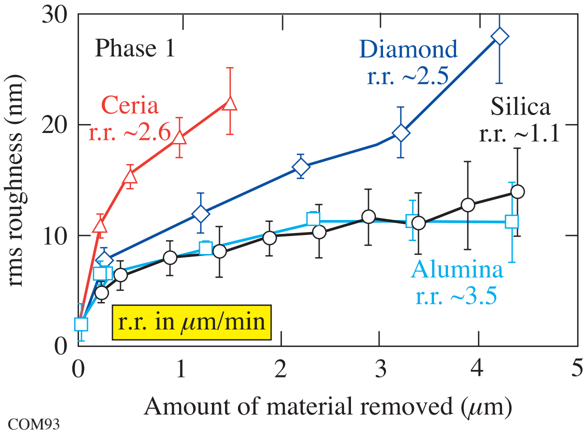

Figure 101.41
Evolution of rms surface roughness with the amount of material removed during dc polishing of pitch-polished CVD ZnS with a hard CI-based fluid prepared with each of four different abrasives.

the ceria-based MR fluid, which was almost two times higher than the removal rate provided by the silica-containing fluid. These results clearly demonstrate the dramatic difference in abrasive polishing efficiency on ZnS, independent of the abrasive concentration. (It was not possible to relate removal rates to the number of abrasive particles of a given abrasive type because of issues of aggregation and agglomeration previously discussed relative to Table 101.IV.)

The two abrasives, ceria and diamond, provided similar removal rates with drastically different surface-roughness characteristics. As shown in Fig. 101.41, rms surface roughness increased dramatically from 2.7 nm for the initially pitch-polished surface up to 11 nm after polishing out 0.2 μm of material with the ceria-based MR fluid. Roughness continued to increase after every subsequent polishing run and approached 22-nm rms with the cumulative removal of 1.5 μm. Roughness values grew slowly but steadily when using diamond abrasives, exceeding 25-nm rms after the removal of 4 μm. Silica and alumina abrasives caused less surface degradation. The silica-based MR fluid provided relatively lower roughness levels with the rms leveling out at around 11 nm after removing as much as 3.5 μm of material. However, this abrasive demonstrated a tendency for increasing roughness with further polishing. The results obtained for the alumina-based fluid were quite similar to those of the silica-based fluid, with rms not exceeding 11 nm after polishing out more than 2 μm. Root-mean-square roughness remained at this same level after polishing out another 2.5 μm of material. Moreover, the p–v surface characteristics showed the lowest values as well. The alumina-based fluid was chosen for further experiments due to its 3.5×-higher removal rate than the silica, a low level of surface roughening, and its excellent rheological properties.

Pebbles were first observed on the S2 surface of the CVD ZnS puck after the first 0.5-μm dc polishing runs were made, regardless of the type of abrasive used. The emergence of pebbles on S2 became more noticeable to the eye after each subsequent polishing run; however, the quantification of these topographic features was difficult to document since they caused no increase to the surface roughness measured with either 20× or 2.5× objectives. On S1, the situation was different. Pebble-like features became noticeable to the eye only with removal of over 1.5 μm of material. As they emerged with additional polishing, the features on S1 exhibited a different shape, areal density, and intensity than those on S2.

Images of S1 and S2 on a 20-mm-thick CVD ZnS puck after 1.5 μm of material was polished out from an initially pitch-polished ZnS surfaces were obtained using a laser interferometer (40-mm aperture) and a white-light interference microscope (2.5×: 7.2-mm × 5.4-mm area). The images are presented in Fig. 101.43 and clearly demonstrate the pronounced difference

