Temperature Dependence of the Dissolution Rates of the (111) Surface of Copper Single Crystals Etched in Young's Solution*

Shigeo Sugawara** and Jirô Watanabé**

The effect of etching temperature on the dissolution rates at edge dislocation and dislocation-free sites of the (111) surface of copper single crystals was studied. The etching was carried out at temperatures 270 to 285 K for 5 to 25 s with Young's etchant 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 $0.3 \text{ kmol} \cdot \text{m}^{-3}$. From the measured data on the width and depth of dislocation etch pits and the dissolved thickness of the (111) matrix surface as a function of etching time, the lateral dissolution rate across the surface at dislocation v_h , the longitudinal one along dislocation v_d , and the dissolution rate normal to the surface at dislocation-free sites v_s , were determined. It was found that the dissolution rates were in the order of $v_h > v_d > v_s$ at any temperature and that they increased as the etching temperature increased. These results were qualitatively discussed on the basis of the kinetic theory of two-dimensional nucleation and step motion for crystal dissolution, and some kinetic quantities relating to the formation of two-dimensional nucleus and the step motion were evaluated.

(Received August 6, 1990)

Keywords: etch pit, dislocation, crystal dissolution, copper crystal, electron microscopy, interferometry, two-dimensional nucleation theory

I. Introduction

As is well known, when a low-index crystal face is subjected to an appropriate chemical or thermal environment, some layers of the crystal surface are removed by etching or evaporation, and simultaneously etch pits are revealed at the intersections of dislocations and the crystal surface. The mechanism of this crystal dissolution is considered as follows⁽¹⁾⁻⁽⁴⁾. As demonstrated schematically in Fig. 1, a two-dimensional nucleus of the etch pit with one atomic depth occurs preferentially at the dislocation site, since the strain energy associated with the dislocation can lower the activation energy for nucleation appreciably. The etch pit grows laterally by the removal of atoms from the step around the nucleus, and it deepens longitudinally by the subsequent nucleation at the exposed dislocation site. Repeating the proc-

Fig. 1 Schematic illustration of dissolution at a dislocation site and a dislocation-free site of low-index crystal surface.

* This paper was originally published in Japanese in J. Japan Inst. Metals, **53** (1989), 1079.

** Department of Materials Engineering and Applied Chemistry, Mining College, Akita University, Akita 010, Japan.

ess of the nucleation and growth would lead to the formation of a visible etch pit at the site of the dislocation. Accordingly, the longitudinal dissolution rate along the dislocation line, v_d , may depend on the nucleation rate of the two-dimensional nucleus of dislocation etch pit, and the lateral one perpendicular to the dislocation line, v_h , may depend on the removal rate of atoms from the step site.

The dissolution of the crystal surface may also occur at dislocation-free sites with the process of nucleation and growth of two-dimensional nuclei. As shown in Fig. 1, two-dimensional nuclei of etch pits are formed randomly at dislocation-free sites, and they grow laterally by the advance of steps due to the removal of atoms, until the mutual annihilation of two-dimensional etch pits occurs by collision of neighboring steps. Successive occurrence of these processes may result in a layer by layer dissolution of matrix surface. Therefore, the dissolution rate of the matrix surface, v_s , may depend on the nucleation rate of the two-dimensional nucleus of the etch pit at the dislocation-free site as well as the removal rate of atoms from the step site.

Previously, the present authors have investigated the effect of concentrations of components in Young's etchant⁽⁵⁾ $((\text{NH}_4)_2\text{S}_2\text{O}_8\text{--NH}_4\text{OH--NH}_4\text{Br})$ on the dissolution at edge dislocation sites and dislocation-free sites of the (111) surface of copper single crystal⁽⁶⁾⁻⁽⁹⁾. We determined the dissolved depth along the dislocation line (the longitudinal dissolution quantity), the dissolved distance across the crystal surface at the dislocation (the lateral dissolution quantity) and the dissolved thickness of the matrix surface after etching for 10 s at 280 K with the etchant of specified composition. As the concentration of NH_4Br inhibitor in the etchant increased, the lateral

