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Study at dislocation etch pits in antimony single crystals by etching in citric acid containing etchants

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Abstract : The (111) cleavages of antimony single crystals were etched in etchants containing 10 parts citric acid, 3 parts fuming nitric acid and 1 part distilled water. The etchant exhibited well-defined triangular etch pits at the sites of dislocations. The reactivity at line defects for lateral motion of ledges in the etch-pits and the frequency factor have been calculated for this etchant.

Keywords : Dislocations, etchants, etch-pits, activation energy, frequency factor.

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Chemical etching is a valuable tool in revealing dislocations in crystals. Etching of antimony crystals have been attempted by many workers [1–7]. The earlier work was reported by Wernick *et al* [1] on antimony by etching in CP4, which had been used by Vogel *et al* [8] to show dislocations on the (100) and (111) planes of germanium. The Dash etchant [9], which is a modified CP4 etch was found to be a polishing agent for antimony without producing etch-pits. However, there are only few standard etchants available to etch antimony cleavages. In the present communication an etchant has been developed consisting of aqueous mixtures of citric acid and nitric acid, which is found to be a fairly good etchant to reveal dislocations.

Single crystals of antimony were grown by Chalmer's technique [10], which has been extensively discussed elsewhere by Thakar and Shah [11]. The metal of 5N purity obtained from Nuclear Fuels Complex, Hyderabad, India, was used. Several crystals were grown under temperature gradient of 92° C/cm and growth velocity of 1.5 cm/hr. The crystals were cleaved at liquid nitrogen temperature in conventional manner.

The etchant used to reveal etch-pits at the sites of dislocations consisted of 10 parts citric acid, 3 parts fuming nitric acid and one part distilled water. The etchant produced triangular, crystallographically oriented etch pits, which revealed dislocations of the (111) [10$\bar{1}$] type. High temperature etching was performed by raising the temperature of the samples and etchants to the required temperatures before etching. The etching was carried out from room temperature to 55°C. It was confirmed through various tests suggested by Amelinckx [12] that this etchant reveals dislocation etch pits. Figure 1 is a photomicrograph showing the types of etch pits obtained at 40°C for etching time of 30 seconds. Whereas, the Figures 2 and 3 are photomicrographs exhibiting the etch pits at 45°C and 50°C. From these photomicrographs one can see that the size of etch pits increases with the temperature. Figure 4 shows the histogram indicating distribution of different size of etch pits and their numbers at 40°C.

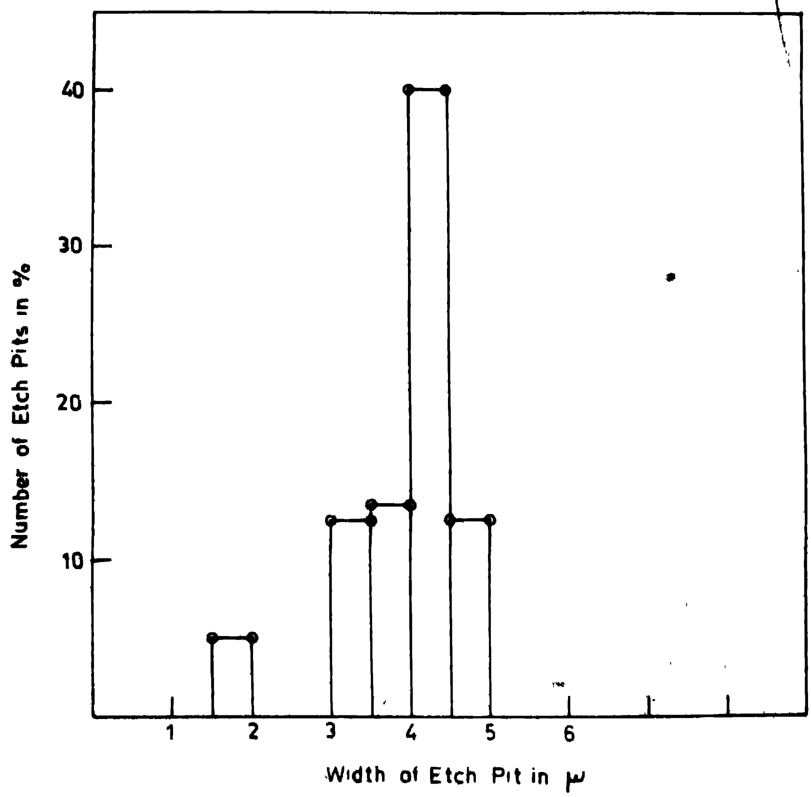

Figure 4. Histogram showing distribution of different size of etch pits in the observed area on (111) cleavage plane of antimony crystal at 40°C.

