# The Discovery of ZnO Grain Boundary Phenomena

**In the words of the man responsible**
**Dr. Michio Matsuoka 1988**

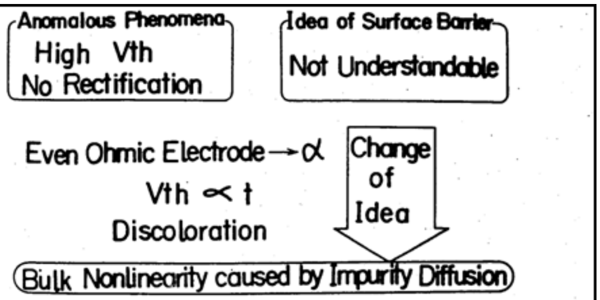


Fig.6 Explanation of anomalous phenomena

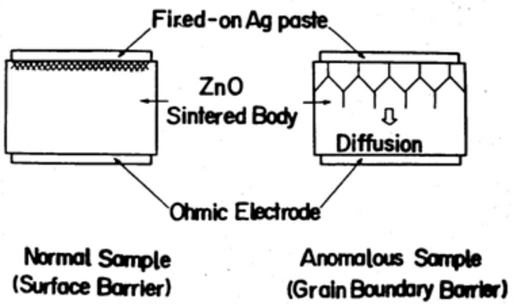


Fig.7 Diffusion effect

# DISCOVERY OF ZnO VARISTORS AND THEIR PROGRESS FOR THE TWO DECADES

Michio Matsuoka
Matsushita Electronic Components Co., Ltd.
1006 Kadoma Osaka 571, Japan

## ABSTRACT

The process of discovery of ZnO varistors are reviewed from the view point of the background and the motive for the development, the concept of development, the episode during the development and the scientific understanding to the new phenomena.

## INTRODUCTION

Since 1968, the nonohmic ZnO ceramics have been widely used as varistors for voltage stabilization and transient surge suppression in electronic circuits and electric power systems[1∿3]. Much attention has been paid to the fundamental research and applications of ZnO varistors and, up to this time, about 700 papers and lectures in total have been published and presented in the world.
The development of ZnO varistors is based on a lucky discovery in July 1967 which can be called "Planned Serendipity". After the discovery of new phenomena, many efforts to convert the serendipity to inevitability were made.
ZnO varistor technology has succeeded in utilizing a popular material, ZnO, as a main ingredient of new useful electronic components and in using grain boundary phenomena which are intrinsic properties in electronic ceramics.
From the view point of application technology in electronics, ZnO varistors have progressed with the stream characterized by the change in technology from vacuum tubes to semiconductor devices in electronic circuits, and now play an important role in transient surge suppression technology.
The process of discovery of ZnO varistors and their progress for the two decades are reviewed.

## MOTIVE FOR DEVELOPMENT

Around 1965, the change of key devices in electronic circuits from vacuum tubes to semiconductors began to extend to consumer and

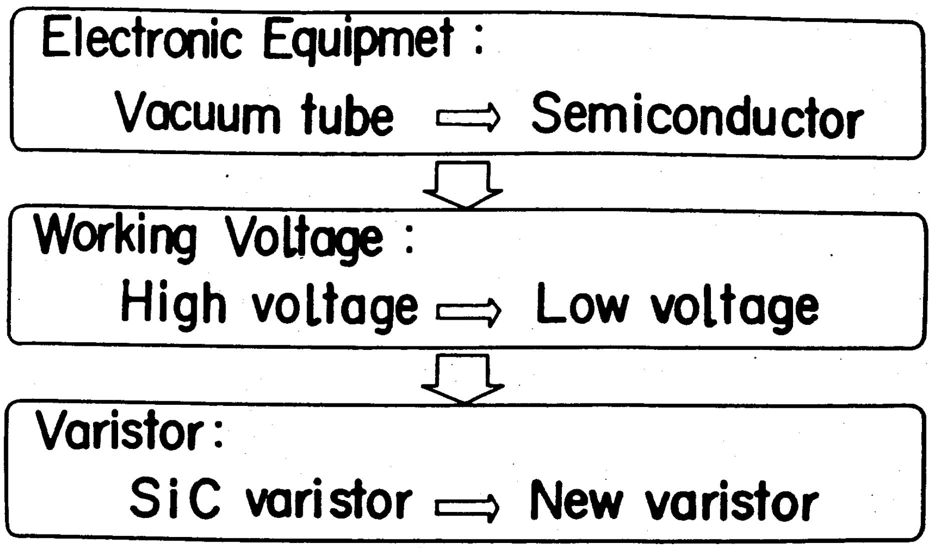


Fig.1 Background for development

industrial equipments. Under the background stated above, the development of new varistor started in November 1965. The change of key devices means the working voltage in electronic circuits becomes lower as shown in Fig.1. Therefore, the new varistor was necessary as a transient surge suppression device in place of SiC varistors which were considered to be the typical surge suppression devices at that time.

