

The Effect of Arsenic on the Brittle-to-Ductile Transition in Si Single Crystals

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The brittle-to-ductile transition (BDT) in arsenic doped (001) CZ silicon single crystals has been experimentally studied. The temperature dependence of apparent fracture toughness was measured by three-point bending tests at various strain rates. The BDT temperature in arsenic doped silicon was found to be lower than that in non-doped. The activation energy was obtained from the strain rate dependence of the BDT temperature. It was found that the value of the activation energy in the arsenic doped silicon is lower than that in non-doped, suggesting that the dislocation velocity in the silicon single crystal was increased by arsenic doping. The effect of increasing in dislocation velocity on the BDT temperature was also investigated by two-dimensional discrete dislocation dynamics simulations, indicating that the BDT temperature is decreased by increasing in dislocation velocity. [doi:10.2320/matertrans.MAW200919]

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1. Introduction

Since silicon crystal shows a sharp brittle-to-ductile transition (BDT),¹⁾ it has been used as a model crystal to understand the mechanism behind the BDT. The values of activation energy for the controlling process of the BDT behavior were obtained in several materials such as semi-conductors,¹⁻³⁾ ceramics,⁴⁾ bcc metals⁵⁻⁸⁾ and so on. It was found that controlling process of the BDT was dislocation glide since the values of the activation energy obtained were closed to those for dislocation glide in each material.

The effects of several dopants on the dislocation velocity in silicon single crystals were investigated.⁹⁻¹¹⁾ It was found that the dislocation velocity is strongly affected by dopants, for example, the dislocation velocity in a silicon single crystal was increased by phosphorous or arsenic doping which makes silicon n-type semi-conductor. Samuels and Roberts²⁾ measured temperature dependence of fracture stress of phosphorous doped silicon single crystal by using pre-cracked specimen. They showed that the BDT temperature in phosphorous doped silicon is lower than that in non-doped, and the activation energy obtained from the rate dependence of the BDT temperature is close to that in dislocation glide. It implies that the BDT behavior is affected by the doped elements via change of dislocation velocity. Since heavily arsenic doped silicon wafers are commercially used for the demands of the low resistivity of silicon wafers, it is necessary to investigate the effect of arsenic doping on the BDT behavior. Therefore, in this study, the effect of arsenic on the BDT behavior will be discussed, based on the dislocation shielding theory.¹²⁾ The effect of the change in dislocation velocity on the BDT was also investigated by a two-dimensional discrete dislocation dynamics simulation.

2. Experimental Procedure

Two kinds of one-side mirror polished (001) CZ wafers were employed, the thickness of which were 0.62 mm. One is arsenic doped and the other is non-doped silicon wafer. The

Table 1 The chemical composition of silicon single crystals used.

	B	As	O
Arsenic doped Si	—	2.83×10^{19}	8.7×10^{17}
Non-doped Si	1×10^{15}	—	4×10^{17}

unit: atoms/cm³

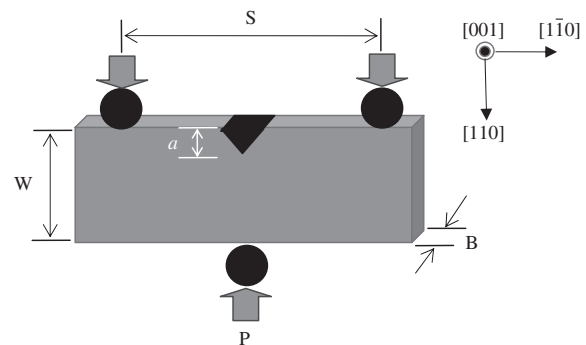


Fig. 1 Schematic drawing of a miniature three-point bending sample.

chemical compositions were shown in Table 1. Rectangular specimens of $8 \times 35 \times 0.62$ mm³ were cut out from the wafer for subsequent three-point bending tests. Figure 1 shows the schematic drawing of a specimen for the three-point bending tests. A V-shaped notch with the curvature of 1.9 rad^{-1} was introduced by a diamond blade at the middle of the tensile surface in the specimen for a crack to extend along the [110] direction. The apparent fracture toughness, K_Q , was obtained by the following equations:

$$K_Q = \frac{3SP\sqrt{\pi a}}{2W^2B} F(\xi),$$

with

$$F(\xi) = 1.090 - 1.735\xi + 8.20\xi^2 - 14.18\xi^3 + 14.57\xi^4,$$

$$\text{and } \xi = \frac{a}{W}, \quad (1)$$

where S is the distance between bars at a tensile surface of the bending specimen, P is the load at fracture, and a is the depth of the notch ($= 0.5$ mm). W and B are the height and