dissolution quantity decreased remarkably, while it increased with an increase of concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidizer or NH_4OH complexing agent in the etchant. The longitudinal dissolution quantity reached a maximum value at an intermediate concentration of each component in the etchant. The dissolved thickness of matrix surface showed a slight increase or a constant value when the concentration of each component in the etchant increased. It was shown that these results could be explained qualitatively on the basis of the two-dimensional nucleation theory by considering the variations of the coverage of crystal surface by Br^- ions, the interfacial energy and the difference in chemical potentials when the concentration of each component in the etchant was increased⁽⁶⁾⁻⁽⁹⁾.

It is very interesting how the dissolution at dislocations is influenced by the etching temperature. Although research in this field is rather scant, some researchers have developed some information. Ives and Hirth⁽¹⁰⁾ studied the effect of etching temperature on the growth rate of dislocation etch pit on LiF (100) face which was etched with water containing a small amount of Fe^{3+} ion. They found that the widening rate of the etch pit became larger at high temperatures. It was shown experimentally by Toropov and Udalov⁽¹¹⁾ that the rates of widening and deepening of dislocation etch pit on KBr (100) face, etched with isopropyl alcohol containing a small amount of PbBr_2 and H_2O , increased exponentially with the increase of the etching temperature.

In this paper, we present the experimental results of the effect of etching temperature on the dissolution rates at dislocation and dislocation-free sites of Cu (111) surfaces in Young's standard etchant⁽⁵⁾.

II. Experimental Procedure

Copper single crystal used as a specimen and the procedure taken for preparing (111) face and its etching were the same as those described in our previous report⁽¹²⁾⁽¹³⁾ on the dissolution rates of Cu (111) surface in Young's standard etchant at 290 K. The mirrorlike (111) surface was obtained by polishing chemically and electrolytically. Two pieces of vinyl tape 2 mm in width were affixed on the polished surface. After the specimen was beforehand held at the same temperature as that to be tested, the etching was carried out for 5, 10, 15, 20 and 25 s in Young's standard etchant which consisted of $1 \text{ kmol} \cdot \text{m}^{-3}$ $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $6 \text{ kmol} \cdot \text{m}^{-3}$ NH_4OH and $0.3 \text{ kmol} \cdot \text{m}^{-3}$ NH_4Br . Tested temperatures were 270, 275, 280 and 285 K, respectively.

As illustrated in Fig. 2, a step was produced along the boundary line between the masked surface and the exposed surface, the step height S corresponding to the dissolved thickness of the matrix surface. Two-beam interferometry was used to determine the step height. The width h and the depth d of the triangular pyramid etch pits which were observed at the edge dislocation sites on the exposed surface were measured by means of replica electron microscopy.

Fig. 2 Schematic structure of Cu crystal etched with Young's etchant. h and d are the width and depth of an etch pit on the (111) surface, respectively and S is the dissolved thickness of (111) matrix surface. (a) Normal view and (b) sectional one.

Fig. 3 Electron micrographs of an etch pit formed at the intersection of edge dislocation with the (111) surface of Cu crystal. Etching was carried out in Young's etchant for 20 s at (a) 270 K and (b) 285 K.

Figure 3 illustrates typical electron micrographs of dislocation etch pits on Cu (111) surface etched with Young's etchant for 20 s at 270 and 285 K. It was experimentally confirmed that these etch pits appeared dark under an optical microscope of low magnification, and they corresponded with an edge dislocation of positive sign⁽¹⁴⁾⁽¹⁵⁾. When the etching temperature or time increased, the etch pit increased in size keeping the shape of a triangular pyramid.

