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Chemical etching of gadolinium-gallium garnet substrates

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The etching of mechanically polished gadolinium-gallium garnet substrates by phosphoric acid, sulphuric acid and sulphuric-oxalic acid mixture was investigated in order to find an etchant which would remove the damaged surface layer and provide a substrate surface suitable for liquid phase epitaxial growth of magnetic garnets. Optimum surface properties were obtained when substrates were etched for 10 sec in phosphoric acid which had been maintained for 1 to 2 h at temperatures of 350 or 400° C. The disadvantage of this etchant is that it increases the surface roughness of the substrate. Surface smoothness was retained when substrates were etched in sulphuric acid; however, this acid revealed residual scratch marks introduced into the platelet during mechanical polishing. The sulphuric-oxalic acid mixture and phosphoric acid at 160° C revealed defects due to coring, faceting and scratch marks.

1. Introduction

Single crystal films of mixed rare-earth substituted iron garnets with an easy axis of magnetization normal to the film are proposed [1] for use in magnetic domain devices. Magnetic garnet can be grown on a non-magnetic rare-earth gallium garnet substrate by liquid phase epitaxy [2]. Surface imperfections present in the substrate adversely affect the quality of the epitaxial film [3]. Although numerous articles have been published on the preparation of thin films of magnetic garnets, very little useful information is recorded in the area of substrate preparation.

Rare earth gallium garnets can be obtained readily by the Czochralski technique. Gadolinium-gallium garnet, which is available commercially as a single crystal boule, is commonly used. To obtain substrates suitable for epitaxial film growth, the crystal boule is cut into platelets with a definite crystallographic orientation using either a wire saw or a diamond saw. The platelets are mechanically polished with various grades of aluminium oxide or diamond and finally with Syton*. Although the Syton polishing yields very smooth surfaces, films grown on these surfaces showed various imperfections. The mechanical polishing creates an amorphous Beilby [4, 5] layer which covers the mechanical damage. This layer apparently has a high solubility and dissolves immediately when the platelet is submerged in the molten salt solution. The epitaxial film then nucleates on the damaged crystal and the defects are propagated through the magnetic film. Imperfections in the film can often be related to defects in the substrate.

The defects in the substrate can be divided into two types. Type I defects are present in the garnet due to growth imperfections. These defects can be due to coring, faceting and the inclusion of second phase or air bubbles. Type II defects are introduced during cutting and mechanical polishing; these defects are saw marks, scratch marks and surface strain. In addition solid particles sometimes remain embedded in the surface of the substrate after Syton polishing and are difficult to remove. These surface impurities also cause growth imperfections in the film.

Type I defects which are introduced into the gadolinium-gallium garnet crystal during crystal growth cannot be removed by either chemical or mechanical polishing, Type II defects can be eliminated by the combination of careful mechanical polishing and subsequent chemical etching.

Various chemical etchants are used, either to remove the damaged surface layer, to or expose

*Trade name of Monsanto Company, St Louis, Missouri, USA.