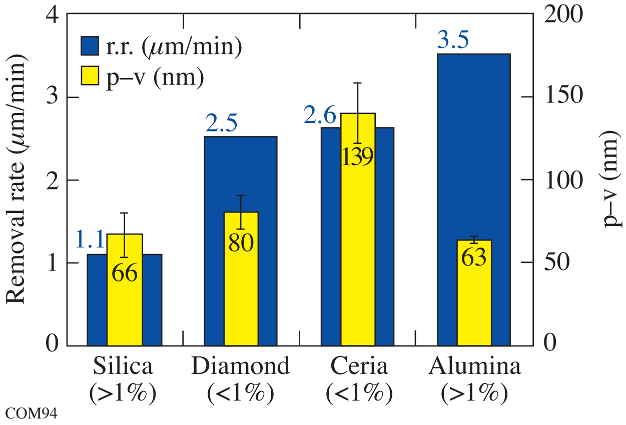

Figure 101.42
The removal rates and p–v surface-roughness values measured after polishing out 1 μm of material with hard CI-based fluids prepared with four different abrasives. Approximate abrasive concentration is indicated in volume percent.

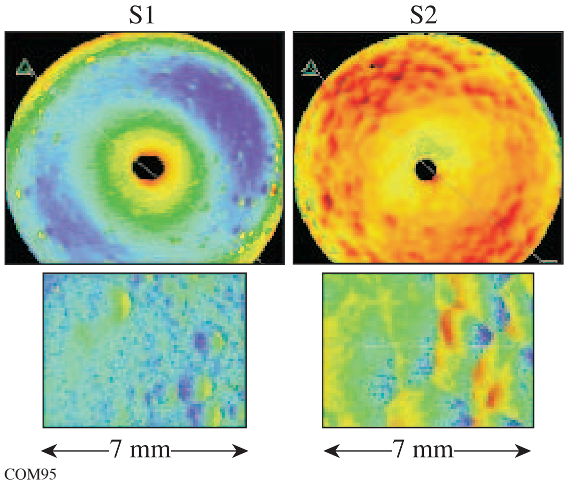

Figure 101.43
Laser interferometer images (40-mm aperture) and white-light interferometer intensity maps (2.5×, 7.2-mm × 5.4-mm field) for two opposite sides of a 20-mm-thick CVD ZnS puck after polishing out 1.5 μm of material by a hard CI-based nanoalumina fluid.

in the shape and density of the artifacts. Pebbles on S1 resemble distinct, separated craters, having a circular shape with a diameter smaller than 1 mm, while the pebbles observed on S2 appear as large, overlapped petals of a flower. The features on S2 are quite different in size, with some being larger than 5 mm across. In terms of visual appearance, the S2 side showed significant decoration to the eye, whereas S1 looked nicely polished with no observable artifacts. These micro- and macrostructures fit previous descriptions and microphotographs of CVD ZnS that indicate cones of material growing up and away from S1 (mandrel/side) toward S2 (free side).[4]

Composition and Chemistry Alterations (Phase 2)

The necessity for making further improvements to surface roughness and surface visual appearance resulted in the second phase of our experiment, during which MR fluid composition and chemistry were altered employing alumina as the nonmagnetic polishing abrasive. Use of a soft type of CI improved long-term stability of the altered alumina-based fluid and provided removal rates of ~1 μm/min. Additional alterations of fluid chemistry gave very beneficial results. The evolution of p–v and rms surface roughness as a function of material removed by these MR fluids with soft CI and altered chemistry are plotted in Figs. 101.44(a) and 101.44(b) for initially pitch-polished surfaces. The use of soft CI led to the noticeable improvement in the surface roughness although there was a 3× reduction in the removal rate from phase 1. The alteration of both CI type *and* chemistry lowered the surface roughness to below 20 nm p–v and 2-nm rms after polishing out as much as 2 μm of material from an initially pitch-polished surface. Further polishing to remove a total of 3.5 μm led to a modest increase in both roughness parameters to 25 nm p–v and 2.5-nm rms.

The other significant advantage of using the altered fluid was the fact that no pebbles were observed on either S1 or S2 [see Fig. 101.44(c)], providing good visual appearance after polishing out a total of 3.5 μm. These results made the chemically altered, alumina-based, soft-CI MR fluid an advantageous choice for figure correction of prepolished CVD ZnS.

