

CHEMICAL POLISHING OF GARNETS WITH PHOSPHORIC ACID

D. C. Miller

Phosphoric acid between 250 and 450°C has been used to chemically polish as-sawn rare earth gallium garnet substrates, principally $\text{Gd}_3\text{Ga}_5\text{O}_{12}$. Yttrium aluminum garnet laser rods have also been successfully polished. Difficulties associated with phosphoric acid etching at high temperatures such as precipitate formation on the specimen surface and rapid deterioration of the acid bath due to dehydration and polymerization have been overcome by stabilizing the moisture content of the acid with steam. The surfaces of the etch-polished substrates are smooth, but have undulations with an amplitude of .25 μm or less and a wave length of 80 μm or more. Epitaxial magnetic garnet layers grown on etch-polished substrates appear to have magnetic properties and defect densities identical to those grown on substrates polished in the conventional way using diamond and Syton. A ten thousand bit shift register has been successfully operated in a film grown on an etch-polished substrate.

Introduction

Phosphoric acid has been shown previously to chemically polish several single crystal oxide materials¹⁻⁴ including yttrium iron garnet.⁵ It therefore seemed likely that the rare earth gallium garnets⁶ used as substrate material for epitaxial magnetic garnet films^{7,8} could also be chemically polished with phosphoric acid. The chemistry of concentrated phosphoric acid and its etching characteristics on the garnets at lower temperatures where selective etching occurs has also recently been studied.⁹ The purpose of this investigation was first to determine the etching conditions which would result in the surfaces of as-sawn garnet slices being chemically polished well enough for the crystals to be examined for inclusions, dislocations, and strain. Since chemical polishing of a slice from a garnet boule is orders of magnitude faster than mechanical polishing, a considerable saving could be realized in the time required to determine if the boules were sufficiently perfect to be processed into substrates.

In addition, it was thought that the etch polished substrates could be used with only one side of the substrate mechanically polished, rather than both sides. This would reduce the total polishing time required per substrate by a factor of three since the reversing operation requires about as much time as the polishing of one side. The "back" side of the substrates must be damage free so that crystallites do not nucleate and grow there during film growth, and smooth enough that domains may be easily observed in the magnetic layer on the "front" side. Finally, the possibility existed that the etch-polished substrates could be used directly for film growth.

In previous work,¹⁻⁴ however, precipitate formation on the specimen surface and rapid deterioration of the acid bath appeared to limit the reproducibility and the large scale applicability of high temperature phosphoric acid etching. These problems have been overcome by stabilizing the properties of the acid by passing steam through the bath.

Additions of various compounds such as CrO_3 , KMnO_4 , etc. will increase the etch rates slightly, but no polishing mixture proved superior to pure, stabilized phosphoric acid. Mixtures of phosphoric acid with other acids were also investigated and it was found that additions of H_2SO_4 increased the etch rate, probably because it retards dehydration and aids dissociation of the H_3PO_4 . However, its usefulness as a polishing solution is limited because evolution of SO_3 reaches objectionable proportions above about 250°C .

EXPERIMENTAL PROCEDURE

Commercial 85% orthophosphoric acid, H_3PO_4 , is heated in a platinum crucible to about 180°C until rapid boiling causes, whereupon the temperature is increased to the etching temperature, between 250 and 450°C . Platinum sheathed chromel-alumel thermocouples were used for temperature measurement and control.

The platinum crucibles used were etched very slowly. Alternatives to platinum for crucible fabrication are boron nitride, which is also etched very slowly, graphite, which is completely unaffected by the acid, and possibly gold. Pyrex and quartz are attacked too rapidly to be useful as container materials. The samples to be etched were held by the edges with platinum tipped forceps. Enhanced etching of the garnet occurs in the vicinity of the point of contact between the forceps and crystal, but this effect can be minimized by using boron nitride or graphite instead of platinum.

