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A comparison of AC and DC electrochemical etching techniques for the fabrication of tungsten whiskers

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Abstract. The relative merits of the AC and DC methods for electrochemically etching tungsten whiskers have been studied. Examination under a 1 MeV electron microscope has shown that the tip radius is comparable in both cases, and in the region 5–10 nm. The AC method, however, produces more robust whiskers with larger cone angles and is probably more suitable for the manufacture of whiskers used in metal–insulator–metal diodes.

1. Introduction

Various methods have been used in the past for fabricating the metal whiskers used in, for example, field emission microscopy and metal–insulator–metal (MIM) diodes. These methods have included electron bombardment (Drechsler and Prulhiere 1970), and chemical and electrochemical etching (Dyke and Dolan 1956). Electrochemical etching is almost certainly the most satisfactory and simplest method of fabrication for tungsten, perhaps the metal most commonly used for whiskers, although little detailed information on the technique has been published. This is partly because production of these whiskers has been considered somewhat of an art dependent upon the experience and skill of the worker. Recently, however, Twu (1975) reported a reproducible method of DC electrochemical etching using sodium hydroxide as the etchant. This study considered only the general shape of the etched portion of the whisker and did not include a detailed study of the tip radius and shape. The National Physical Laboratory has been involved for several years with the production of metal whiskers for use in MIM diodes using electrochemical etching with an AC current. It was decided therefore to do a comparative study of the AC and DC techniques, with regard to the detailed tip parameters, using a 1 MeV electron microscope.

MIM diodes have been used as harmonic mixers of infrared lasers (Blaney *et al* 1977). Important requirements of these diodes are (1) small tip radii (<10 nm) so that the junction capacitance, which degrades the high-frequency response of the diode, is minimised, and (2) a sturdy shape to the whisker tip so that it will not distort appreciably on contact, and any heat generated in the tip by incident radiation is readily dissipated (cone half angle $\geqslant 10°$). This second requirement is not so critical for whiskers produced as field emitters.

2. Apparatus and procedure

Circuits were designed and built for both AC and DC etching using a digital technique based on that described by Lilburne *et al* (1970). In the case of DC etching the only modification to Lilburne's circuit was that the DC current was square wave modulated at 1 kHz instead of 1 MHz, as it was found that better tip shapes were produced at this lower frequency (unmodulated DC was briefly investigated and found to give apparently similar results). The AC circuit used the same basic concept and is shown in figure 1. In both cases the current through the etching bath switches off within one cycle of the

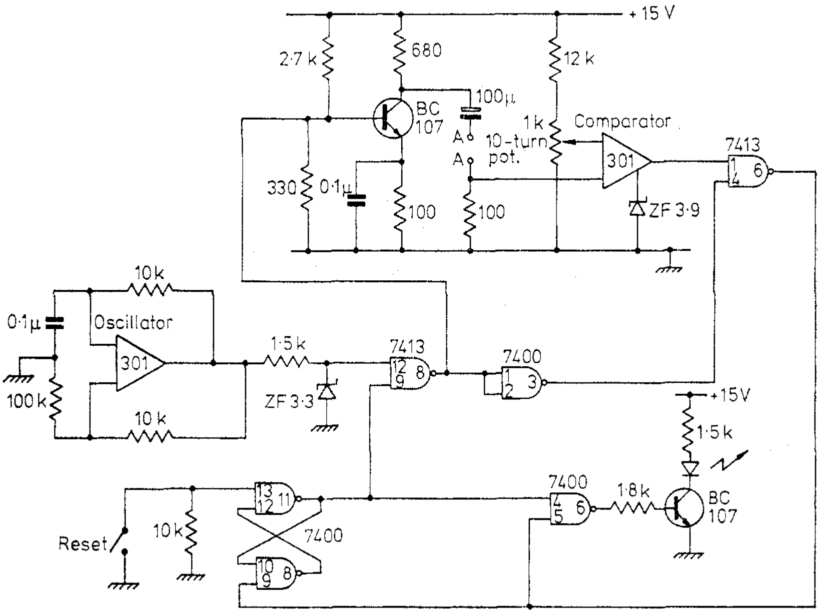

Figure 1. The circuit used for AC electrochemical etching. The etching cell is connected across the terminals A.

