ETCHING INVESTIGATIONS ON SINGLE CRYSTALS OF V_2O_5

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(Received December 1, 1976)

V_2O_5 single crystals were grown from melt. Effects of different etchants and heat-treatments in different atmospheres were investigated on "upper" and "intermediate" (010) faces. Dislocation density was $(3-8) \cdot 10^3\ cm^{-2}$ obtained in 5n H_2SO_4 with an etching time of 2 to 8 minutes.

Introduction

Several methods of preparing V_2O_5 single crystals are known. A short summary of some methods can be found in paper [1]. Single crystals prepared by different methods also differ from one another in size, colour, dislocation density and many other physical properties, too. A part of the preparing methods makes possible to grow needle-like single crystals of small dimensions. In many cases thin crystal faces with a relatively large area are needed for optical and electrical measurements. These faces can be made by the cleavage of the grown crystals [2].

Some articles dealt with the etching and dislocation structure of V_2O_5 single crystals [3—6]. The different results obtained may be connected with the different crystal-growing methods. According to KLEBER *et al.* [4] the chemical agent suitable for etching the (010) faces of V_2O_5 single crystals is $3n$ H_2SO_4 at boiling temperature; again, according to ABDULLAJEV *et al.* [5] a mixture of concentrated acids of HCl, HF and HNO_3 in equal ratios is convenient for detecting and counting dislocations. To investigate these questions we studied the effects of several chemical agents on (010) faces of V_2O_5 single crystals.

Preparation of single V_2O_5 crystals

KENNEDY'S modified method was used for preparing single crystals [7]. A design of the apparatus can be seen in Fig. 1. The temperature of the V_2O_5 melt placed in the Pt crucible was regulated by two electrical heaters. The optimum thermal gradient in the melt and its surface, determining the sizes and growth rates of crystals, was controlled by the heating current and the diaphragm.

The melt was heated to 800 °C, held at this temperature for some hours, then cooled down below its melting point and at the same time a crystal seed was placed to the melt surface in order to obtain oriented growth. Platelets of V_2O_5 single

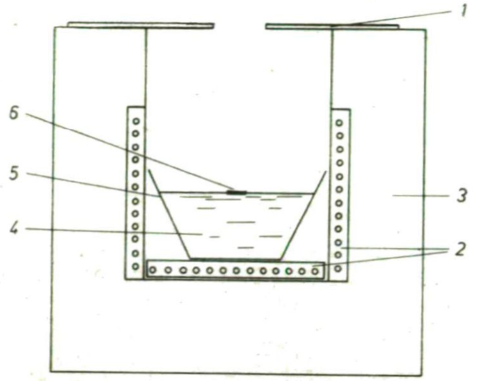


Fig. 1. 1 — diaphragm, 2 — electrical heaters, 3 — insulation, 4 — V_2O_5 melt, 5 — Pt crucible, 6— V_2O_5 crystal seed

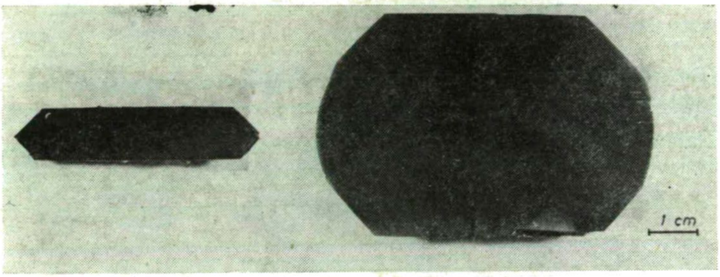


Fig. 2. Single crystals of V_2O_5

crystals, having dimensions of 7 cm×4,7 cm×0,7 cm, could be prepared in this way. This method was suitable for growing doped V_2O_5 single crystals, too. Typical crystal products are shown in Fig. 2. Data of mass spectroscopic analysis on single crystals are given in Table I. The results are given in weight-ppm.

