Development of "TPE3000" Polyimide Etching Solution, and Polyimide Processing using that Solution

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1. Introduction
Polyimide film is widely used in applications such as base film for FPCs, but there is a need for technology to process that film with even higher precision due to the increasing definition, higher functionality and miniaturization of LCD screens in mobile electronic devices such as mobile phones, 1seg TVs and mobile game machines. Due to the recent economic conditions, it will be difficult to survive the intense cost competition if low cost cannot be maintained in high-precision processing.
Polyimide processing technologies can be roughly divided into three types: mechanical processing (the conventional processing technique), laser processing (primarily using UV lasers for forming microholes), and chemical etching using etching solution. Each of these technologies has both advantages and disadvantages.
This paper describes the features of each processing method, and presents examples of processing using recent chemical etching methods.

2. Polyimide etching processes
2.1. Mechanical processing
With this method, polyimide is processing by shearing, grinding or otherwise applying physical force. Punching using dies, and drilling, are also examples of this type.
Advantages
The greatest advantage is the simplicity of the technique. Pre-processing and post-processing are basically unnecessary.
Secondly, the technique does not use chemicals.
Therefore there is no need for exhaust gas or waste liquid treatment equipment.
Mass production is possible in the case of punching. (With drilling, the drilling speed is affected by the number of holes drilled.)
Disadvantages
The greatest disadvantage is limitations on the processing of microholes. The method can produce microholes with a diameter of φ0.1mm or less, but since there is a large replacement loss due to die and drill damage, it is not realistic from the standpoint of cost.
Secondly, the method cannot produce blind-via. Therefore, it is limited to forming through-holes.
It is not suited to processing involving frequent model changes. In the case of punching in particular, a new investment in dies is necessary when changing models, and thus the method has problems in terms of delivery times and cost when there are model changes.
Features
Due to the above, this technique is most suitable for processing comparatively large through-holes (diameter φ0.2mm or greater), when model changes are infrequent.

2.2. Laser processing
With this method, polyimide is processed by thermal decomposition using light or heat energy.
Today, UV lasers are the most commonly used, but CO2 lasers are also used in some cases.
Advantages
The greatest advantage is the ease of producing
microholes with a diameter of φ0.1mm or less.

Secondly, the method can also produce blind-via.

Disadvantages

The greatest disadvantage is the technique's unsuitability for mass production when there are many points to be processed, or a processing on a large area. Since the processing speed is determined by the number of shots and the movement distance, when there are many microholes lined up at a narrow pitch, or processing is done on a large area, the number of shots increases, and equipment investment in multiple machines becomes necessary.

When processing blind-via, carbon is deposited on the copper at the bottom, and desmear treatment using chemicals such as potassium permanganate becomes necessary to remove the carbon. This makes the process more complex, and other equipment is needed for tasks such as waste liquid treatment. For environmental reasons, industry is phasing out heavy metals such as manganese.

Features

For the above reasons, this technique is suitable for producing microholes (diameter φ0.1mm or less) when there are comparatively few processing points.

2.3. Chemical etching

With this method, processing is done by chemically decomposing the polymer. Previously, simple alkaline aqueous solutions and hydrazine have been used for this purpose. TPE3000 is a new alkali etching solution which improves the problems with previous etching solutions.

Advantages

The greatest advantage is the ability to selectively etch polyimide without damaging copper or sputtered film. Thus the method is suitable for forming blind-via.

Secondly, the technique can simultaneously process numerous processing points or processing on a large area.

Thirdly, it enables half-etching or soft-etching for surface modification by adjusting etching temperature and time.

Disadvantages

The greatest disadvantage is that the technique is not applicable when metals corroded by alkali are exposed, i.e. amphoteric metals such as aluminum.

Secondly, it is difficult to achieve a processing taper angle (angles of 45-60° are typical), and there are limits on forming microholes with a narrow pitch.

Even with the same polyimide, there are large differences in processing time depending on the type of substrate.

A patterning process is necessary, and equipment is needed for waste liquid and exhaust gas treatment.

Features

Due to the above, this technique is most suitable for fine patterning at parts adjacent to metals such as copper or SUS, e.g. forming fine blind-via or etching flying lead parts.

Hydrazine is problematic because it contains carcinogenic components, is difficult to manage because the solution degrades quickly, and is only applicable to a limited number of polyimide types.

Alkaline aqueous solutions are effective for some types of polyimide such as Kapton (Du Pont-Toray) and Apical (Kaneka), but there are problems because some decomposition products do not dissolve, thus making the etching solution unstable, and etching solution is not applicable to Espanex (Nippon Steel Chemical) or Uplex (Ube Industries). "TPE3000 Solution" is a polyimide etching solution developed to solve these problems.

