Growth of antimony single crystals and dislocation etching

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Abstract : Antimony single crystals have been grown by the horizontal Chalmer's technique The furnace for the growth was designed and fabricated in the laboratory A specially designed graphite boat was used as a container for the growth For dislocation studies, the crystals were cleaved at liquid nitrogen temperature in a conventional manner Optically smooth (111) cleavage surfaces were selected for etching in the etchants consisting of different compositions of malic acid, nitric acid and distilled water Crystallographically oriented triangular etch pits were obtained at sites of dislocations The reaction is characterised by kinetic as well as thermodynamic parameters.

1. Introduction

Antimony, a silver white brittle metal, finds numerous applications in various fields. Antimony metal available with a purity of 99.999% finds its applications in semiconductor technology for making infrared detectors, diodes and Hall – effect devices [1, 2]. Antimony expands on solidification which finds its uses in solder and decorative casting of britannia metal and some pewter. The growth of antimony single crystals is well reported, various growth techniques were employed by different workers [3-7]. Ogg [8] experimentally confirmed the crystal structure of antimony, which consists of two inter-penetrating face-centered lattices. Lampert and Reichelt [9] described the crystal lattice of Antimony having point group R $\bar{3}$ m and it is isomorphous to arsenic. The negative resistance effect in antimony single crystals were studied by Marimoto and Yoshida [10] at 1.6 °K. Moreover, the diamagnetic nature of susceptibility of Antimony [11] and neutron strength function data for target $^{50}_{121}$Sb and compound nucleus $^{51}_{122}$Sb [12] have been obtained.

The etching technique is widely used to reveal dislocations on surface of single crystals of metals, organic and inorganic

crystals. The composition of an etchant remains empirical but the basic requirement of an etchant is an oxidizing agent and a complexing agent, sometimes as many as three to four components are involved. Many workers have explored chemical etching technique to reveal dislocations on (111) cleavage plane of antimony single crystals [7, 13-18]. In the present investigation, the single crystals of antimony are grown by the horizontal Chalmer's technique and etched by etchants containing malic acid to reveal dislocations.

2. Experimental techniques

2.1 Crystal growth :

In the Bridgman method, the furnace is kept steady and the charge is moved, whereas in the Chalmer's technique, the charge is kept steady and the furnace is moved horizontally along the charge [19]. The crucibles play an important role in crystal growth. The types and designs of crucibles or containers are selected carefully for every type of crystal growth technique, which are summarised by Shah and Wills [20]. In the present investigation, the metal is kept in a specially designed graphite boat which is pointed at one end and flat at the other. This type of boat provides the freezing of the melt at a point because of constriction. In this way, very few seed crystals are formed.

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The graphite boat is kept at the centre of the quartz tube of one meter in length and 2.5 c.m. in diameter. The trolly furnace which moves along the quartz tube is made according to the standard procedure. The arrangement is shown schematically in Figure 1. The X, Y and Z are the three different furnaces where X and Z are connected in series with separate power supply for Y. The X and Z are the preheating and after heating furnaces respectively, their temperatures being less than the melting point of antimony. The central furnace Y is kept at a temperature 50°C to 70°C above the melting point of antimony. The temperature gradient is controlled by changing the temperature of X and Z, and could also be changed by changing the distances from the central furnance Y. The horizontal movement of the furnace is facilitated with a motor. Many crystals were grown under temperature gradient of 92 °C/cm and growth velocity of 1.5 cm/hr. Antimony metal of 5N purity obtained from Nuclear Fuels Complex, Hyderabad, India, was used.
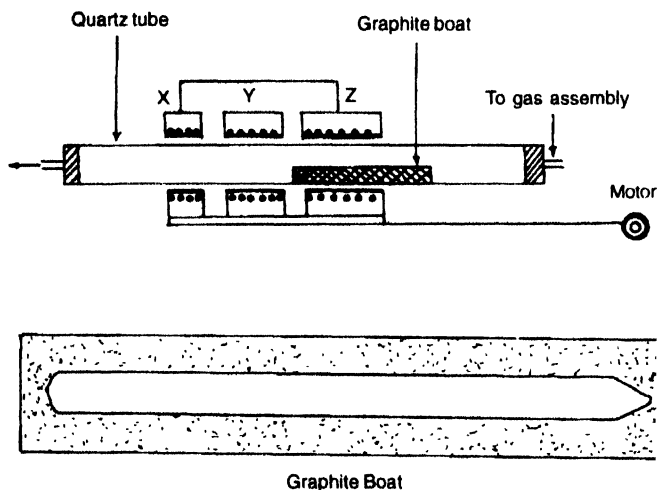

Figure 1. A schematic diagram of Chalmer's setup used for growth of antimony single crystals and a graphite boat for the growth

During the growth of crystals, a continuous flow of hydrogen gas is mantained over the charge, the gas is produced in Kipp's apparatus and subsequently passed through a column of water to remove the HCl vapour and through a tower containing calcium chloride to absorb the moisture. The gas is then passed over hot copper filling kept in a separate furnace to remove the traces of oxygen present in it.

