Effect of the Concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NH_4OH in Young's Etchant on the Dissolution of (111) Surface of Cu Single Crystals*

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The dissolution of the (111) surface of Cu single crystals was studied as a function of concentration of oxidizer $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and complexing agent NH_4OH in Young's solution $((\text{NH}_4)_2\text{S}_2\text{O}_8\text{--NH}_4\text{OH--NH}_4\text{Br})$. The etching was carried out for 10 s at 280 K with a crystal rotation 4 s^{-1} using the rotation disc method. The dissolved depth of matrix surface S was obtained by two-beam interferometric measurement of the step height produced at the boundary between the masked surface and the exposed surface to the etching. The width h and depth d of etch pits formed at edge dislocation sites on the exposed surface were determined by replica electron microscopy. The dissolved quantities along lateral and longitudinal directions at dislocation H and D were determined from S , h and d , respectively.

As the concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH in the etchant was increased, the following features were observed: (a) the lateral dissolution at the dislocation site, H , increased monotonically, (b) the longitudinal dissolution at the dislocation site, D , attained a maximum value at the intermediate concentration and (c) the matrix dissolution, S , increased slightly. These results were discussed on the basis of the two-dimensional nucleation theory of crystal dissolution.

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I. Introduction

Several chemical etchants for revealing dislocation sites by surface pits in copper single crystal have been developed^{(1)–(6)}. Young⁽³⁾ recommended a solution containing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ $1\text{ kmol}\cdot\text{m}^{-3}$, NH_4OH $6\text{ kmol}\cdot\text{m}^{-3}$ and NH_4Br $0.3\text{ kmol}\cdot\text{m}^{-3}$ as a good one for revealing dislocation pits on the (111) surface of copper crystal. In this solution, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ reacts as an oxidizer and will ionize Cu atoms on the dissolving surface. The Cu ions are complexed with ammonium ions when NH_4OH is added, and the rate of attack is increased. While, with addition of NH_4Br , bromic ions are adsorbed on the dissolving surface as poisons and retard the dissolution of Cu atoms into the solution. Previously, the present authors⁽⁷⁾⁽⁸⁾ have investigated the effect of the concentration of NH_4Br from 0.2 to $2.0\text{ kmol}\cdot\text{m}^{-3}$ in the etchant on the dissolution at edge dislocation sites on Cu (111) surface and discussed the experimental results on the basis of the two-dimensional nucleation theory of crystal dissolution. The lateral dissolution at the dislocation site decreased markedly with an increase of NH_4Br concentration. It was considered that a fraction of step sites which were poisoned by bromic ions increased with an increase in NH_4Br concentration, thereby slowing down remarkably the step motion due to a removal of atoms from the step. The longitudinal dissolution along disloca-

tion line attained a maximum value at the intermediate concentration of NH_4Br . This could be ascribed to the variation of formation energy of critical etch pit nucleus at the dislocation site arising from the concentration dependence of the interfacial energy and the difference in chemical potential between Cu atoms at the step and in the etchant. The dissolution of matrix surface was practically constant regardless of the concentration of NH_4Br . This could be interpreted in terms of the concentration dependence of formation energy of critical nucleus at the dislocation-free site and the poison adsorption at the step of nucleus.

It is interesting to know how the oxidizer $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and complexing agent NH_4OH affect the dissolution at dislocation site as well as dislocation-free site on Cu (111) surface. So, we have now examined this problem as an extension of our previous investigation⁽⁷⁾⁽⁸⁾.

II. Experimental Procedure

The method of preparing a Cu single crystal, revealing the (111) face and its etching is quite the same as that reported in a previous paper⁽⁷⁾⁽⁸⁾. A crystal piece (99.998% pure Cu, $\sim 10\text{ mm}$ in diameter and $10\text{--}15\text{ mm}$ in length) which was cut out from Czochralski Cu [111] crystal with an acid cutter was embedded in a PVC holder so as to expose the (111) face. A mirrorlike (111) surface was obtained by a chemical polishing followed by an electrolytic polishing in conc H_3PO_4 at a voltage of 1.5 V for about $1.1 \times 10^4\text{ s}$ (3h). After a piece of vinyl tape with a hole 6 mm in diameter was affixed on the polished surface, the etching was carried out in Young's solution at 280 K for 10 s with a crystal rotation 4 s^{-1}

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Fig. 1 Relation between etch-pit formation and dissolution of a matrix surface. (a) Normal view and (b) sectional view.

using the rotation disc method. As described in I, Young's solution consists of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ $1 \text{ kmol} \cdot \text{m}^{-3}$, NH_4OH $6 \text{ kmol} \cdot \text{m}^{-3}$ and NH_4Br $0.3 \text{ kmol} \cdot \text{m}^{-3}$, which will be referred to as standard solution in the following. In the present investigation,

- (1) the concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was varied from 0.4 to $1.5 \text{ kmol} \cdot \text{m}^{-3}$, keeping the concentration of the other two components at the standard ones, and
- (2) the concentration of NH_4OH was varied from 4 to $10 \text{ kmol} \cdot \text{m}^{-3}$, keeping the concentration of the other two components at the standard ones, respectively.

