United States Patent [19]

Hanazono et al.

[11] **3,905,883**

[45] **Sept. 16, 1975**

[54] **ELECTROLYTIC ETCHING METHOD**

[75] Inventors: **Masanobu Hanazono; Osamu Asai,** both of Hitachi, Japan

[73] Assignee: **Hitachi, Ltd.,** Japan

[22] Filed: **June 18, 1974**

[21] Appl. No.: **480,472**

[30] **Foreign Application Priority Data**

June 20, 1973 Japan 48-68734

[52] **U.S. Cl.** **204/129.65;** 204/129.8

[51] **Int. Cl.** **B23p 1/00**

[58] **Field of Search** 204/129.75, 129.8, 129.65, 204/129.2

[56] **References Cited**

UNITED STATES PATENTS

3,013,956	12/1961	Hugle et al.	204/129.65
3,560,357	2/1971	Shaw	204/129.65
3,560,358	2/1971	Black	204/129.65
3,721,592	3/1973	De Werdt	204/129.65
3,728,237	4/1973	Heijenbrok et al.	204/129.75

Primary Examiner—T. M. Tufariello

Attorney, Agent, or Firm—Craig & Antonelli

[57] **ABSTRACT**

A precise pattern figure can be formed on a thin film of permalloy, iron, nickel, cobalt and copper through an electrolysis with a mixture of ammonium persulfate and nitric acid electrolyte under control of the electrode potential. Particularly, a desired part of an electrode whose surface is in coexistence with aluminum can be electrolytically etched without damaging the aluminum.

