Electrochemical Diode

Katsuya YAMAGUCHI* and Hiroshi OGAWA**

Abstract

Tantalum electrochemical diode has been developed. It consists of tantalum needle (anode) having an oxidized film metamorphosed by heating treatment, carbon electrode (cathode) and electrolyte (4%(v/v)H_2SO_4 solution).

Maximum applicable reverse voltage of tantalum diode is 300 volts and reverse leakage current of tantalum diode is less than a micro-ampere when applied reverse voltage is below 35 volts.

It works as a good diode when the frequency of input signal is below 100 KC. Temperature dependence of tantalum diode is obtained experimentally.

1. Introduction

The surface oxidized film of tantalum, Ta_2O_5 is an n-type semiconductor and the tantalum electrolytic rectifier which utilizes the rectifying characteristic of this oxidized film is one of the well known rectifiers.

Recently, Yamaguchi[1] has reported the improvement of tantalum rectifier by using the new method (heating treatment) to metamorphose the oxidized film.

The authors have succeeded in constructing the electrochemical diode which had the tantalum needle having an oxidized film metamorphosed by heating treatment.

Tantalum diode works satisfactory in low frequency region.

2. Principle

The electrochemical reactions of each electrode are as follows, when electrolyte used is H_2SO_4 solution, and anode is biased positively.

Anode (Tantalum)

$$SO_4^{--} - 2e \rightarrow SO_4$$

$$H_2O + SO_4 = H_2SO_4 + \tfrac{1}{2}O_2$$

Cathode (Carbon)

$$H^+ + e \rightarrow \tfrac{1}{2}H_2$$

It is reported that the rectifying layer does not exist between host tantalum metal and Ta_2O_5 film but between Ta_2O_5 film and electrolyte, the existance of p-n junction at the surface of the Ta_2O_5 film is believed[2].

We believe that the p-type region is thin surface Ta_2O_5 layer which contacts with electrolyte and is rich in oxygen (acceptor) captured.

This is shown schematically in Fig. 1.

A detailed study of the p-n junction of tantalum diode may be presented in a later report.

* *Department of Applied Physics*
** *Department of Electrical Engineering*

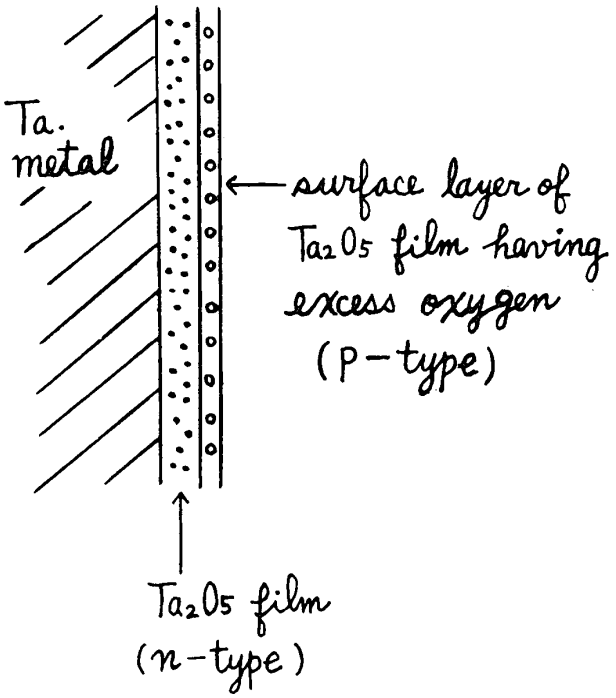


Fig. 1. *p-n* junction of tantalum diode.

3. Experimental and Results

Fig. 2 shows the construction of tantalum diode and Fig. 3 shows the view of it.

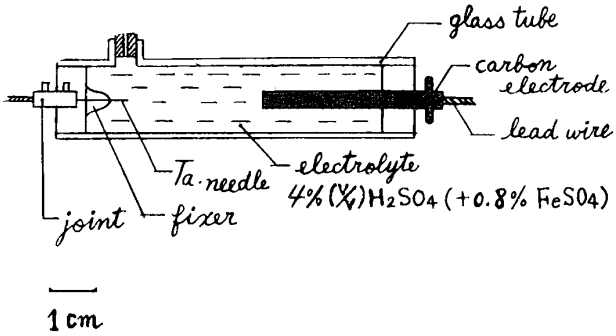


Fig. 2. Construction of tantalum diode.