START OF NEW VARISTOR PROJECT

First problem for the new varistor project was how to select the basic policy for the development, that is, (1) the development based on the improvement of SiC varistors or (2) the development based on the new principle and new material. After the discussion, the second concept was selected as the basic policy for the new varistor project.

Approach to development (I) Principle

After the preliminary discussions and experiments, the nonohmic properties due to the surface barrier formed at the contact between semiconductor and metal electrode was selected as the basic principle for the new varistor having low threshold voltage as shown in Fig.2. In this case, the symmetry of V-I curve depends on the symmetry of electrodes formed at opposite surfaces of the semiconductor.

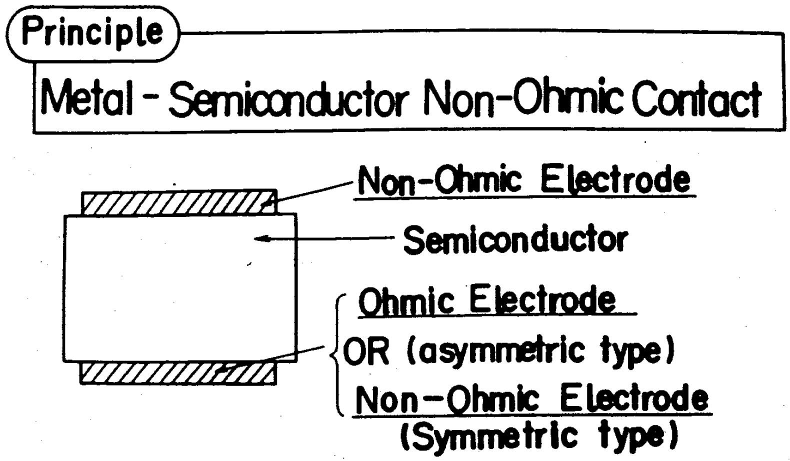


Fig.2 Approach to development (I) Principle

Approach to development (II) Semiconductor material

In the application of surface barrier property, the most important problem was what kind of semiconductor material should be used. As shown in Fig.3, at first, the ceramics were selected in comparison with single crystals from the view point of production cost. And next, the oxide was selected from the view point of productivity. Oxide can be sintered in air, and this is a very important advantage in mass production. According to the preliminary experiments for many kinds of oxides, ZnO was finally selected as a semiconductor material for new varistor. ZnO has the features of easiness in sintering and control of electrical resistivity.

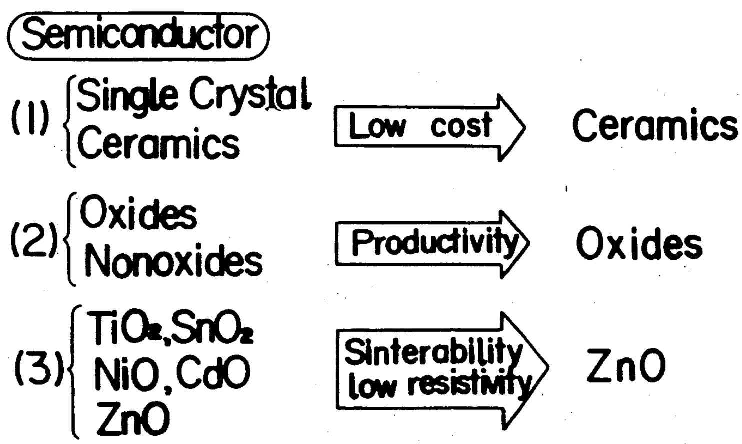


Fig.3 Approach to development (II) Semiconductor

Approach to development (III) Electrode

There are many kinds of electroding methods in order to obtain the nonohmic contact between semiconductor and electrode. As shown in Fig.4, typical methods are evaporation, plating and firing. According to the preliminary experiments, the fired-on Ag paste method was selected as a nonohmic electrode. This method has the advantages in productivity and variation in composition.

