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TECHNIQUE FOR ELECTROETCHING THIN FILM METALLIZATION

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FIG. 1

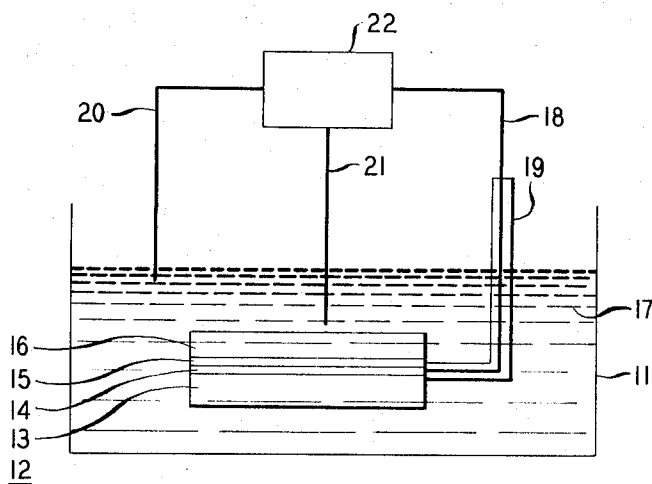
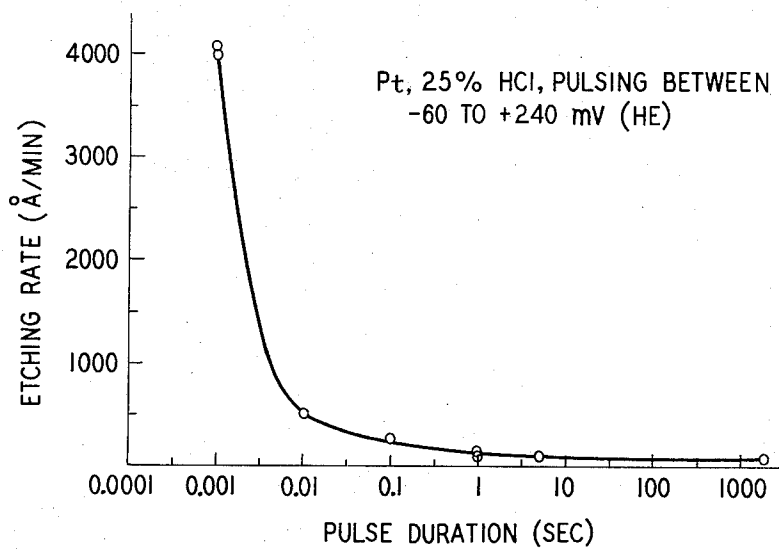


FIG. 2



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TECHNIQUE FOR ELECTROETCHING THIN FILM METALLIZATION

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7 Claims

ABSTRACT OF THE DISCLOSURE

Pattern delineation of thin film metallizations including gold, platinum and rhodium is effected electrolytically in the presence of a strong acid having a pH less than one. The described technique permits controlled etching of noble metals which heretofore have been etched only with difficulty.

This invention relates to a technique for electrochemically etching thin film metallizations. More particularly, the present invention relates to a technique for selectively etching thin film metallization including noble metals by electrochemical means.

In recent years miniaturization of components and circuitry coupled with the increasing complexity of modern electronic systems have created an unprecedented demand for reliability in thin film circuitry and the need for the total exploitation of the technology. This is particularly true in the case of lead attachment which has long been recognized as being a critical factor in the stability of circuit characteristics.

Early workers in the art recognized that the metallurgical compatibility of the various metallic constituents of the joining and conducting system played a prominent role in determining the parameters of interest, so motivating the use of a single metal for this purpose. Although such systems were found to be ideal from a metallurgical standpoint, they suffered from inherent defects in that the manufacturer was necessarily restricted from the standpoint of obtaining optimum circuit characteristics. Accordingly, the interest of workers in the art was focused upon multi-metal joining or conducting systems.

Unfortunately, studies have revealed that thermal degradation of adhesion of gold-transition metal thin film composites often occurs, such being attributed to diffusion and migration affects. In order to obviate this limitation, workers in the art proposed inserting a barrier, typically platinum or palladium between the gold and the other member of the composite. Although rhodium was also considered for this purpose, attempts at pattern delineation proved fruitless.

Studies of composites prepared utilizing palladium as the barrier layer revealed that interdiffusion between the gold and the palladium occurred at high temperatures, thereby resulting in a reduction in the conductivity of the gold and altering circuit parameters.