Table I

Impurity	Concentration [weight-ppm]
Pt	60
Fe	30
Ti	2.5
Ni	0.5
Si	100
Al	3
As	2
P	170
S	50
Cl	2.5
Na	12
K	10
Mg	6
Ca	10

Experimental results

Effects of several solutions (see Table II) were studied at a boiling-point temperature in order to select the best etching agent for determining the dislocation density of V_2O_5 single crystals. The changes in surfaces induced by etching procedures were observed by a Polmi A type Zeiss polarization microscope. Some typical photomicrographs obtained by etching the uppermost (010) faces — exposed to air during the growing procedure (in followings "upper") — are shown in Fig. 3*a*—*h*. On the basis of the photomicrographs it can be noted, that 3*n* HCl and 3*n* HNO_3 solutions develop tetragonal

Table II

Etchant	Concentration (n)	Etching time (minutes)
H_2SO_4	0.0001 0.01 1 3 5 7	0,25 to 20
HCl	1 3 5 7	0,25 to 6
HNO_3	1 3 5	0.25 to 6
NaOH	0.0001 0.01 0.1 1 3	0.25 to 4
KOH	0.01 0.1 1 3	0.25 to 4

as well as

Etchant	Combination	Etching time (minutes)
$HCl:HF:HNO_3$	1:1:1 1:2:1 1:2:2 2:1:1 2:2:1 2:1:2	0.25 to 6

etch pits, while 5*n* H_2SO_4 solutions hexagonal ones. Again a mixture of concentrated acids of HCl, HF and HNO_3 in different ratios forms lenticular etch pits expanding along *a* axis; 0.1*n* NaOH, as well as 0.1*n* KOH, develop pits of bacilliform shape expanding along *c* axis. Moreover the development ot the etch pits depends on the concentration of the etching agent: for example H_2SO_4 of a concentration less than 5*n* results in tetragonal pits, H_2SO_4 in a concentration of 5*n* develops symmetrical hexagonal pits and concentrations more than 5*n* form hexagonal etch pits expanding along *a* axis (see Figs. 3*a*—*c*). The form of the etch pits depended on the concentration in cases of other chemical agents, as well. This indicates that etching agents of different combinations and concentra-