As is easily seen from Fig. 2, the longitudinal dissolution quantity along the dislocation line, D , is given by

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

and the lateral dissolution quantity, H , perpendicular to the dislocation line is expressed by

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

III. Experimental Results

Figure 4(a)–(d) illustrates the etching-time variation of the matrix dissolution S and width h , depth d and side face slope d/h of the edge dislocation etch pits on Cu (111) surface for temperatures 270 to 285 K together with the data at 290 K which were obtained in the previous

investigation⁽¹²⁾⁽¹³⁾. Each value of S , h and d increases linearly with the etching time t except for the early stage of etching. The time dependence of steady dissolution is written as⁽¹²⁾⁽¹³⁾

$$\left. \begin{aligned} S &= \dot{S}t + S_0 \\ h &= \dot{h}t + h_0 \\ d &= \dot{d}t + d_0 \end{aligned} \right\} \quad (3)$$

in which $\dot{S}$, $\dot{h}$ and $\dot{d}$ are the rates of increase in S , h and d with time t , and S_0 , h_0 and d_0 are constants, respectively. $\dot{S}$ corresponds to the dissolution rate of the matrix surface v_s as defined by

$$\dot{S} = \frac{dS}{dt} = v_s. \quad (4)$$

From eq. (3), d/h is written as⁽¹²⁾⁽¹³⁾,

$$\begin{aligned} \frac{d}{h} &= \frac{\dot{d}t + d_0}{\dot{h}t + h_0} \\ &= \frac{\dot{d}}{\dot{h}} \left(1 - \frac{t_h - t_d}{t + t_h} \right), \end{aligned} \quad (5)$$

where

$$t_h = \frac{h_0}{\dot{h}}, \quad t_d = \frac{d_0}{\dot{d}}. \quad (6)$$

Equation (5) indicates that d/h approaches a constant value $\dot{d}/\dot{h}$ asymptotically with an increase of t . It can be seen from Fig. 4(d) that the measured value of d/h changes very little with t at any temperature so that it can be practically regarded as constant. According to the descriptions in the previous report⁽¹²⁾⁽¹³⁾, when d/h is constant, the lateral dissolution rate at dislocation site v_h and the longitudinal one v_d are given, respectively, by

$$\left. \begin{aligned} v_h &= \frac{dH}{dt} = (\dot{S} + \dot{d}) \frac{h}{d}, \\ v_d &= \frac{dD}{dt} = (\dot{S} + \dot{d}). \end{aligned} \right\} \quad (7)$$

Figure 5 shows the temperature variation of v_h , v_d and v_s as calculated from eqs. (4) and (7) using the value of $\dot{S}$, $\dot{h}$ and $\dot{d}$ that are determined from Fig. 4. It can be seen that the dissolution rates v_h , v_d and v_s increase as the etching temperature is increased.

IV. Discussion

1. Temperature dependence of the lateral dissolution rate at dislocation

As described in the Introduction (I), a two-dimensional nucleus of an etch pit can be easily produced at the intersection of a dislocation and a crystal surface. The nucleus grows laterally by the removal of atoms from the resultant step around the nucleus, and then the next nucleus is formed at the exposed dislocation outcrop. By a repetition of the nucleation and growth process, the dissolution at the dislocation site would occur^{(1)–(4)}. Ac-

Fig. 4 Changes in S , h , d and d/h with etching time t at temperatures 270 to 285 K. The data at 290 K are those obtained in the previous investigation⁽¹²⁾⁽¹³⁾.

Fig. 5 Temperature dependence of the dissolution rates v_h , v_d and v_s . The data at 290 K are those obtained in the previous study⁽¹²⁾⁽¹³⁾.

cordingly, the lateral dissolution rate at dislocation v_h may depend on the removal rate of atoms from step sites, and the longitudinal dissolution rate at dislocation v_d may depend on the nucleation rate of the two-dimensional etch pit nucleus. If v_h is much larger than v_d , the etch pit would become so shallow that it could not be observed under an optical microscope. In a readily observable etch pit, the slope of the side faces exceeds ~ 0.1 giving the ratio $v_d/v_h \geq 0.1$. Therefore, a dislocation etchant usually contains a poison which is adsorbed at the step sites, thereby slowing down the removal rate of atoms from the step⁽¹⁾. In Young's etchant, bromic ion may act as the poison⁽⁵⁾⁻⁽⁷⁾. It is to be added that the removal of atoms from the $\langle 110 \rangle$ straight steps occurred during dissolution of Cu (111) face in Young's etchant (see Figs. 2 and 3).

