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Dynamics and characters of dislocations in ZnSe

I. YONENAGA*, K. WATANABE, S. ITOH
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
E-mail: yonenaga@imr.tohoku.ac.jp

S. FUJIWARA
Sumitomo Electric Industries, Semiconductor R & D Laboratories, Itami 664-0016 Japan

The mechanical strength of single-crystal ZnSe is investigated at elevated temperatures by means of compressive deformation. The yield stress of ZnSe in the temperature range 150–300°C is around 7–13 MPa, easily deformed even at low temperature. From the temperature dependence of the yield stress an activation energy for dislocation motion in the ZnSe is deduced to be 0.5–0.7 eV. The stacking fault energy is estimated to be 7–9 mJ/m^2 from the dissociation width of dislocations into partials.

1. Introduction

Zinc selenide (ZnSe) is a typical II–VI compound semiconductor in the sphalerite structure with a direct band-to-band transition with an energy of 2.67 eV at 300 K. This material and related alloys have been of keen interest as wide band-gap semiconductors for applications in blue and recently white light emitting devices. Several works have been done on dislocation properties in CdTe, among the II–VI compounds, with respect to the photoplastic and electro-plastic phenomena in the 1970s and 1980s. Nevertheless, up to now far less is known about the dislocation mobility and the mechanical properties of other II–VI compounds, including ZnSe, except for the stacking-fault energy [1, 2]. Information on the mechanical strength at elevated temperatures is essential in order to control dislocation generation and plastic deformation during crystal growth and device processing and also to improve the optical and electronic properties and their homogeneities in the material. From such a viewpoint, Yonenaga and Suzuki [3] reported the Vickers hardness of ZnSe to be 1.1 GPa at room temperature, which is much lower than that of Si. Although the mechanical instability of ZnSe has been informed from their result, the yield strength of such single crystals should ideally be measured by conventional mechanical testing for physically reliable information. The difficulty of large-size ZnSe crystal bulk preparation was a limiting factor in obtaining such information. Recently, Fujiwara *et al.* succeeded in growing high-quality ZnSe bulk crystals using the chemical vapor transport (CVT) method [4].

The purpose here is to determine the mechanical strength of ZnSe single crystals at elevated temperatures using a compressive deformation method in comparison with that of other typical semiconductors such as Si, GaAs, and GaN and to clarify the stacking fault energy, characteristic in II–VI compounds. Understanding how dislocations behave under stress is very important if one is to clarify the elementary mechanism of dislocation glide in a series of semiconductors.

2. Experimental procedure

ZnSe bulk single crystals were grown on a ZnSe (seed) substrate by the CVT method using iodine as a transport agent. Details of the growth technique and structural characterization of the crystals are given elsewhere [5]. The crystals with orange color were semi-insulating and the density of grown-in dislocations was about 10^5 cm^{-2} evaluated by counting pits etched by the dilute bromine–methanol solution.

Specimens for mechanical tests were rectangular, approximately $1.9 \times 2.0 \times 7.6$ mm^3 in size suited for compression tests, prepared by chemical polishing with a reagent of 1 g $K_2Cr_2O_7$ + 10 ml H_2SO_4 + 20 ml H_2O at 20°C following mechanical polishing. The long axis was parallel to the [123] direction and the side surfaces,

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*Author to whom all correspondence should be addressed.

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parallel to the (111) and (541) planes. The specimen was compressed along the long axis with a constant strain rate using an Instron-type machine at various temperatures in a high-purity argon atmosphere. The details of the experimental procedure for mechanical testing are described elsewhere [6].

To observe dislocation structure developed by deformation, 3-mm diameter discs were cut parallel to the primary slip plane (111) from the deformed specimens and thinned to electron transparency. The foils were examined using a JEM 2000EX-II transmission electron microscope operating at 200 kV.

3. Results and discussion

3.1. Stress-strain characteristics

Specimens were deformed at temperatures higher than 150°C without brittle fracture under the application of rather low compressive stress. Fig. 1 shows stress–strain curves for ZnSe crystals under a shear strain rate of 2.3×10^{-4} s^{-1} at temperatures of 150, 200, 250, and 300°C. The stress-strain curves at all temperatures are characterized by an apparent elastic increase in the stress, a smooth yield behavior, and a subsequent gradual increase in the stress with respect to the strain, i.e., plastic deformation accompanying the work hardening. Stress drop in the yield region, typical for various elemental and compound semiconductors such as Si [7, 8], GaAs [9], and so forth, deformed at relatively low temperatures, was not observed except for deformation at 150°C, though the yield drop is quite small at this temperature. The observed stress-strain curves for ZnSe are similar to those of CdTe [10–12]. The yield stress and flow stress decrease with increasing temperature. Similarly, stress-strain behavior depends on the strain rate for deformation and the yield stress and flow stress increase with increasing strain rate. The most striking feature of the stress-strain curves is the low levels of yield and flow stresses of around 13 MPa even at 150°C. This is in good agreement with previous results on the remarkable mechanical susceptibility of ZnSe obtained from micro-indentation tests [3].