7 Claims, 10 Drawing Figures

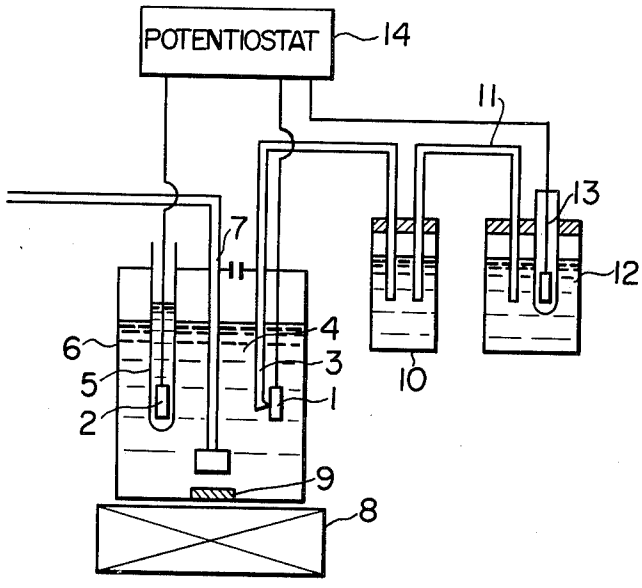


FIG. 1

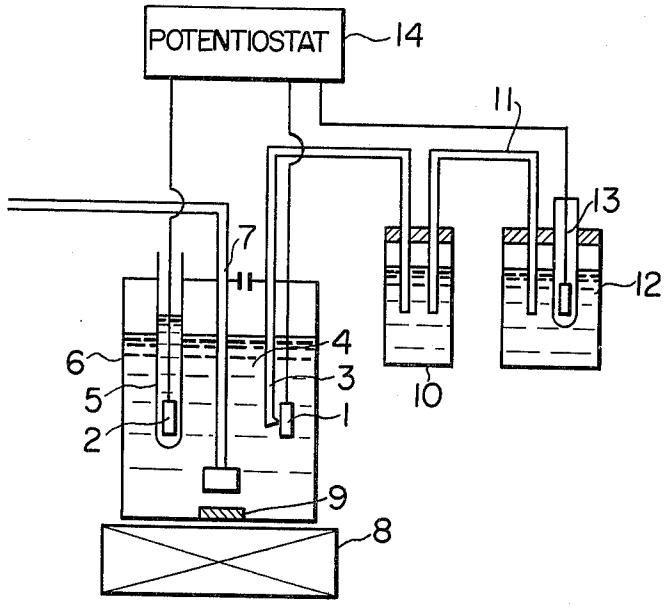

POTENTIOSTAT
14
11
13
12
7
6
5
2
4
3
1
10
9
8

FIG. 2

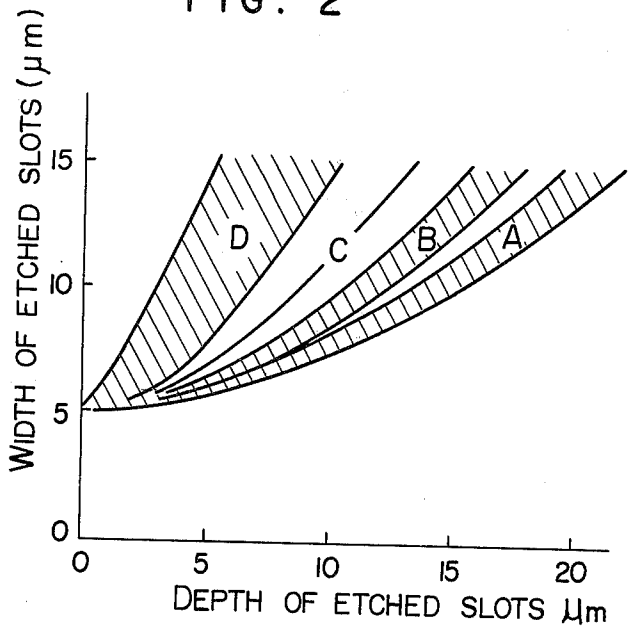

WIDTH OF ETCHED SLOTS (μm)
15
10
5
0
D
C
B
A
0
5
10
15
20
DEPTH OF ETCHED SLOTS μm

FIG. 3(a)

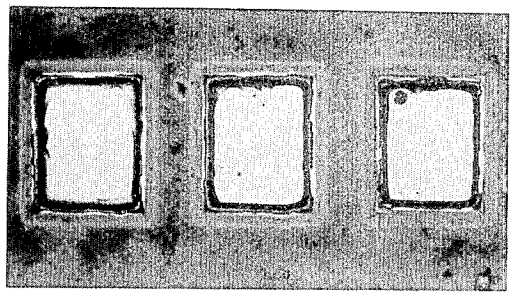


FIG. 3(b)

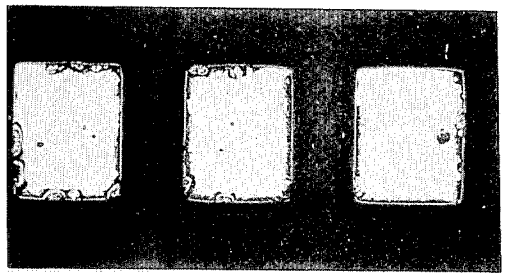


FIG. 3(c)

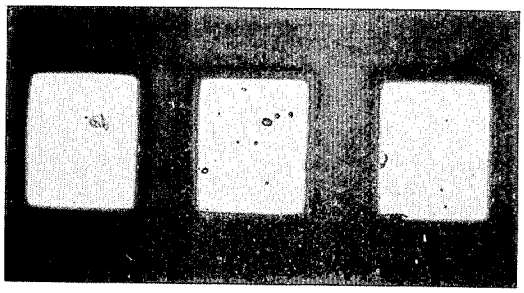
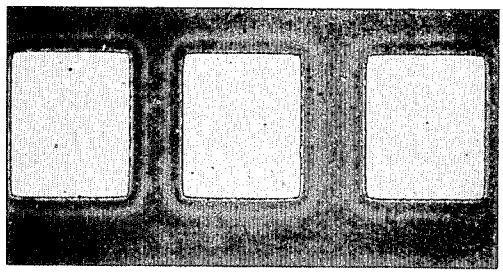


FIG. 3(d)



(x100)

