

SOME REMARKS ON ELECTROLYTICAL ETCHING OF GERMANIUM SURFACES

By

L. MICHAILOVITS and M. I. TÖRÖK

Research Group on Luminescence and Semiconductors of the Hungarian Academy
of Sciences, Szeged

(Received May 10, 1970)

Anodic polarization of weakly *n*-type germanium samples treated in different ways was investigated in neutral aqueous solutions. It was found that black germanium monoxide was produced in the etching pits characteristic for (111) orientation of the surface. At anodic polarization, with decreasing current density an increasing part of the charge flowing through the surface produced monoxide. The formation of surface structure was followed continuously by means of a microscope, without interrupting the electrolysis.

Introduction

The investigations reported here are connected with the problems arising from the measurement of field effect and electrode capacity under electrolyte [1, 2]. According to JIRSA [3] and others [4—6], anodic dissolution of Ge in the range of small and moderate current densities takes place with transfer of four electrons per atom. BECK and GERISCHER [7] pointed out that *n*-type and weakly *p*-type Ge samples were covered with a well visible orange-red GeO layer when applying great polarization current densities, while the surface of strongly *p*-type samples remained blank during the process. On the basis of these experimental results, they concluded that, in presence of sufficient hole concentration on the surface, the reaction leads to the formation of GeO₂ and its dissolution in form of H₂GeO₃, whereas in case of low hole concentrations GeO is partly formed.

REID [8], investigating the anodic dissolution of Ge, found about 8 percent of germanium ions present in form of Ge⁺⁺, independently from the current density in the range of 5 to 90 mA/cm². He does not mention the quality of the surface formed by anodic polarization, it is known, however, (see e.g. [9]) that germanium monoxide is of low solubility in neutral alkaline solutions; therefore it may be assumed, that GeO produced in electrode reaction partly remains on the surface. This is in accordance with the results of cyclic current step polarization [10], according to which the value of the electrode potential measured in the period of switching off is between the equilibrium potentials of germanium monoxides and dioxides.

The aim of the present work was to investigate and to follow up continuously the change of the surface structure under anodic polarization. The presence of small quantities of reaction products as well as the surface structure were observed and photographed microscopically.

Experimental set-up

A cell containing the sample and a Pt electrode was placed on the objective table of a Zeiss microscope Type Polmi A (Fig. 1). By using this arrangement it was possible to observe the processes on the surface without interrupting the polarization and removing the sample from the electrolyte.

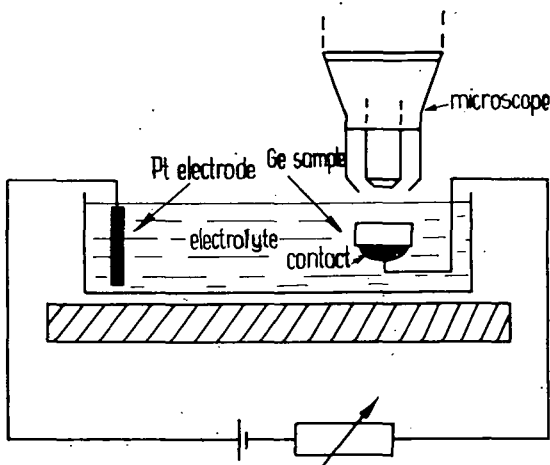


Fig. 1. Diagram of the experimental set-up

The measurements were made on *n*-type disk samples of 7 mm diameter, 0.5 mm thickness and of 27 cm resistivity. The samples were provided with an ohmic contact on their back surface. The samples oriented in (111) direction were anodized in neutral aqueous 0.1 N K_2SO_4 solution. All measurements were performed at room temperature. Three different surface treatments were used for the investigations:

- (a) samples polished on a glass plate to obtain a mat surface
- (b) samples polished to mirror brilliance
- (c) samples polished to mirror brilliance and then etched in CP4A.

Anodic polarization was applied at constant current densities of 1, 5 and 25 mA/cm², respectively, for about 400 minutes. In the beginning of the polarization, visual observations and microphotographs were taken simultaneously at intervals of 5 to 10 and later of 30 minutes. During a polarization process a set of 20 photos was taken from the same place of the surface. The magnification of the microphotographs was 60×.