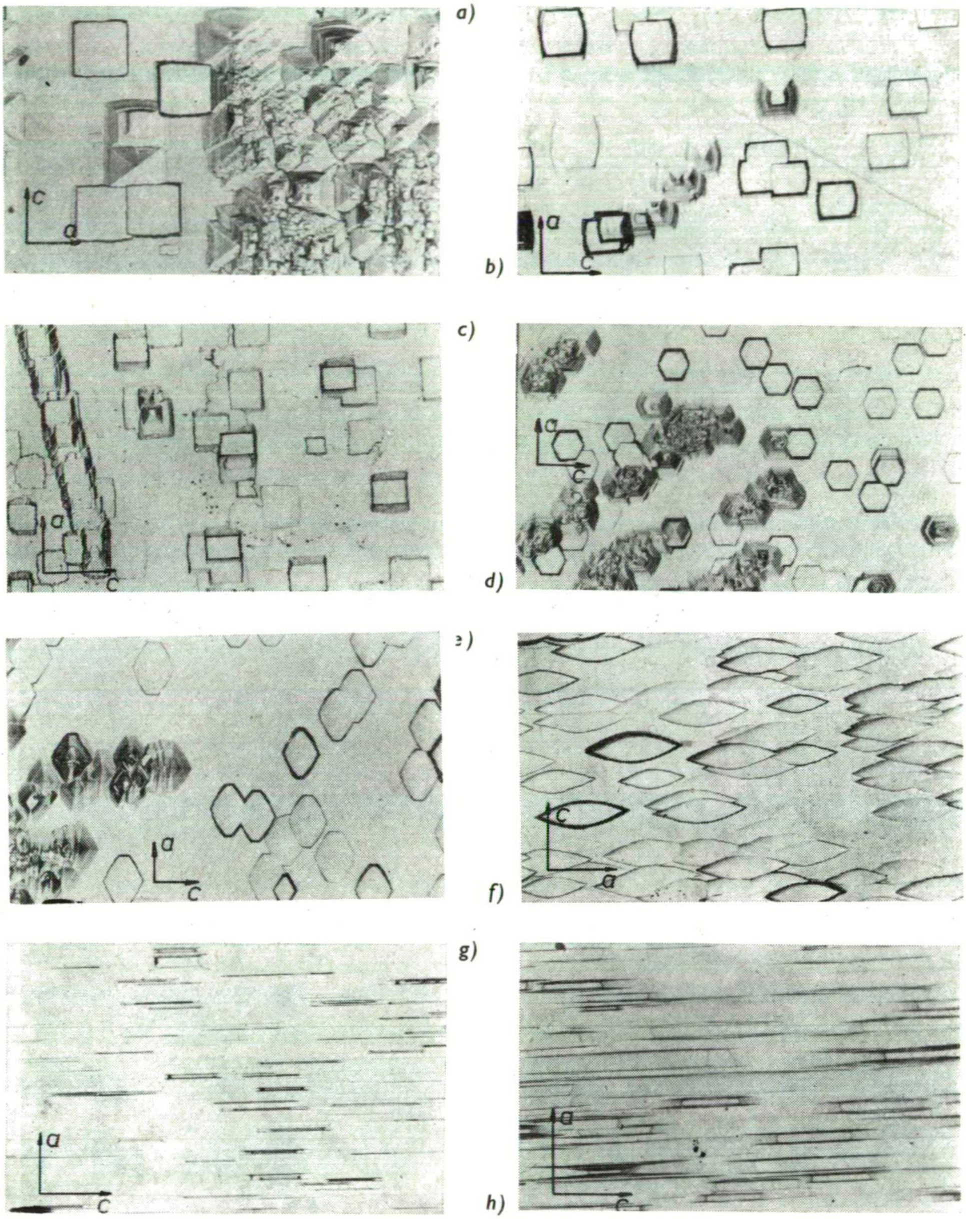


Fig. 3a—h. Etching figures formed by different etchants on the "upper" (010) faces. Etching was made at boiling temperature. *a* — 3n HCl, *b* — 3n HNO_3, *c* — 1n H_2SO_4, d — 5n H_2SO_4, *e* — 7n H_2SO_4, *f* — a mixture of concentrated acids of HCl, HF and NHO_3 in equal ratios with an etching time of 4 minutes in all cases, as well as *g* — 0.1n NaOH, *h* — 0.1n KOH with an etching time of 15 seconds in both cases (×50)

tion develop specific etching pictures, namely that the solution rates along *a* and *c* axes change together with the concentration and combination of the solvents.

According to our investigations made on (010) faces of V_2O_5 single crystals, $5n$ H_2SO_4 proved to be a well reproducible and suitable agent for the detection of dislocations with an etching time of 2 to 8 minutes at boiling-point temperature. The density, shape and symmetry of the pseudohexagonal etch pits were independent of etching time within this period. An increase in the diameters of etch pits, determined by successive etching and microscopic measurements, was a linear function of the etching time. The etching rate was 8 μ/min on an average, along both *a* and *c* axis.

As already mentioned thin crystal faces with relatively large areas are often needed for certain optical and electrical measurements. These faces can be prepared by cleavage. Such platelets may be "upper" or intermediate (010) faces (not exposed to air during the growing procedure) — in followings "intermediate". According to our experiments the "upper" and the "intermediate" faces show different etching pictures independently of the chemical agent and its concentration.

a) In all the cases two types of pits appear on the "upper" faces. The shapes of the pits are the same, while their dephts are different (see Fig. 3). The deep etch pits grow further along *b* axis by the increase in etching time, while the flat ones disappear after about 20 min. of etching in $5n$ H_2SO_4 (see Fig. 4*a*—*c*). According to our microscopic examinations the thickness of the dissolved layer along *b* axis was about 2 to 4 μ during this period.