Steam was introduced into the 400 cc bath at the rate of about 30 cc/min. at approximately 200°C through a quartz nozzle, as illustrated in Fig. 1. No attempt was made to accurately measure the flow rate or temperature of the steam.

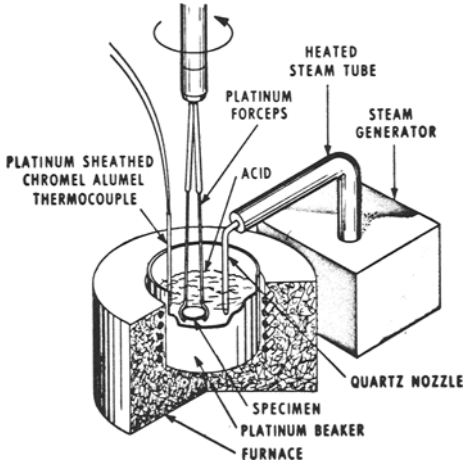


Fig. 1. Schematic illustration of etching apparatus.

However, both were kept as uniform as possible while etching and from one run to the next. The quartz steam nozzles were renewed each time the bath was replaced, usually after about 10 hours at the etching temperature. After etching, the samples were quickly quenched in a mechanical vacuum pump oil bath at 70°C and then washed in three consecutive hot Alconox solutions also at 70°C, the first two containing approximately 15 wt% KOH. Etch rates were determined by weight loss and thickness change measured using a micrometer. Densities of the acid were measured as described previously.⁹

RESULTS AND DISCUSSION

The etch rate of a material in the ideal chemical polish should vary inversely with only the radius of curvature of the specimen surface and with no other property or condition of the crystal such as crystallographic orientation or strain and chemical heterogeneities intersecting the surface. This behavior is approximated by the phosphoric acid garnet system above about 300°C. For example, there is no preferential etching in the presence of either residual surface damage or dislocations. However, the extremely complex and unstable chemical nature of hot concentrated phosphoric acid has made the determination and maintenance of optimum etching conditions extremely difficult.

As orthophosphoric acid (H_3PO_4) is heated, it dehydrates and other, polyphosphoric acids begin to form.¹⁰ The rate of moisture loss increases with temperature, but at any given temperature and partial pressure of moisture in the ambient, some equilibrium state of hydration

will be obtained. The hydration state, or equivalent concentration of P_2O_5 , governs the ratios of the different phosphoric acids present in the bath.¹¹ The equivalent P_2O_5 concentration may in turn be determined from the density (d) of the acid using the following empirical relationship¹²

$$\text{wt\% } P_2O_5 = \frac{d - .66}{.0167} \quad (1)$$

The relative proportions of orthophosphoric, pyrophosphoric ($H_4P_2O_7$), triphosphoric ($H_5P_3O_{10}$) and the other polyphosphoric acids present in an etching bath may then be determined by measuring the density and using Eq. (1) and the results of Bell¹³ and others,¹¹ as shown in Fig. 2.