FIG. 4a

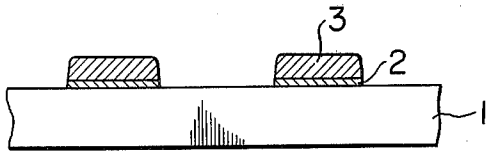


FIG. 4b

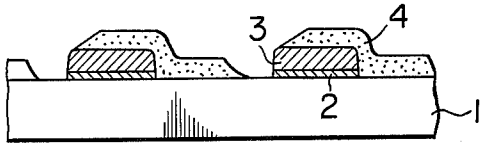


FIG. 4c

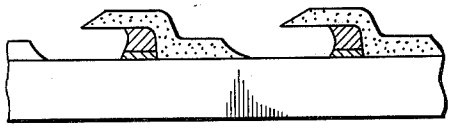
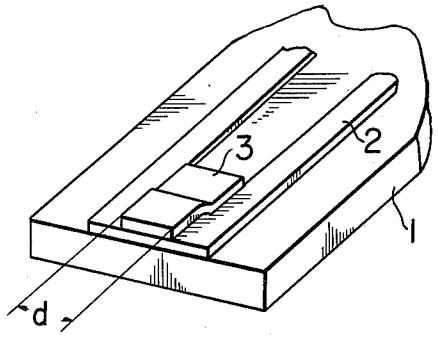


FIG. 5



ELECTROLYTIC ETCHING METHOD

BACKGROUND OF THE INVENTION

1. Field Of The Invention

The present invention relates to an electrolytic etching method available for preparation of large size integrated circuits incorporated with a number of highly concentrated elements and circuits formed on a substrate, formation of electrodes of semiconductor elements and preparation of other elements and circuits as well.

2. Description Of The Prior Art

As measures for preparing thin film circuits, vacuum evaporation, sputtering, plating, chemical etching, electrolytic etching, ion beam etching and sputter etching are known, and these measures are used in combination for forming a highly concentrated desired pattern.

By means of vacuum evaporation or sputtering through a pattern mask, it is possible to form under a dry process a desired pattern on a thin film comparatively readily. However, precision in the pattern figure thus prepared varies widely dependent on precision in the pattern mask and bonding ability of the mask to an object to be patterned, and by the usual mask evaporation method the formation of the pattern is achieved with precision of 20 to 50 μm at most.

A mask pattern of photoresist can have highly precise dimension and therefore with photoresist it is possible to form a mask pattern with 1 μm precision. However, when a pattern is formed through chemical etching by using such a highly precise mask pattern as the photoresist mask, precision in a completed pattern is reduced to about 10 μm on account of the irregularity of etching and the damage of the photoresist mask. Especially, in the chemical etching it is usual to raise the temperature for the purpose of promoting the dissolving speed and this often damages the photoresist film.

As compared to the chemical etching, an electrolytic etching softly acts on an object to be etched. However, electrolysis creates gases which are liable to cause the photoresist film to be peeled off, thus degrading precision in the pattern. Incidentally, a so-called selective electrolytic etching method wherein only one of two kinds of metals electrically connected and exposed from the electrode surface is dissolved has not been used for forming thin film circuit patterns since it requires a special combination of different metals and special conditions.

SUMMARY OF THE INVENTION

A principal object of the present invention is to provide an electrolytic etching method for forming a precise pattern figure on thin films of permalloy, iron, nickel, cobalt, copper and molybdenum.

A second object of the present invention is to provide an electrolytic etching method wherein a metal thin film a part of which is coated with a photoresist pattern film can be etched without damaging the photoresist pattern film.

A third object of the present invention is to provide a selective electrolytic etching method wherein permalloy, iron, nickel, cobalt, copper, and molybdenum are each electrically connected to aluminum and under this electrical connection the permalloy, iron, nickel, cobalt, copper or molybdenum is selectively dissolved.

A fourth object of the present invention is to provide an electrolytic etching method capable of suppressing the creation of gases.

A fifth object of the present invention is to provide an electrolytic etching method wherein etching performance of metals can be observed during the etching process.

A sixth object of the present invention is to provide measures of preparing precise electronic parts such as an aluminum strip lead and thin film magnetic heads.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic representation of one type of electrolytic etching device embodying the invention.

FIG. 2 is a graphic representation of etching pattern figures in accordance with different electrolytes and materials of a pattern mask.