Although platinum has not proven as convenient to use as palladium, it has not evidenced the interdiffusion problem with gold. However, platinum was found to be very difficult to etch and the only material found suitable for this purpose has been aqua regia, a material which attacks photoresists. Further investigation revealed that pattern delineation of the platinum containing composite could only be effected by back sputtering, a technique which is economically undesirable and which often results in the deposition of residues. Still further, back sputtering could not be used in the fabrication of MOS devices due to the likelihood of damaging the dielectric. Accordingly, the platinum composites have been utilized primarily in the fabrication of bipolar devices. Recognizing these limita-

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tions, workers in the art have focused their interest upon the development of a technique suitable for pattern delineating all noble metals with a universal etchant.

In accordance with the present invention, this end has been attained by means of a novel electrochemical etching technique. Briefly, the invention involves etching at least one thin film material selected from among gold, rhodium and platinum in a non-oxidizing electrolyte having a pH less than one by applying a potential difference between the sample to be etched and an auxiliary electrode so as to develop a potential on the sample with respect to a reference electrode which varies periodically between an upper and a lower value. In a preferred embodiment, etching of a gold-transition metal metallization composite having a barrier layer selected from the group consisting of platinum and rhodium is effected selectively in an electrolyte comprising a non-oxidizing acid having a pH less than one. Composites may be etched in the described manner in controllable fashion at a significantly higher rate than that attainable by conventional electroetching techniques, the metals being removed selectively by adjusting the height of the potential.

The invention will be more readily understood by reference to the following detailed description taken in conjunction with the accompanying drawing wherein:

FIG. 1 is a schematic representation of a typical system suitable for use in the practice of the present invention; and

FIG. 2 is a graphical representation on coordinates of pulse duration in seconds against etching rate in Angstroms per minute for a titanium-platinum-gold composite pulse etched in accordance with the present invention.

With reference now more particularly to FIG. 1 there is shown an etching vessel 11 having disposed therein thin film composite 12 comprising an insulating substrate 13 having deposited thereon a transition metal or glue layer 14; a noble metal 15 selected from among platinum and rhodium, and patterned gold layer 16. An electrolyte 17 is employed in an amount sufficient to cover the metallized composite. Electrolyte 17 is a non-oxidizing acid having a pH less than one. Typical acids suitable for use in the practice of the present invention are hydrochloric, sulphuric, hydrofluoric, phosphoric and the like. The electrical system employed includes contacting electrode 18 which is connected to layer 14, electrode 18 being insulated from electrolyte 17 by means of insulating sheath 19. A second electrode 20 functions as the counter or auxiliary electrode in the system and is immersed in electrolyte 17. The third electrode 21 is a conventional reference electrode, typically a calomel electrode, which serves to maintain the composite 12 at a controlled potential with respect to the electrolyte, thereby permitting control of the etching process. Each of the electrodes is shown connected to a pulsing means 22, typically a potentiostat including a pulse generator.

In the operation of the process, the apparatus depicted in FIG. 1 is set up and etching initiated by applying a difference of potential between the sample and the auxiliary electrode so as to develop a potential on the sample with respect to the reference electrode which varies periodically between an upper and lower value. With respect to the composite described herein, this potential may range from 1450 to 1600 mv. (hydrogen scale) at the upper value and from 550 to -60 mv. (hydrogen scale) at the lower value. Studies have revealed that for slow etching, the lower value may range from 550 to 240 mv. and from 240 to -60 mv. for rapid etching. It has also been found that the described technique may be used selectively with respect to platinum, gold and rhodium. Thus, the use of higher potentials ranging from 1450 to 1600 mv. results in the etching of gold, platinum and rhodium. However,

rhodium may be etched selectively with respect to platinum and gold by maintaining the upper value of potential between 900 and 1100 mv. and rhodium and platinum selectively etched with respect to gold at upper potential values ranging from 1100 to 1450 mv. (all potential being on the hydrogen scale). The upper limit of 1600 mv. is dictated by considerations relating to undesirable gas evolution. The lower potential limit is determined by etching rate considerations. The period of time that the sample is maintained at either the upper or lower potential may conveniently range from 1 to 10 milliseconds, the shorter time periods corresponding with the higher etching rates and the converse. It has been found that platinum may be etched at 1 millisecond durations at the rate of 4000 A. per minute and rhodium at 2000 A. per minute. However at 10 millisecond durations etching of platinum may be effected at the rate of 500 A. per minute and rhodium at the rate of 250 A. per minute.

With reference now to FIG. 2, there is shown a graphical representation on coordinates of duration of time that the sample is maintained at either the upper or lower potential with respect to the reference electrode versus etching rate in Angstroms per minute for a titanium-platinum-gold thin film composite etched in a 25 percent hydrochloric acid solution to potentials (on the hydrogen scale) from -60 to 240 mv. It will be noted that a one millisecond duration results in etching of platinum at 4000 A. per minute and at 10 milliseconds at 500 A. per minute. It will be understood that removal of the base or glue layer may also be effected by lowering the potential to a constant negative value, or by etching to a potential between -500 and -300 mv. at durations ranging from 1 to 10 milliseconds, so resulting in a universal etching bath. A final chemical etching step will, of course, be used as required to remove detached residues.