The procedure of measuring the dissolved quantities was also similar to that taken in a previous investigation⁽⁷⁾⁽⁸⁾. As illustrated in Fig. 1, dislocation etch pits of triangular pyramidal shape are formed on the exposed surface and a step is developed along a boundary line between the exposed surface and the masked surface. The step height S which corresponds to the dissolved depth of matrix surface was determined by means of two-beam interferometry. Previously, we found that etch pits which were seen dark and light under an optical microscope of low magnification corresponded to edge dislocations of positive and negative signs⁽⁹⁾⁽¹⁰⁾, respectively. The width h and depth d of the dark etch pits were measured by replica electron microscopy. The net dissolved depth along the dislocation line, D , is given by

$$D = S + d \quad (1)$$

and the dissolved distance parallel to the surface, H , is expressed by

$$H = \frac{(S + d)h}{d} \quad (2)$$

III. Experimental Results

1. Effect of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration on crystal dissolution

Figure 2 is typical electron micrographs showing a morphological change of edge-dislocation etch pit with the concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the etchant. The etch pit produced by the etchant containing $0.4 \text{ kmol} \cdot \text{m}^{-3}$ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ has a triangular pyramidal shape of which sides are somewhat rounded and stepped (Fig. 2(a)). The side faces of etch pit become flat gradually with an increase of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration and they are sharply outlined at the concentration more than $1.0 \text{ kmol} \cdot \text{m}^{-3}$ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Fig. 2(b)).

Figure 3 shows the results of measurement of the width h , the depth d and the side slope d/h of dislocation etch pits and the dissolved depth of matrix surface S of Cu crystal etched with Young's etchant containing various concentrations of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. S increases monotonically with an increase of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration, while both h and d increase first, attain a maximum value and then decrease with an increase of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration. Corresponding to the variation of h and d , d/h tends to take a maximum at the intermediate concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Changes in dissolved quantities along lateral and longitudinal directions at dislocation sites, H and D , which are calculated from measured values of S , h and d , with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration are shown in Fig. 4.

Fig. 2 Electron micrographs of etch pits revealed at edge dislocation site on the (111) surface of Cu crystal after etching in Young's solution for 10 s at 280 K with a rotation of crystal 4 s^{-1} . The compositions of solution were NH_4OH $6 \text{ kmol} \cdot \text{m}^{-3}$, NH_4Br $0.3 \text{ kmol} \cdot \text{m}^{-3}$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (a) 0.4 and (b) $1.0 \text{ kmol} \cdot \text{m}^{-3}$, respectively.

Fig. 3 Changes in (a) dissolved depth of matrix surface S , (b) width h , (c) depth d and (d) slope d/h of edge-dislocation etch pits on the (111) surface of Cu crystal with concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in Young's solution. Etching was carried out for 10 s at 280 K with a rotation of crystal 4 s^{-1} .

Fig. 4 Changes in dissolved quantities along (a) lateral and (b) longitudinal directions at an edge dislocation site on the (111) surface of Cu crystal with concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in Young's solution. Etching was carried out for 10 s at 280 K with a rotation of crystal 4 s^{-1} .

H increases slightly with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration. D attains a maximum value at the concentration of $1.0 \text{ kmol} \cdot \text{m}^{-3}$ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ which corresponds to the standard solution.

2. Effect of NH_4OH concentration on crystal dissolution

Figure 5 shows typical electron micrographs of edge-dislocation etch pits on Cu (111) surface etched with Young's solution which contains 4 and $10 \text{ kmol} \cdot \text{m}^{-3}$ NH_4OH . When the etchant contains $4\text{--}8 \text{ kmol} \cdot \text{m}^{-3}$ NH_4OH , etch pits of triangular pyramid are sharply outlined (Fig. 5(a)), while they are rounded and stepped when the concentration of NH_4OH exceeds $10 \text{ kmol} \cdot \text{m}^{-3}$ (Fig. 5(b)). This morphological change is in reverse sequence to that occurred when the concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was varied.