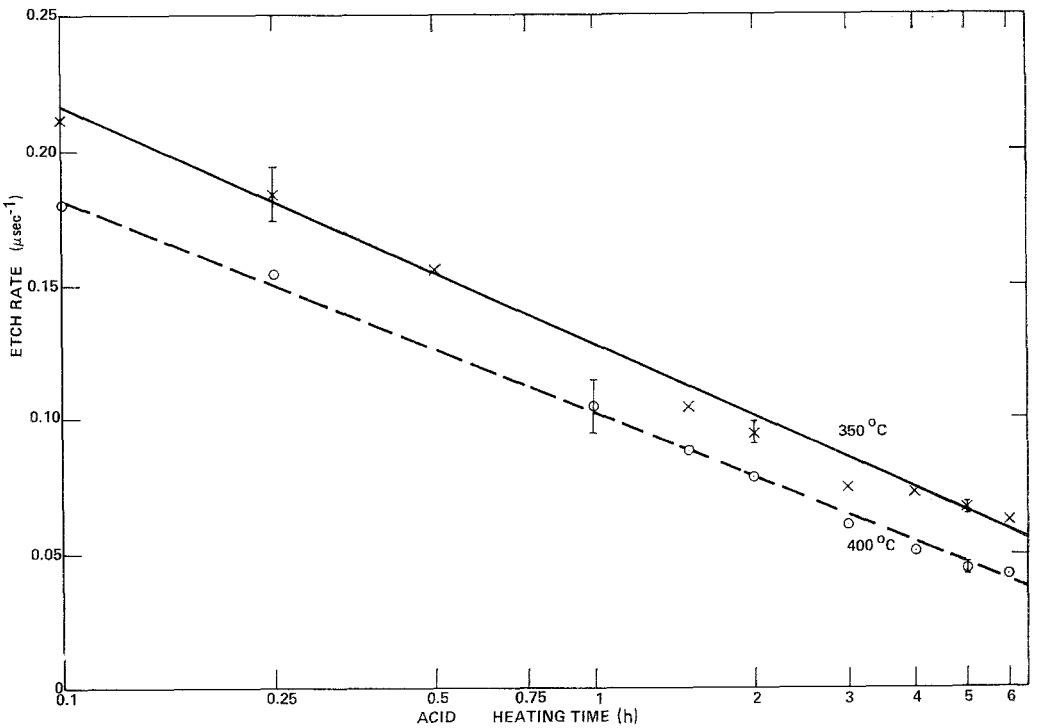

Figure 1 The etch rate of phosphoric acid with acid heating time (t) at temperatures 350° C (X) and at 400° C (0).

imperfections in the surface of the substrate. A thorough analysis of etching behaviour of flux grown single crystal YIG and GdIG was reported by Hanke [6]. She used a sulphuric-oxalic acid mixture, azeotropic (20.24%) hydrochloric acid, aqua regia and a nitric-acetic acid mixture. Linares [3] attempted to remove surface damage with boiling hydrochloric and with hot phosphoric acid. Aeschlimann [7] and more recently Schick [8] reported the use of hot phosphoric acid for chemically polishing rare-earth ortho-ferrites.

In this report we present the etching by phosphoric acid, sulphuric acid and sulphuric acid-oxalic acid mixture of mechanically polished gadolinium-gallium garnet substrates. Attempts were made to find an etchant which would remove damaged surface layers as well as provide a substrate surface suitable for liquid phase epitaxial growth of magnetic garnets. We also investigated the possibility of using chemical etchants to reveal defects in the surface of mechanically polished substrates.

2. Experimental results

The platelets used in the following experiments were all mechanically polished with various grades of aluminium oxide and finally with Syton.

2.1. Phosphoric acid etching

Concentrated phosphoric acid in a platinum crucible (~ 100 ml) was heated in a Kanthal wound furnace. The furnace temperature was first increased slowly getween 120 and 160° C until water evaporation from the acid ceased. Then the acid was heated at a constant rate to either 350 or 400° C and held at that temperature. The temperature was determined by a Pt-Pt/10% Rh thermocouple immersed in the acid. The substrate to be etched was held by platinum tipped tweezers, preheated for 2 min above the acid, immersed for 10 sec and then washed in de-ionized water and in isopropyl alcohol.

To determine the etch rate, a platelet which had been mechanically polished on both sides was used. Prior to etching the acid bath was preheated to 350 (or 400° C) and maintained for a heating time (t) from 0 to 6 h. The platelet was immersed for 10 sec in time intervals from $t = 0$ to $t = 6$ h. The platelet was weighed before and after each etching. The etch rate was calculated