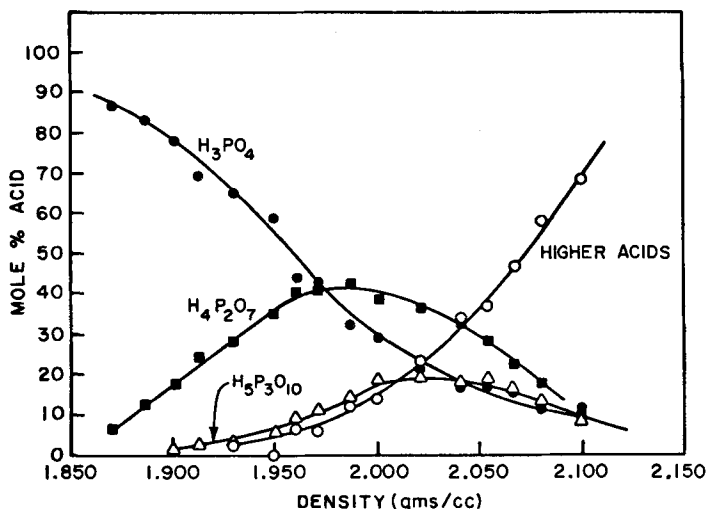


Fig. 2. Composition of phosphoric acid as a function of density.^{10,11}

Since the composition of the acid changes upon heating as a result of dehydration, the etching properties of the bath may be expected to change. It has been found that only the H_3PO_4 present in the solution contributes to the etching reaction at lower temperatures⁹ and, as is illustrated in Fig. 3, the same behavior occurs at higher, polishing temperatures. However, the exponential dependence of the etch rate, on the H_3PO_4 concentration is an unexpected result. It is possible, but unlikely, that by some chance the activity coefficient of H_2PO_4 changes exponentially with concentration at low H_3PO_4 concentrations, but where the dilution is not yet enough for Henry's Law to apply. It is also unlikely that a dissociation step preceding the etching reaction is responsible for the behavior because if this were the case, the concentration of the reaction products should not be exponentially dependent on the reactant concentration. The appearance of spiral streaming patterns

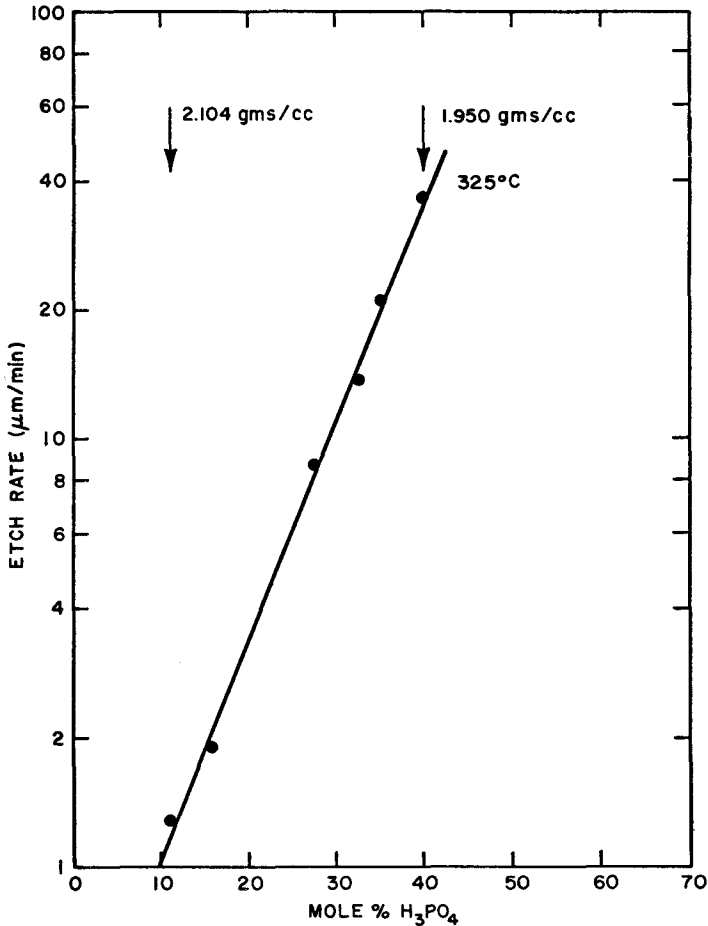


Fig. 3. Etch rate of the {111} surface of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ at 325°C as a function of H_3PO_4 concentration.

on horizontally rotated specimens, and other evidence, suggests both that the reaction products alter the etch rate and that a boundary layer forms which is enriched in etch products and depleted of reactants. Thus, boundary layer effects may be responsible for the exponential behavior observed. At lower temperatures where the etch rate is much slower, and at higher H_3PO_4 concentrations this would not be the controlling effect and dissociation equilibria may then be expected to play the primary role.

