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The role of the oxidising agent and the complexing agent on reactivity at line defects in antimony

A H Raval, M J Joshi and B S Shah

Solid State Physics and Materials Science Laboratories, Department of Physics,
Saurashtra University, Rajkot-360 005, Gujarat, India

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Abstract : The (111) cleavage planes of antimony single crystals were etched in the etchants containing malic acid, nitric acid and distilled water. The composition of malic acid (complexing agent) and nitric acid (oxidising agent) was varied in such a manner that the total composition of the etchants remained the same The values of kinetic parameters, such as the frequency factor and the activation energy, were calculated The oxidising agent and the complexing agent modify the kink kinetics within the etch pits which has been discussed.

Keywords : Antimony single crystals, etchants, line defects

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1. Introduction

Dissolution and vaporization may be considered to a great extent as the reverse process of crystal growth. These two processes are useful for the revealation of emergent ends of dislocations on free surfaces. Both the processes, together in general, rely on the fact that some extra energy is associated with dislocation lines; hence preferential attack of the surfaces occurs. Many workers [1–8] have carried out their investigations to study the revealation of dislocations; in order to do so, they developed new etchants and modified a few of them also [1,2,6–8].

In the present study, the etchants containing aqueous solutions of nitric acid and malic acid were selected to etch (111) cleavages of antimony single crystals.

2. Experimental technique

Single crystals of antimony were grown by Chalmers method, which has been elaborately discussed by Thaker and Shah [9]. The metal was kept in a specially designed graphite boat.

The boat is pointed at one end and flat at the other end. The tip provides the freezing of the melt at a point and because of the constriction, very few crystals are formed. The graphite boat was kept at the centre of a silica tube having 2–5 cm diameter and 75 cm length. The trolley furnace, which moved along the silica tube, was prepared by the standard techniques. Several crystals were grown under a temperature gradient of 92°C/cm and a growth velocity of 1–5 cm/hr. The crystals were cleaved at liquid nitrogen temperature in the conventional manner.

The etchants containing malic acid had been selected to etch the (111) cleavages of antimony single crystals. The composition of the selected etchants are as follows :

Etchant A : 9 parts malic acid + 3 parts HNO_3 + 1 part distilled water.
Etchant B : 9.5 parts malic acid + 2.5 parts HNO_3 + 1 part distilled water.
Etchant C : 10 parts malic acid + 2 parts HNO_3 + 1 part distilled water.

The etchants were made from AR grade chemicals. For high temperature etching, the crystals were first heated separately and brought to the temperature of etchant before etching. All the etchants were tested by the standard technique and found to be revealing dislocation etch pits.

The values of activation energy and frequency factor were calculated using the Arrhenius law :

$$W = Ae^{-E/kT}, \tag{1}$$

where W is the average width of the etch pits, T is the absolute temperature, E is the activation energy and A is the frequency factor.

Figure 1 is the photomicrograph revealing crystallographically oriented triangular etch pits corresponding to the dislocations of the (111) $[10\bar{1}1]$ type by etching in the etchant

Table 1. The values of activation energy and frequency factor for different etchants

Etchants	Activation energy	Frequency factor
[A] 9 parts malic acid + 3 parts HNO_3 + 1 part distilled water	0.63 eV	5.32×10^4 cm/s
[B] 9.5 parts malic acid + 2.5 parts HNO_3 + 1 part distilled water.	1.07 eV	1.31×10^{12} cm/s
[C] 10 parts malic acid + 2 parts HNO_3 + 1 part distilled water	0.79 eV	4.00×10^7 cm/s

Plate I

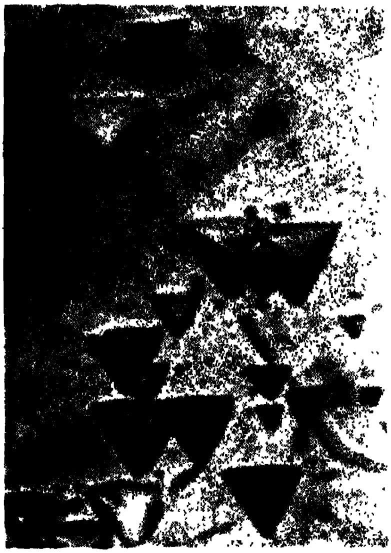

Figure 1. Photomicrograph revealing the type of etch pits produced on (111) cleavage plane of antimony single crystals by etching in the etchant A at 33°C for 120 seconds.