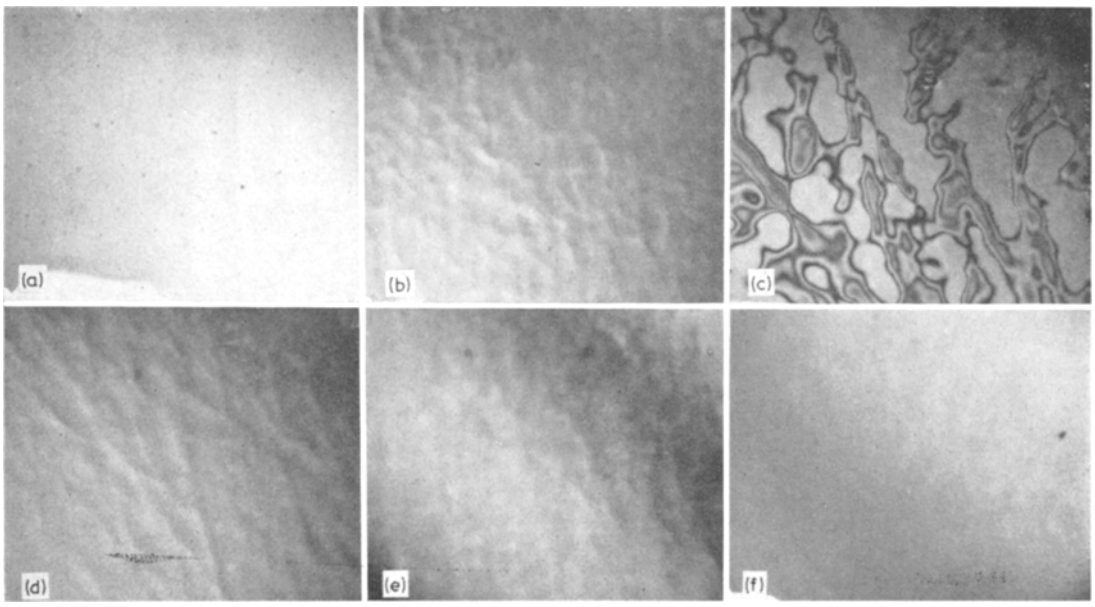

Figure 2 The surface features of gadolinium-gallium garnet substrates before etching (a) and after etching in phosphoric acid at 350 or 400°C at $t = 0$ h (b and c), at $t = 0.5$ h (d), at $t = 1.0$ h (e) and at $t = 2$ h (f) (approx. × 40).

from the density and surface area, assuming uniform etching on both sides of the substrate. The etch rate was determined using a fresh substrate for each experiment and showed similar results.

The etch rate decreased exponentially with the time (t) for which the acid had been maintained and was higher at 350°C than at 400°C (Fig. 1). The decrease of etch rate with t is probably due to increasing polymerization of the phosphoric acid. The lower etch rate at 400°C can be explained by the faster polymerization of the acid at higher temperature.

To determine surface features, an un-etched gadolinium-gallium garnet substrate, mechanically polished on one side was used in each case. Platelets were etched individually in phosphoric acid heated to and maintained at 350 or 400°C for 6 h ($t = 6$ h).

The surface features observed microscopically were independent of the acid temperature but depended on t. Photomicrographs (b) and (c) in Fig. 2 show the surface of substrates etched in phosphoric acid at $t = 0$ while photomicrograph (a) shows the mechanically polished surface before etching. The impurity particles (black dots) were removed by the etching. In 90% of the cases where the substrate was etched at $t = 0$ layers of substrate material had not been removed by the etch in certain areas (Fig. 2c). This uneven removal of surface layers was probably caused by the high etch rate of the fresh acid and the higher solubility of strained areas. These un-etched areas could be removed only by further etching. Where this film did not appear, the surface appeared to be rough (Fig. 2b) and the Talysurf, which directly measures surface irregularities, indicated an amplitude of approximately 0.25 μm. The amplitude of the surface roughness of the mechanically polished sample was only 0.05 μm.