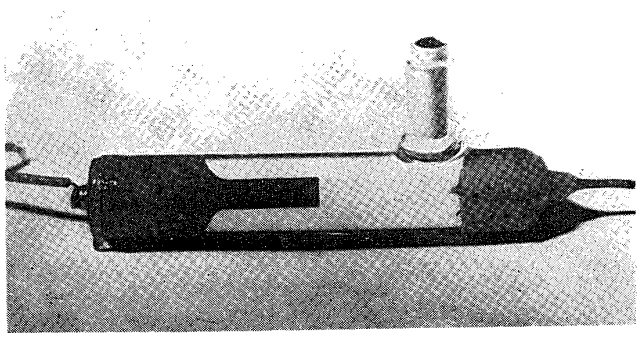


Fig. 3. Tantalum diode.

By incorporating few drops of $FeSO_4$ solution, the deterioration of the oxidized film due to the adsorption of H_2 gas is avoided[3].

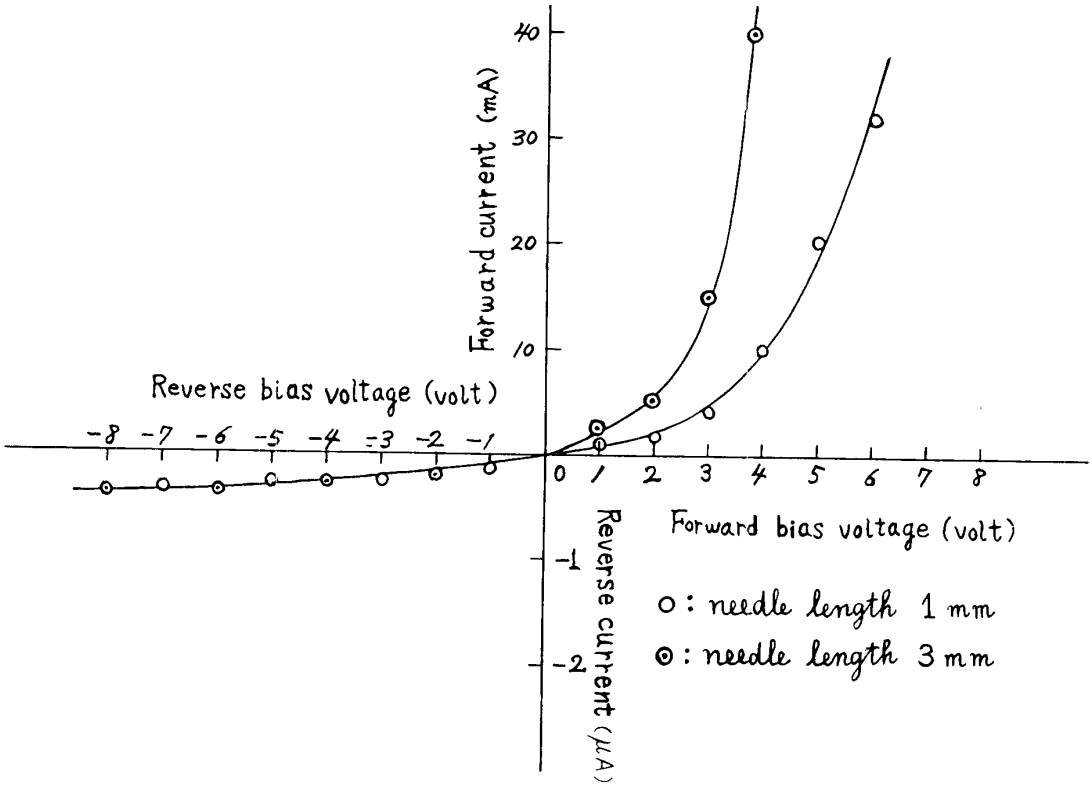
Purity of the tantalum needle used is 99.9%, its diameter and length are 0.08 mm and 10 mm respectively. A half of the tantalum needle was inserted into the electric furnace (670°C, heater was not exposed, air atmosphere) and was heated for 2 seconds to metamorphose the oxidized film.

Tantalum needle having an oxidized film juts out into the electrolyte about 1 mm～3 mm and is fixed by resin paste.

Fig. 4 shows the relation between current and voltage of the tantalum diode.

As is shown in Fig. 4, an obvious rectifying characteristic is observed.

Fig. 5 shows the relation between reverse leakage current and reverse voltage of tantalum diode.



Temperature of electrolyte : 25°C

Fig. 4. Voltage and current characteristics of Ta diode.

As shown in Fig. 5 it should be remarked that the applicable maximum reverse voltage of this diode is 300 volts approximately, this value of reverse voltage is larger than that of some germanium diode, for example, the applicable maximum reverse voltage of OA-79 (NATIONAL) is 30 volts.