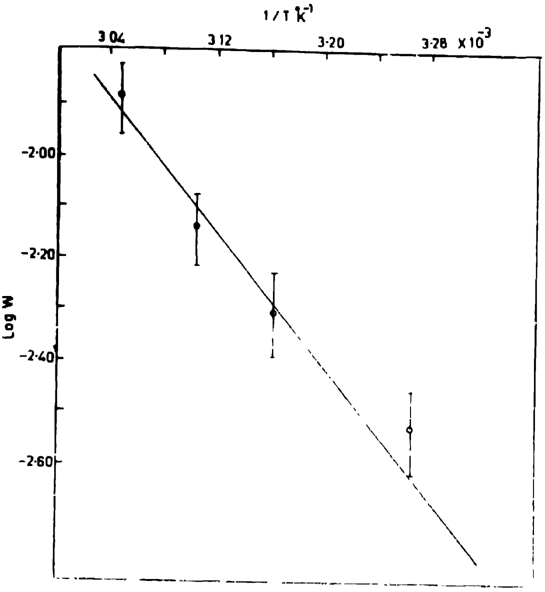

Figure 2. A plot of logarithm of average width of etch pit W *versus* $1/T$ for etchant A

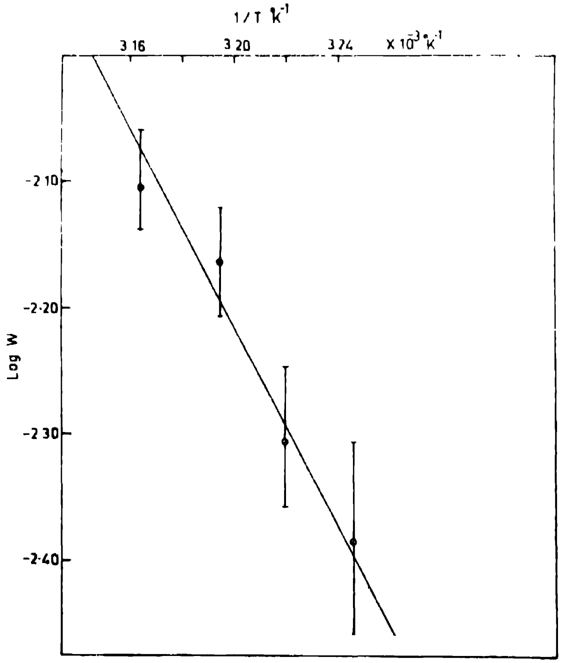

Figure 3. A graph of logarithm of average width of etch pit W *versus* $1/T$ for etchant B.

A at 38°C for 120 seconds. Figures 2–4 are the plots of logarithm of average value of etch pit width *W* *versus* reciprocal of absolute temperature *T* for etchants A, B and C, respectively.

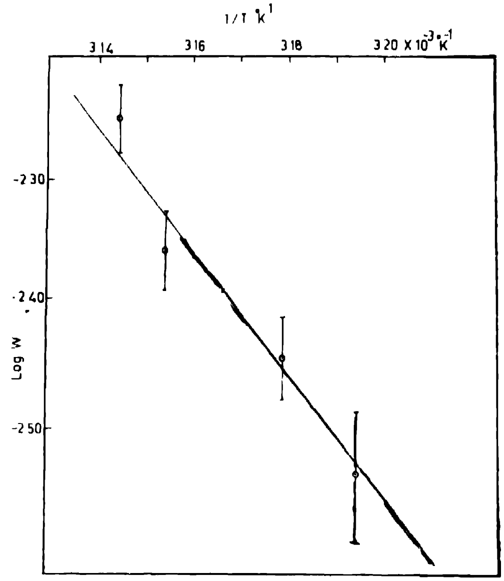

Figure 4. A graphical relation between the logarithm of average width of etch pit and the reciprocal of absolute temperature for etchant C.

The values of activation energy for the lateral motion of steps as well as the frequency factors were found out from the plots and are tabulated in Table 1.