2.2 Chemical Etching :

The crystals were cleaved at liquid nitrogen temperature in a conventional manner. The freshly cleaved surfaces were rinsed in alcohol followed by rinse in ether and hot air dried. The crystal dimensions were kept constant such that the surface to volume ratio was large. For high temperature etching, the crystals were first heated separately and brought to the temperature of etchant before etching. The etch pit width W was measured by using a filer eye piece of Carl Zeiss NU-2 microscope with resolution of 0.4 microns. The tests were carried out to check whether the

etch pits were at dislocation sites [21]. The crystals were found to have dislocation densities of 10^5 lines/cm^2.

The following mentioned etchants have been selected for etching (111) cleavages of Antimony single crystals.

(1)   Etchant A : 8 c.c. 1 M malic acid + 3 c.c. nitric acid + 1 c.c. distilled water.

(2)   Etchant B : 9 c.c. 1 M malic acid + 3 c.c. nitric acid + 1 c.c. distilled water.

(3)   Etchant C : 10 c.c. 1 M malic acid + 3 c.c. nitric acid + 1 c.c. distilled water.

The chemical structure of malic acid is as follows :

$$
\begin{array}{c}
COOH \\
| \\
H—C—H \\
| \\
HO—C—COOH \\
| \\
H—C—H \\
| \\
COOH
\end{array}
$$
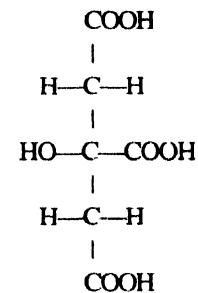
The etching was carried out at different temperature from room temperature to 45 °C. The etching times were 120 sec. for etchant A and 45 sec. for etchants B and C. Crystallographically aligned triangular etch pits of (111) [10$\overline{1}$] type were observed

Figure 2 is a photomicrograph exhibiting triangular etch pits on (111) cleavage plane at temperature of 45° C by etching in etchant B. Similarly Figure 3 is a photomicrograph showing the types of etch pits obtained in etching by etchant C at 40° C.
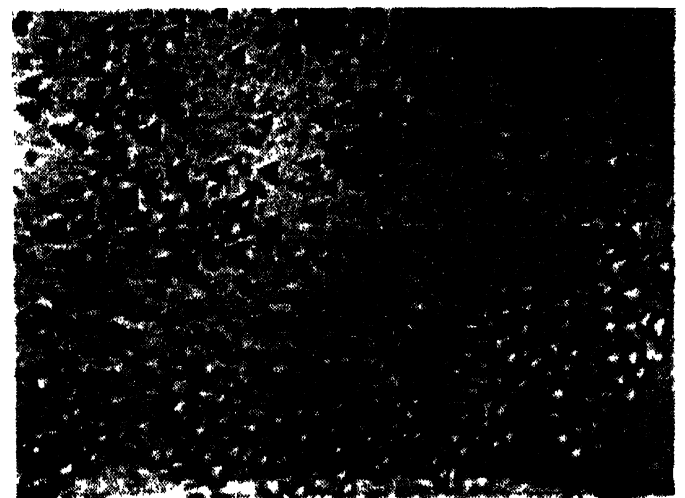

Figure 2. A photomicrograph of typical etch pits observed on etching (111) cleavage plane of antimony in etchant B at 45°C for 45 seconds

3. Results and discussions

Various workers have grown antimony single crystals. Maslova et al [3] have grown antimony single crystals by Bridgman

method in a hard crucible. They studied dislocations when crystals were grown in split graphite moulds at different rates. They found that the dislocations arose mainly due to plastic
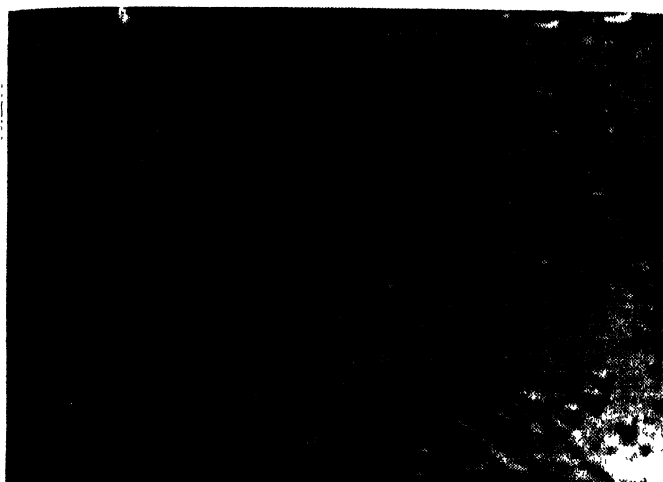