Fig. 6 shows the experimental apparatus which was used for measuring the frequency response of tantalum diode and Fig. 7 shows the result of measurement, comparing it with the frequency response of germanium diode SD-46 (NEC).

When the frequency of the input signal is over 100 KC, the decreasing rate of D.C. output current is inferior to that of SD-46, but in lower frequency region, D.C. output current is superior to that of SD-46.

Fig. 8 shows the temperature dependence of D.C. output current of tantalum diode.

With the rise of the temperature of electrolyte, a gradual increase in D.C. out put current was observed but frequency response showed no temperature dependence in the temperature range of 5°C～90°C.

When the third electrode (carbon or platinum) was inserted into the electrolyte and biased as shown in Fig. 9, an increase in D.C. output current was observed.

Fig. 10 shows the relation between increase in D.C. output current (ΔI) and the current (I_t) which flows from the third electrode to the cathode.

Fig. 11 shows the cathode-ray oscillographical observation of the increase in D.C. output current due to the insertion of positively biased third electrode.

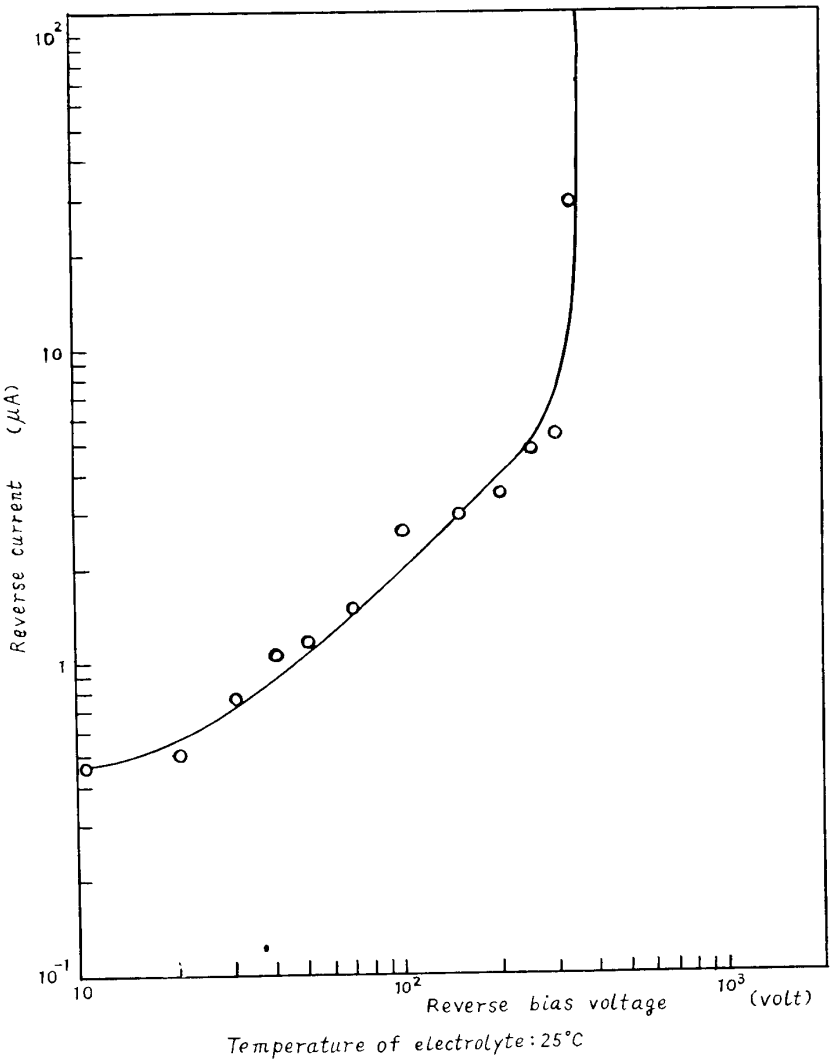


Fig. 5. Reverse voltage vs. reverse leakage current.