3. Discussions

The approach to etch pit control through the study of the kinetics of pitting must have some relevance, since even if a thermodynamically stable shape is eventually attained, the pits are certainly kinetic phenomena immediately following nucleation of an appropriate 'hole' at the defect. The two aspects of kinetics, namely, the nucleation of monomolecular steps at the defects and the motion of steps away from the source, have been outlined by Gilman *et al* [10] and Cabrera [11]. Successive nucleation of steps at the defects gives rise to dissolution rate V_d at the defects. If the height of the steps is h, then V_d/h steps are produced in unit time. This model takes no account of the shape of the steps, and hence that of the pit they comprise, and it is best thought of as a two-dimensional model. Following nucleation, the steps move out by removal of atoms and can be assigned a velocity V_s. The dependence of V_s on the position of the steps is unknown; but as pointed out by Cabrera [11], it is likely to be controlled by superimposed diffusion fields, particularly close to the defect source. An analysis of moving steps in terms of the surface concentration gradient has been performed by Hirth and Pound [12] in developing the idea of Burton *et al* [13] for crystal evaporation. They predict that a series of steps emanating from a source, after sufficient distance of travel, will achieve a uniform steady velocity V_s^∞ and also a uniform spacing. Such a conclusion indicates that the velocity V_s^∞, at a sufficient distance from the source, is independent of the rate of production of steps and hence, is independent of V_d. Consequently, if the steady state is achieved at a small distance comparable to the size of a pit, it will be difficult to perform an analysis, due to ignorance of the boundary conditions. If, however, the steady state is achieved well inside the pit, its slope and rate of widening will be independent of the type of defect. In this connection, the results of Ives and Hirth [14] and Ives and McAusland [15] are quite important.

There are many kinks in the ledges and their nucleation is primarily controlled by the effective undersaturation of the dissolving species in the solvent and the principal effect of the etchant inhibitor is the retardation of kink motion. These two effects are in no way independent. Whereas an uninhibited solvent attacks crystal surfaces very roughly, etchants containing inhibitor produce pits in an otherwise relatively smooth surface. It appears, therefore, that the inhibitor produces some modification in kink mechanism rate, in addition to its effect on kink motion [16]. Many etchants for bismuth [17,18] and antimony [6–8] have been reported which are believed to be modifying the kink kinetics.

The present study is a part of the investigations carried out to verify the use of different hydroxy acids as a component in the dislocation etchants. The earlier studies on citric acid containing etchants [8] and dextro-tartaric acid and levo-tartaric acid containing etchants [6] are already reported by the present authors. The values of activation energy for the lateral motion of ledges and frequency factors, *i.e.* the kinetic parameters, have been calculated for the etchants containing malic acid for the present investigation and compiled in Table 1. One can notice from the table that the activation energy and the frequency factor increase initially and then decrease on increasing the content of malic acid. The activation energy, which is defined as the difference between the mean energy of all the collisions of the reactants and the average energy of collision in which the reaction takes place, is thought of as a barrier to the occurrence of reactions. The greater the activation energy, the lower the rate of reaction. This also further suggests that the reaction rate decreases first and thereafter increases, *i.e.* a critical point is observed. The critical point shows a deviation in the normal trend of reaction. This type of behaviour was reported by Shah *et al* in bismuth [17]. They observed a presence of critical composition in the ethyl alcohol containing etchants and propyl alcohol containing etchants, where the critical point exhibited the maximum value of the activation energy in the case of the former and the minimum value in the case of the latter. They conjectured that at critical dilution, changes in the kink kinetics took place. In antimony single crystals, the citric acid containing etchants indicated that the critical point had minimum values of the activation energy and the frequency factor [8]. In contrast, the present study suggests that the critical point indicates the maximum values of the activation energy and the frequency factor. Nitric acid is serving as an oxidising agent in the composition of the etchants [19], the variation in its composition seems to modify the kink kinetics in the ledges within the etch-pits which also depends upon the type and composition of the complexing agent (*i.e.* malic acid or citric acid) so that the critical point either indicates maximum values or the minimum values of the kinetic parameters.

4. Conclusions

(1) All the etchants exhibited dislocations of (111) [101] type.

(2) Increasing the composition of malic acid and reducing the composition of nitric acid in such a way that the total composition of the etchants remains constant, a critical point is observed where a deviation in the normal behaviour is observed, which corresponds to the earlier results in bismuth and antimony. However, the specific composition of oxidising agent (nitric acid) as well as the type and composition of complexing agent (malic acid or citric acid) is responsible for modifying the kink kinetics in the ledges in such a way, either to indicate the critical composition with maximum values of kinetic parameters or the minimum values.

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