Figure 3. A photomicrograph of typical etch pits observed on etching (111) cleavage plane of antimony in etchant C at 40°C for 45 seconds

deformation condition by the crystal – wall adhesion in the crucible. The dislocation density can be reduced and the size effect suppressed by weakening the adhesion between crystal and wall of the crucible. Also, the formation of dislocations in antimony crystals grown by pulling from melt have been reported by Tsivinskii *et al* [4]. Apart from this, Thakar and Shah [7] grew antimony single crystals by modified Chalmer's technique and reported preferred orientation of (111) cleavage plane with the growth axes.

It is well known that the reaction rate increases with temperature and follows the empirical Arrhenius law. The activation energy for the lateral motion of ledges of dislocation etch pits and the frequency factor can be calculated using the following equation :

$$W = A \exp(-E / RT),$$ (1)

where W is the average width of the etch pit, E is the activation energy, A is the frequency factor, R is the gas constant and T is the absolute temperature. The values of activation energy and the frequency factors have been calculated from the plots of logarithm of W versus $1/T$. Figures (4-6) are the plots of log W vs. $1/T$ for the etchants A, B and C, respectively. The reactions
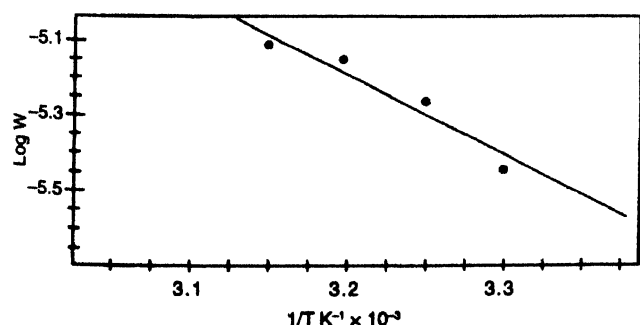

Figure 4. A plot of log W versus $1/T$ for etchant A.

were further characterised by Gibb's free energy of activation given by

$$\Delta^*G^0 = \Delta^*H^0 - T\Delta^*S^0,$$ (2)

where Δ^*S^0 is the standard entropy of the activation, Δ^*H^0 is the standard enthalphy of activation. The Δ^*H^0 is given by

$$\Delta^*H^0 = E - RT.$$ (3)
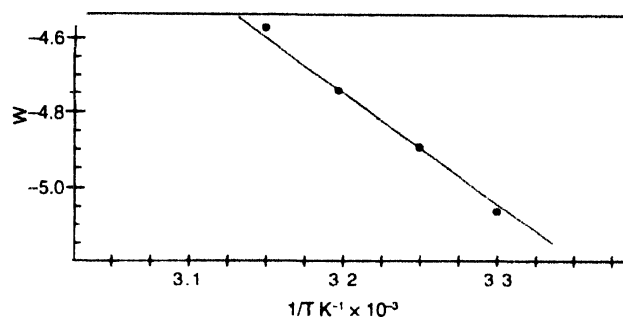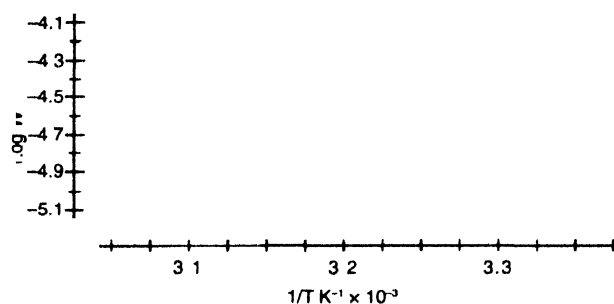

Figure 5. A plot of log W versus $1/T$ for etchant B

Figure 6. A plot of log W versus $1/T$ for etchant C

The Δ^*S^0 can be calculated as

$$W = \left(\frac{k_b T}{h}\right) \exp(\Delta^*S^0 / R) \exp(-\Delta^*H^0 / RT),$$ (4)

where k_B is the Boltzman constant, h is the Planck constant.

The estimation of kinetic and thermodynamic parameters has been made by using the above eqs. (1-4), which are elaborately discussed elsewhere [22-24]. The values of these parameters are listed in Table 1.