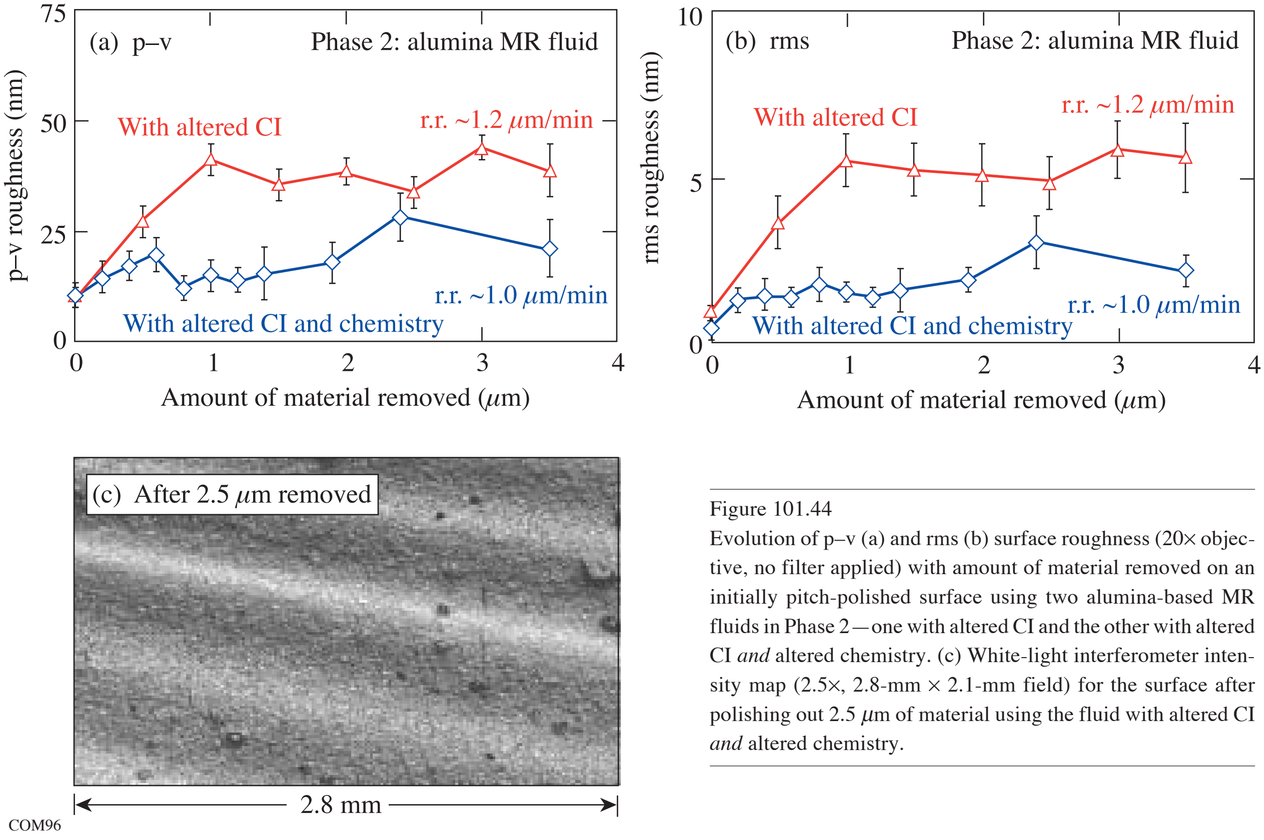

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Figure 101.44
Evolution of p–v (a) and rms (b) surface roughness (20× objective, no filter applied) with amount of material removed on an initially pitch-polished surface using two alumina-based MR fluids in Phase 2—one with altered CI and the other with altered CI *and* altered chemistry. (c) White-light interferometer intensity map (2.5×, 2.8-mm × 2.1-mm field) for the surface after polishing out 2.5 μm of material using the fluid with altered CI *and* altered chemistry.

