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Etching and dissolution kinetics of $MoSe_2$ single crystal

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Etching and dissolution kinetics of $MoSe_2$ single crystals in aqueous chromic acid at different concentrations and temperatures have been studied. The dependence of the etch rate upon the concentration and temperature of the etchant has been established. The mechanism of the process of dissolution has been explained on the basis of an oxidation-reduction process. The process of etching has been found to be purely diffusion controlled.

1. Introduction

Recently, layered crystals of transition-metal dichalcogenides have found potential application in the fabrication of photoelectrochemical (PEC) solar cells [1]. PEC solar cells using $MoSe_2$ single crystal as photoelectrode and platinum grid as counter electrode in an aqueous iodine solution have been fabricated [2]. It is our observation that the surface condition of the crystal plays a dominant role in deciding the efficiency of the cell and, therefore, it is worthwhile to undertake a detailed study of the etching behaviour of these crystals. An attempt has therefore been made in the present study to develop a dislocation etchant for $MoSe_2$ crystals and to study the kinetics of dissolution.

Molybdenum diselenide has a hexagonal closed-packed stacking structure of two kinds of atoms that can be represented by the sequence $a\beta ab\alpha ba\beta ab\alpha b$..., where a and b refer to selenium atoms and α and β refer to molybdenum atoms. The structure is hexagonal with $a = 0.3286$ nm and $c = 1.297$ nm. The unit-cell contains two $MoSe_2$ layers. The bonds between two selenium layers are mainly of Van der Waal-type and, hence, are considerably weaker. This enables an easy cleavage along the basal plane.

2. Experimental procedure

The $MoSe_2$ crystals selected for our study were grown by the direct vapour transport method according to the procedure described elsewhere [3]. Plate-like samples of basal surface area up to 0.5 cm × 0.5 cm were selected. Etchant solutions of 5, 6, 7.5, 8.5 and 10 N were prepared by dissolving appropriate amounts of analytical grade chromium trioxide in double-distilled water. The crystals were dipped in the etchant contained in a 50 ml beaker for periods ranging from 1 to 20 min. Subsequently, the crystals were washed in distilled water and were dried in air on filter paper. Etching at higher temperatures (between 30 and 60° C) was carried out by placing the beaker containing the etchant in a constant-temperature bath having a toluene temperature-controlling system with a constancy of temperature within ± 0.5° C.

Etch-pit size determination was carried out by an optical microscope having a calibrated eye-piece.

3. Results

The etch pits produced are usually uniform in size and have hexagonal shape (see Fig. 1a). It is seen that these pits exhibit many phenomena associated with dislocation etch pits. For example, on prolonged etching (see Fig. 1b), most of the pits, while retaining their shape, become larger. The pit density remains constant. The pits observed on the congruent faces (see Fig. 2a and b) and on the opposite sides of a thin flake (see Fig. 3a and b) have one-to-one correspondence in their positioning.

The fact that etch pits are preferentially formed at the apex of the spirals (see Fig. 4) and at the

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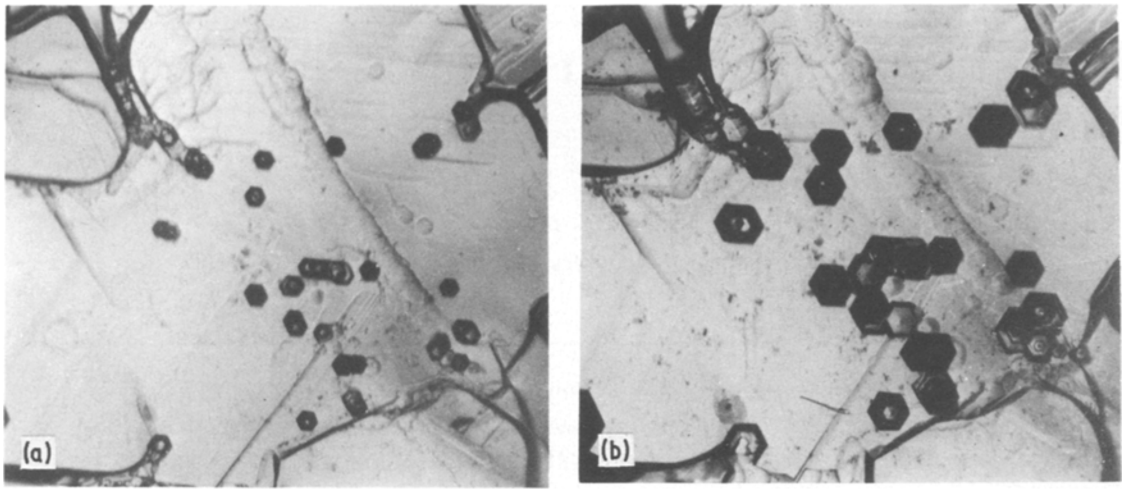

Figure 1 (a) Etch pattern obtained after 5 min of etching in the solution 7.5 N at room temperature, × 160; (b) Etch pattern produced by successively etching the same crystal for 10 min, × 160.

termination points of the cleavage steps strongly suggests that the etching procedure here described can reveal the sites of the dislocation.

