Reactivity at line defects in bismuth : effect of chlorine substitution in acetic acid in the etchant

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Abstract : Etching studies were carried out to study the effect of chlorine substitution in the etchant on the lateral motion of steps at dislocations on the (111) cleavage surfaces of bismuth single crystal. The activation energies for the lateral motion of ledges at dislocations, the frequency factors, the standard enthalpy of activation, the entropy and the standard Gibbs energy for activation were calculated for the etchants containing monochloro-, dichloro- and trichloro-substituted acetic acids as well as trifluoro-substituted acetic acid and mono-substituted acetic acid

1. Introduction

The heterogeneity of reactivity of crystal surfaces have been known since long times. In the case of etch-pits, the existence of an interrelation between the heterogeneities and dislocations in crystals was suggested by Read and Schokley [1]. Recent advances in the theories of crystal growth, electrochemistry and metal physics help in understanding how a metal dissolves and why the rates vary over its surfaces.

Dissolution and vaporization could be considered to a great extent the reverse process of crystal growth. These two processes are useful in the revelation of the emergent ends of dislocations on free surfaces. Both the processes, together with chemical reactivity, in general, rely on the fact that some extra energy is associated with dislocation lines, hence, a preferential attack occurring on the surface.

Studies of the reactivity at line defects in bismuth crystals have been reported from the authors' laboratory earlier [2–8]. In the present investigation, the authors have calculated

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the values of activation energy for lateral motion of steps at dislocations, the frequency factors, the standard enthalpy of activation and the standard change in internal energy in passing from initial state to the activated state.

2. Experimental

Single crystals of bismuth used in the present study, were grown by the horizontal zone-levelling method. The container was a pyrex glass tube, 10 cm in length and 1 cm in diameter. Metal of 5N purity, obtained from Nuclear Fuels Complex, Hyderabad, was placed in the container, evacuated and sealed. This was then placed in the zone-levelling setup. A trolley furnace having a temperature gradient of 52°C/cm travelled with a speed of 1 cm/hr and after several passes, good quality single crystals were obtained. The crystals were cleaved at liquid nitrogen temperature in conventional manner. The crystals were then rinsed in alcohol followed by ether and air dried.

The etchants used in the present study were freshly prepared from AR grade chemicals. The freshly cleaved surfaces were etched, washed in water followed by a rinse of alcohol, ether and finally air dried. High temperature etching was performed by raising the temperature of the samples and the etchants. The etchants were tested for their reliability of revealing dislocations by testing for the one-to-one correspondence of etch-pits on the counterparts of cleavages and successive etching to see if any increase in the etch-pit density took place. The etch pit widths were measured using a comparator.

The following mentioned etchants were used to etch (111) cleavages of bismuth single crystals.

(A) The etchants having chlorine substitution for hydrogen :

    (1) Etchant E-1, 2 cc fuming HNO_3 + 3 cc 1N $CH_2ClCOOH$

    (2) Etchant E-2, 2 cc fuming HNO_3 + 3 cc 1N $CHCl_2COOH$

    (3) Etchant E-3, 2 cc fuming HNO_3 + 3 cc 1N CCl_3COOH

(B) The etchants containing mono substituted acetic acid :

    (4) Etchant E-1, 2 cc fuming HNO_3 + 3 cc 1N $CH_2ClCOOH$

    (5) Etchant E-4, 2 cc fuming HNO_3 + 3 cc 1N $CH_2BrCOOH$

    (6) Etchant E-5, 2 cc fuming HNO_3 + 3 cc 1N CH_2ICOOH

(C) The etchants containing tri-substituted acetic acid :

    (7) Etchant E-3, 2 cc fuming HNO_3 + 3 cc 1N CCl_3COOH

    (8) Etchant E-6, 2 cc fuming HNO_3 + 3 cc 1N CCF_3COOH

Table 1 indicates the etchants used in the present investigation. All the etchants produced triangular crystallographically oriented etch pits revealing the dislocation of (111)
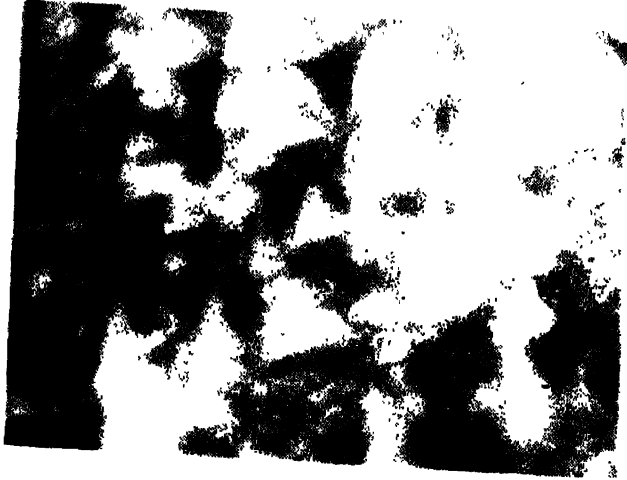
Plate I

Figure 1. Triangular etch pits are produced on (111) cleavage plane of bismuth in monochloro acetic acid containing etchant for 5 seconds at 313° K.