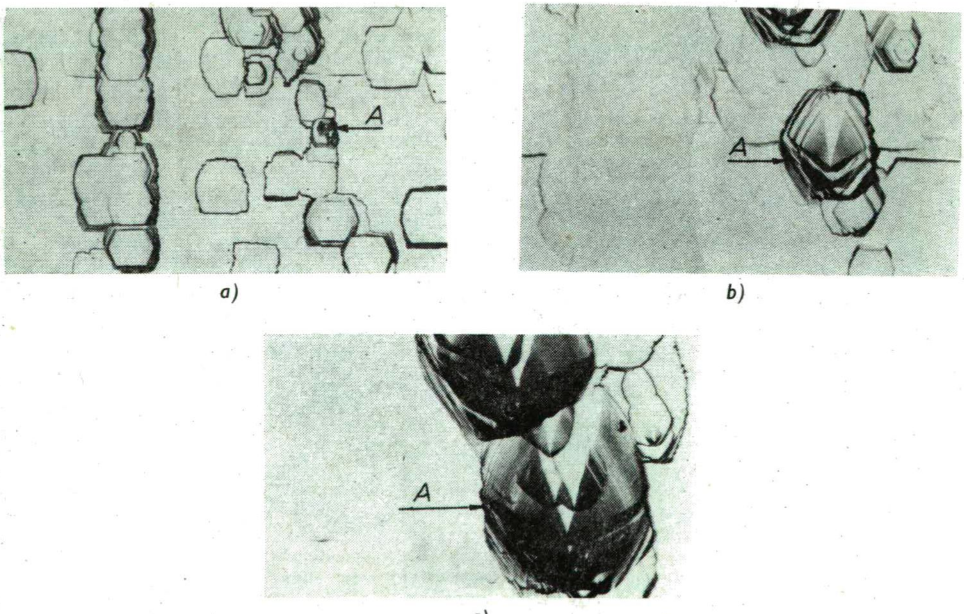


Fig. 4a—c. Succesive etching figures of the same places of "upper" (010) faces. Etchant was 5n H_2SO_4 with an etching time of *a* — 5 minutes, *b* — 12 minutes and *c* — 20 minutes (×67)

b) The dislocation density of our single crystals was $(3—8) \cdot 10^3\ cm^{-2}$, of both "upper" and "intermediate" (010) faces.

It can be concluded the from the symmetry of etch pits that the dislocation lines are parallel to the axis of growth *b*. To investigate whether a connection between the etch pits and intersection points of dislocation lines exists the etching pictures of faces separated by cleavage were compared. The etched images were to be symmetrical namely the pits formed the same places of the cleavaged surfaces were intersected by line-like imperfections (see Fig. 5*a*, *b*).

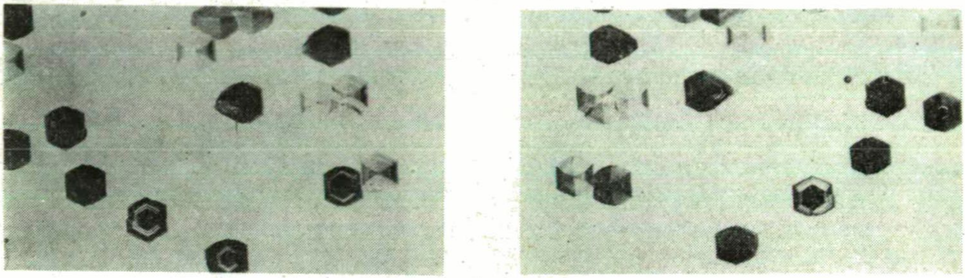
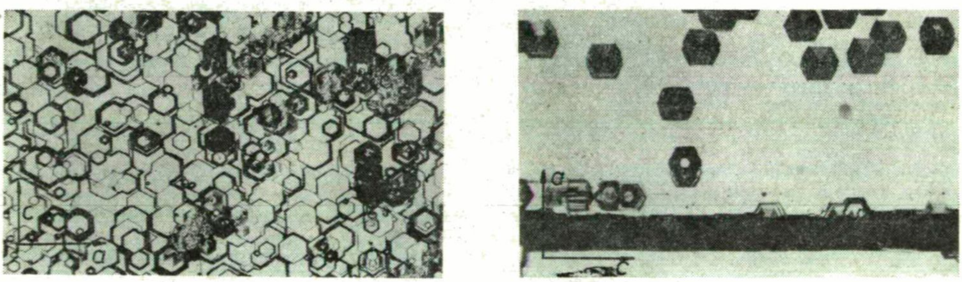


Fig. 5. Etched images of the cleaved "intermediate" (010) faces. Etchant was 5n H_2SO_4 with an etching time of 4 minutes (×50)

To decide whether a connection between the flat etch pits and the impurities exitsts, V_2O_5 crystals doped with 2 weight % of SnO_2 were grown [5]. The etching pictures of both "upper" and "intermediate" faces were investigated. An increase in the density of etch pits was observed (dislocation density: $2 \cdot 10^4\ cm^{-2}$); and flat pits were characteristic of the "upper" deep faces of the "intermediate" surfaces (see Fig. 6*a*, *b*).



a) *b)*

Fig. 6a—b. Etching of figures "upper" *a* and "intermediate" *b* (010) faces of crystals doped with 2 weight % of SnO_2. Etchant was 5n H_2SO_4 with an etching time of 4 minutes (×50)

The next investigation was made to reveal the cause of flat etch pits. Crystal faces were treated at the temperature of 300, 450 and 600 °C in O_2, N_2 and Ar, at 300 °C in H_2 and at 200 °C in $5 \cdot 10^{-6}$ Torr air during five hours. Then they were cooled to room temperature at the rate of 5 °C/min. Etching was made in 5*n* H_2SO_4.