4. Mechanism and kinetics of dissolution

The concentration, temperature, viscosity of the etchant, activation energy for etching, intensity of illumination at the surface (possibly, if the etching mechanism is governed by an oxidation-reduction process) etc., are the various parameters that decide the etch rate. A basic formula for etch rate, V, is described by the Arrhenius equation,

$$V = V_0 \, e^{-E/kT}, \qquad (1)$$

where E is the activation energy for etching, T is the temperature of the etchant, V_0 is the pre-exponential factor and k is the Boltzmann's constant. All other parameters affecting the etch rate are taken into account by the V_0 term.

Experimental data connecting etch rate with concentration and temperature are given in Table I and fit the relation

$$V = (10\,344)\,C - 43\,356\, e^{-2600/T}, \qquad (2)$$

where C is a constant.

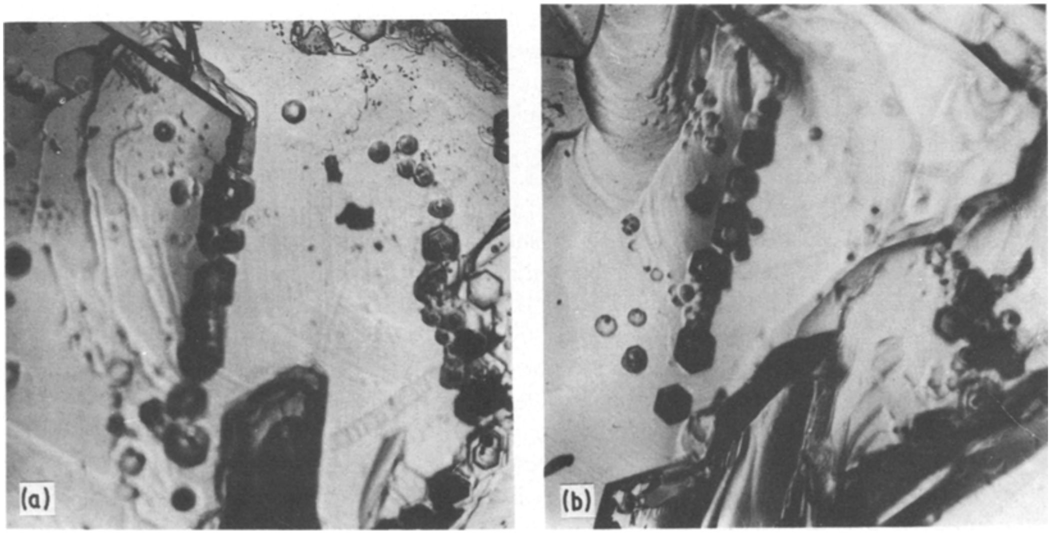

Figure 2 (a) and (b) Etch patterns produced on the opposite sides of a thin flake, × 200.

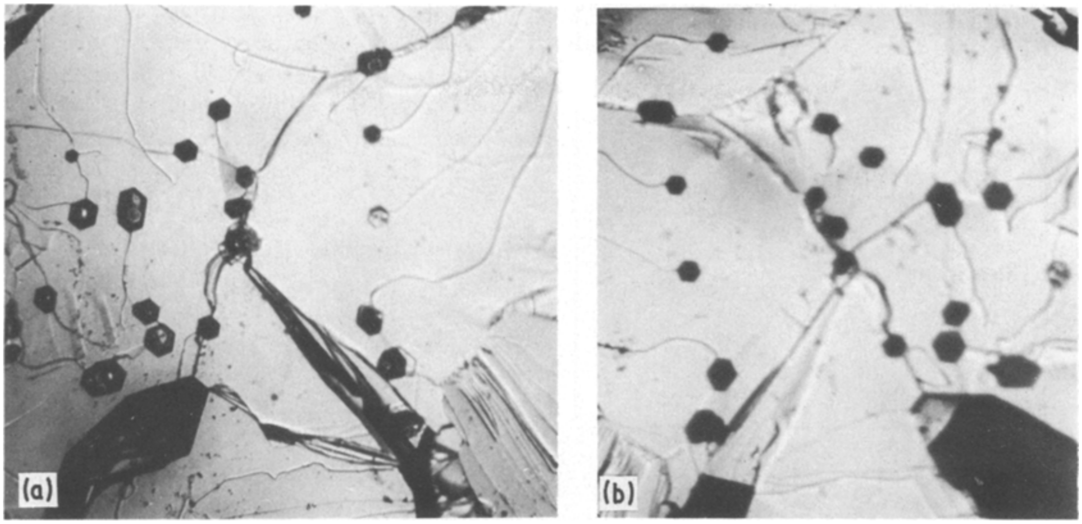

Figure 3 (a) and (b) Pit showing one-to-one correspondence of a cleavage face, × 200.