Examples of the present invention are described in detail below. These examples are included merely to aid in the understanding of the invention and variations may be made by one skilled in the art without departing from the spirit and scope of the invention.

EXAMPLE 1

A composite comprising successively 500 A. titanium, 500 A. platinum and 10,000 A. of gold deposited upon a ceramic substrate member was immersed in an apparatus of the type shown in FIG. 1, a 25 weight percent hydrochloric acid solution having a pH of about 1 being employed as the electrolyte. The auxiliary electrode was comprised of carbon and the reference electrode was a calomel electrode. Etching was then effected by establishing a potential of -60 mv. on the sample with respect to the reference electrode for a duration of 1 millisecond and then establishing a potential of 1600 mv. for a duration of 1 millisecond. The procedure was continued successively until the gold was removed. Then, the procedure was repeated using a lower potential value of -60 mv. and an upper value of 1240 mv. to remove the platinum at a rate of 4000 A. per minute.

EXAMPLE 2

The procedure of Example 1 was repeated using a duration of 10 milliseconds. The platinum was etched controllably at the rate of 500 A. per minute.

EXAMPLE 3

The procedure of Example 1 was repeated using a composite comprising 500 A. of rhodium rather than platinum. The rhodium was etched at one millisecond durations at a rate of 200 A. per minute.

EXAMPLE 4

The procedure of Example 2 was repeated using a composite comprising 500 A. of rhodium rather than platinum, the rhodium being etched using a duration of 10 milliseconds at a rate of 250 A. per minute.

What is claimed is:

1. Technique for electrochemical etching of a thin film selected from the group consisting of gold, platinum and rhodium which comprises immersing said thin film together with an auxiliary electrode and a reference electrode in an electrolyte comprising an acid having a pH less than one and etching the thin film by applying a difference of potential between the thin film and the auxiliary electrode so as to develop a potential on the thin film with respect to the reference electrode which varies periodically between an upper value ranging up to 1600 mv. and a lower value ranging down to -60 mv., the potentials being on the hydrogen scale, the upper value of the potential ranging from 900 to 1100 mv. for selective etching of rhodium with respect to platinum and gold, 1100 to 1450 mv. for selective etching of rhodium and platinum with respect to gold and from 1450 to 1600 mv. for etching of rhodium, platinum and gold.

2. Technique for electrochemical etching of a gold-transition metal thin film composite having a noble metal selected from the group consisting of platinum and rhodium deposited intermediate the gold and the transition metal which comprises immersing the composite together with an auxiliary electrode and a reference electrode in an electrolyte comprising an acid having a pH less than one and etching the composite by applying a difference of potential between the composite and the auxiliary electrode so as to develop a potential on the composite with respect to the reference electrode which varies periodically between an upper value ranging up to 1600 mv. and a lower value ranging down to -60 mv., the potentials being on the hydrogen scale, the upper value of the potential ranging from 900 to 1100 mv. for selective etching of rhodium with respect to platinum and gold, 1100 to 1450 mv. for selective etching of rhodium and platinum with respect to gold and from 1450 to 1600 mv. for etching of rhodium, platinum and gold.

3. Technique in accordance with claim 2 wherein said potential varies at a periodicity ranging from 1 to 10 milliseconds.

4. Technique in accordance with claim 3 wherein said lower value ranges from 550 to -60 mv.

5. Technique in accordance with claim 3 wherein said upper value ranges from 1450 to 1600 mv.

6. Technique in accordance with claim 2 wherein said acid is hydrochloric acid.

7. A technique for pattern delineation of a thin film composite comprising an insulating substrate having deposited thereon a transition metal, a noble metal selected from the group consisting of platinum and rhodium and a patterned gold layer which comprises immersing the composite together with an auxiliary electrode and a reference electrode in an electrolyte comprising an acid having a pH less than one and etching the composite by applying a difference of potential between the composite and the auxiliary electrode so as to develop a potential on the composite with respect to the reference electrode which varies periodically between an upper value ranging up to 1600 mv. and a lower value ranging down to -60 mv., the potentials being on the hydrogen scale, the upper value of the potential ranging from 900 to 1100 mv. for selective etching of rhodium with respect to platinum and gold, 1100 to 1450 mv. for selective etching of rhodium and platinum with respect to gold and from 1450 to 1600 mv. for etching of rhodium, platinum and gold.

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