The products of the etching action which tend to reduce the etch rate also favor precipitate formation. These products are more dense

than the acid and will flow off of the specimen often producing uneven etching. This can be avoided by maintaining a uniformly thin boundary layer of these etch products at the garnet surface by rotation of the specimen, stirring the bath, etc. The precipitates which often form appear to be small crystals of Gd-Ga phosphate. Crystals similar to the precipitates, only much larger, were grown on the sides of the crucible by cooling the bath slowly after etching many garnet specimens. The crystals are hard, non-cubic and insoluble in water. The crystal structure, lattice parameter and composition of these crystals will be reported at a later date.

Above about 300°C, the acid is non-selective with respect to the gallium garnets, and the polishing action as well as the etch rates continue to increase with increasing temperature. However, with dehydration the higher acids form and dilute the H_3PO_4 , thus reducing the etch rate without changing the polishing properties of the acid. This is very useful since it is the aim of chemical polishing to achieve as flat a surface as possible, while removing a minimum of material, reproducibly. Thus in order to polish the garnets chemically successfully with phosphoric acid, both the temperature and density of the acid must be within certain values.

In order to polish without steam a fresh charge of acid should be used with each batch. The acid should be heated to 160°C, the crystals inserted and then the bath temperature raised to 300°C in 10 minutes, the samples removed, quenched in oil and the acid thrown out or rehydrated. In this way the proper temperature and density are achieved for a short period during etching. The bath may be stirred or the crystals rotated at about 40 RPM to eliminate streaming or non-uniform boundary layer effects. Alternatively, the sample may be suspended at an angle of about 6° from the horizontal in a still bath. This results in an extremely flat upper surface, as the etch products will drift slowly off of the specimen fast enough so that precipitates will not form and not so fast as to produce streaming. The bottom surface, however, becomes extremely uneven due to non-uniform flow of the etch products from the lower side.

These techniques have several disadvantages. Material removal is excessive and it is difficult to achieve reproducibility. It is a batch process which would be costly and inconvenient if it were necessary to prepare large numbers of specimens in this way.

These difficulties are overcome using the steam stabilized bath where the moisture content and thus the composition and etching characteristics of the acid bath can be controlled. Even at 450°C the density of the acid can be maintained below 1.90 gms/cc, the equilibrium value at 160°C. Thus, the combination of temperature and composition giving favorable etch properties can be achieved and maintained. The steam provides bath stirring action as well, so it is not necessary to rotate the specimens. However, more uniform results may be obtained by rotating the specimens at 40 RPM. Pre-etching the specimens in a separate bath at 160°C in phosphoric acid for 1-5 minutes immediately before polishing and without rinsing is very useful in eliminating the possi-

bility of precipitate formation. The reason for this behavior is not clear except that a garnet-acid interface is already established before contact with the 300°C acid is made which may avoid some transient reaction favoring precipitate formation which may occur between room temperature garnet and 300°C acid. This step also removes the saw damage and any abrasive or dirt remaining on the surface as well as heating the specimen which reduces the thermal shock it experiences when lowered into the high temperature bath.

Gadolinium gallium garnet has been successfully polished with as-sawn surfaces at 300°C in phosphoric acid having a density of 1.95 gms/cc. It has not been established what the optimum conditions are for the various other garnets which etch at different rates; however, the above conditions have proved to be satisfactory for a range of gallium garnets including Sm, Eu, Dy, Ho, Y, Sc, Nd, and various solid solutions of these.⁶ Excellent polishing of YAG can be accomplished at 435°C and a density of 1.98 gms/cc.

The resulting surfaces of the etch polished crystals are undulating, but smooth. A Tally-Surf of a typical substrate etch-polished from the as-sawn condition at 300°C for two minutes with steam is shown in Fig. 4.