FIGS. 3*a* to 3*d* show photographs of etched permalloy films provided on a glass substrate.

FIG. 4 is a diagramatic representation of preparing process of a strip lead to which the invention is applied.

FIG. 5 is a perspective view of a thin film magnetic head.

DESCRIPTION OF THE PROFERRED EMBODIMENTS

The present invention contemplates a method of electrolytic etching with a mixture of ammonium persulfate and nitric acid electrolyte for dissolving permalloys as well as iron, nickel, cobalt, copper and alloys thereof. Disclosed herein is an electrolytic etching method wherein an electro-chemical action is intentionally applied to an etching reaction. It also involves a case where some electro-chemical means are added for promoting, or sometimes suppressing, the chemical etching reaction. The electro-chemical means is identical to means for changing electrode potential of an object to be etched from the natural electrode potential, which the object bears when immersed alone in an electrolyte, to a desired potential, and it may be constituted, for example, by application of voltage with an external power source or coupling of the object to be etched with a different metal.

The electrolyte used herein is an aqueous solution which contains 0.1 to 2.5 mol/l ammonium persulfate [$(NH_4)_2S_2O_8$] and 0.2 to 10 mol/l nitric acid.

Where an aqueous solution of ammonium persulfate devoid of nitric acid is used as the electrolyte, the dissolving speed of permalloy is caused to differ markedly dependent on compositions of the permalloy and preparing conditions therefor. For example, since the dissolving speed of a vacuum evaporation deposited film is less than that of casting material and plated material by 1/10 to 1/100, the aqueous solution of ammonium persulfate alone is unsuitable for electrolyte for making an etching pattern of an object coexistent with the casting and plating materials.

In addition, the electrolyte of ammonium persulfate aqueous solution has a comparatively small etching speed and it will tend to damage anti-etching photoresist films. For example, under an electrolysis 20 % ammonium persulfate aqueous solution at 50°C temperature, copper and cobalt-vanadium-iron alloy bear dissolving speeds of about 0.2 μm/min and 1 μm/min, respectively, while the photoresist film of about 2 μm thickness can assume the protective ability within about 10 minutes. Accordingly, with the anti-etching

photoresist film the depth of etching is restricted to less than 2 μm for copper and within 10 μm even for irons.

When the ammonium persulfate aqueous solution is added with nitric acid, the electrolytic etching speed is markedly increased owing to the oxidization action of nitric acid and especially difference in the dissolving speed due to different preparation processes such as plating or evaporation becomes almost negligible. Further, since the addition of nitric acid acts to reduce the polarization of an iron object and to increase the passivating range of aluminum, the ammonium persulfate aqueous solution added with nitric acid is advantageous to such a selective etching as to etch only the iron and copper of metals coexisting with aluminum.

Instead of nitric acid, ferric chloride, cupric chloride, potassium bichromate, and cerium sulfate are useful as oxidizing acids adapted to be added to the ammonium persulfate. Since chlorides induce etch pits on an aluminum surface, other additional substances than chlorides should be used when it is necessary to avoid the etch pits on the aluminum surface. To facilitate oxidization, supplemental injection of oxygen gas and addition of hydrogen peroxide are effective. The concentration of ammonium persulfate within the electrolyte is 0.1 to 2.5 mol/l but 0.8 to 1.5 mol/l is preferred to the practical use, at which the solution assumes pH representation of 1.8 to 1.9. However, since negative ions HSO_4^- takes place in the dissolving reaction of metals by ammonium persulfate, it is necessary to select conditions for easy creation of the negative ions HSO_4^- for the purpose of facilitating the dissolving reaction of the metals. This enforces reduction in pH of ammonium persulfate electrolyte to below 1.6. Ordinary acids such as chloride, sulfuric acid, and nitric acid may be used for reducing the pH representation. Especially, for the reason set forth above, oxidizing acids are preferred to the present invention end.