Previously, the present authors⁽⁶⁾⁻⁽⁹⁾ have made an approximate treatment of the removal rate of atoms from a straight step, taking account of the coverage of adsorption of poisons and the resistance for the dissolution due to poisoning. An obtained expression for v_h is

$$v_h = b^* \chi v \left[1 - \theta_1 \left\{ 1 - \exp \left(-\frac{\eta}{kT} \right) \right\} \right] \times \exp \left(-\frac{\Delta H}{kT} \right), \quad (8)$$

where

$$\theta_1 = \frac{A_1 C_1}{1 + A_1 C_1 + A_2 C_2 + A_3 C_3}, \quad (9)$$

$$A_i = K_i \exp \left(\frac{\Delta H_i}{kT} \right). \quad (10)$$

In eq. (8), b^* is one atomic spacing along the advance

direction of the step; χ is a degree of undersaturation; v is a frequency of atomic vibration; θ_1 is a fraction of the step sites occupied by poisons; ΔH is an activation energy for dissolution of poison-free Cu atom; η is an increment of activation energy for dissolution of poisoned Cu atoms; k is a Boltzmann constant, and T is an absolute temperature. In eq. (9), C_1 denotes a concentration of poisonous species (bromic ion due to a dissociation of NH_4Br molecules) in the etchant, C_2 and C_3 those of other adsorbent species (those concerned with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NH_4OH molecules) in the etchant, respectively and A_i ($i=1, 2$ and 3) is a function of a heat of adsorption ΔH_i and a reverse of the rate constant for i component K_i as given in eq. (10).

Based on the previous paper⁽⁶⁾⁻⁽⁹⁾, it can be reasonably assumed that a degree of undersaturation χ is nearly equal to 1 irrespective of the etching temperature. Therefore, the temperature dependence of v_h can be attributed to the term of poison adsorption, $[1 - \theta_1 \{1 - \exp(-\eta/kT)\}]$, and the term of probability for removal of poison-free atoms, $\exp(-\Delta H/kT)$. In the former term, θ_1 decreases with T as seen from eqs. (9) and (10) and $\{1 - \exp(-\eta/kT)\}$ decreases also with T , both giving an increase of the poison-adsorption term with T . It is needless to say that the latter term is an increasing function with T . In this way, we can explain the dependence of v_h on T shown in Fig. 5.

2. Temperature dependence of the longitudinal dissolution rate at dislocation

According to the nucleation theory for crystal dissolution, the longitudinal dissolution rate v_d which may depend on the nucleation rate of two-dimensional nucleus of the etch pit at the dislocation site is given by⁽⁶⁾⁻⁽⁹⁾

$$v_d = a \chi v \exp \left(-\frac{\Delta G_d^* + \Delta H}{kT} \right), \quad (11)$$

where a is one atomic spacing along the dislocation line and ΔG_d^* represents free energy of formation of a critical, two-dimensional nucleus of etch pit which is given by the following expression taking into account the strain energy of the dislocation core⁽³⁾.

$$\Delta G_d^* = \left\{ \gamma - \frac{\alpha \mu b^2}{8\pi^2(1-\sigma)r_0} \right\}^2 \frac{\pi a \Omega}{|\Delta g|}. \quad (12)$$

In eq. (12), γ is the specific interfacial energy; α is a factor depending on dislocation characters, e.g., $\alpha=1.8-2$ for an edge dislocation; μ is the rigidity modulus; b is the magnitude of Burgers vector; σ is the Poisson's ratio; r_0 is the dislocation core radius; Ω is the volume of single atom; Δg is the difference of chemical potential between Cu atoms at the step and in the etchant.