The Effect of Initial Surface Preparation (Phase 3)

The effect of initial surface preparation on the polishing and smoothing performance of MRF was studied using the chemically altered, alumina-based, soft-CI MR fluid on five types of CVD ZnS surfaces from the two manufacturers described earlier.

The removal rate was measured to be 1.2 to 1.4 μm/min with no significant dependence on the initial surface preparation in the tested range of initial roughness parameters. The evolution of roughness with the amount of material polished out from domestic CVD ZnS with different initial surface preparation is presented in Figs. 101.45(a) and 101.45(b). Similar roughness levels were achieved on all three tested surfaces after polishing out 2 μm of material, with the p–v falling to below 20 nm and the rms going below 2 nm. This was accomplished despite the fact that p–v values for the initial surfaces were in a range that varied from 10 nm p–v for the pitch-polished surface to more than 400 nm p–v for the microground surface. This result is of great importance for the MRF process because it widens the range of initial surface conditions that can be processed. The other noteworthy result is that no signs of surface decoration (e.g., pebble-structure formation) were observed on any surfaces of ZnS after removing up to 4 μm of material.

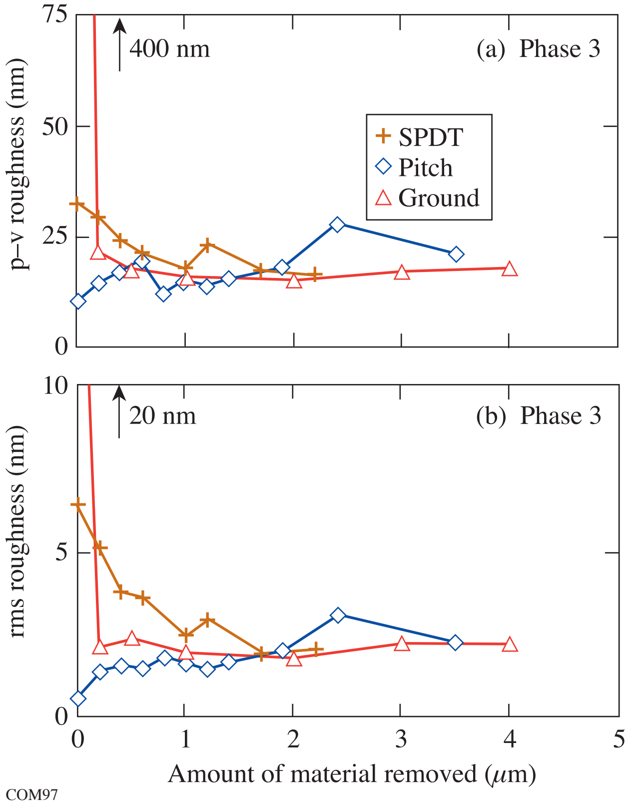

Figure 101.45
Evolution of p–v (a) and rms (b) surface roughness with the amount of material polished out for three types of initial surfaces—pitch-polished, ground, and SPDT—using the chemically altered, soft-CI MR fluid (domestic material from II-VI, Inc).

The surface of an SPDT ZnS part before and after MRF polishing was examined using PSD analysis of lineouts from roughness scans. This analysis is useful for showing the evolution of various spatial frequencies in the surface. The initial surface exhibited primary peaks in power density (e.g., diamond-turning grooves) with several periodicities between 8 μm and 15 μm (spatial frequencies from 1.2×10^{-4}/nm to 7×10^{-5}/nm), with a broad secondary peak (grooves presumably caused by misalignment or chatter) between 100 μm and 500 μm (spatial frequencies from 1×10^{-5}/nm to 2×10^{-6}/nm).