Table 1. Values of activation energy, frequency factor, standard enthalpy of activation, standard entropy of activation and Gibb's free energy are compiled in the table for etchants A, B and C.

Etchant	Activation Energy E kJMol⁻¹	Frequency Factor A	Δ^*H^0 kJMol⁻¹	Δ^*S^0 JK⁻¹Mol⁻¹	Δ^*G^0 kJMol⁻¹
A	42.12	7.07×10^1	39.56	−219	107.02
B	61.27	3.16×10^5	58.71	−149	104.60
C	90.95	4.87×10^{10}	88.39	−50	103.79

The activation energy can be thought of as a barrier to the reaction, therefore, the greater is the activation energy slower is the reaction rate. The pre-exponential factor or the frequency factor A is composed of collission frequency and steric factor [25].

One can notice from Table 1 that the values of standard entropy of activation and standard enthalpy of activation increase with increasing the amount of malic acid in the etchants, while the values of standard Gibb's energy remain more or less constant. The negative values of standard entropy indicates the presence of activated complexes. The Gibb's energy of activation is assumed to follow linear relationship by eq. (2). Any effect that leads to stronger binding between a solute molecules and solvent molecules, will lower the enthalpy; it will lower the entropy by restricting the freedom of vibration and rotation of the solvant molecules. This may lead to a type of compensation between $\Delta^{\neq}H^0$ and $T\Delta^{\neq}S^0$ and hence a very little change in the values of $\Delta^{\neq}G^0$ is expected. This can be observed from Table 1.

The large negative value of the entropy and a moderate value of the frequency factor indicates the formation of intermediate complex as rate determining step in the case of etchant A [23, 26], while for etchants B and C, the intermediate mechanism of reaction may not contain such intermediate complex. If the entropy of activation corresponding to the standard state is about minus 50 $JK^{-1}M^{-1}$, the pre-exponential factor is close to that given by simple collision theory [22], which is expected in etchant C, as it is having entropy of -50 J $K^{-1}M^{-1}$.

Etch pit distributions for the three etchants are depicted in Figure (7a, b, c). From these histograms, it is observed that the complete distribution of etch pits shift towards the larger etch pit width ; also, the distribution gets widened as the malic acid content increases in the etchant. This suggests that the malic acid reacts strongly at dislocation sites on (111) planes of antimony crystals. The frequency factor predominates the activation energy, which is the barrier to the reaction; and as a result, the histograms are shifting towards higher pit width and gets widened. Usually, the higher the activation energy, lower the reaction rate is observed; but in the present investigation, the predominance of frequency factor is found to be important than the activation energy and higher reactions, *i.e.* larger etch-pit widths, are found for higher values of the frequency factor

Figure 7c. Histogram of different etch pit size distribution for etchant (at 40°C

Angus and Dyble [27] have given a mathematical analysis of etching of (111) diamond surfaces. The slopes of etch pit have been computed by them in terms of specific rate constants k_2 and k_3, for removal of 2 and 3 bonded atoms along $<\bar{1}10>$
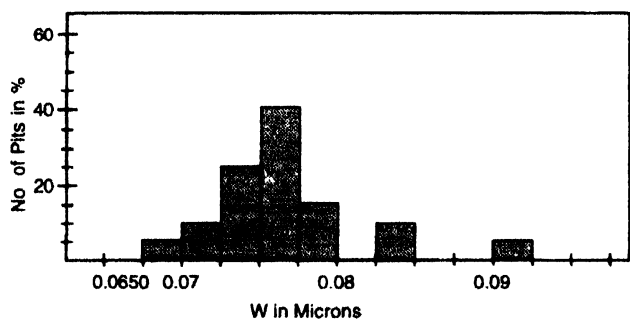
Figure 7a. Histogram of different etch pit size distribution for etchant A at 45°C.
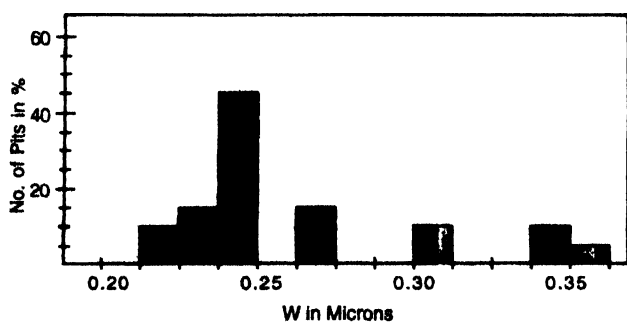
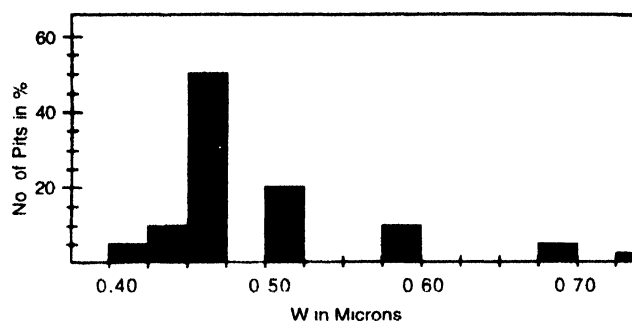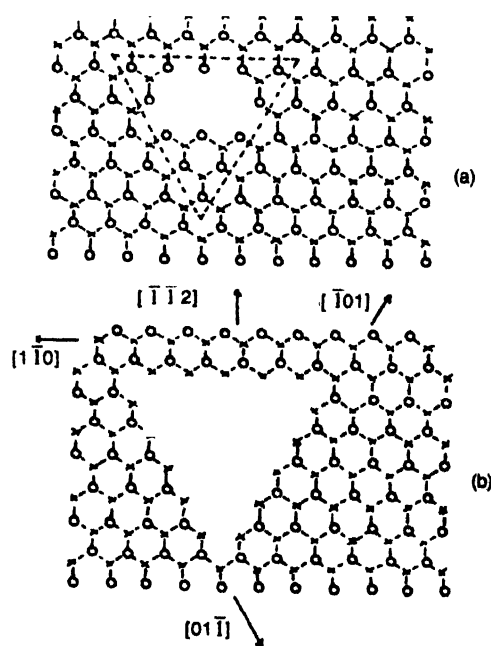Figure 7b. Histogram of different etch pit size distribution for etchant B at 45°C.

