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Tingting Zhu,[1] Kuan Ding,[1] Yu Oshima,[2] Anahid Amiri,[1] Enrico Bruder,[1] Robert W. Stark,[1] Karsten Durst,[1] Katsuyuki Matsunaga,[2,3] Atsutomo Nakamura,[2,4,a),b)] and Xufei Fang[1,a)]

AFFILIATIONS

[1]Department of Materials and Earth Sciences, Technical University of Darmstadt, 64287 Darmstadt, Germany
[2]Department of Materials Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464–8603, Japan
[3]Nanostructures Research Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta, Nagoya 456–8587, Japan
[4]PRESTO, Japan Science and Technology Agency (JST), 7, Gobancho, Chiyoda-ku, Tokyo 102–0076, Japan

[a)]**Authors to whom correspondence should be addressed:** nakamura@me.es.osaka-u.ac.jp and fang@ceramics.tu-darmstadt.de
[b)]**Present address:** Department of Mechanical Science and Bioengineering, Osaka University, Osaka 560–8531, Japan.

ABSTRACT

An enormous change in the dislocation-mediated plasticity has been found in a bulk semiconductor that exhibits the photoplastic effect. Herein, we report that UV (365 nm) light irradiation during mechanical testing dramatically decreases the fracture toughness of ZnS. The crack tip toughness on a (001) single-crystal ZnS, as measured by the near-tip crack opening displacement method, is increased by ~45% in complete darkness compared to that in UV light. The increase in fracture toughness is attributed to a significant increase in the dislocation mobility in darkness, as explained by the crack tip dislocation shielding model. Our finding suggests a route toward controlling the fracture toughness of photoplastic semiconductors by tuning the light irradiation.

Most bulk inorganic semiconductor materials are well known for their brittleness and limited plasticity at room temperature because of their strong ionic/covalent bonds.[1] The poor mechanical properties, especially the low fracture toughness, of inorganic semiconductors greatly limit their application in extreme environments. Various approaches to actively control the mechanical properties of semiconductor materials have witnessed rising interest in the last few years.[2–4] In addition, inorganic semiconductor materials that could display large deformability and high flexibility[4,5] as well as fracture toughness are highly desirable as potential candidates for the up-surging flexible electronic applications,[6,7] where real-time controlling and switching of the strength and toughness of such materials would greatly promote its application considering the versatile working environment that involves, for instance, light-emitting processes.[7]

The light effect on the mechanical deformation of certain semiconductors was reported by Osip'yan and Savchenko,[8] who later coined the term "photoplastic effect" (PPE).[9] It was found that for positive PPE materials (e.g., II-VI semiconductors), light irradiation with the wavelength at or close to the absorption edge increases the yield stress or the hardness.[8–12] As the underlying mechanism, it has been proposed that the dislocations get pinned by the light-excited electrons and holes, hence decreasing the dislocation mobility.[9,10,12–14] The majority of previous studies focus on the light effect on the plastic yield and hardness of these materials. Recently, Oshima *et al.*[2] reported a surprisingly large plastic strain up to 45% on single-crystal ZnS during bulk compression when the sample is deformed in complete darkness. Under UV light (365 nm), in contrast, the sample fractures almost immediately after plastic yield.

One of the major carriers for the plastic deformation of crystalline materials is dislocation, one-dimensional defect. Dislocation is also the main reason for the enhanced fracture toughness by blunting the crack tip, as readily evidenced in metallic materials. In addition, the brittle-to-ductile transition is proposed to be controlled by dislocation activity (to be specific, dislocation nucleation, multiplication, and dislocation mobility) at the crack tip.[15,16] The dislocation crack tip shielding model[15,17,18] has been proposed to account for the dislocation toughening, which applies not just for metals but also for inorganic crystals such as Si[15,18] at elevated temperatures. Since the light irradiation with a wavelength of 365 nm drastically decreases the dislocation mobility in ZnS,[19] it is, therefore, logical to ask the questions: would light irradiation decrease the fracture toughness of ZnS? If so, how strong is the effect?