Figure 2. The types of etch pits are revealed by etching (111) cleavages of bismuth in etchants containing dichloro acetic acid for 5 seconds at 313° K.

[10$\bar{1}$] type. Figures 1 and 2 show the types of etch pits produced by etching in monochloro acetic acid and dichloro acetic acid containing etchants, respectively.

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

	Etchant	Activation energy	Frequency factor	Entropy	Enthalpy of activation	Gibbs energy for activation
		KJ mol^{-1}		$\Delta^{\neq}S^{\circ}$ JK^{-1} mol^{-1}	$\Delta^{\neq}H^{\circ}$ KJ mol^{-1}	$\Delta^{\neq}G^{\circ}$ KJ mol^{-1}
	E–1	38.53	3.990	–233.84	35.92	109.12
'A'	E–2	27.93	1.700	–240.92	25.33	100.74
	E–3	36.6	3.55	–234.81	33.99	107.49
	E–1	38.53	3.990	–233.84	35.92	109.12
'B'	E–4	57.79	6.73	–233.95	55.18	128.41
	E–5	39.49	2.77	–236.87	36.88	111.02
'C'	E–3	36.6	3.55	–234.81	33.99	107.49
	E–6	23.12	2.24	–238.64	20.51	95.21

A = Chlorine substitution for hydrogen in acetic acid.

B = Mono substituted acetic acid.

C = Tri substituted acetic acid.

3. Results and discussion

The reactivity at line defects on (111) cleavage planes of bismuth single crystals have been extensively studied by using etchants containing monocarboxylic acids [4], alcohols [5,6], monosubstituted acetic acid [7] and trifluoroacetic acid and trichloroacetic acid [8]. In the present study, the authors report the thermodynamic and kinetic parameters for monosubstituted acetic acid and trifluoroacetic acid and trichloroacetic acid containing etchants in continuation of earlier studies [7,8].

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

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

where W is the 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 frequency factors have been calculated from plots of logarithm of W versus $1/T$.

The theory of reaction rates were published almost simultaneously by Eyring [9] and Evans and Polanyi [10] is now referred to as Conventional Transition-State Theory (CTST) [11-]. Sometimes, it is convenient to express rate constants in terms of thermodynamic

quantities. The thermodynamic formulation of CTST is due to Wynne-Jones and Eyring [14]. The standard entropy of activation $\Delta^* S^\circ$ can be calculated by using the following equation ;

$$A = (kT / h)e^{\Delta^* S^\circ / R},\tag{2}$$

where k is the Boltzmann constant and h is the Planck's constant. The standard enthalpy of activation $\Delta^* H^\circ$ can be calculated for various temperatures using the activation energy as mentioned below :

$$\Delta^* H^\circ = E - RT.\tag{3}$$

The standard Gibbs energy of activation $\Delta^* G^\circ$ is also possible to calculate at different temperatures with the help of the following expression

$$\Delta^* G^\circ = \Delta^* H^\circ - T\Delta^* S^\circ.\tag{4}$$

Table 1 lists the values of activation energy, frequency factor, standard enthalpy of activation, standard Gibbs energy of activation and standard entropy of activation. The values of $\Delta^* H^\circ$, $\Delta^* S^\circ$ and $\Delta^* G^\circ$ were calculated at 313°K temperature. It can be observed that on increasing chlorine substitution for hydrogen in acetic acid, the activation energy, the frequency factor, the Gibbs energy for activation and the enthalpy of activation decrease initially and then increase; whereas in the case of mono-substituted etchants, the behaviour is just opposite to that of the chlorine substituted etchants. For tri-substituted etchants, the values are low in the case of trifluoro acetic acid with comparison to trichloro acetic acid. Moreover, the values of entropy remains more or less constant for all etchants. Also, the large negative values of $\Delta^* S^\circ$ and small values of A indicate that the formation of the intermediate complex compound is the rate determining step, which corresponds to the results of Garchar and Parsania [15] for bromination of bis-phenol-C and bis-phenol-S in acetic acid.

Shah *et al* [5] have reported that etching (111) cleavages of bismuth in propyl alcohol containing etchants, a critical dilution is observed at which the activation energy and frequency factor are low with comparison to other concentrations. However, this trend is opposite to that of ethyl alcohol containing etchants. The critical point indicates a deviation in the normal trend of the reaction. It can be conjectured that at the critical concentration, a change in the kink kinetics is taking place. Recently, Raval *et al* [16] have supported these results in antimony crystals. In the present study, the existence of critical point further supports earlier observations and indicates the change occurring in the kink kinetics.

4. Conclusions

(1) All the etchants reveal dislocations of (111) [10$\bar{1}$] kind.

(2) The variation of thermodynamic parameters, such as, the entropy, the standard enthalpy of reaction and the Gibbs energy for activation is similar to that of the activation energy and frequency factor.

(3) The large negative values of entropy and small values of frequency factor indicate that the formation of intermediate complex compound is the rate determining step.

(4) A critical point is observed where a deviation in normal behaviour is observed for chlorine substituted for hydrogen in the etchants and mono-substituted etchants. This corresponds to the earlier results in bismuth and antimony and suggests a modification in kink kinetics in the ledges within the etch pits.

Acknowledgments

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