Experimental results

Some photographs of a set, made on a sample previously polished to mirror brilliance and electrolyzed with a current density of 1 mA/cm², are shown in Fig. 2. At the beginning of the polarization some scratches which were not visible originally begin to appear and then the quick dissolution of the damaged surface layer starts. Two different kinds of pits appear on the surface. The pits of the first type are round and their surface remains blank and glossy. These pits are mostly situated along the scratches mentioned above. Similar pitting effects can be observed with the use of non-structural etchants [11, 12].

The pits of the other kind formed by electrolytic dissolution are located at random on the surface of the sample; their surface is covered with a black layer. They are of nearly tetrahedral form, each tetrahedron being oriented in the same direction. In this aspect these pits are similar to those produced by structural etchants; however, the edges of the pits obtained by anodization are rounded off,

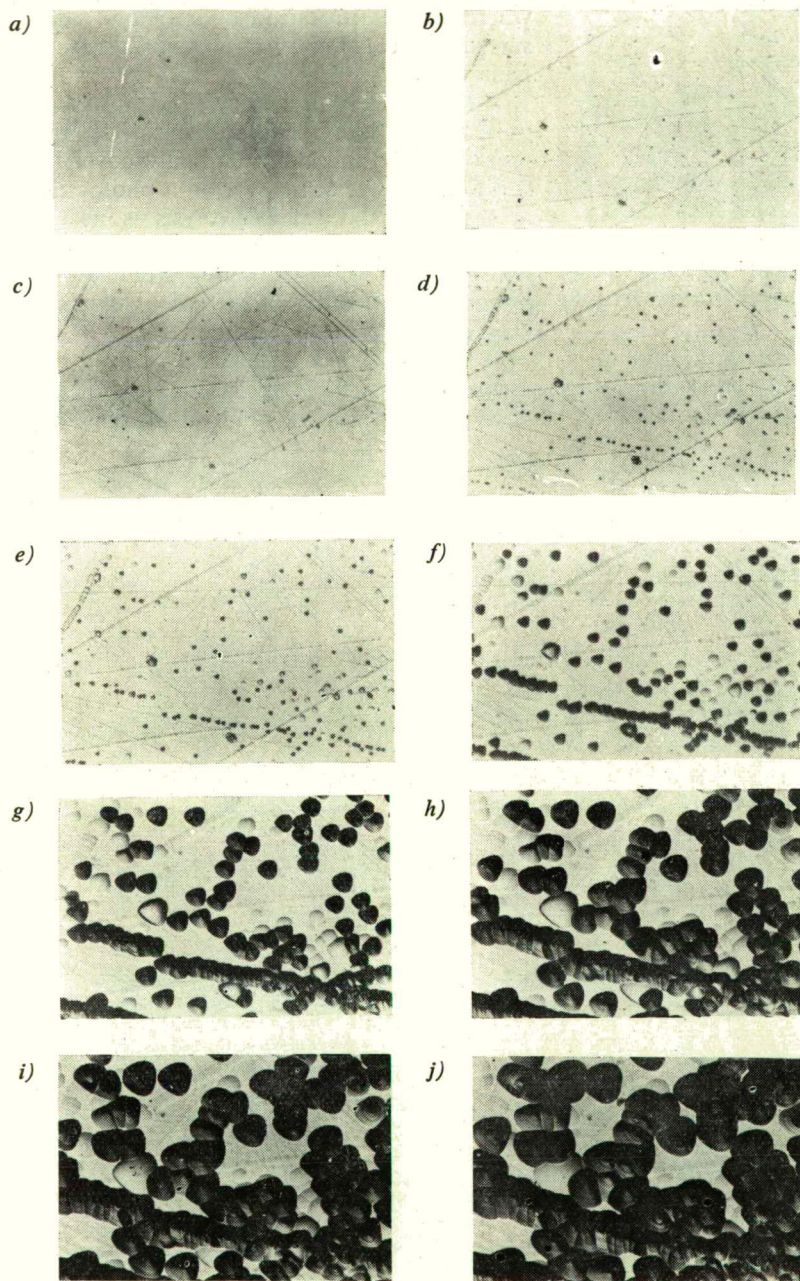


Fig. 2. Microphotograms of a set, made from a sample polished to mirror brilliance and polarized with a current density of 1 mA/cm^2 , after 0, 10, 15, 30, 50, 100, 200, 300, 440 minutes of polarization, respectively: Figs. (a) to (j). Magnification $60\times$