The PSD data in Fig. 101.46 demonstrate that the primary diamond-turning grooves (8 to 15 μm) were eliminated after the removal of only 0.2 μm of material. Removal of 1 μm was sufficient to decrease the signature near 200 μm (5×10^{-6}/nm) by over on order of magnitude. This demonstrated ability of MRF to reduce the intensity and even eliminate the periodic

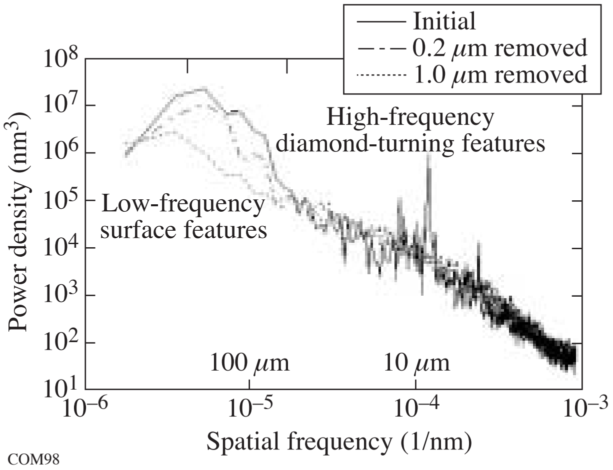

Figure 101.46
PSD plots on an SPDT ZnS surface showing the removal of high-frequency diamond-turning grooves after polishing out 0.2 μm of material. Additional polishing reduced the power density of low-frequency artifacts by 10×.

marks of different frequencies, accompanied by a dramatic improvement in surface roughness without introducing artifacts, makes the altered MR fluid a strong candidate for improving SPDT surfaces of CVD ZnS.

CVD ZnS manufactured in Beijing was evaluated in a series of dc polishing runs using the chemically altered, soft-CI MR fluid. Both as-received surfaces and surfaces prepolished in-house on pitch were processed with MRF without uncovering any surface artifacts. As shown in Fig. 101.47, it was impossible to improve the roughness of as-received surfaces (initial: 300 nm p–v/9-nm rms) to less than 30 to 40 nm p–v/5-nm rms. Starting from an in-house pitch prepolish, however, it was possible to bring the Chinese material to p–v and rms roughness levels comparable to those achieved for the domestic material.

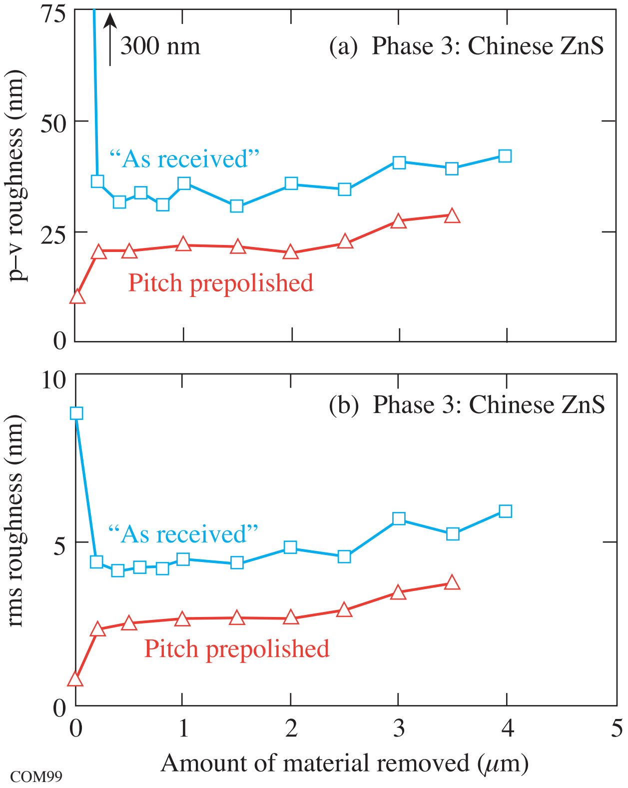

Figure 101.47
Evolution of p–v (a) and rms (b) surface roughness with the amount of material removed for CVD ZnS from China using chemically altered, soft-CI MR fluid. Two initial surfaces were used in the experiment: as received and after in-house prepolishing on pitch.