oscillator frequency when the voltage across a resistor monitoring this current drops to an adjustable reference voltage. It was found advantageous in both cases to use the spare gate of one of the quad-nand integrated circuits to switch on a light-emitting diode to indicate when the etching process had stopped.

The whiskers were prepared from 25 μm diameter tungsten wires (manufactured by Lamp Metals Ltd, purity >99·95%) approximately 5 mm in length. Each wire was soldered to a brass post and degreased in acetone in an ultrasonic cleaner. The wire was positioned vertically by a micrometer screw and to a known immersion depth in a solution of potassium hydroxide in distilled water (no significant difference was observed in the results when sodium hydroxide was used as the etchant). The etching bath (a glass dish) and positioning device were fixed to a heavy brass base mounted on a foam rubber to lessen vibrational disturbances. During etching the bath was covered by a piece of polythene, with a small hole providing access for the tungsten wire, to reduce movement by draughts of the solution surface. The tungsten wire itself formed one of the electrodes, the anode in the case of DC etching, while the other was a sheet of pure gold foil positioned approximately 20 mm from the whisker.

Vigorous bubbling around the tungsten wire was observed throughout the whole process of AC etching. This bubbling did not adversely affect the whisker shape and indeed may form an essential part of the process. In the first few seconds of DC etching, however, only a few bubbles tended to form around the tungsten wire and adhere to the metal surface, consequently protecting the whisker from the etchant and producing very irregular tip shapes. This problem may be resolved by either tapping the whisker (Lilburn *et al* 1970) while current passes through the bath or by removing the tungsten wire from the etching bath some 15 s after the electrochemical process has begun (Twu 1975). The wire may then be reimmersed to its original depth and the etching process resumed whereupon no more bubbles evolve. We followed the second of these methods in the production of whiskers, using a DC current. After etching, the whiskers were again cleaned in acetone in an ultrasonic cleaner.

3. Results

Initial studies concentrated on varying several parameters common to both techniques and looking at the general tip shape under a compound microscope with a magnification of up to $\times 1000$. The parameters involved were the solution strength, immersion depth, cut off voltage, and to a limited degree the age of solution, although this last condition did not appear to affect the results.

Investigation of approximately 100 whiskers for each technique showed that the shape of the whisker was a consistent function of these parameters for a particular solution of potassium hydroxide, the strength of which was varied by diluting the initial solution appropriately. This consistency was not quite so good for different solutions and occasionally results were obtained completely at variance with the norm. Overall, the uniformity of the results was at least 80% and the cause of the extreme fluctuations is not known.

A sample of ten whiskers produced by AC etching and similarly by DC etching were examined under a 1 MeV electron microscope at magnifications ranging from 1000 to 100 000, using what appeared to be the optimum etching parameters for producing a sharp tip. These were a 2 N solution of potassium hydroxide, immersion depth of 1 mm and a cut off reference voltage of 0·3 V representing a current of 3 mA through the etching bath (etching time in both cases 20–25 s).

The photographs show a typical example of this examination, for both high and low magnification. Vibration of the tip degraded slightly the resolution of the microscope although this was still better than 5 nm. There was also a clearly defined deposit on the surface of the AC whiskers which was almost certainly caused by a build-up of a hydrocarbons present as an impurity in the electron microscope at the time the photographs were taken.

The low-magnification photographs show the differences in the overall tip shape for AC and DC etching. In the former case the cone angle is fairly constant whereas it decreases steadily towards the tip for the latter.