The surface roughness decreased with increasing t (Fig. 2d, e and f) to an amplitude between 0.15 and 0.20 μm at $t = 2$ h. Only a few small pits were observed after etching. Micrographs of two mechanically polished substrates (Fig. 3a and c) after etching for 4 and 6 h are shown in Fig. 3b and d respectively. While the amplitude of the roughness decreased to between 0.10 and 0.15 μm, several small pits were observed. Some of these formed at places where impurity particles were embedded in the surface, and were observed only for $t > 2$ h.

As shown above two types of effects were observed when substrates were etched in phosphoric acid. One was the surface roughness which decreased with increasing acid heating time (t) the other was pitting which showed a

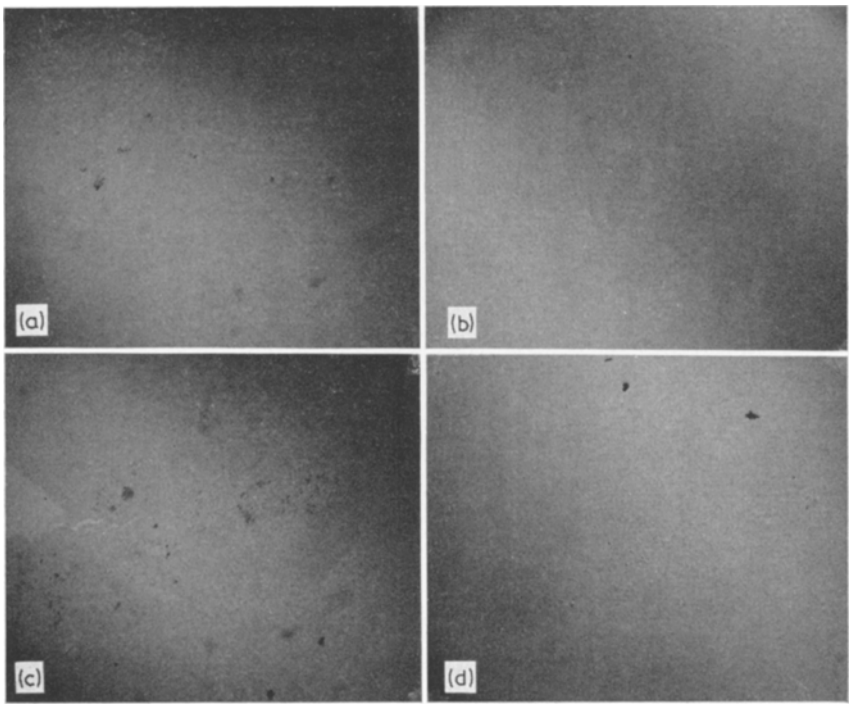

Figure 3 The surface features of gadolinium-gallium garnet substrates before etching (a and c), and after etching in phosphoric acid at 350 or 400°C at $t = 4$ h (b) and at $t = 6$ h (d) (approx. × 40).

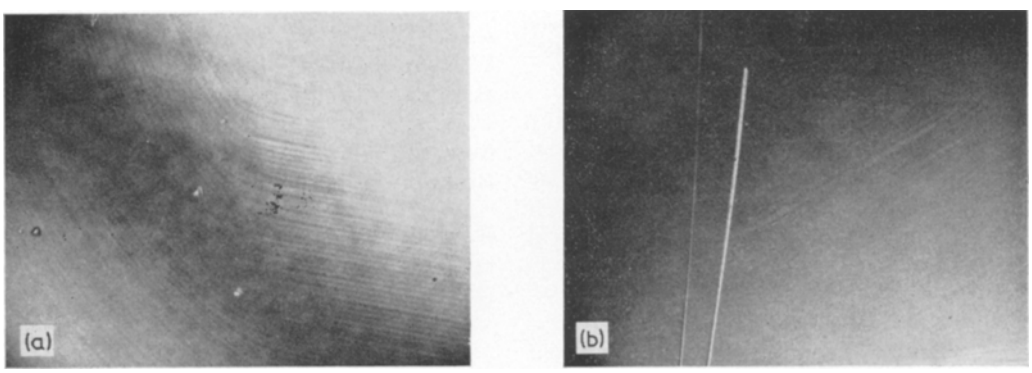

Figure 4 The surface features of gadolinium-gallium garnet substrates etched in phosphoric acid at 160°C (approx. × 80).