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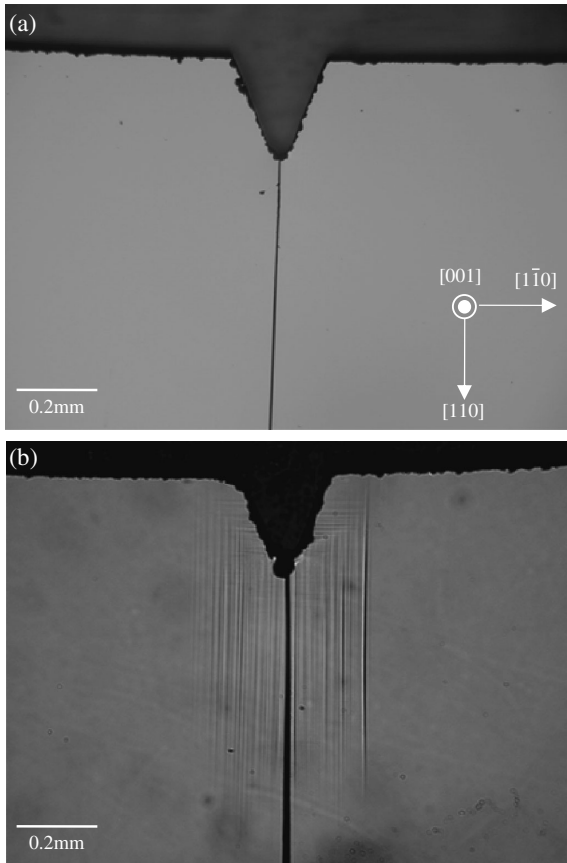


Fig. 2 Optical micrographs around notches in arsenic doped specimens fractured at (a) below the BDT temperature at 1053 K, (b) above the BDT temperature at 1086 K. Lines which parallel to the [110] are slip bands.

width of the specimen, respectively. The fracture tests were carried out at temperatures between 773 K and 1123 K. The cross-head speed was set to be 0.002 mm/min, 0.02 mm/min and 0.2 mm/min. The BDT temperature was determined as the highest apparent fracture toughness in each cross-head speed. The activation energy for the controlling process of the BDT was obtained from Arrhenius plots between reciprocal transition temperatures and logarithm of the cross-head speeds.

3. Results and Discussion

3.1 Effect of arsenic doping on the behavior of brittle-to-ductile transition

Figures 2(a) and (b) show optical micrographs around notches in arsenic doped specimens fractured at 1053 K and 1086 K, respectively, with the cross head speed of 0.2 mm/min. A crack was extended along the [110] direction from the root of the notch. No apparent plastic deformations are found in Fig. 2(a) while slip bands are seen along the [110] and $[1\bar{1}0]$ directions around the notch in Fig. 2(b). The dominant slip bands are parallel to the [110] direction, which indicates that the $(\bar{1}11)$ and/or $(1\bar{1}\bar{1})$ slip planes mainly contributed to the deformation at 1086 K. Slip bands parallel to the $[1\bar{1}0]$ direction indicate that new slip planes of (111) and/or $(\bar{1}\bar{1}\bar{1})$ were also activated, resulting from double-slip due to the crystal rotation at the middle stage of deformation around the notch at 1086 K.

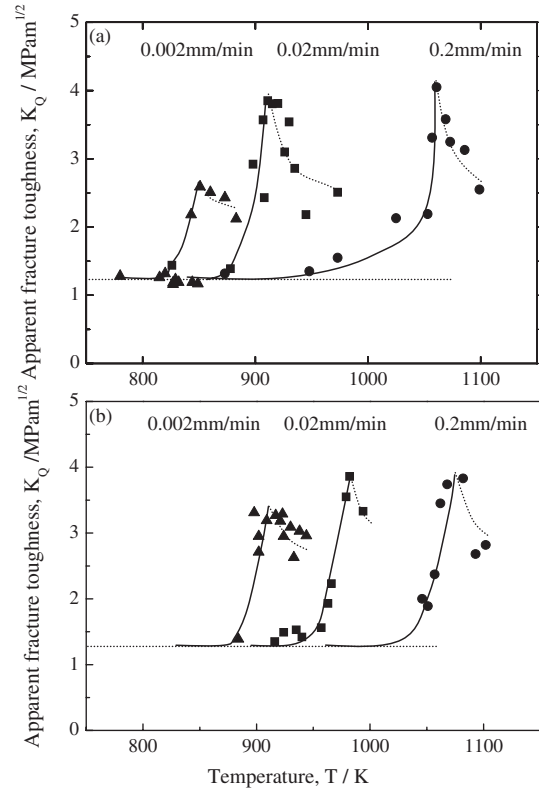


Fig. 3 Temperature dependence of apparent fracture toughness in silicon single crystals. The cross-head speed was set to be 0.002, 0.02 and 0.2 mm/min. (a) arsenic doped (b) non-doped silicon single crystal.