Since $\chi \approx 1$ irrespective of T as already noted, the temperature dependence of v_d can be ascribed to the term $\exp \{-(\Delta G_d^* + \Delta H)/kT\}$ in eq. (11). In this term, ΔH is constant, but ΔG_d^* is a function of γ and Δg (rf. eq. (12)) both of which are temperature-dependent. The change of interfacial energy accompanying adsorption is given by⁽¹⁶⁾

$$\gamma = \gamma_0 + kT\Gamma_m \ln \{(1-\theta_1)(1-\theta_2)(1-\theta_3)\} \quad (13)$$

where γ_0 is the interfacial energy without adsorption, Γ_m is the saturated amount of all the adsorbents per unit area and θ_2 and θ_3 represent the fractional coverage by adsorbents other than poison (those concerned with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NH_4OH molecules) which are given, respectively, by

$$\left. \begin{aligned} \theta_2 &= \frac{A_2 C_2}{1 + A_1 C_1 + A_2 C_2 + A_3 C_3}, \\ \theta_3 &= \frac{A_3 C_3}{1 + A_1 C_1 + A_2 C_2 + A_3 C_3} \end{aligned} \right\} \quad (14)$$

We can see from eqs. (9), (10) and (14) that θ_1 , θ_2 and θ_3 diminish with an increase of T . This may lead to a decrease of γ and hence of ΔG_d^* (eq. (12)) with T , since the logarithmic term which contains θ_i (eq. (13)) always takes an increasing negative value.

On the assumption that Young's etchant represents an ideal solution, we can write the difference of chemical potential Δg as

$$\Delta g = kT \ln \left(\frac{C_0}{C_s} \right), \quad (15)$$

where C_0 is the initial concentration of Cu in the etchant and C_s is the saturated one in the etchant. As T is increased, $|\Delta g|$ increases and consequently ΔG_d^* (eq. (12)) decreases. Therefore, both γ and Δg may produce a lowering of ΔG_d^* with T . Accordingly, an increase of v_d with T is expected from the temperature dependency of ΔG_d^* and $\exp \{-(\Delta G_d^* + \Delta H)/kT\}$.

Using the experimentally determined values of the dissolution rates, an estimation is made on some kinetic quantities relating to the formation of a two-dimensional nucleus and the step motion. Let the nucleation rate of the two-dimensional nucleus of the etch pit at dislocation, that is the number of nucleus formed per unit time, be $\dot{n}_d$. Then, since one atomic depth a is dissolved along the dislocation line whenever a nucleation occurs, $\dot{n}_d$ is given by

$$\dot{n}_d = \frac{v_d}{a}, \quad (16)$$

and a time interval of nucleation, τ_d , that is, a waiting time for the next nucleation, is expressed by

$$\tau_d = \frac{1}{\dot{n}_d}. \quad (17)$$

Table 1 Values of $\dot{n}_d$, τ_d , λ , $\dot{n}_s$ and τ_s calculated from the measured dissolution data using eqs. (16), (17), (18), (21) and (22), respectively.

T (K)	$\dot{n}_d$ (s ⁻¹)	τ_d (s)	λ (μm)	$\dot{n}_s$ ($\mu\text{m}^{-2} \cdot \text{s}^{-1}$)	τ_s (s)
290	2.9×10^2	3.4×10^{-3}	1.2×10^{-3}	8.7×10^6	8.4×10^{-3}
285	2.4×10^2	4.2×10^{-3}	1.3×10^{-3}	8.5×10^6	9.1×10^{-3}
280	2.2×10^2	4.5×10^{-3}	1.0×10^{-3}	8.1×10^6	10×10^{-3}
275	2.2×10^2	4.5×10^{-3}	1.0×10^{-3}	7.6×10^6	12×10^{-3}
270	2.0×10^2	5.0×10^{-3}	0.8×10^{-3}	6.8×10^6	15×10^{-3}

The advance distance of $\langle 110 \rangle$ step during the period τ_d is obtained from

$$\lambda = v_d \cdot \tau_d. \quad (18)$$

Table 1 gives the values of $\dot{n}_d$, τ_d and λ calculated from the measured data of v_d and v_h for various temperatures taking $a = 2.09 \times 10^{-4} \mu\text{m}$ for (111) spacing of Cu crystal. The value of $\dot{n}_d$ lies in the order of 10^2 s^{-1} and that of λ is of $10^{-3} \mu\text{m}$, both of which tend to increase with T . On the other hand, the value of τ_d is in the order of 10^{-3} s , and it diminishes with T .