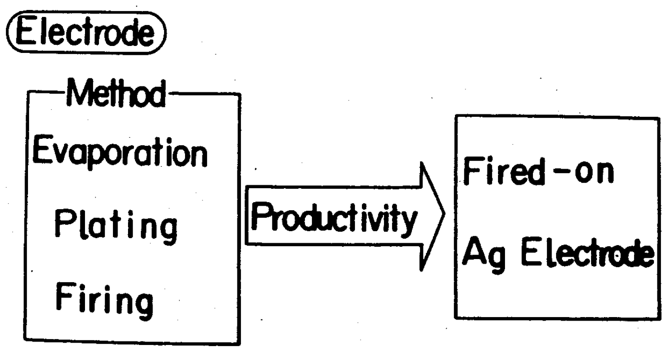


Fig.4 Approach to development (III) Electrode

DISCOVERY OF ANOMALOUS PHENOMENA

The development of ZnO varistors using surface barrier property was succeeded in March 1967. Then, the next target of development started for the purpose of extending the region of threshold voltage. Many kinds of experiments were carried out concerning the effect of additives in ZnO ceramics and variation of glass frit in Ag paste.
In the process of these experiments, very interesting and anoma-

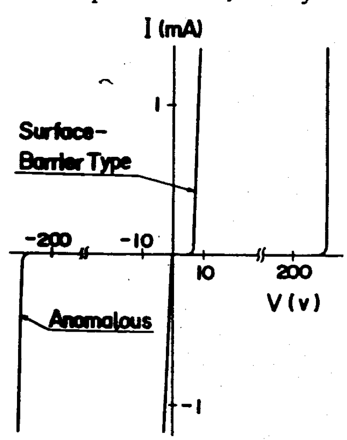


Fig.5 V-I curve of anomalous sample

lous phenomena which can be called "Planned Serendipity" were found out in July 1967. These anomalous phenomena were observed in the samples fired at a temperature higher than normal firing temperature for Ag paste due to the thermal runaway of electric furnace. The anomalous samples show the very high threshold voltage and no rectification even for the asymmetrical electrodes as shown in Fig.5.

## EXPLANATION OF ANOMALOUS PHENOMENA

The observed anomalous phenomena were divided into (1) high threshold voltage, (2) no rectification, (3) dependence of threshold voltage on the thickness of sintered body and (4) discoloration of sintered body as shown in Fig.6. All of these phenomena could not be explained by the concept based on the surface barrier property. Therefore, the basic concept for the development of new

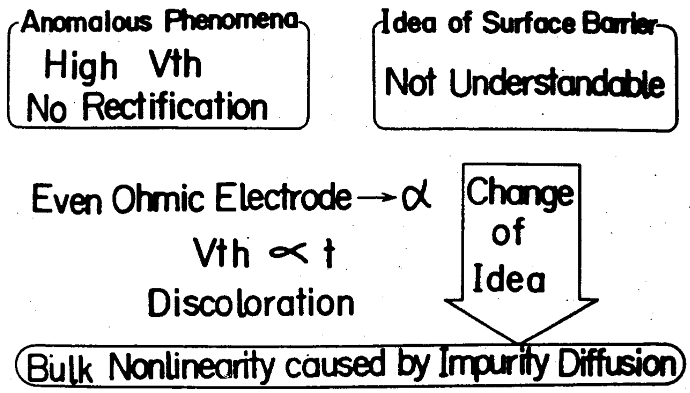


Fig.6 Explanation of anomalous phenomena

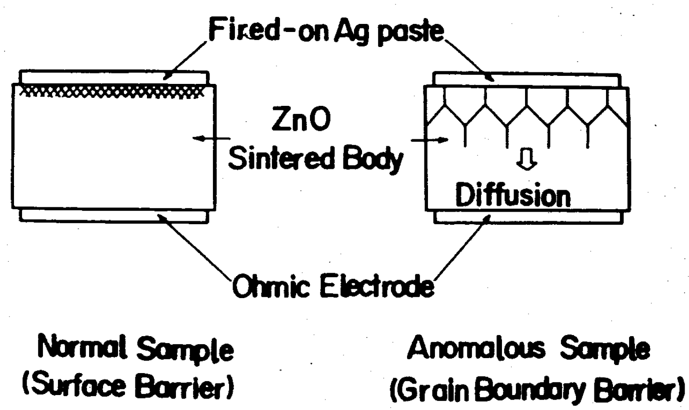


Fig.7 Diffusion effect

varistor was obliged to change in order to get the reasonable explanation for the anomalous phenomena stated above. As a result, these anomalous phenomena could be explained reasonably by assuming that the varistor action came from the sintered body itself. According to the analytical results, it became clear that the bulk nonohmic property was caused by the diffusion of Bi and Mn components contained in glass frit of Ag paste at grain boundary of ZnO sintered body as shown in Fig.7.