Figure 8. Atom removal process considered for (111) surfaces of antimony. Here x indicates a top layer atom bonded to layer below, and o indicates a top layer atom not bonded to layer below. (a) An arbitrary hole in outer layer. (b) A triangular initial pit developed after sequential removal of two-bonded atoms from (a).

steps and the specific rate constant K_j, for step nucleation at the central initiating defect. The model of atom removal process on (111) surfaces of antimony can be shown by Figure (8a, b), where X is a top layer atom bonded to layer below, and O is the top layer atom not bonded to layer below. Figure 8a shows a portion of top layer of (111) surface with several atoms in the central portion removed. The atoms in lower layers are not shown. Assuming that the probability of removal of four and three bonded atoms is very low compared to that of the two bonded atoms. All the atoms within the dashed triangle could be removed by sequential removal of two bonded atoms only. The triangle formed in this way is bounded by <$\overline{1}$10> steps made by only three bonded atoms. Subsequent enlargement of triangle is slower and expected to take place only by first removing a three bonded atom from one of the steps. This way, the formation of triangle etch pit on (111) cleavage plane of antimony can be explained which corresponds to the formation of pits suggested by Angus and Dyble [27].

Raval *et al* [18] selected the etchants containing malic acid in different amounts by keeping the total volume of the etchant constant and found that the values of activation energy and frequency factor increase initially, then decrease with the increase of malic acid content; which indicates the presence of a critical point where a deviation from the normal behaviour takes place. Also, they suggested that the specific composition of oxidizing agent (nitric acid) as well as composition of complexing agent (malic acid) is responsible for modifying the kink kinetics in such a way that a critical point is observed. This has been discussed in detail by the same authors. In the present case, the total compositions of etchants are not kept constant as in the earlier study conducted by Raval *et al* [18]. Hence, no critical point is observed and the activation energy and frequency factor increase with the content of malic acid in the etchants which suggest that the kink kinetics are not modified.

4. Conclusions

(i) Antimony single crystal is grown by horizontal Chalmer's technique in a specially designed graphite boat. The dislocation etching by malic acid containing etchants produce well-defined crystallographically oriented triangular etch pits, which reveal the dislocations of (111)[10$\overline{1}$] type.

(ii) As the amount of malic acid increases in the etchants, the values of activation energy, frequency factor and the distribution of etch pit size on higher widths also increase. The activation energy is a barrier to the reaction and as its value increases the reaction rate is expected to decrease. The higher values of etch-pit widths are observed for higher malic acid contents, though the values of activation energy are high, which are due to the influence of the frequency factors.

(iii) The higher negative values of entropy suggests the presence of activated complex. As the amount of malic

acid increases, the presence of activated complex diminishes.

(iv) There is an absence of critical point which otherwise indicates a deviation from normal behaviour of variations, observed earlier in antimony [18].

Acknowledgment

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