The activation energy for lateral motion of ledges were obtained by using an Arrhenius type law

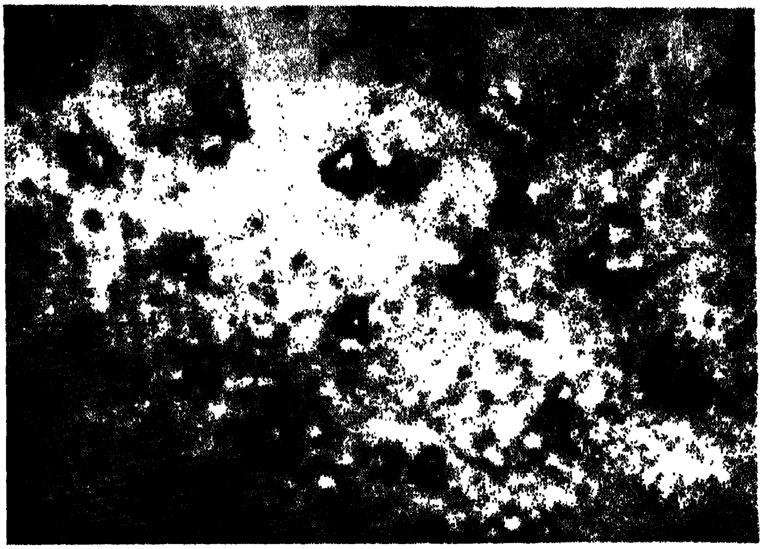

Figure 1. Type of etch pits observed by etching (111) cleavages of antimony at 40°C for 30 seconds.

Figure 2. Type of etch pits revealed by etching (111) cleavages of antimony at 45°C for 30 seconds.

Plate II

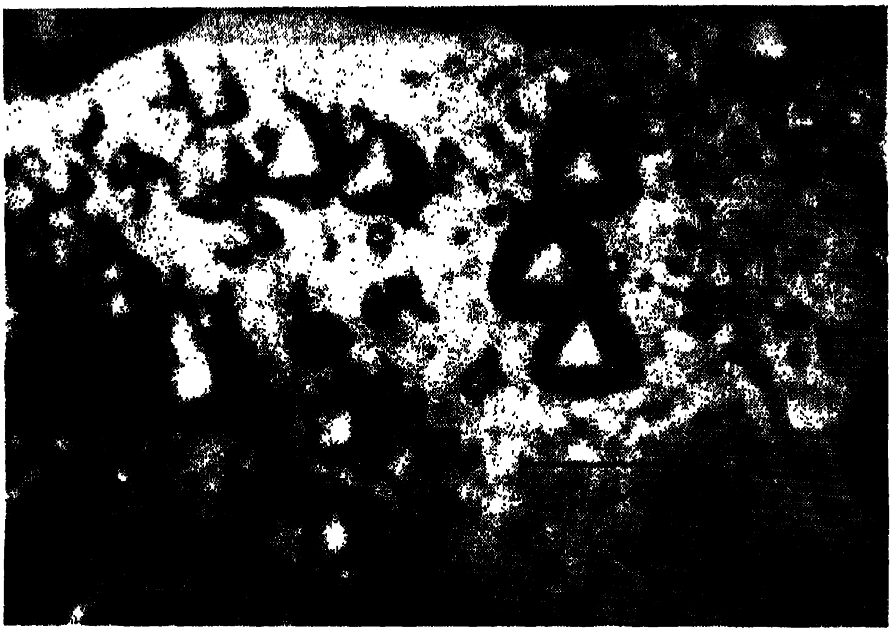

Figure 3. The large size etch pits exhibited on (111) plane of antimony by etching at 50°C for 30 second.

$$W = A \exp(-E/kT) \tag{1}$$

where W is the average width of etch pits, T the absolute temperature, k the Boltzmann constant, A the frequency factor related to the collisional frequency and steric factor and E the activation energy. Figure 5 shows the Arrhenius plot of log W versus $1/T$ and the activation energy, which is calculated from the plot, is found to be 0.41 eV. The frequency factor calculated using eq. (1) is found to be 5.4×10^2 cm/sec.