To our great surprise, there is scarce research on the light effect on the fracture toughness of PPE materials. Very few studies[14,20] were carried out to study the crack formation induced by Vickers indentation under different illumination conditions. The focus was on the crack length and dislocation structures around the cracks, yet the fracture toughness was not evaluated. Moreover, large bulk semiconducting materials are extremely costly and difficult to fabricate, making it almost impossible to measure the fracture toughness using the standard fracture toughness measurement (e.g., single edge V-notched beam test[21]). On the other hand, the anisotropic behavior of the crack formation also makes it ineffective to adopt the crack length fracture toughness measurement using Vickers indentation.[22] Very often, only one major crack, instead of four symmetric radial cracks, is induced in PPE materials.[14,20] In this study, we adopt the near-tip crack opening displacement (COD) method[23–26] to measure the crack tip toughness (K_{I0}) of single-crystal ZnS under different light conditions.

The sample used in this study was a single crystal of ZnS (sphalerite) with a size of $2.9 \times 2.9 \times 7.5$ mm. The sample was grown along $[\bar{1}11]$ using the seeded vapor-phase free growth technology method.[2] The sample surfaces were coated with three pulses (*K950X Turbo Evaporator, EMITech, Ashford, UK*) of transparent carbon in vacuum prior to Vickers indentation (a detailed experimental protocol is presented in the supplementary material) for later surface characterization in scanning electron microscopy (SEM) (*Mira3 FEG, Tescan, Brno, Czech Republic*). The cracks were induced by Vickers indentation on the (001) surface of the single-crystal ZnS in complete darkness and under UV light with a wavelength of 365 nm (*NU-15, Herolab GmbH, Wiesloch, Germany*), which is near the absorption edge of ZnS (3.52 eV[2]). The irradiance of the UV light on the sample surface is measured using a UV-Optometer (SUSS MicroTec SE, Garching, Germany), which gives a value of $\sim$510 μW/cm^2. On the one hand, this intensity is sufficiently large for this material to exhibit the largest PPE during mechanical testing according to Oshima *et al.*,[19] who reported a saturation intensity of 400 μW/cm^2. On the other hand, this intensity is sufficiently low not to cause the material's degradation or surface damage. The diagonals of the Vickers indenter were aligned in the [110] and $[1\bar{1}0]$ directions. An optimized load of 0.98 N was used to perform more than 10 indents in each condition to ensure the reproducibility. The load function consisted of a loading time of 10 s and a dwell time of 10 s. 'Load optimization' means that the load was adjusted to obtain an appropriate a/b ratio ($1.4 < a/b < 3.5$,[23,25] where a is the total length of the crack length and half of the diagonal; b is half of the diagonal) as shown in Fig. 1(a). After indentation, the sample was immediately preserved in a dark box to avoid any further light exposure. In order to avoid subcritical crack growth during the measuring time span, a waiting time of 24 h is planned. The same waiting time for different light conditions gives a defined time regime for crack opening analysis.

The visualization of dislocations was realized by electron channeling contrast imaging (ECCI) using a backscattered electrons (BSE) detector in the SEM, with an acceleration voltage of 20 kV at a scan speed of 320 μs/pixel. The surface slip patterns were measured using an atomic force microscope (AFM) (*Bruker AXS, Bruker, Santa Barbara, USA*) in the tapping mode. Stiff probes (rectangular shape with a tip radius of $R = 10$ nm, a half-opening cone angle of $\leq 25°$, and the flexural resonance frequency of 300 kHz) with a nominal force constant of 40 N/m (*RTESPA*-300, *Bruker, Santa Barbara, USA*) were used for imaging.