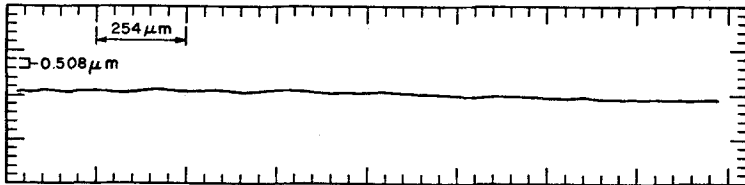


Fig. 4. Tally-Surf trace of a $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ substrate etch-polished in phosphoric acid at 300°C and 1.95 gms/cc.

Twenty-five substrates were etch-polished in the bath over a period of four hours with no significant, observable changes occurring in the surface topology or etch rate. Surfaces with undulations having an amplitude of $0.25\mu\text{m}$ and a frequency of $80\mu\text{m}$ can be routinely achieved.

In order to determine the applicability of the etch-polished substrates for use in magnetic bubble domain devices,⁷ $\text{Er}_2\text{Eu}_1\text{Ga}_{1.7}\text{Fe}_{1.3}\text{O}_{12}$ magnetic garnet films were grown on substrates which were etch polished on one side and conventionally polished (diamond plus Syton*) on the other by the dipping⁸ LPE technique. The films on both sides proved to have identical properties and similar low defect densities. Circuit application to a film on the etch polished side also proved to be straightforward and a 10,000 bit shift register has been successfully operated in a film on an etch-polished substrate.

* Product of Monsanto Chemical Corporation

SUMMARY AND CONCLUSIONS

It has been shown that phosphoric acid in the temperature range 250-450°C is capable of chemically polishing rare earth garnets with the resulting surfaces having undulations with an amplitude of .25 μ m or less and a frequency of 80 μ m or longer. The problems of precipitate formation on the specimen surface and deterioration of the etching properties of the acid due to dehydration have been overcome by pre-etching the substrates at 160°C in phosphoric acid and stabilizing the density (moisture content) of the acid at the etching temperature by passing steam through the bath. The etch rate was found to vary directly with the temperature and inversely with the density of the acid due to the formation of higher acids which do not contribute to the etch rate but merely serve to dilute the H₃PO₄. The flatness of the etched surfaces varied directly with the temperature and to a small extent inversely with the density. The etching reaction products modify the etch rate and if properly controlled could be used to improve surface flatness.

ACKNOWLEDGMENTS

The author would like to thank C. D. Brandle for growing the garnet crystals, J. W. Nielsen and L. K. Shick for helpful comments and suggestions, and P. I. Bonyhard for the shift register evaluation.

REFERENCES

1. B. Cockayne and D. S. Robertson, *Brit. J. Appl. Phys.*, 15, 643 (1964).
2. R. Aeschlimann, F. Gassmann and T. P. Woodman, *Mat. Res. Bull.*, 5, 167 (1970).
3. L. K. Shick, *J. Electrochem. Soc.*, 118, 179 (1971).
4. A. Reisman, M. Berkenblit, J. Cuomo and S. A. Chan, *J. Electrochem. Soc.*, 118, 1653 (1971).
5. J. Basterfield, *Britt. J. Appl. Phys. (J. Phys. D.) Series 2*, 2, 1159 (1969).
6. C. D. Brandle and A. J. Valentino, *J. Crystal Growth*, 12, 195 (1972).
7. A. H. Bobeck, *IEEE Trans. on Magnetics*, MAG-6, 445 (1970).
8. H. J. Levinstein, S. Licht, R. W. Landorf, and S. L. Blank, *Appl. Phys. Lett.*, 19, 486 (1971).
9. D. C. Miller, ECS Spring Meeting, Houston, Texas, 1972, to be published.
10. L. V. Kubasova, *Russian Chemical Reviews*, 40, 1 (1971).
11. A. L. Huhti and P. A. Gartaganis, *Canadian J. Chem.*, 34, 785 (1956).

12. J. R. Van Wazer, J. Amer. Chem. Soc., 72, 640 (1950).
13. R. N. Bell, Ind. Eng. Chem., 408, 1464 (1948).