marked increase when substrates were etched in the acid heated for more than 2 h at 350 (or 400°C). Although the aim of chemical polishing of substrates is to obtain as smooth a surface as possible a compromise had to be made between surface smoothness and pit density. Acceptable surface smoothness and low pit density were obtained when substrates were etched for 10 sec in phosphoric acid heated for 1 to 2 h at temperature 350 (or 400°C).

To lessen the surface roughness, the etch rate was reduced by lowering the temperature of the phosphoric acid but this caused preferential etching. Photomicrographs of platelets etched at 160°C (Fig. 4a and b) showed evidence of coring, faceting, triangular pit marks and scratch marks. None of these features was found in platelets mechanically polished in the same way but etched in phosphoric acid at 350 or 400°C.

2.2. Sulphuric acid etching

Concentrated sulphuric acid in a glass beaker

was maintained at 110 ± 5°C, and mechanically polished substrates in a Teflon* holder were etched for times up to 10 min. The etch rate was 0.012 μm min^{-1}, which is approximately 0.2% of the rate for phosphoric acid at 350°C.

Although the surface did not increase in roughness with etching time, surface features became evident. For example, the micrograph in Fig. 5 shows scratch marks revealed by etching for 10 min. No such marks were observed in the mechanically polished surface.

Since surface roughness did not increase with etching time, sulphuric acid may be used as a

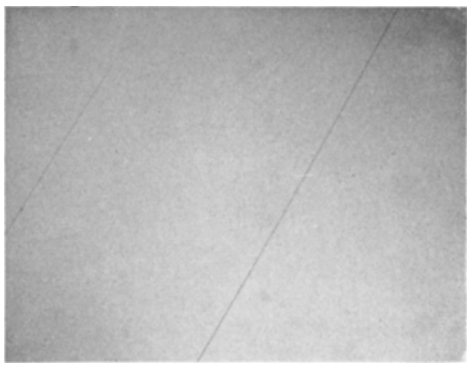

Figure 5 The surface features of gadolinium-gallium garnet substrate etched in sulphuric acid (approx. × 40).

chemical polish to remove the amorphous Beilby layer and provide a surface suitable for epitaxial film deposition. However, this acid can only be used on substrates without residual damage such as scratch marks produced by mechanical polishing.

2.3. Sulphuric-oxalic acid etching

An equal mixture of concentrated sulphuric acid and saturated oxalic acid in a glass beaker was maintained at 135 ± 5°C and mechanically polished substrates in a Teflon* holder were etched for times up to 2 h. The surface features obtained by this acid mixture were similar to the features obtained by phosphoric acid etching at 160°C. Although sulphuric-oxalic acid mixture is not suitable for chemical polishing, it is useful to reveal defects in the substrate crystal. Features such as coring and faceting can be revealed using this etchant. Although these defects may be observed using X-ray topography, etching provides a simpler and faster method.

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3. Conclusions

The etching properties of phosphoric acid, sulphuric acid and sulphuric-oxalic acid mixture on the mechanically polished gadolinium-gallium garnet platelets were determined.

Phosphoric acid at high temperatures removed the damaged surface layer. Optimum surface properties were obtained when substrates were etched for 10 sec in the acid maintained for 1 to 2 h at temperatures of 350 or 400°C. The disadvantage of this etchant is that it increases the surface roughness by a factor of two or three over the mechanically polished surface. Smooth surfaces can be retained by using sulphuric acid as etchant, but this acid can only be used on platelets which do not have residual damage such as scratch marks produced by mechanical polishing.

Scratch marks introduced into the substrate surface by mechanical polishing become visible when etched in sulphuric acid. Sulphuric-oxalic acid mixture and phosphoric acid at 160°C revealed coring, faceting and scratch marks.

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