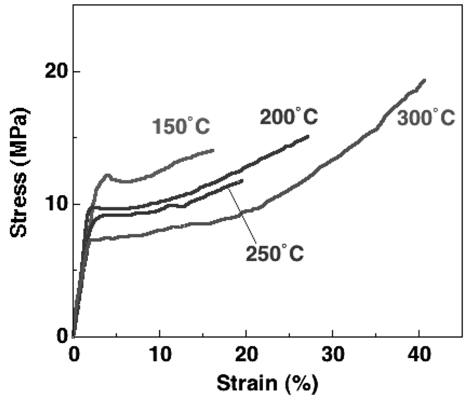

Figure 1 Stress-strain curves of ZnSe single crystals at temperatures of 150, 200, 250, and 300°C under a shear strain rate of 2.3×10^{-4} s^{-1}.

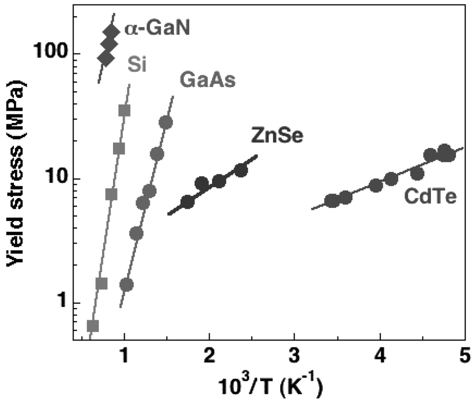

Figure 2 Yield stresses of ZnSe crystals plotted against reciprocal temperature $1/T$ for deformation under a strain rate of 2.3×10^{-4} s^{-1}, in comparison with those of Si (1.2×10^{-4} s^{-1}) [7, 8], GaAs (1.8×10^{-4} s^{-1}) [9], GaN (4.5×10^{-4} s^{-1}) [6], and CdTe (2.8×10^{-4} s^{-1}) [13].

The yield stress, τ_y, of the ZnSe crystals is plotted against reciprocal temperature in Fig. 2 for deformation under a shear strain rate of 2.3×10^{-4} s^{-1}, together with the lower yield stress of Si [7, 8], GaAs [9], GaN [6], and CdTe [13]. In the case of accompanying a stress drop after yielding, the lower yield stress is adopted. The yield stress of ZnSe is more than two orders of magnitude lower than that of Si, GaAs, and GaN, and is about one order of magnitude higher than that of CdTe.

In Fig. 2 the logarithms of the yield stresses for all the crystals are linear with respect to reciprocal temperature across the whole range investigated. The temperature dependence of the yield stress of ZnSe is similar to that of CdTe [13]. Generally, the yield stress of a semiconductor crystal is described as a function of temperature T and strain rate $\dot{\varepsilon}$ by the following empirical equation [14]:

$$\tau_y = A\dot{\varepsilon}^{1/n} \exp(U/k_B T), \tag{1}$$

where A, n, and U are constants and k_B is the Boltzmann constant. The magnitude of U determined experimentally from the temperature dependence of the (lower) yield stress of ZnSe is 0.09–0.12 eV. The magnitude of n is also determined to be 5–6.

In semiconductor crystals, the dislocation velocity v is described using the following empirical equation as a function of the stress τ and temperature T:

$$v = v_0(\tau/\tau_0)^m \exp(-Q/k_B T), \tag{2}$$

where $\tau_0 = 1$ MPa. The constants v_0, m, and Q have been determined experimentally for dislocations with various semiconductors [15]. The constants m and Q are known to be related to n and U in Equation 1 through the following

Figure 3 Bright-field transmission electron micrograph of dislocations along the primary slip plane after deformation at 300°C to 29% shear strain. The diffraction vector is $\boldsymbol{g} = 2\text{–}20$.

equations:

$$n = m + 2, Q = U^{*}(m + 2). \qquad (3)$$

These relationships are based on the collective motion of microscopic dislocations that rate-control the macroscopic deformation of crystals [16, 17]. If the relations remain valid in ZnSe, then it can be presumed that the magnitude Q is 0.5–0.7 eV which fits well to the phenomenological relationship where the activation energy Q for dislocation motion increases linearly with the band-gap energy in the group of semiconductors, i.e., the elemental and IV–IV compound, III–V compound, and II–IV compound, possibly related to the fact that II–VI and III–V compound semiconductors have a comparatively stronger ionicity [18]. The obtained activation energy implies that dislocations are highly mobile in ZnSe. Further work on the direct measurement of the velocities of isolated dislocations within ZnSe crystals under a defined stress distribution is a task for the future.