The cut-off current is more critical for DC etching than for AC if a sharp point is to be achieved. In the DC case lower currents produce short blunted whiskers, whereas higher currents can give a very elongated weak tip. In general, we found that altering the cut-off current was the simplest way of modifying the tip length if the tip radius is not critical, and we did not find that this length could be simply changed by altering the solution strength in the manner indicated by Twu (1975).

With the AC method although too high a reference setting will cause etching to cease too early, it is in general not possible to severely blunt the whisker with too low a setting as the etching tends to be self-terminating in that when the process has reached a certain stage the liquid meniscus drops away from the whisker. Probably this is an effect produced by the vigorous bubbling, mentioned earlier, around the whisker.

It was found under high magnification that the whiskers, whether AC or DC-etched, possessed in general sharp points of $\sim$5–10 nm radius. The tips produced by AC etching had a polished clearly defined conical shape with a half angle ranging from 8° to 12°. In contrast, the DC-etched whiskers were, in all cases, very long and drawn out towards the point with pronounced irregularities. These irregularities may be caused by the formation of tiny bubbles on the tungsten anode or by preferential etching of the metal microstructure.

4. Conclusions

In conclusion we find that AC electrochemical etching can consistently produce tungsten whiskers of small tip radii coupled with a sturdy conical shape, and polished metal surface, a combination particularly useful in MIM diodes. With DC etching, although consistently sharp points are produced, tips are of an extremely fragile nature and irregular shape towards the end.

Acknowledgments

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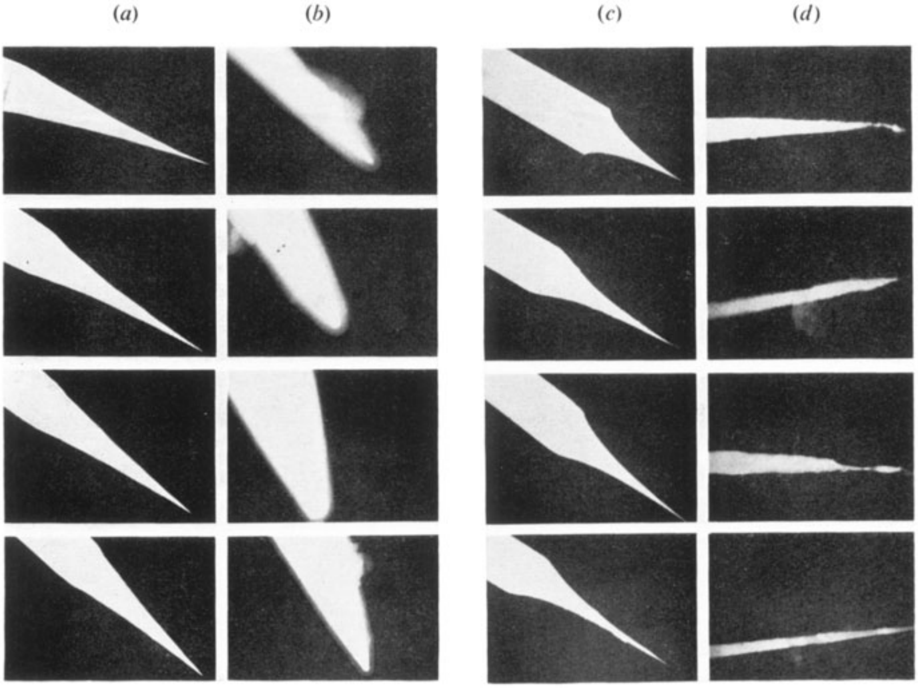

Figure 2. Examples of electron microscope photographs of tungsten whiskers etched by the (*a*, *b*) AC and (*c*, *d*) DC methods. For each whisker, two magnifications are shown: (*a*) 1″ ≡ 100 μm; (*b*) 1″ ≡ 600 nm; (*c*) 1″ ≡ 100 μm; (*d*) 1″ ≡ 2 μm.