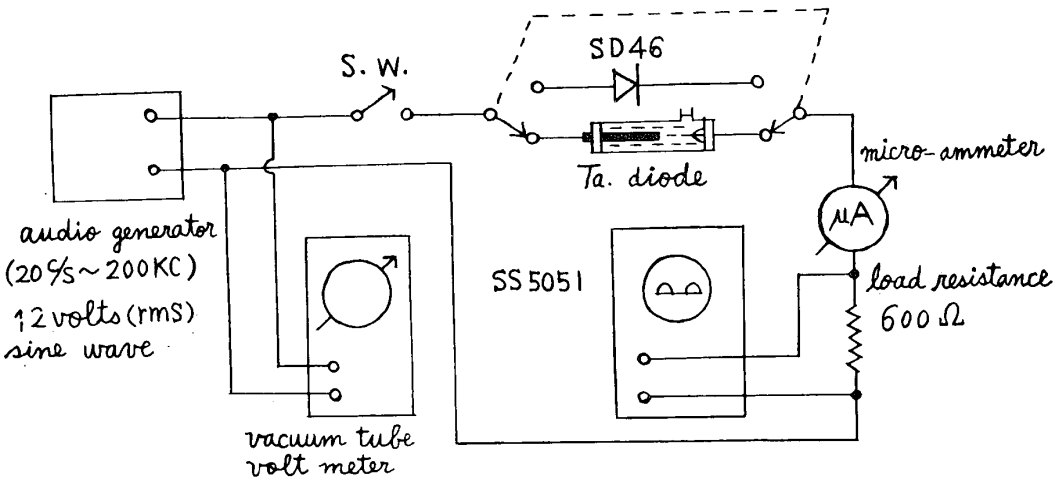


Fig. 6. Experimental apparatus.

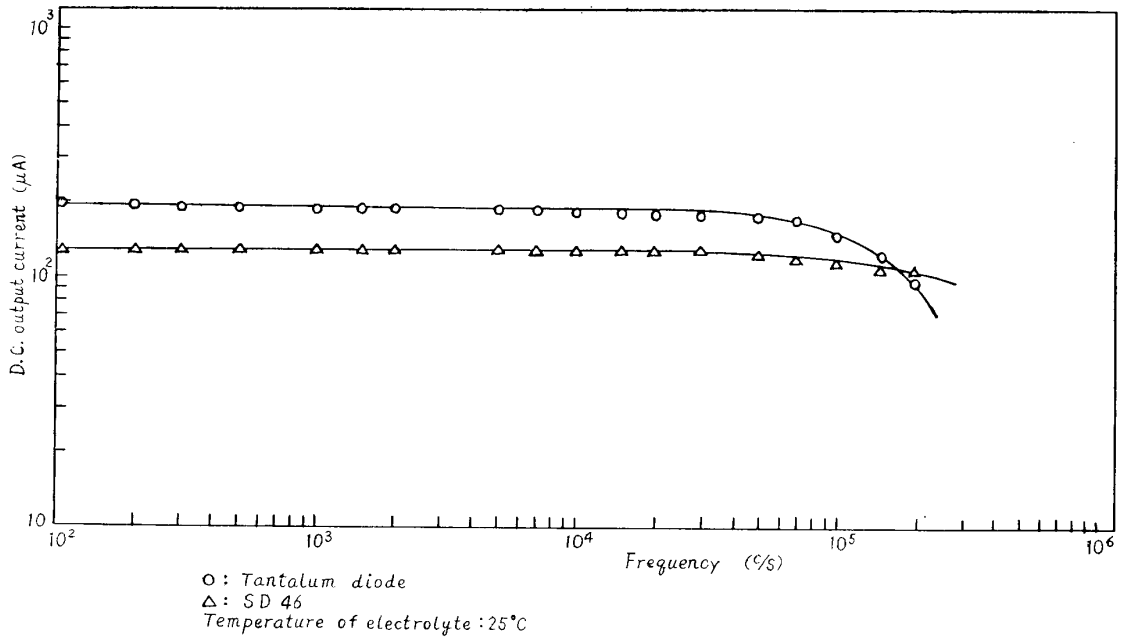
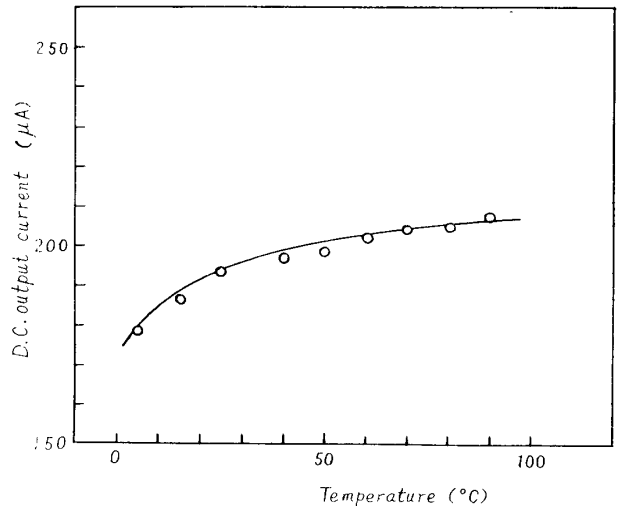


Fig. 7. Frequency response.