3. Temperature dependence of the dissolution rate of matrix surface

As described before (rf. I), the two-dimensional nuclei of etch pits are produced homogeneously at dislocation-free sites on a matrix surface, and they grow laterally by the removal of atoms from steps, until the mutual annihilation of the two-dimensional etch pits occurs by collision of neighboring ones. Repeating the process of the nucleation and growth may lead to a layer by layer dissolution of the matrix surface. To obtain the dissolution rate of matrix surface v_s , Johnson-Mehl's approximation⁽¹⁷⁾ which treated the rate of phase transformation can be applied. The treatment yields⁽⁶⁾⁽⁷⁾

$$v_s = 3^{1/6} a \left(\frac{b^*}{b} \right)^{1/3} \left[1 - \theta_1 \left\{ 1 - \exp \left(-\frac{\eta}{kT} \right) \right\} \right]^{2/3} \times \chi v \exp \left(-\frac{\Delta G_s^* + 3\Delta H}{3kT} \right), \quad (19)$$

where ΔG_s^* is the free energy of formation of critical two-dimensional nucleus of etch pit at the dislocation-free sites which is given by

$$\Delta G_s^* = \frac{\pi a \Omega \gamma^2}{|\Delta g|}. \quad (20)$$

Since $\chi \approx 1$ as noted before, the variation of v_s with T may primarily depend upon the term of poison adsorption $[1 - \theta_1 \{1 - \exp(-\eta/kT)\}]$ and the last exponential term $\exp \{-(\Delta G_s^* + 3\Delta H)/3kT\}$ in eq. (19). As described in IV.1, the former term enables v_s to increase with T . The parameter ΔG_s^* in the latter term becomes small through the variations of γ and $|\Delta g|$ with an increase of T . These factors may result in an increase of v_s with T .

Now the authors estimate the nucleation rate of two-dimensional nucleus of etch pit, $\dot{n}_s$, that is the number of nuclei formed on a matrix surface of a unit area in unit time. If each nucleus grows in size triangularly by an advance of three $\langle 110 \rangle$ steps with a velocity of v_h , the time required to dissolve the whole area of the matrix surface is given from Johnson and Mehl's approximation by the following equation⁽¹⁰⁾:

$$\tau_s = 3^{-1/6} \dot{n}_s^{-1/3} v_h^{-2/3}. \quad (21)$$

Since the matrix surface dissolves by one atomic spacing a during the period τ_s , the dissolution rate of the matrix

surface is given by $v_s = a/\tau_s$. Putting this relation into eq. (21), we obtain

$$\dot{n}_s = 3^{-1/2} a^{-3} v_s^3 v_h^{-2}. \quad (22)$$

Table 1 contains values of $\dot{n}_s$ and τ_s calculated from measured values of v_s and v_h taking the value of a as (111) spacing for Cu crystal. $\dot{n}_s$ is on the order of $10^6 \mu\text{m}^{-2} \cdot \text{s}^{-1}$ which tends to increase with T , while τ_s is of 10^{-3} s which decreases with increasing T .