2.4. Summary

There are many options for forming through-holes with a comparatively large area, including punching, drilling, CO2 laser and wet etching. Therefore, it is best to select the processing method with the greatest cost advantages, based on an overall judgment taking into account the number of processing points, model changes, outsourcing vs. in-house processing, current equipment and so on.

However, when processing blind-via (even those with a large area) the methods change, and the options are limited to UV laser or wet etching. The reason for this is the need to consider damage to copper foil.

When forming microholes, the primary methods are UV laser and wet etching. Whereas the processing taper angle for wet etching is a small 45-60°, the processing taper angle for UV laser can be set to about 80°. Thus UV laser is advantageous for fine pitch patterns (pitch of 100μm or less).

When forming blind-via, or when there are many processing points, wet etching is advantageous because it enables selective etching of polyimide and the processing time is not affected by the number of processing points.
"Half etching" is a technique for thinning polyimide by etching part of the substrate to improve flexibility, or for obtaining a desired polyimide thickness which is not available commercially by etching the entire substrate. There is no technique other than wet etching capable of half etching.

Surface treatment (modification) is a technique for improving wettability of the polyimide surface, or improving the anchor effect when applying catalyst. Various options are possible: excimer laser, plasma processing and wet soft etching. Since each of these have unique features, it is best to evaluate which technique is most suitable.

3. Etching Process

3.1. Mask techniques for etching

This section describes the etching process from commercially available polyimide substrate to etching using TPE3000 solution. Three techniques are shown in Fig. 1. These differ only in the approach to the mask for polyimide etching. The basic process flow is the same.

1. Dry film mask technique

With this technique, a dry film is directly laminated onto the polyimide film surface, and a mask for polyimide etching is formed by performing exposure and development. When polyimide etching is finished, the dry film is peeled off, but the interesting point here is that peeling can be done without peeling solution, simply by rinsing with hot water. This is because, bringing a strong alkaline etching solution into the hot water rinsing bath causes dilution to a PH which is just right for peeling of the dry film surface.

There are two important points regarding this technique. First, the dry film used is not the type for fine patterning, but rather a type with outstanding heat-resistance for gold plating. The reason for this is that commercially available dry film is the alkali-soluble type, and etching solution is strongly alkaline. Therefore, if it is used at a high temperature of 70-80°C, an ordinary dry film for fine patterning will have inadequate chemical resistance, and will not function as a mask material. Second, the acrylic resin which comprises the dry film is a water repellent material. Therefore even if a dry film mask substrate with microholes is dipped directly into etching liquid, air in the hole will not be adequately released, and thus there is a high probability of causing etching defects. An effective solution for this is to perform etching after a pre-treatment where air release is promoted by dipping in a surfactant.

The greatest advantage of this technique is that it enables processing using inexpensive polyimide film, without using a copper clad substrate. Also, for bumpy substrates where copper or SUS has been etched, the bumpiness can be absorbed if a thick dry film resist is used, and thus it is possible form openings where required in the polyimide part. The disadvantage, on the other hand, is that even if a chemical-resistant dry film is used, as in gold plating applications, side etching will progress as etching time elapses, thus resulting in a small processing taper angle of 40-45°, and there are also limits on the processing precision of the bottom diameter.

Therefore, this technique is suitable for processing with comparatively large areas, such as the HDD suspension processing example in the sample applications described below.

2. Copper mask technique

This technique uses a copper clad substrate, such as a sputtered substrate or cast substrate. In this technique, a dry film for fine patterning is laminated onto the copper surface, and after exposure and development, a mask for polyimide etching is formed by performing copper etching.

The advantage of this technique is that it enables high-precision processing of microholes. Since copper is not corroded by alkaline solution and there is outstanding adhesion between copper and polyimide, there is almost no side etching with an etching time of about 5 mins., and it is possible to obtain processing taper angles of 50-60°. Therefore, the bottom diameter is also stable, and processing precision is improved. The disadvantage of this technique is that the substrate cost is relatively high compared to polyimide film, and copper etching increases the steps in the process.

Due to these features, this technique is suitable for microhole via processing applications.

3. Copper mask technique (Double-sided etching)

Recently, there has been an increasing need to form microholes of less than 30μm with higher precision than the copper mask technique. Basically, this is the same process as the copper mask technique described above, but the etching time for performing etching from both sides is half that of single-sided etching, and effects due to process taper are also reduced by half. As a result,
it is possible to obtain a through-hole processing precision of $10\mu m \pm 1\mu m$. The disadvantage of this technique is that a double-sided exposer is needed to perform patterning.