Variations of the dissolved depth of matrix surface S , the width h , the depth d and the side slope d/h of dislocation etch pits with NH_4OH concentration are shown in Fig. 6. S increases slightly with increasing NH_4OH concentration and reaches a constant value. h increases somewhat largely with NH_4OH concentration, while d attains a maximum value at the intermediate concentration. d/h decreases slightly with NH_4OH concentration.

Figure 7 shows changes in dissolved quantities along lateral and longitudinal directions at dislocation sites, H and D , with NH_4OH concentration. H shows a small increase with increasing NH_4OH concentration, while D takes a maximum value at the medium concentration.

Effects of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidizer and NH_4OH complexing agent on dissolution of Cu (111) surface in Young's solution are summarized together with our previous results⁽⁷⁾⁽⁸⁾ of NH_4Br inhibitor as follows.

Fig. 5 Electron micrographs of etch pits revealed at edge dislocation site on the (111) surface of Cu crystal after etching in Young's solution for 10 s at 280 K with a rotation of crystal 4 s^{-1} . The compositions of solution were $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 1 kmol m^{-3} , NH_4Br 0.3 kmol m^{-3} and NH_4OH (a) 4 and (b) 10 kmol m^{-3} , respectively.

Fig. 6 Changes in (a) dissolved depth of matrix surface S , (b) width h , (c) depth d and (d) slope d/h of edge-dislocation etch pits on the (111) surface of Cu crystal with concentration of NH_4OH in Young's solution. Etching was carried out for 10 s at 280 K with a rotation of crystal 4 s^{-1} .

Fig. 7 Changes in dissolved quantities along (a) lateral and (b) longitudinal directions at an edge dislocation site on the (111) surface of Cu crystal with concentration of NH_4OH in Young's solution. Etching was carried out for 10 s at 280 K with a rotation of crystal 4 s^{-1} .

(1) The lateral dissolution perpendicular to a dislocation line decreased markedly with an increase of NH_4Br concentration. Contrarily it increased with increasing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH concentration.

(2) The longitudinal dissolution along a dislocation line attained a maximum value as the concentration of any component in the etchant was increased.

(3) The dissolution of matrix surface was nearly constant or slightly increased with an increase of concentration of any component in the etchant. These facts indicate that the effect of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH on the lateral dissolution at dislocation site is the reverse of NH_4Br , while all of these components affect similarly the longitudinal dissolution at dislocation site and the dissolution of matrix surface. These phenomena will be discussed on the basis of the two-dimensional nucleation theory of crystal dissolution.

IV. Discussion

According to thermodynamic considerations on the kinetics of crystal dissolution⁽¹¹⁾⁽¹²⁾, a two-dimensional nucleus of etch pit with one atom depth is nucleated at a site where dislocation line intersects with a close-packed singular plane, and subsequently it grows laterally by a removal of atoms from kink sites of the resultant steps around the nucleus. Repeated nucleation and growth of a two-dimensional etch pit nucleus can give rise to visible etch pit at the dislocation site. Accordingly, the lateral dissolved quantity at a dislocation site H depends on the advance rate of step due to a removal of atoms from it, and the longitudinal one D depends on the nucleation rate of two-dimensional etch pit at a dislocation. The dissolution of matrix surface can also occur by a nucleation and growth process. Two-dimensional nuclei of etch pit with one atom depth are produced randomly at dislocation-free sites on the crystal surface, and they grow laterally until the mutual annihilation occurs by collision of neighboring pits. Successive occurrence of these processes may lead a layer by layer dissolution of matrix surface. Therefore, the dissolved depth of matrix surface S depends on the nucleation rate of two-dimensional etch pit at dislocation-free site as well as the advance rate of step.

1. Variation of the lateral dissolution at a dislocation site H

Previously, the present authors have shown that the removal rate of atoms from a straight step, v_h , which is reflected in the lateral dissolution H , is given by

$$v_h = b^* \chi \nu \left[1 - \theta_1 \left\{ 1 - \exp \left(-\frac{\eta}{kT} \right) \right\} \right] \exp \left(-\frac{\Delta H}{kT} \right) \quad (3)$$

where b^* is one atom spacing normal to the step, χ is an undersaturation, ν is a frequency of atomic vibration, θ_1 is a fraction of poisoned atom at the step, k is Boltzmann constant, T is absolute temperature, ΔH is an activation energy for dissolution of poison-free atom and η is an increment of activation energy for poisoned atom. In eq. (3), b^* , ν , η and ΔH are assumed to be constant and χ is given by

$$\chi = 1 - \exp\left(-\frac{|\Delta g(C)|}{kT}\right) \quad (4)$$

in which $\Delta g(C)$ is the difference in chemical potential between the Cu atoms at the step and in the etchant. If we assume that the etchant is an ideal solution, $\Delta g(C)$ can be written as

$$\Delta g(C) = kT \ln\left(\frac{C_0}{C_s(C)}\right) \quad (5)$$

where C_0 is the initial concentration of Cu in the etchant and $C_s(C)$ is the saturated one. Since $C_s(C) \gg C_0$ regardless of the concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH , we can put $\chi \approx 1$. Accordingly, a main factor creating the variation of v_h (eq. (3)) with the concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH would be a fraction of poisoned atoms with addition of $0.3 \text{ kmol} \cdot \text{m}^{-3}$ NH_4Br in the etchant.