In put signal : f = 1 KC. sine wave. 12 volts (rms)

Fig. 8. Temperature dependence of output current.

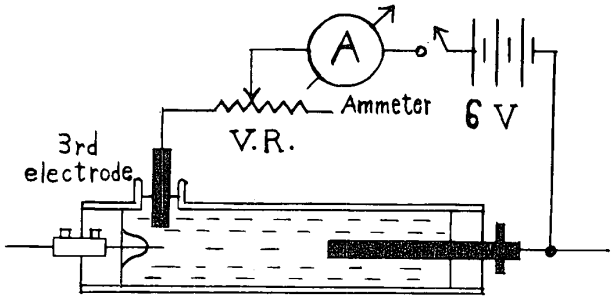


Fig. 9. 3rd electrode insertion.

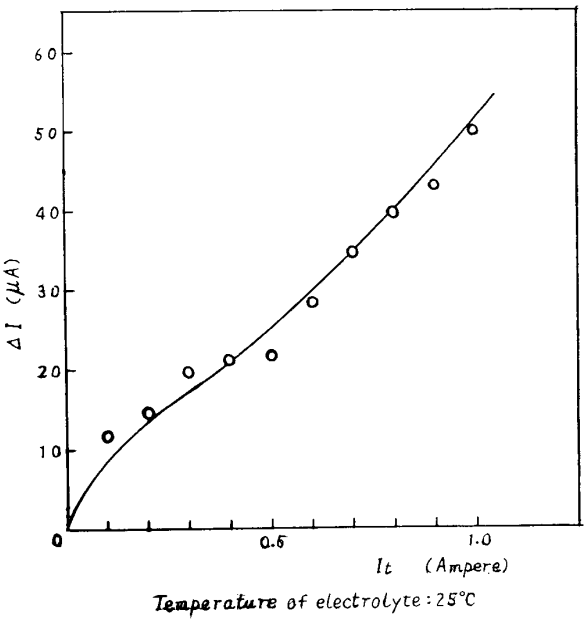


Fig. 10. ΔI-It characteristic.

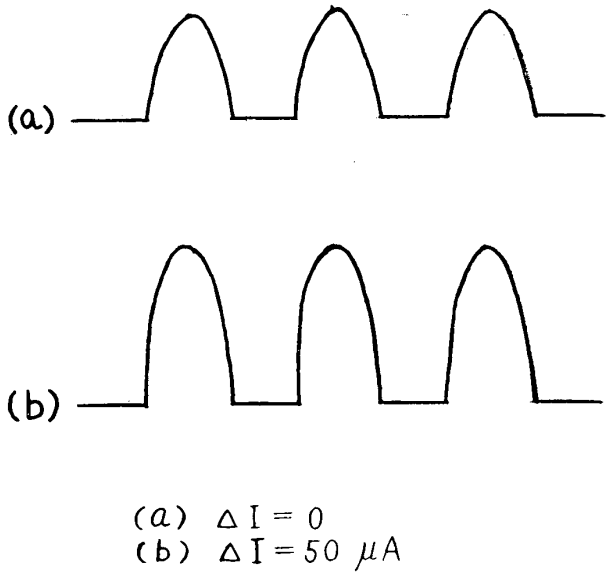


Fig. 11. Oscillographical observation of ΔI.

4. Discussion and Summary

As the tantalum diode is an electrolytic liquid diode, it has some difficult points in conservation but it is very easy to construct.

Comparing tantalum diode with the solion liquid diode,[4] it is obvious that tantalum diode is much superior in working voltage (solion, below 0.9 volts) and frequency response (solion, below about 60 caps).

Tantalum diode has less temperature dependence than solion diode (solion, variation of current and voltage characteristic per 1°C is about 14%).

Comparing tantalum diode with germanium diode, tantalum diode has higher applicable reverse voltage (about 300 volts) and less reverse leakage current (below a micro-ampere when applied reverse voltage is below 35 volts) than some germanium diodes.

By inserting the third electrode, control of the D.C. output current of tantalum diode is possible to some extent.

References

1) Katsuya Yamaguchi : Ôyô Buturi, 32, 344 (1963)
2) Hajime Shiratori and Tamotsu Shirogami : Denkikagaku, 30, 892 (1962)
3) DENKIGAKKAI : "Denkikogaku pocket book" (1956) p. 385
4) Isao Oshida : Denkikagaku, 28, 475 (1960)

(Received Sept. 10 1963, in final Sept. 1 1964)