Summary

The finishing performance of magnetorheological (MR) fluids prepared with a variety of magnetic and nonmagnetic ingredients was studied on CVD ZnS flats from different manufacturers. Surfaces studied were used as received, after polishing on pitch, after single-point-diamond-turning (SPDT), and after deterministic microgrinding. MR polishing using hard CI and standard MR fluid chemistry yielded a surface with high roughness and pebble-like structures. The severity of pebble-like decoration was shown to be related to the processed side of the ZnS puck. Pebbles were more pronounced on the free surface farthest from the graphite growth mandrel. Experiments on pitch-polished surfaces showed nanoalumina abrasives to be the least detrimental of four nanoabrasives tested. These abrasives were then combined with soft CI and altered MR fluid chemistries to enable several microns of ZnS material to be removed with suppression of pebble-like decoration. Surfaces that were initially microground, diamond turned, or pitch polished were all processed with this altered MR fluid to ~20 nm p–v and 2-nm rms. Diamond-turning marks were eliminated.

REFERENCES

1. R. Lane and B. Battat, Advanced Materials and Processes Technology Information Analysis Center (AMPTIAC), **AMPT-18,** IIT Research Institute, Rome, NY, Contract No. SPO700-97-D-4001 (December 1999).
2. H. H. Karow, *Fabrication Methods for Precision Optics* (Wiley, New York, 1993), Chap. 2.
3. C. S. Chang, J. L. He, and Z. P. Lin, Wear **225**, 115 (2003).
4. K. L. Lewis, A. M. Pitt, and J. A. Savage, in *Proceedings of the Ninth International Conference on Chemical Vapor Deposition 1984*, edited by Mc. D. Robinson *et al*. (Electrochemical Society, Pennington, NJ, 1984), pp. 530–545.
5. S. D. Jacobs, S. R. Arrasmith, I. A. Kozhinova, L. L. Gregg, A. B. Shorey, H. J. Romanofsky, D. Golini, W. I. Kordonski, P. Dumas, and S. Hogan, Am. Ceram. Soc. Bull. **78**, 42 (1999).
6. D. Golini, in *Precision Science and Technology for Perfect Surfaces*, edited by Y. Furukawa, Y. Mori, and T. Kataoka, JSPE Publication Series No. 3 (The Japan Society for Precision Engineering, Tokyo, Japan, 1999), pp. 132–137.
7. S. D. Jacobs, S. R. Arrasmith, I. A. Kozhinova, S. R. Gorodkin, L. L. Gregg, H. J. Romanofsky, T. D. Bishop II, A. B. Shorey, and W. I. Kordonski, in *Initiatives of Precision Engineering at the Beginning of a Millennium*, edited by I. Inasaki (Kluwer Academic Publishers, Boston, 2001), pp. 501–505.

8. A. B. Shorey, S. D. Jacobs, W. I. Kordonski, and R. F. Gans, Appl. Opt. **40**, 20 (2001).

9. J. E. DeGroote, H. J. Romanofsky, I. A. Kozhinova, J. M. Schoen, and S. D. Jacobs, in *Manufacturing and Testing V*, edited by H. P. Stahl (SPIE, Bellingham, WA, 2004), Vol. 5180, pp. 123–134.

10. II-VI, Inc., Saxonburg, PA 16056-9499.

11. Research Institute of Synthetic Crystals State Administration of Building Materials, Industry, Beijing, Peoples Republic of China.

12. Q22Y, Commercial MRF machines manufactured by QED Technologies, LLC, Rochester, NY 14607.

13. Zygo GPIxpHR phase shifting interferometer system, Zygo Corporation, Middlefield, CT 06455.

14. Zygo New View™ 5000 White Light Optical Profilometer, Zygo Corporation, Middlefield, CT 06455.

15. New View™ 5000 setting for roughness measurements with 20× objective: scan length: 20 μm bipolar; min. mode: 5.0%; min. area size: 7; FDA: high. The reported roughness values are the average of eight to ten measurements at different sites.

16. Corning NetOptix, Diamond Turning Division, Keene, NH 03431.