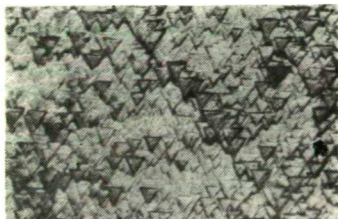


Fig. 3. Regular tetrahedral pit produced by etching with WAg structural etchant for 2 minutes

whereas those produced by structural etchants on surfaces of (111) orientation are of regular tetrahedral form (see Fig. 3).

The black pits appear later in the course of polarization than the blank ones, but they grow more quickly and they gradually cover the whole surface. The size of the pits on a photograph taken at the same state of electrolysis is nearly equal.

A comparison of different sets of photos, made with the same current density, but with samples pretreated in a different way, showed that, during the same time of polarization, a less number of black pits was produced on samples with mat surface. The size of pits produced under the same conditions of polarization was the largest on samples pretreated by chemical etching. This can be clearly seen in Fig. 4, which shows photos of three

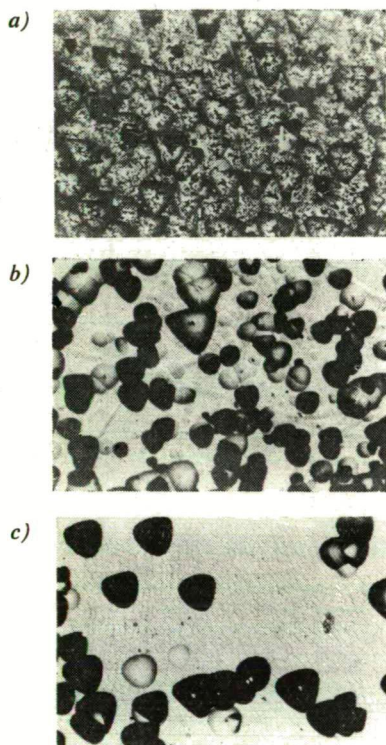


Fig. 4. Microphotograms taken after 180 min. polarization with 1 mA/cm^2 current density from surfaces of different pretreatment: (a) mat; (b) polished to mirror brilliance; (c) chemically etched. Magnification $60\times$

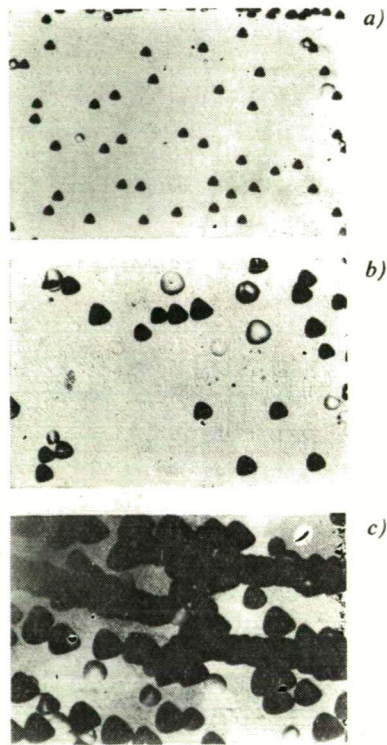


Fig. 5. Microphotograms of samples with chemically pre-etched surfaces after anodizing with different current densities for 90 minutes. (a) 1 mA/cm^2 ; (b) 5 mA/cm^2 ; (c) 25 mA/cm^2 . Magnification $60\times$