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Fig. 1. Via formation

3.2. Steps in the progression of etching

Fig. 2 shows observations of a sample where a hole $30\mu m$ in diameter was formed in copper in a double-sided copper clad Kapton substrate ($25\mu m$). The images were captured by removing the sample at one minute intervals until the proper etching (5 mins.) was attained.

- After 1 minute of etching, a few $\mu m$ of erosion has begun over the entire opening. At the etching surface, polyimide is being hydrolyzed, and a swollen layer has formed.
- At the stage after 2 minutes, etching has progressed to a depth of approx. $15\mu m$.
- After 3 minutes, etching has reached the bottom, but at this stage the shape of the bottom is not circular, and there are large variations in bottom dimensions between different holes.
- After 4 minutes, the bottom shape is close to circular, but observed in cross-section, it has a conical shape.
- After 5 minutes, the processing taper part is straight, and the bottom shape and dimensions are stable. This stage is defined as the end of etching.

The interesting point here is that close inspection of the taper part shows that it is not flat, and there are fine faults which look like tree rings. This is a phenomenon seen with all polyimides, and this characteristic is used in sputter residue treatment and half etching processing, described below.
3. Sample applications

The following describes typical applications using TPE3000 solution.

Via processing

Fig. 3 shows an example where a blind-via (bottom diameter=100µm) was formed by using a single-sided copper clad substrate (sputtered, copper thickness=12µm) made of Kapton En (25µm), laminating a dry film onto the polyimide surface, performing exposure and development, and etching from the surface at the openings in the dry film. The processing time was 5 mins. (80 °), and the top diameter is 150µm (processing taper angle=45 °).

Recently, there has been a growing need to form 30-50µm via. Fig. 4 shows a via produced by etching copper on one side of double-sided copper clad substrate (cast) made from Espanex M Series (25µm) to form a mask for polyimide etching, and etching using the copper mask. Processing time was 6 mins. (80 °), and the top diameter is 40µm (processing taper angle=60 °).

Processing for HDD suspension

An HDD (Hard Disk Drive) has the structure shown in Fig. 5, and this etching liquid was used to process a part called the HDD suspension located inside the drive. This part has the distinctive feature that it requires flex resistance, and thus is made by combining SUS, polyimide and copper.

As shown in Fig. 6, this is a technique where polyimide is partially etched while using a substrate on which part of the copper circuit pattern and SUS have been pre-etched. This is one application which can most effectively exploit the advantages of chemical etching.

Application to liquid crystal polymers

Fig. 7 shows an example where roughening treatment was achieved by using TPE3000 solution to etch the surface of liquid crystal polymer (a material often regarded as the next-generation insulation material for polyimide). Treatment was done for 5 mins. at 60 °. An Ra (arithmetic average roughness) of less than 0.1µm before treatment was increased to 0.6µm after treatment, and a porous surface ideal for the anchoring effect
was obtained.

Before treatment

After treatment

Fig. 7. Surface roughening of liquid crystal Polymer (LCP)

Fig. 8 shows an example of via processing in liquid crystal polymer. In this example, blind-via processing (bottom diameter=250µm) was performed in a 25µm thick liquid crystal polymer. Treatment was done for 4 mins. at 80 º.

Fig.8. Via processing of LCP

4. Physical characteristics and etching liquid

Fig. 9 shows the etching speeds of different polyimide materials using TPE3000 solution.

This graph shows how polyimide film thickness decreases with time when TPE3000 in a beaker is heated to a specified temperature while stirring with a stirrer, and small pieces of polyimide are placed in the beaker and etched from one side.

Apical-NPI and Kapton V (each 50µm thick) are etched in approx. 3 mins., and Kapton En (50µm thick) is etched in approx. 5 mins.

The submerged spray system is used in actual equipment because etching speed is reduced by approx. 1.5 times when a submerged spray is applied to the processing surface.

This graph is based on data obtained by etching with the polyimide etching liquid from the early stage of development (TPE3000). A newer liquid was also subsequently developed to enable efficient etching of Espanex substrate and thermoplastic polyimide (TPE3000T).

5. Conclusion

The information presented in this paper can be summarized as follows.

Polyimide processing using wet etching is a unique technique which can handle a broad range of tasks, from processing comparatively large areas to forming 10µm microholes, half etching and surface treatment.

With this technique, it is easy to selectively process polyimide without damaging metals such as SUS or copper.

Processing time does not increase when processing large areas or many processing points.

The technique can handle mixed patterns and design changes by just changing the patterning.

The solution is safer and more stable than the previous etchant (hydrazine).

References