Figures 3(a) and (b) show temperature dependence of apparent fracture toughness of arsenic doped and non-doped silicon single crystals, respectively. Symbols of triangles, squares and circles represent the results with the cross-head speeds of 0.002 mm/min, 0.02 mm/min and 0.2 mm/min, respectively. The apparent fracture toughness increases with increasing temperature, from the lowest value of $1.3 \text{ MPa}\cdot\text{m}^{1/2}$ (dashed lines in Fig. 3), the bottom level of which is slightly higher than the fracture toughness of $1 \text{ MPa}\cdot\text{m}^{1/2}$ for silicon single crystals at room temperature.¹⁾ It is due to the lower stress concentration at a notch tip than that at a crack tip. The BDT temperature, T_{BDT} , is defined as the highest apparent fracture toughness in this study. The BDT temperatures in arsenic doped silicon single crystals were found to be 851 K, 911 K and 1061 K at the cross-head speeds of 0.002 mm/min, 0.02 mm/min and 0.2 mm/min, respectively. The BDT temperatures in non-doped silicon single crystals were found to be 913 K, 982 K and 1075 K at the cross-head speeds of 0.002 mm/min, 0.02 mm/min and 0.2 mm/min, respectively. The BDT temperature shows the strain rate dependence as reported.¹⁾ It should be noted here that the BDT temperature in arsenic doped silicon is lower than that in non-doped in any strain rate, indicating that the BDT temperature is decreased by arsenic doping. It can be understood by the increase in the dislocation velocity in the arsenic doped silicon. In order to investigate the effect of the arsenic doping on the dislocation velocity, the activation energy was measured from the strain rate dependence of the BDT temperature.

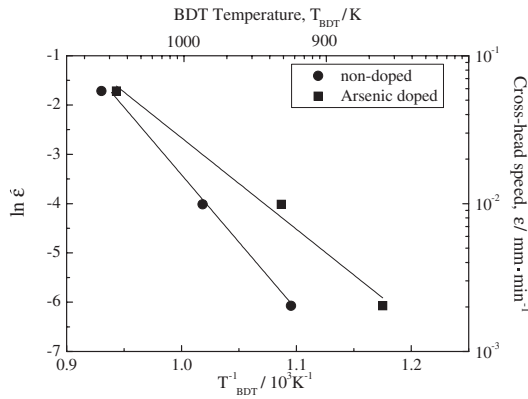


Fig. 4 Arrhenius plots between the reciprocal BDT temperatures and logarithm of the cross-head speeds in non-doped and arsenic doped silicon single crystals.

3.2 Effect of arsenic doping on the activation energy for the brittle-to-ductile transition

The relation between transition temperatures and strain rates in silicon crystals is empirically given by an Arrhenius type of equation:¹⁾

$$\dot{\varepsilon} = \varepsilon_0 \exp\left(-\frac{Q_E}{kT_{BDT}}\right), \quad (2)$$

where ε_0 is a pre-experimental factor, k is Boltzmann constant. T_{BDT} is the BDT temperature and Q_E is the activation energy. Figure 4 shows Arrhenius plots between logarithm of the cross-head speed and the reciprocal BDT temperature. Solid squares and circles represent results from arsenic doped and non-doped silicon single crystals, respectively. The slopes of each Arrhenius plot give the activation energies of 1.6 eV and 2.3 eV for arsenic doped and non-doped silicon crystals, respectively. It exhibits that the value of activation energy obtained from arsenic doping is lower than that from non-doped silicon. Here, the value of the activation energy obtained from arsenic doped silicon will be discussed.

Yonenaga^{10,11)} demonstrated that dislocations in silicon are pinned by dopants, which invokes the kinds of threshold stress for dislocations to be released from the pinning dopants. It is one of the thermally activated processes so that the values of activation energy in several dopants were measured; 3.7 eV for arsenic doped silicon and 3.6 eV for oxygen doped CZ silicon. The values of activation energy for unpinning dislocations are much higher than those obtained from the BDT, indicating that the thermally activated processes which controls the BDT behavior is not unpinning of dislocations from the dopants. Roberts and Samuels²⁾ investigated the BDT behavior in a heavily phosphorus doped silicon. They showed that the BDT temperature was decreased and the activation energy obtained from the BDT was 1.63 eV in the phosphorus doped silicon. The value of the activation energy is nearly the same as that for arsenic doped silicon used in this study. It indicates that n-type dopants decrease the BDT temperature and the activation energy obtained from the BDT, no matter what kinds of dopants are added. It suggested that the decrease in activation energy for the BDT in phosphorus silicon is due to the increase in the dislocation velocity since the values of

activation energy obtained from the BDT and the dislocation glides are nearly the same.