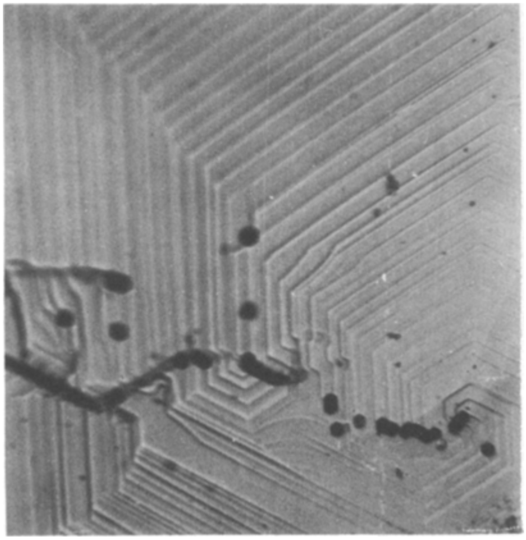

Figure 4 Etch pattern produced at the centre of the spirals, × 210.

TABLE I Data relating the etch rates with temperatures and concentrations of the etchant H_2CrO_4 for $MoSe_2$ single crystal

Temperature (K)	Etch rate concentration (μm min^{-1})				
	5 N	6 N	7.5 N	8.5 N	10 N
295	1.25	2.63	5.00	6.61	8.32
303	1.43	3.47	6.31	8.51	11.33
313	1.62	4.00	8.40	11.40	15.40
323	2.60	5.60	12.00	14.40	19.60
333	3.40	7.60	14.50	18.00	24.40

Table II shows a comparison of the observed etch rate, V_{obs}, and the calculated etch rate V_{cal}, calculated from Equation 2.

In the present case the activation energy for etching, E, is as small as 0.236 eV. Because of this, as soon as the reacting species reach the surface of

TABLE II Comparison of observed etch rate, V_{obs}, with calculated etch rate, V_{cal}

V_{obs} (μm min^{-1})	V_{cal} (μm min^{-1})
1.25	1.24
1.43	1.57
1.62	2.06
2.60	2.67
2.63	2.78
3.40	3.40
3.47	3.51
4.00	4.62
5.00	5.09
5.60	5.97
6.31	6.42
6.61	6.63
7.60	7.61
8.32	8.93
8.51	8.36
8.40	8.45
11.33	11.28
11.40	11.00
12.00	10.92
14.40	14.23
14.50	13.91
15.40	14.83
18.00	18.12
19.60	19.18
24.40	24.43

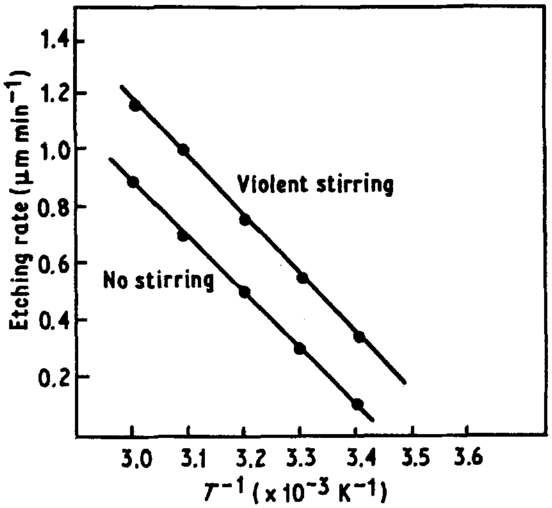

Figure 5 Etch rate plotted as a function of reciprocal temperature, T^{-1}, with and without stirring.

the crystal they get immediately reduced and a thin reactant-depleted layer is formed at the surface of the crystal. Under these circumstances the etch rate will solely depend upon the rate at which the reacting species diffuse through this layer. The thickness of the reactant depleted layer can be reduced by stirring the solution, which increases the rate of diffusion of the reacting species and consequently the etch rate. This is verified from Fig. 5, which shows the graph of etch rate against reciprocal of temperature for $MoSe_2$ with and without stirring. The etch rate increases upon stirring but the activation energy derived from the slope of the graph does not change.

The mechanism of the process of dissolution of $MoSe_2$ in the etchant H_2CrO_4 can be explained on the basis of an oxidation-reduction process as follows.

H_2CrO_4 is a strong oxidizing agent. Each Mo atom at the surface (at the site of etching), upon coming into contact with the etchant, becomes oxidized liberating one electron. The electron thus "spared" is taken up by the oxidizing agent (etchant, H_2CrO_4). The oxidizing Mo^+ atom subsequently combines with the reduced H_2CrO_4 giving water-soluble reaction products $Mo(CrO_4)_2$ and H_2Se. The entire process of dissolution can be described by

$$MoSe_2 + H_2CrO_4 \rightarrow (MoSe_2)^+ + (H_2CrO_4)^- \quad (3)$$

and

$$(MoSe_2)^+ + 2(H_2CrO_4)^- \rightarrow Mo(CrO_4)_2 + 2H_2Se + e^-. \quad (4)$$

This explanation for the dissolution process of $MoSe_2$ seems to be most probable since it is supported by our observation that the rate of dissolution increases upon illuminating the crystal surface while being etched.

5. Conclusion

It is concluded that the dissolution mechanism of $MoSe_2$ in aqueous chromic acid is of an oxidation-reduction type.

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