In ammonium persulfate aqueous solution of 1 mol/l concentration, the oxygen creation potential (relative to saturated caromel electrode, hereinafter abbreviated as SCE) is about 1.0 volt. On the other hand, in order to dissolve a plated coating of 22 % iron-78 % nickel permalloy at 2 μm/min etching speed in this solution, it is necessary to maintain the oxygen creation potential (relative to SCE) about 1.3 volts, naturally resulting in that oxygen gas taking place at a large amount. However, where nitric acid concentrated above 0.2 mol/l is added to the 1 mol/l concentration ammonium persulfate aqueous solution, since the dissolving speed of permalloy is increased and accompanied by decrease in the polarization of permalloy, the electrode potential at the permalloy electrode adapted to be dissolved can be decreased below the oxygen creation potential, particularly below 1.0 volt (relative to SCE), thereby enabling etching of the permalloy without causing the creation of oxygen gas.

For etching the permalloy with electolyte of 0.8 to 1.5 mol/l ammonium persulfate and 0.5 to 8 mol/l nitric acid, the electrode potential at permalloy object to be etched may be selected to −0.1 to 0.5 volts (relative to SCE).

In the 1 mol/l concentration ammonium persulfate electrolyte, aluminum is passivated over a wide range of the oxygen creation potential of 0.5 to 2.5 volts (relative to SCE). When added with nitric acid, however, the passivation becomes unstable and the etch pit potential is observed. As the additional amount of the nitric acid increases, the etch pit potential decreases, especially, at the nitric acid concentration of above 10 mol/l a current flow necessary for maintaining the passivation exceeds 1 mA/cm². Accordingly, it will be seen that the additional amount of the nitric acid ranges from 0.2 to 10 ml/l to obtain an aluminum etch pit potential of above 1.7 volts (relative to SCE) and the current flow necessary for passivation of below 0.5 mA/cm². Preferably it ranges from 0.5 to 8 mol/l.

As understood from the foregoing description, a rapid etching for magnetic objects such as iron, nickel and cobalt and alloys thereof as well can be achieved with an electrolyte which contains 0.1 to 2.5 mol/l concentration ammonium persulfate and 0.2 to 10 mol/l nitric acid under the application of a potential between the natural electrode potential and the oxygen creation potential to the object. Under these conditions, gas evolution is avoided, and it leads to the prevention of the photoresist film from being peeled off, and so aluminum will not be damaged. In addition to it the aluminum is maintained in the passivation range, so it will not be dissolved.

EXAMPLE 1

A permalloy sheet of 30 μm thickness provided with a precise mask pattern was subjected to an electrolytic etching to examine the respective preferable kinds of mask material and electrolyte from the etching figure.

The experiment was made with an electrolytic etching device shown in FIG. **1**. In the figure, numeral **1** designates a permalloy sample to be etched, which sample constitutes an anode electrode. Numeral **2** designates a platinum cathode electrode in the form of a plate, which cathode electrode **2** is separated by an unglazed tube **5** such that gas created therein is prevented to prevail into the electrolyte but is electrically communicated with the etching electrolyte through the unglazed tube **5**. Numeral **3** disignates a glass capillary vessel for measuring the electrode potential. There are further provided electrolyte **4**, an electrolytic bath **6**, a gas injection pipe **7** through which gas is injected into electrolyte with need to control the circumferential conditions thereof a magnetic stirrer **8** and a stirrer piece **9** adapted for stirring the electrolyte, saturated KNO_3 solution **10**, a salt bridge **11**, saturated KCl solution **12**, a saturated calomel electrode **13** and a potentiostat **14** for measuring the anode potential relative to the saturated calomel electrode and maintaining the anode potential at a desired value.

The electrolitic etching in accordance with the present invention was carried out by maintaining the anode electrode potential and the oxygen creation potential of the permalloy sample to be etched with a D.C. voltage being applied between the platinum cathode electrode and the anode electrode of the permalloy sample.

Listed in Table 1 are permalloy compositions of the sample to be etched.