Although the activation energy of dislocation glide in arsenic doped silicon crystals has not been measured as far as the authors are aware, the value can be deduced from the previous work by Yonenaga.¹⁰⁾ It was indicated that the dislocation velocity is increased with doping phosphorus or arsenic. The dislocation velocity in the phosphorus doped silicon is almost the same as that in arsenic doped when the concentrations of the dopants are nearly the same (10^{19} cm^{-3}). It indicates that the activation energy of around 1.6 eV in arsenic doped silicon is close to that in phosphorus doped to be around 1.6 eV. The value of activation energy obtained from the BDT in the present study was 1.6 eV, indicating that the activation energy corresponds to that for dislocation glide in the arsenic doped silicon crystal. It is thus considered that the BDT temperature lowered in arsenic doped silicon crystal is due to the decrease in the activation energy for dislocation glide. In order to investigate the effect of decrease in the activation energy for the dislocation glide on the BDT temperature, a two-dimensional discrete dislocation dynamics simulation was performed.

3.3 Simulation for the effect of activation energy of a dislocation glide on the BDT behaviour

3.3.1 Fracture toughness increased by dislocation shielding

When an external stress is applied on a system with a crack, where no dislocations are introduced, the stress, σ_{ij} , at (r, θ) around the crack in Fig. 5 is given by:

$$\sigma_{ij} = \frac{K_A}{\sqrt{2\pi r}} f_{ij}(\theta), \quad (3)$$

In this simulation, we considered only mode I. Where r is the distance from crack tip and $f_{ij}(\theta)$ is the function of θ . K_A is the applied stress intensity factor. When a dislocation is introduced around the crack tip and stay there, where no external stress is applied, the stress due to dislocation near the crack tip is given by the following equation:

$$\sigma_{ij}^D = \frac{k_d}{\sqrt{2\pi r}} f_{ij}(\theta), \quad (4)$$

where k_d is the local stress intensity factor due to dislocations. When the applied stress and dislocations are present at the same time, the total stress, σ_{ij}^T , near the crack tip is derived from the summation of eqs. (3) and (4) thus:

$$\sigma_{ij}^T = \sigma_{ij} + \sigma_{ij}^D = \frac{K_A}{\sqrt{2\pi r}} f_{ij}(\theta) + \frac{k_d}{\sqrt{2\pi r}} f_{ij}(\theta), \quad (5)$$

where $k_1 = K_A + k_d$,

Here, k_1 is defined as a local stress intensity factor at mode I.

Fracture occurs when the local stress intensity factor reaches the Griffith level:

$$k_1 = K_A + k_d = \sqrt{\frac{2E\gamma}{1-v^2}}, \quad (6)$$

where E is the Young's modulus, γ is the surface energy of fracture planes and v is Poisson's ratio. The fracture toughness is given by the applied stress intensity factor at fracture:

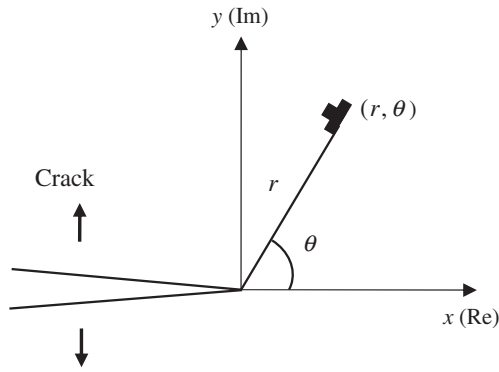


Fig. 5 Schematic drawing of a complex coordinate used in a two-dimensional model for discrete dislocation dynamics simulations.

$$K_{IC} = K_A = \sqrt{\frac{2E\gamma}{1-\nu^2}} - k_d, \quad (7)$$

Here, the local stress intensity factor due to dislocations is given by the following equation:¹³⁾

$$k_d = \sum_i \left(\frac{3\mu b_i}{(1-\nu)\sqrt{2\pi r_i}} \cos \frac{\theta_i}{2} \sin \theta_i \right), \quad (8)$$

where μ is shear modulus, b is the scalar of the Burgers vector. In the present study, only the edge component of the Burgers vector was taken into account for simplification. Direct TEM observations^{14,15)} of dislocations emitted from a crack tip has revealed that the k_d term has the negative value, indicating that fracture toughness increases when dislocations are emitted from the crack tip as shown by eq. (7). Since k_d is the function of the dislocation position in the coordinate, K_{IC} can be derived from the position of each dislocation.