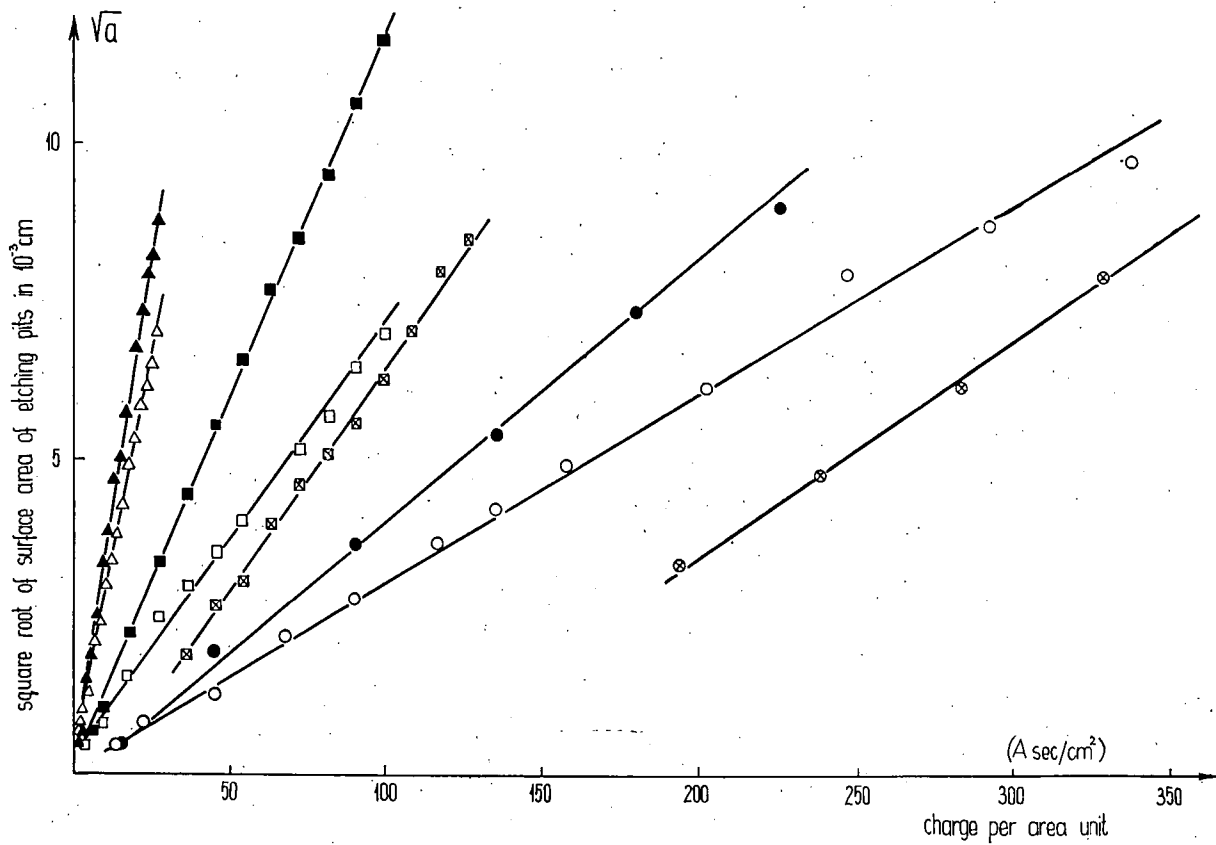


Fig. 6. Linear dimensions (square roots of the area) of pits as a function of the charge passing through the surface during anodization with different current densities: (Δ 1 mA/cm²; \square 5 mA/cm²; \circ 25 mA/cm²), and after different pretreatment (filled signs: chemically etched; blank signs: polished to mirror brilliance; crossed signs: mat).

samples of different pretreatment, each after polarization with a current density of 5 mA/cm^2 for 180 minutes.

By comparing sets of microphotographs made with different anodizing current densities on surfaces pretreated in the same way, it could be observed that the size of the black pits did not increase in such a degree as it was to be expected from the current density. This is illustrated by Fig. 5, in which microphotographs of surfaces pretreated by chemical etching are shown after anodizing with current densities of 1, 5, and 25 mA/cm^2 , respectively, for 90 minutes.