V. Summary

The dependence of temperature on the dissolution rates of the (111) surface of copper crystal in Young's etchant was studied. The etching was carried out for 5 to 25 s at temperatures 270 to 285 K applying Young's standard etchant which contains $(\text{NH}_4)_2\text{S}_2\text{O}_8$ $1 \text{ kmol} \cdot \text{m}^{-3}$, NH_4OH $6 \text{ kmol} \cdot \text{m}^{-3}$ and NH_4Br $0.3 \text{ kmol} \cdot \text{m}^{-3}$. The width h and the depth d of the etch pits which were observed at the intersections of the edge dislocations and the (111) face was determined by replica electron microscopy, and the dissolved thickness of (111) matrix surface S was determined by two-beam interferometry. From the time dependency of the measured values of h , d and S , the lateral dissolution rate at dislocation v_h , the longitudinal one at dislocation v_d and the dissolution rate of matrix surface v_s were determined, respectively. The results obtained are as follows.

(1) The etch pit size h and d increased linearly after 5 s etching for all etching temperatures tested. The slope of the side face d/h remained constant irrespective of the etching time, indicating that the etch pit increased in size but keeping its initial shape.

(2) The matrix dissolution S increased also linearly after 5 s etching.

(3) The dissolution rates at dislocation v_h and v_d and that of matrix surface v_s increased as the etching temperature rose.

(4) The increase of v_h with the increase of the etching temperature can be attributed to a decrease of poisoned Cu atoms and an increase of probability for removal of poison-free Cu atoms at the step sites. The temperature

dependence of v_d can be attributed to an enhanced nucleation of the critical two-dimensional nucleus of the etch pit at dislocation with high etching temperatures. The variation of v_s with the etching temperature can be explained by a decrease of poisoned Cu atoms and an enhanced nucleation of a critical two-dimensional nucleus of the etch pit at dislocation-free sites on the matrix surface with the increase of etching temperature.

(5) Using the values of v_h , v_d and v_s , the nucleation rate of the two-dimensional nucleus of the etch pit at dislocation $\dot{n}_d$ was estimated to be in the order of 10^2 s^{-1} per dislocation and that at dislocation-free sites on the matrix surface $\dot{n}_s$ was of $10^6 \mu\text{m}^{-2} \cdot \text{s}^{-1}$.

Acknowledgment

The authors wish to thank Messrs. K. Kikuchi, K. Wakae, A. Funato, K. Obuse and M. Yanagisawa for their assistance with the experiments.

REFERENCES

- (1) J. J. Gilman, W. G. Johnston and G. W. Sears: *J. Appl. Phys.*, **29** (1958), 747.
- (2) N. Cabrera and M. M. Levine: *Phil. Mag.*, **1** (1956), 450.
- (3) W. Schaarwächter: *Phys. Status Solidi*, **12** (1965), 375.
- (4) W. Schaarwächter: *Phys. Status Solidi*, **12** (1965), 865.
- (5) F. W. Young, Jr.: *J. Appl. Phys.*, **32** (1961), 192.
- (6) S. Sugawara and J. Watanabé: *J. Japan Inst. Metals*, **52** (1988), 1199.
- (7) S. Sugawara and J. Watanabé: *Mater. Trans., JIM*, **30** (1989), 973.
- (8) S. Sugawara and J. Watanabé: *J. Japan Inst. Metals*, **53** (1989), 565.
- (9) S. Sugawara and J. Watanabé: *Mater. Trans., JIM*, **31** (1990), 829.
- (10) M. B. Ives and J. P. Hirth: *J. Chem. Phys.*, **33** (1960), 517.
- (11) N. A. Toropov and Yu. P. Udalov: *Soviet Phys.-Dokl.*, **10** (1965), 259.
- (12) S. Sugawara and J. Watanabé: *J. Japan Inst. Metals*, **47** (1983), 820.
- (13) S. Sugawara and J. Watanabé: *Trans. Japan Inst. Metals*, **25** (1984), 797.
- (14) J. Watanabé and S. Sugawara: *J. Japan Inst. Metals*, **41** (1977), 612.
- (15) J. Watanabé and S. Sugawara: *Trans. Japan Inst. Metals*, **19** (1978), 511.
- (16) O. Knacke and I. N. Stranski: *Z. Electrochem.*, **60** (1956), 816.
- (17) W. A. Johnson and R. F. Mehl: *Trans. AIME*, **135** (1939), 416.