3.3.2 Two-dimensional simulation for brittle-to-ductile transition

Dislocation distribution emitted from a crack tip is calculated by using a two-dimensional discrete dislocation dynamics simulation, the detail of which is given elsewhere.¹⁶⁾ The position of each dislocation is calculated from the force on the dislocations at each step of time at given strain rate and temperature. Figure 5 illustrates the schematic drawing of a two-dimension complex coordinate used in the simulation where an edge dislocation is locate at (r, θ) in polar coordinates. The x axis is the direction of crack extension and the y axis is perpendicular to the crack plane. A single dislocation source is located at the distance of r from the crack tip. The slip plane is inclined by θ against the x axis.

The first dislocation is emitted when the force on dislocation, f_d , exceeds 0:

$$f_d > 0 \quad \text{with} \quad f_d = f_{Kd} + f_m, \quad (9)$$

where f_{Kd} is the force on the dislocation due to the mode I applied stress and f_m is the image force. When more than one dislocation is emitted, the dislocation-dislocation interaction force, f_{dd} , needs to be considered, hence eq. (9) is now:

$$f_d = f_{Kd} + f_m + f_{dd}, \quad (10)$$

The dislocation velocity in a silicon single crystal at certain temperature is given by the following equation:⁹⁾

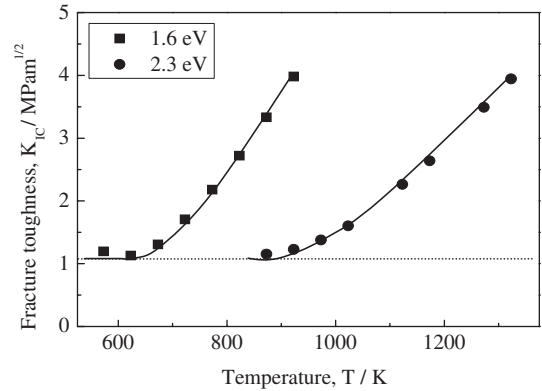


Fig. 6 Calculated fracture toughness against temperature where the activation energy for dislocation glide was set to be 1.6 eV and 2.3 eV, respectively. The BDT temperature decreased with decreasing the activation energy for dislocation glide.

$$v = v_0 \left(\frac{f_d}{b} \right)^m \exp \left(-\frac{Q_E}{kT} \right), \quad (11)$$

where v_0 ($= 733.3 \times 10^{-3}$ m/s) and m ($= 1$) are constants, k is the Boltzmann constant. Q_E is the activation energy for dislocation glide. The value of Q_E used in the present study is those obtained in Fig. 4, that is, 1.6 eV from arsenic doped silicon and 2.3 eV from non-doped silicon. Dislocations are generated on the $(11\bar{1})$ slip plane ahead of the (111) crack tip and glide away from the crack. Dislocations do not cross slip in this model.

Figure 6 shows the temperature dependence of fracture toughness calculated by using the two-dimensional model. Solid squares and circles indicate demonstrate results from the activation energy of 1.6 eV and 2.3 eV for dislocation glide, corresponding of that for arsenic doped silicon and non-doped silicon, respectively. The experimental values of the BDT temperatures were lower than those from the present simulation, which is because such a simplified model that the multiplication processes of dislocations are neglected around the crack tip was employed. It is to be noted here that the BDT temperature decreases with decreasing in the activation energy for dislocation glide. Therefore, it is concluded that decrease in the BDT temperature by arsenic doping is due to the increase in the dislocation velocity in silicon single crystals.

4. Conclusions

Three-point bending tests revealed that the BDT temperature in arsenic doped silicon single crystal is lower than that in non-doped. The activation energy for the controlling process of the BDT was obtained from the rate dependence of the BDT temperature, indicating that the activation energy in arsenic doped silicon was found to be lower than that in non-doped. It indicated that the dislocation velocity is increased by arsenic doping in silicon single crystals. Two-dimensional dislocation dynamics simulations, based on the dislocation shielding theory, indicated that the BDT temperature decreased with decrease in the activation energy for dislocation glide, which corresponds to the experimental results in the present study. It is concluded that the decrease in the BDT

temperature in arsenic doped silicon is due to the increase in the dislocation velocity.

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