The density of flat pits increased after the heat-treatment. The greatest numerical change was caused by heat-treatment in H_2 (dislocation density increased by an order), while the heat-treatment in O_2 did not cause any change.

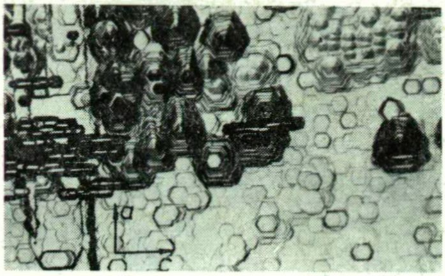
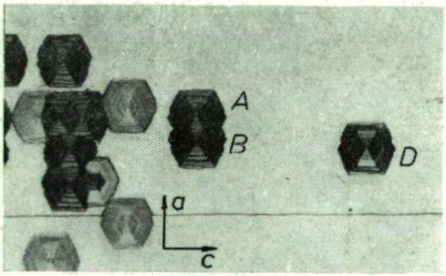
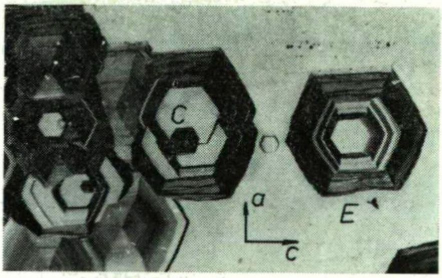


Fig. 7. "Upper" face treated at 300 °C in H_2 for five hours. Etchant was 5n H_2SO_4 with an etching time of 2 minutes (×50)

According to our investigation, cleavages in crystals can be made easier if heat-treated. The same place of "intermediate" face was etched before (Fig. 8*a*) and after (Fig. 8*b*) heat-treatment, to investigate the above mentioned empirical fact. As also shown by the photographs, some dislocation lines leave their places as their densities are reduced (see Fig. *a, b*; A, B→C and D→E).



a)



b)

Fig. 8a—b. The etched "intermediate" (010) face of V_2O_5 before heat-treatment *a* and the same place after heat-treatment followed by a second etching *b* (×67)

Conclusions

According to our experiments, in the field of the chemical etching of (010) faces of V_2O_5 single crystals, well-reproducible results were achieved with 5*n* H_2SO_4, in an etching time of 2 to 8 minutes. Kleber *et al.* designated the solution of 3*n* H_2SO_4 as presenting well reproducible results and reported on etch pits with hexagonal symmetry. In addition, rhombus-shaped etch pits were formed by 1*n* NaOH at a temperature of 90 °C with an etching time of 6 minutes [4]. Surfaces of our crystals became damaged at this etching time. Abdullayev *et al.* found the concentrated acids of HCl, HF and HNO_3 mixed in equal ratios to result in well reproducible etching pictures. These authors brought the flat etch pits into connection with impurities and supposed the impurities to be spread in layers along the grown axis of *c* [5]. Our investigations do not confirm this conception: *a)* If the flat etch pits were connected only with impurities, those would be present in about equal concentrations on the "intermediate" surfaces, as well (see etching pictures of V_2O_5 doped with SnO_2). *b)* Again, their densities ought to be independent of heat-treatment in different atmospheres. These pits can be supposed to be in connection partly with dislocations (intersecting the surface and then leaving their places during crystal growth), partly with the oxigen-loss of the crystal and its surface. It was made evident by LEED as well as by electrical measurements that (010) faces of V_2O_5 single crystals had an oxigen-loss and were probably transformed into $V_{12}O_{26}$ [8—12].

On the basis of our results (chemical etching and heat-treatments in different atmospheres) the defects of V_2O_5 single crystals may be said to be in connection both with the circumstances of growth and deviation of stoichiometric ratio. Further investigations are under way to clear these problems.

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The authors wish to acknowledge and express their indebtness to R. Schiller (Central Research Institute for Physics of the Hungarian Academy of Sciences) for the chemical analysis, and to professor I. Ketskeméty for his kind interest in the work.

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ИССЛЕДОВАНИЕ ТРАВЛЕНИЯ МОНОКРИСТАЛЛОВ V_2O_5

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В работе описано влияние различных травителей и тепловых обработок в различных атмосферах, на «верных» и «промежуточных» (010) плоскостях монокристалла V_2O_5, выращенные из расплава. Плотность дислокаций полученная травлением 5н H_2SO_4 со временем травления от 2 до 8 минут оказалось $(3—8)\cdot 10^3$ см$^{-2}$.