## DEVELOPMENT OF ZnO VARISTOR

After the discovery of bulk nonohmic property, the most important problem was how to convert the diffusion effect obtained by the lucky experimental accident to the designed addition effect. In order to find out the desirable composition, many experiments were carried out from the view point of combined addition effect. As a result, some kind of rule was found out and then, typical composition of ZnO with $Bi_2O_3$, CoO, MnO, $Sb_2O_3$ and $Cr_2O_3$ which is widely used for actual products was obtained. ZnO varistors having the typical composition are characterized by the features of excellent nonohmic property and surge withstand capability. These

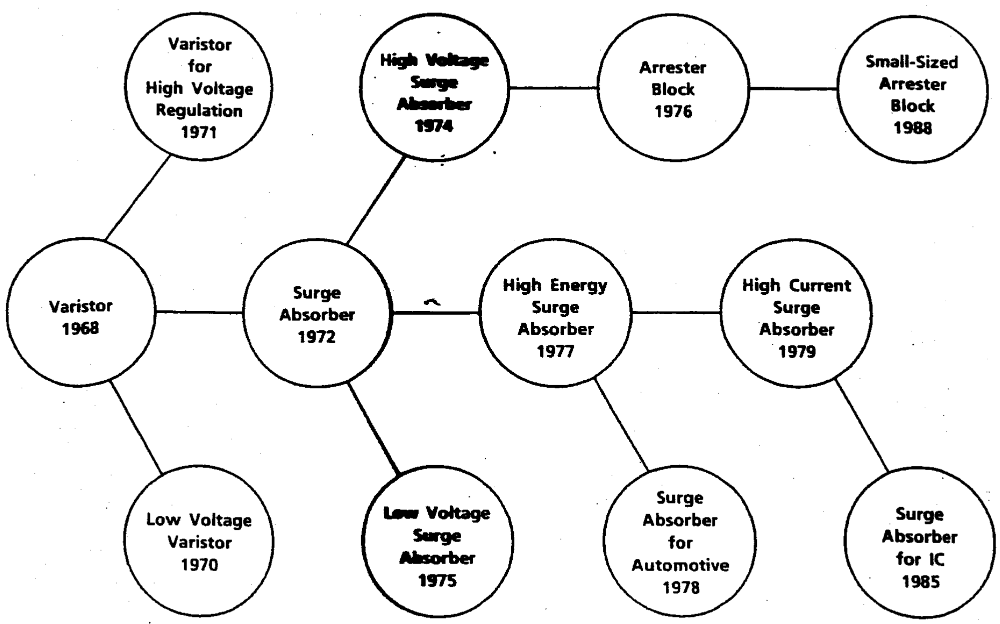


Fig.8 Development process of ZnO varistors

features are attributed to grain boundary phenomena which are an intrinsic property in electronic ceramics.
From the view point of the structure characterized by the multi-connection of small nonohmic elements in the sintered body in series and parallel, ZnO varistors are similar to SiC varistors, and this feature results in the very large surge withstand capability. The indivisual nonohmic element of ZnO varistors has highly nonohmic properties similar to those of Si zener diodes. Therefore, ZnO varistors can be considered to have the features of both Si zener diodes and SiC varistors.
As shown in Fig.8, the application of ZnO varistors extends year by year on the basis of the improvements of threshold voltage region, nonohmic exponent, surge withstand capability and long term reliability.

## SUMMARY

For the two decades, ZnO varistors have shown the remarkable progress in fundamental research and application technology due to the strong interests of many scientist and engineers in the world. And, ZnO varistors will have a possibility in futher improvements of electrical properties and indicates a possibility in finding new devices using grain boundary phenomena in electronic ceramics.

## ACKNOWLEDGMENTS

The author is greatly indebted to Dr. Y. Iida and Dr. T. Masuyama for their useful advice and encouragement through this study.

## REFERENCES

1) M. Matsuoka, T. Masuyama and Y. Iida, "Nonlinear Electrical Properties of Zinc Oxide Ceramics", Proceedings of the 1st Conference on Solid State Devices, Tokyo, 1969, Suppl. J. Jpn. Soc. Appl. Phys., 39, 94-101 (1971).
2) M. Matsuoka, "Nonohmic Properties of Zinc Oxide Ceramics", Jpn. J. Appl. Phys., 10, 736-46 (1971).
3) M. Matsuoka, "Progress in Research and Development of Zinc Oxide Varistors", Advances in Ceramics, 1, Grain Boundary Phenomena in Electronic Ceramics, 290-308 (1981).