Table 1

Compositions	Fe	Ni	Mn	P	S	C
Content (weight %)	20.62	78.88	0.36	0.05	0.03	0.01

After polished, washed and dried, the surface of permalloy film was coated with a photoresist film of a commercial photoresist made of isobutylene rubber and polycinnamic vinyle and deposited with aluminum

by evaporation, with an uncovered partial figure of 5 ± 1 μm width and 50 μm length. Three kinds of electrolytes as listed in Table 2 were used. With a 30°C temperature electrolyte and under 0.1 volts (relative to SCE) electrode potential, the etching was performed to measure relation between the depth and the width of etched slots.

Table 2

Electrolyte No.	(mol/l) $(NH_4)_2S_2O_8$	HNO_3
1	0.4	0.5
2	0.85	1
3	1.5	5

Results are illustrated in FIG. 2. In the figure, symbol A represents a case where No. 2 electrolyte is used with the protective coating of aluminum evaporation deposition, wherein a sharp slot is formed having the smallest extension in the width direction. Symbol B represents a case where No. 2 and No. 3 electrolytes are used with the protective coating of photoresist, and symbol C represents a case where No. 1 electrolyte is used with a photoresist film. Symbol D represents a case where No. 2 electrolyte is used with a photoresist film, wherein a chemical etching is performed without passing a current flow. In chemical etching the etching speed was less than one-half that of the electrolytic etching and the dissolved or etched depth remarkably differs in the direction of width.

EXAMPLE 2

Permalloy was deposited by means of evaporation upon a glass substrate (No. 7059 glass substrate of Corning) to a thickness of about 3,000 A and thereupon a permalloy layer was plated to a thickness of 10 μm. Photoresist film (KMER) was used as the protective mask and an electrolytic etching was performed under a constant potential of 0.05 volts (relative to SCE). After the etching, etched pattern figures were photographed as shown in FIG. 3. FIGS. 3*a* to 3*d* correspond to electrolytic etchings with 1 mol/l ammonium persulfate electrolyte, 1 mol/l ammonium persulfate and 0.1 mol/l nitric acid electrolyte, 1 mol/l ammonium persulfate and 0.5 mole/l nitric acid electrolyte, and 1 mol/l ammonium persulfate and 1 mol/l nitric acid electrolyte, respectively. Especially, in the electrolytic etching corresponding to FIG. 3*d* the anode potential was maintained at 0.05 volts and then permalloy applied with a potential of −0.5 volts (relative to SCE) which is lower than its natural electrode potential was immersed in the electrolyte for five minutes, wherein island-shaped and electrically isolated portions were dissolved. It will be understood from the figure that not only the effect of additional nitric acid is clearly exemplified in the resulted pattern figure but also precision in electrolytic etching pattern is further improved owing to the dissolving ability of electrolyte itself.

EXAMPLE 3

On a glass substrate, a copper evaporation deposition pattern was formed and thereon a nickel plating layer was placed by about 20 μm thick, thereby to form a multiple-layer as shown in FIG. 4*a*. A glass substrate **1**, a copper evaporation deposition layer **2** and a nickel plating layer **3** are illustrated in the figure. The multiple-layer was subjected to a shadowing evaporation with aluminum at 30° incident angle to obtain a resulted structure as illustrated in FIG. 4*b*. Thereafter, the resulted structure was electrolytically etched in 1.5 mol/l ammonium persulfate - 1.5 mol/l nitric acid electrolyte under a constant electrode potential of zero volt (relative to SCE). Thus, an aluminum beam lead which takes a shape as shown in FIG. 4*c* was prepared.

EXAMPLE 4

In manufacturing process of a thin-film magnetic head for writing in and reading out recording signals of a magnetic recording medium, a precise finish of figure is required for increasing recording density. In FIG. 5, there are provided a ferrite substrate **1** on which aluminum conductors **2** having an anodic coating on their surfaces are placed, and an upper permalloy magnetic member **3** across the aluminum conductors **2** magnetically communicating with the ferrite substrate **1** at its rear portion. A magnetic gap between the ferrite substrate and the front portion of an upper magnetic member serves as a magnetic head. In this magnetic head, the width *d* of the upper permalloy magnetic member equals the track width and therefore the upper permalloy magnetic member is required to be formed with high accuracy. Upon preparing the permalloy magnetic member, a permalloy thin film layer having a larger area than a desired figure and 20 μm thickness was formed by means of the evaporation and plating, and thereupon a precise pattern of the desired figure was formed with naphthoquinone-diazo positive type photoresist coating. A resulted structure was subjected to an electrolytic etching in 1 mol/l ammonium persulfate-2 mol/l nitric acid electrolyte under a constant potential of 0.2 volts (relative to SCE), thereby to obtain the upper permalloy magnetic member. Errors in the width of the upper permalloy magnetic member thus obtained were within ±30 μm (±15 μm for one side) with respect to a target width of 200 μm.