3.2. Dislocation structure

Fig. 3 shows a transmission electron micrograph of dislocations on the primary slip plane, cut from a ZnSe crystal deformed at 300°C to a shear strain of 29%. Long dislocations rather smooth in shape are thought to be mobile. A high density of dislocation dipoles along the $\langle 11\underline{2}\rangle$ direction can be seen. The feature of the dislocation distribution is very similar to that in Si [19], GaAs [9], and GaN [20] crystals deformed at rather high temperatures corresponding to the crystals. This may indicate that the dislocation mechanism operating during the deformation of ZnSe is the same as that in semiconductors as Si, GaAs, and so on. An interesting finding is that some dislocations were moved over rather long distances at room temperature due to the irradiation of a focused electron beam. This may be due to the recombination enhanced dislocation motion of dislocations [21].

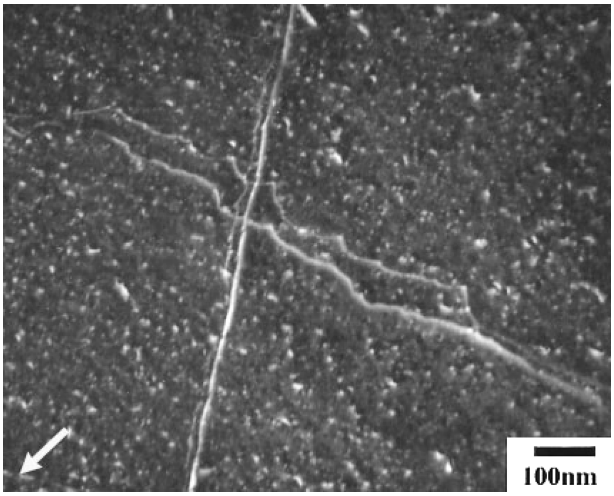

Figure 4 Weak-beam image of dislocations within deformed ZnSe. Images were obtained for the condition of approximately $\boldsymbol{g}$, $3\boldsymbol{g}$ ($\boldsymbol{g} = 2\text{–}20$).

Fig. 4 shows a weak-beam image of dislocations within a ZnSe crystal. Almost all the parts of the dislocations, with the Burgers vector $\boldsymbol{b} = (a/2)\langle 110\rangle$ determined by using the extinction criterion for dislocations for $\boldsymbol{g}^{*}\boldsymbol{b} = 2$ and $\boldsymbol{g}^{*}\boldsymbol{b} = 0$, are dissociated into two Shockley partial dislocations similar to those in Si, GaAs, and other various semiconductors. The bounded stacking faults were of intrinsic type. The 60° dislocation is separated locally narrowing and broadening 20–60 nm, probably due to the point obstacles. The 30° dislocation is rather straight keeping a constant spacing 13–17 nm. The $\pm\boldsymbol{g}$ image pairs showed a strong asymmetric nature with a reversal of the strong contrast from one partial to the other. From the separation of the 30° dislocation, the stacking-fault energy was preliminarily estimated to be 7–9 mJ/m^2. This is slightly lower than the results $\sim$13 mJ/m^2 reported by Rivaud *et al.* [1] and Aristov *et al.* [2] by deformation at room temperature. Quantitative analysis is a task for the future with an investigation for dissociated dislocations along various orientations.

4. Conclusion

This article has shown preliminary results of the mechanical strength of ZnSe single crystals obtained by a direct method. The yield stress of ZnSe in the temperature range 150–300°C is around 7–13 MPa, much lower than those of Si, GaAs, and other III–V compounds, showing the mechanical instability of this material. From the temperature dependence of the yield stress, the activation energy for dislocation motion in ZnSe is estimated to be 0.5–0.7 eV. Dislocations are dissociated into two partials bounding a strip of intrinsic stacking-fault in a width of 15–60 nm observed by the weak-beam method. The stacking fault energy is supposed 7–9 mJ/m^2. The results reported here are expected to provide a solid basis for the future improvement of crystal growth and treatments.

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