Let us denote the concentration of poisoning species in the etchant by C_1 and those of other adsorbent species with addition of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NH_4OH by C_2 and C_3 , respectively. Then, on the assumption of Langmuir adsorption isotherms, θ_1 is expressed by

$$\theta_1 = \frac{A_1 C_1}{1 + A_1 C_1 + A_2 C_2 + A_3 C_3} \quad (6)$$

in which A_i ($i=1, 2$ and 3) is a constant which depends on a kind of adsorbent species and its temperature⁽¹³⁾. In eq. (6) C_1 is practically constant, though C_2 and C_3 increase with an increase in concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH , respectively, resulting in a decrease of θ_1 and hence an increase of v_h in eq. (3). Thus, the variation of lateral dissolution at dislocation site H shown in Figs. 4(a) and 7(a) can be interpreted in terms of the coverage of steps with poisons.

2. Variation of the longitudinal dissolution at a dislocation site D

The longitudinal dissolution rate along a dislocation line v_d is given by⁽⁷⁾⁽⁸⁾

$$v_d \approx a\nu\chi \exp\left(-\frac{\Delta G_d^*(C) + \Delta H}{kT}\right) \quad (7)$$

in which a is an interatomic distance along dislocation line and $\Delta G_d^*(C)$ is a formation energy of critical two-dimensional nucleus of etch pit at a dislocation site. In this equation, a , ν and ΔH are constant and $\chi \approx 1$. According to Schaarwächter⁽¹²⁾, $\Delta G_d^*(C)$ is given as

$$\Delta G_d^*(C) = \left\{ \gamma(C) - \frac{\alpha\mu b^2}{8\pi^2(1-\sigma)r_0} \right\}^2 \frac{\pi a \Omega}{|\Delta g(C)|} \quad (8)$$

where $\gamma(C)$ is the specific interfacial energy between the crystal surface and the etching solution, μ is the rigidity modulus, b is the magnitude of Burgers vector, σ is Poisson's ratio, r_0 is the radius of dislocation core, α is a factor depending on dislocation characters, e.g., $\alpha \approx 1.8$ – 2 for an edge dislocation and Ω is the volume of a single atom in the crystal. The variation of interfacial energy with adsorption is approximated by means of Gibbs and

Langmuir equations as⁽¹⁴⁾

$$\begin{aligned} \gamma(C) = \gamma_0 + kT\Gamma_m \ln \left\{ \left(1 - \frac{A_1 C_1}{1 + A_1 C_1 + A_2 C_2 + A_3 C_3} \right) \right. \\ \times \left(1 - \frac{A_2 C_2}{1 + A_1 C_1 + A_2 C_2 + A_3 C_3} \right) \\ \left. \times \left(1 - \frac{A_3 C_3}{1 + A_1 C_1 + A_2 C_2 + A_3 C_3} \right) \right\} \end{aligned} \quad (9)$$

where γ_0 is the interfacial energy without adsorption and Γ_m is the saturated amount of all the adsorbent per unit area. As C_2 or C_3 increases, $\gamma(C)$ decreases (refer to eq. (9)), which results in a decrease of $\Delta G_d^*(C)$ (refer to eq. (8)) and hence an increase of v_d (refer to eq. (7)). The experimental result shows that v_d first increased with an increase of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH concentration, attained a maximum value at its intermediate concentration and then decreased (see Figs. 4(b) and 7(b)). This fact cannot be explained only by the decrease of $\gamma(C)$ with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH concentration.

It can be seen from eqs. (7) and (8) that v_d depends on the difference in chemical potential $\Delta g(C)$ in the exponential, so that it may vary markedly with a small change of $\Delta g(C)$. Then, if $|\Delta g(C)|$ decreases with an increase of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH concentration, $\Delta G_d^*(C)$ which is given by the product of the increasing function $|\Delta g(C)|^{-1}$ and the decreasing one $\{\gamma(C) - \alpha\mu b^2 / 8\pi^2(1-\sigma)r_0\}^2$ can take a minimum value and hence v_d attains a maximum value at the intermediate concentration of each component. This can explain qualitatively the experimental results on longitudinal dissolution at dislocation site D shown in Figs. 4(b) and 7(b).