For comparison, deviations in the width of the upper permalloy magnetic member prepared by mask evaporation and chemical etching were measured. When prepared by the mask evaporation, deposition entering between the mask and the substrate was twice the thickness of the deposition layer, though fitting precision between the mask and substrate is responsible for reducing the deviation. Accordingly, in view of mass-production, obtainable width of the upper permalloy magnetic member will be about 200±50 μm. When prepared by the chemical etching with the photoresist coating and 1 mol/l ammonium persulfate - 0.1 mol/l sulfuric acid solution, the width of the upper permalloy magnetic member was 200±40 μm and undissolved portions of island shape were retained. Further, as compared to the electrolyte etching, edge figure was not sharp. Effective track width of magnetic head thus obtained was impaired in response to the poor sharpness of edge figure.

As understood from the foregoing description and applications referred to in examples, according to an electrolytic etching method of the invention, it is possible to form precisely figured etching patterns and further it is possible to form comparatively readily a desired pattern figure on an object to be etched, with partly unetched portions if the etching intensity has previously been measured. Easy washing after completion of electrolyte etching and mass-treatment of fine

and sophisticated objects to be etched within a short time permit a readily available etching method.

We claim:

1. An electrolytic etching method for etching precise electrical parts, wherein a 0.1 to 2.5 mol/l concentration ammonium persulfate - 0.02 to 10 mol/l concentration nitric acid electrolyte is used and a DC voltage is applied between a cathode electrode of insoluble metal and an anode electrode including a metal object to be etched, said metal object being made from a member selected from the group consisting of iron, nickel, cobalt, copper and alloys thereof, whereby a constant potential electrolytic etching is performed by maintaining the anode electrode potential between the natural electrode potential and the oxygen creation potential of said objects to be etched.

2. An electrolytic etching method according to claim 1 wherein said electrolyte comprises a 0.8 to 1.5 mol/l concentration ammonium persulfate - 0.5 to 8 mol/l concentration nitric acid solution.

3. An electrolytic etching method according to claim 1, wherein said anode electrode including said metal objects to be etched is covered with isobutylene rubber, polycinamic vinyle, diazo compound photoresist films at a part other than that to be etched.

4. An electrolytic etching method according to claim 1, wherein said anode electrode including said metal objects to be etched is covered with an aluminum film at a part other than that to be etched.

5. An electrolytic etching method for etching precise electrical parts wherein one end of an anode electrode including an object to be etched is connected to a potentiostat, said object being constituted by an electrically insulative substrate or aluminum layer provided thereon with a thin film made from a member selected from the group consisting of iron, nickel, cobalt and alloys thereof said thin film being coated with a photoresist or aluminum pattern, one end of a cathode electrode including an insoluble metal is connected to said potentiostat, and the other ends of said anode electrode and said cathode electrode are immersed in a 0.8 to 1.5 mol/l concentration ammonium persulfate 0.5 to 8 mol/l nitric acid electrolyte, whereby a constant potential electrolytic etching is performed by maintaining the anode electrode potential between the natural electrode potential and the oxygen creation potential of said anode electrode.

6. An electrolytic etching method according to claim 5, wherein after a constant potential electrolysis is performed by maintaining the anode electrode potential between the natural electrode potential of said anode metal and 1.2 volts (relative to SCE), a noble potential than said natural electrode potential is applied to said anode electrode immersed in said electrolyte, whereby a remaining part of metal to be etched which has been electrically insulated is dissolved.

7. An electrolytic etching method according to claim 1, wherein said anode electrode including a metal object to be etched comprises aluminum.

* * * * *