In order to obtain quantitative information concerning the dependence of the pitting process on the time of anodization and the current density employed, sets of microphotographs made with different current densities and pretreatment have been analysed. After adequate magnification of the microphotographs the size of a well defined black spot in each photo of a set was measured by planimetry. The linear dimension of the spot, determined by the square root of its area, showed a linear dependence on the time of polarization. The proportionality factor describing the growth of the pits with time was, however, not identical after different pretreatment of the samples. In Fig. 6 the square root of the area of black spots is plotted against the charge passing through the unit surface area. It appears that the size of the black pits produced by the same charge is much less in case of higher current densities. No correlation between the number of pits and the current density could be found. The latter seemed to be of no marked influence on the number of the pits. Therefore, it has to be assumed that the distribution of charge between the different electrochemical reactions occurring on the surface is not identical in case of different current densities.

On samples polarized with a current density of 25 mA/cm^2 , an orange-red, gel-like layer, translucent in the beginning, appeared without respect to the pretreatment. The thickness of the layer increased gradually; it could be easily removed from the surface by washing. It proved to be slowly soluble in water, more easily, in acids. After drying at room temperature it became dark brown.

Conclusions

As it is shown by the results of these experimental observations, the reaction products obtained by anodic polarization of weakly *n*-type samples in neutral solutions are only in part well soluble. The layer covering the surface becomes inhomogeneous. Taking into account the properties of the known oxides of Ge, the residue formed in the black pits is to be considered as consisting of brown or black germanium monoxide. On mat surfaces, where the density of generation (recombination) centers is high, the quantity of germanium monoxide produced is much less. This is in good agreement with the mechanism of anodic formation of germanium dioxide suggested by TURNER [4] and GERISCHER [7].

The linear size of the pits covered with monoxide, calculated from the square root of the area of the black spots on the photos, is a linear function of time. This suggests that the kinetics of the pitting process is determined by the activation energy required to remove the surface Ge atoms from the brim of the pits. The dissolution of the atoms from the lateral faces of the tetrahedron should proceed much faster.

With decreasing current density, an increasing part of the charge passing through

a unit area of the surface will be used to form monoxide. This results differ from those found by REID [8] in the range of current densities from 5 to 90 mA/cm²; however, a careful analysis of his data of measurements speaks in favour of our conclusions.

References

- [1] Michailovits, L., A. Süli: Acta Phys. et Chem. **16** (1970).
- [2] Konorov, O. V.: Fiz. Tverd. Tela **8**, 13 (1966).
- [3] Jirsa, F.: Z. anorg. Chem. **268**, 81 (1952).
- [4] Turner, D. R.: J. electrochem. Soc. **103**, 252 (1956).
- [5] Palatova, M. N.: Zhur. Prikl. Khim. **35**, 344 (1962).
- [6] Kucheragov, V. M., E. A. Ziablova and F. I. Zaburdaeva: Zhur. Prikl. Khim. **37**, 1492 (1964).
- [7] Beck, F., H. Gerischer: Z. Elektrochem. **63**, 500 (1959).
- [8] Reid, W. E. Jr.: J. Phys. Chem. **69**, 3168 (1965).
- [9] Carasso, J. I., M. M. Factor: in „The Electrochemistry of Semiconductors”, Ed. P. J. Holmes, Academic Press, London and New York (1962). Chapter 5.
- [10] Giber, J.: to be published.
- [11] Holmes, P. J.: in „The Electrochemistry of Semiconductors”, Ed. P. J. Holmes, Academic Press, London and New York, (1962). Chapter 8.
- [12] Flietner, H.: phys. stat. sol. **2**, 222 (1962).

ЗАМЕЧАНИЕ К ВОПРОСУ ЭЛЕКТРОЛИТИЧЕСКОГО ТРАВЛЕНИЯ ГЕРМАНИЕВОЙ ПОВЕРХНОСТИ

Л. Михайлович и М. И. Тёрёк

Исследовано в нейтральных водных растворах анодное растворение германиевого электрода, приготовленного различным образом. Установлено образование чёрной окиси германия в травленных дырках, характеризующихся кристаллографической гранью (III). Тем большей части заряда, протекающего через единицу поверхности, использована для образования GeO, чем меньше плотности тока. Изменение структуры поверхности исследовано непрерывно с помощью микроскопа, без прекращения электролиза.