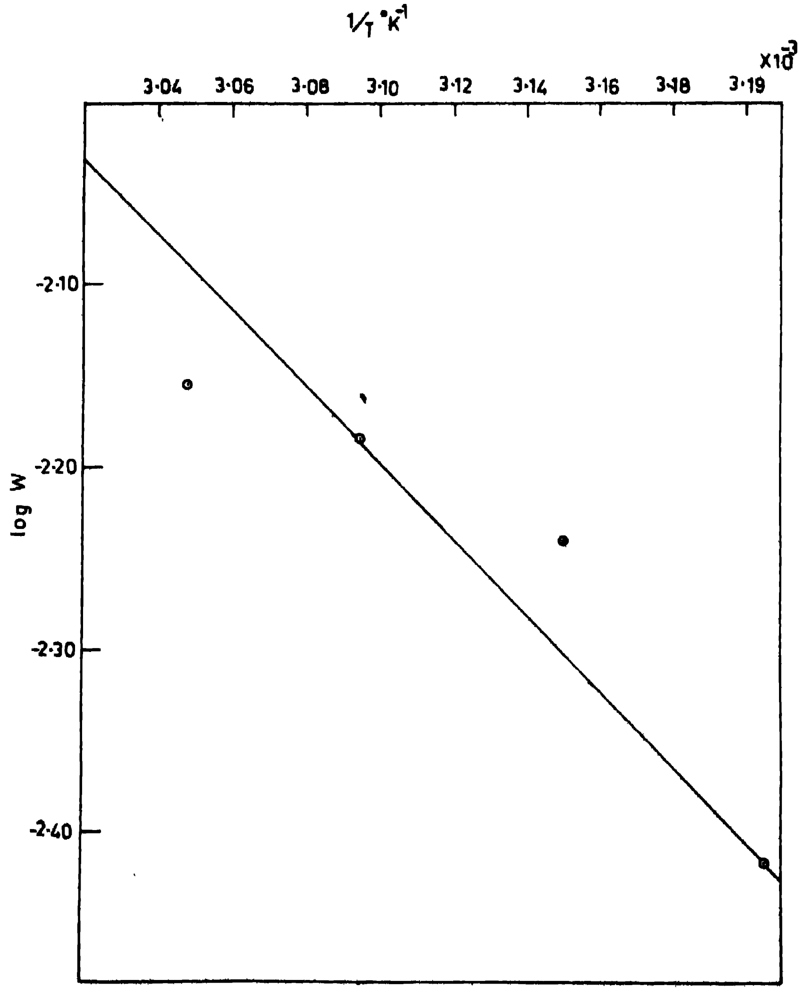

Figure 5. A plot of logarithm of average width of etch pits *versus* reciprocal of absolute temperature.

Wernick *et al* [1] used CP4 etchant containing 3 parts HF, 5 parts HNO_3, 3 parts CH_3COOH and 1 part Br_2 to etch (111) cleavages of antimony. While the Dash reagent, which contains 1 part HF, 3 parts HNO_3, and 12 parts CH_3COOH, was found to be good polishing agent. The superoxol reagent, which consists of 1 parts 30% H_2O_2, 1 part 48%

HF, and 4 parts H_2O [13], is used as a crystallographic etch for germanium. Theuerer [13] found that the amplification characteristics of germanium transisters were improved by etching of the face upon which two point electrodes were applied. However, the modified form of the superoxol reagent brought out spiral terraces in shallow etch pits in antimony [1]. Kosevich [2] had also etched (111) plane of antimony with CP4 etchant. He studied etch patterns on the faces of blocks, slip lines, and elastic and stable twinned layers. He had also modified the CP4 etchant by using composition of 28 parts glacial CH_3COOH, 5 parts HNO_3, 4 parts HF and 3 parts Br_2. Shigeta *et al* [4] used the etchant comprising of 10 gms $FeCl_3$, 30 cc HCl and 120 cc H_2O to etch (111) plane of antimony. Pandya and Bhatt [5] and Pandya and Balasubramanian [6] have tried a solution of tartric acid and nitric acid for the purpose of revealing dislocations. The surface remained bright after prolonged etching. Thakar [7] carried out in detail the chemical and thermal etching of antimony crystals. A systematic study of the relative merits of various etchants had been made and it is found that the purity of metal and reagent composition of the etchants were very sensitive parameters. Pile-ups had also been observed by the author [7] which supports the view that the etch pits were formed at the sites of dislocations.

In conclusion, the etch pits were observed, using the developed etchant, at the sites of dislocations. The activation energy for the lateral motion of ledges was found to be 0.41 eV. Also, the frequency factor was found to be 5.4×10^2 cm/sec. Further work is in progress.

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