3. Variation of the matrix dissolution S

The dissolution rate of matrix surface v_s is given by⁽⁷⁾⁽⁸⁾

$$\begin{aligned} v_s \approx a\nu \left(\frac{b^*}{b}\right)^{1/3} \left[1 - \theta_1 \left\{ 1 - \exp\left(-\frac{\eta}{kT}\right) \right\} \right]^{2/3} \\ \times \chi \exp\left(-\frac{\Delta G_s^*(C) + 3\Delta H}{3kT}\right) \end{aligned} \quad (10)$$

where $\Delta G_s^*(C)$ is a formation energy of critical two-dimensional nucleus of etch pit at dislocation-free sites on the matrix surface which is given by⁽¹²⁾

$$\Delta G_s^*(C) = \frac{\pi a \Omega \gamma(C)^2}{|\Delta g(C)|} \quad (11)$$

As described in IV.1, θ_1 decreases with increasing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH concentration. This leads to an increase in v_s . In the similar manner as $\Delta G_d^*(C)$ described in IV.2, $\Delta G_s^*(C)$ decreases through the term $\gamma(C)^2$ but it increases through the term $|\Delta g(C)|^{-1}$ with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH concentration. As easily seen from a comparison of eq. (8) with eq. (11), the increase due to the term $|\Delta g(C)|^{-1}$ contributes to $\Delta G_s^*(C)$ with the same extent as to $\Delta G_d^*(C)$, while the decrease due to the term $\gamma(C)^2$ contributes to $\Delta G_s^*(C)$ larger than to $\Delta G_d^*(C)$. Consequently, the competition between these two terms may yield a slight decrease of $\Delta G_s^*(C)$ and hence an increase

of v_s with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH concentration. It is considered that v_s is increased through the twofold effects due to θ_1 and $\Delta G_s^*(C)$ as the concentration of each component in the etchant increases (see Figs. 3(a) and 6(a)).

V. Conclusion

The effect of concentrations of oxidizer $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and complexing agent NH_4OH in Young's etchant $((\text{NH}_4)_2\text{S}_2\text{O}_8\text{--NH}_4\text{OH--NH}_4\text{Br})$ on the dissolution at edge dislocation site on (111) surface of Cu single crystal was examined. The concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was varied from 0.4 to 1.5 $\text{kmol}\cdot\text{m}^{-3}$, keeping the concentration of NH_4OH at 6 $\text{kmol}\cdot\text{m}^{-3}$ and that of NH_4Br at 0.3 $\text{kmol}\cdot\text{m}^{-3}$, and the concentration of NH_4OH was changed from 4 to 10 $\text{kmol}\cdot\text{m}^{-3}$, keeping the concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at 1.0 $\text{kmol}\cdot\text{m}^{-3}$ and that of NH_4Br at 0.3 $\text{kmol}\cdot\text{m}^{-3}$, respectively. The etching was carried out at 280 K for 10 s by the rotating disc method with a crystal rotation of 4 s^{-1} . The width h and depth d of dislocation etch pit were determined by replica electron microscopy and the dissolved depth of matrix surface S was measured by two-beam interferometry. From the measured values of h , d and S , the dissolved quantities along lateral and longitudinal directions at dislocation site were obtained. The experimental results were discussed on the basis of the two-dimensional nucleation theory of crystal dissolution. The results are summarized as follows.

(1) The lateral dissolution at dislocation site H increased with an increase of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH concentration. This can be attributed to a reduction of poisoning by adsorption of bromic ions at steps. Since a fraction of step sites covered by poisons decreases as the concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH increases, the step motion due to a removal of atoms from kink sites becomes easier and hence H increases.

(2) The longitudinal dissolution along dislocation line D attained a maximum value at the intermediate concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH in the etchant. It is

inferred that a formation energy of critical two-dimensional nucleus of etch pit decreases due to the lowering of interfacial energy, while it increases due to the lowering of absolute value of chemical potential difference as the concentration of each component increases. The cancellation of these terms yields a minimum value of the formation energy of critical nucleus and hence D attains a maximum value at the intermediate concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH .

(3) The matrix dissolution S increased slightly with increasing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or NH_4OH concentration. This can be ascribed to an enhancement of dissolution due to the lowering of formation energy of two-dimensional critical nucleus of etch pit at dislocation-free sites on matrix surface and that due to a reduction of the poison adsorption at the step of nucleus.

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