In order to determine the crack tip toughness K_{I0} using the COD method, the crack tip opening displacement [$2u$ in the inset of Fig. 1(b)] as a function of the distance x from the crack tip (indicated by the yellow triangle, Fig. 1(a), where $x = 0$ denotes the crack tip) was measured based on the SEM images. The step size is shown in Fig. 1(b) as the distance of the vertical white lines, and so the crack opening was measured every 10 pixels (66.7 nm in this case). The Irwin parabola in Eq. (1) is used to fit K_{I0} based on the crack opening profile.[24–27] For plane strain condition $E' = E/(1-\nu^2)$, where ν is Poisson's ratio and E is the Young's modulus. With $1.4 < a/b < 3.5$ (in our case, $a/b = 2.4$ is obtained under the optimized indentation load of 0.98 N), the Irwin parabola gives satisfactory accuracy for the crack tip toughness measurement.[23,26] Due to the low UV light irradiation intensity, the Young's modulus and Poisson's ratio are unchanged in comparison with darkness, as shown by Nakamura *et al.*[28] using photoindentation tests. For ZnS, we take $E = 74.5$ GPa and $\nu = 0.27$,[28]

$$u(x) = \frac{K_{I0}}{E'}\sqrt{\frac{8x}{\pi}}. \tag{1}$$

The crack tip opening displacement (dots) and fitted Irwin parabola (solid lines) to obtain the crack tip toughness K_{I0} are represented in

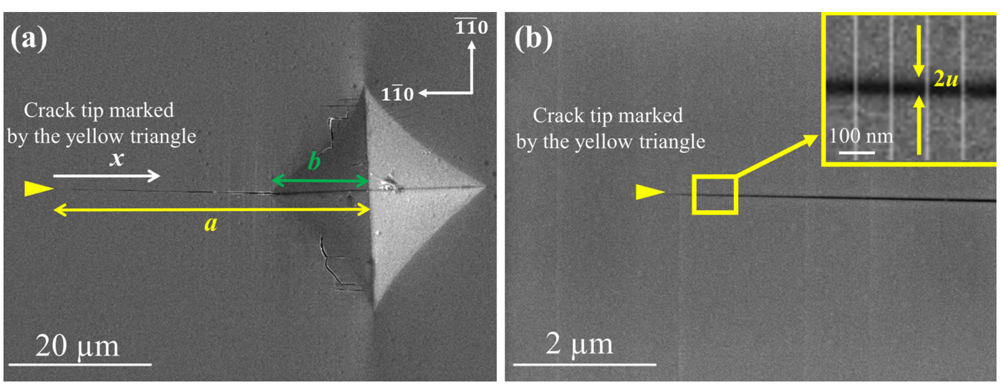

FIG. 1. Representative SEM images showing (a) one major crack induced by the Vickers indenter with an optimized load of 0.98 N, where a is the total length from the center of indent imprint to the crack tip and b is the half of the indent imprint diagonal; x is the distance from the crack tip (indicated by the yellow triangle); (b) determination of the crack opening profile near the crack tip, where the inset image shows the area marked by the yellow rectangle.

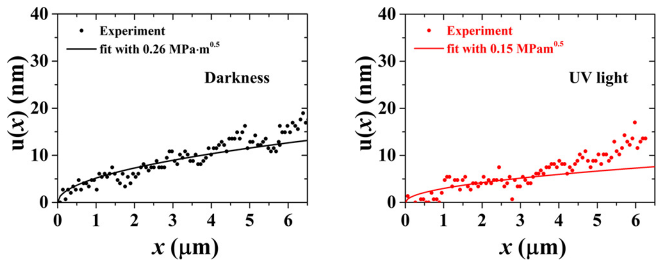

FIG. 2. Representative near-tip crack opening displacements *u(x)* measured from Vickers indentations with an optimized load of 0.98 N in darkness and under UV light.

Fig. 2 for two different light conditions (one in complete darkness and the other in UV light). A larger crack tip opening developed for the indentation in darkness [hence a higher K_{I0} according to Eq. (1)] in comparison with UV light. Based the average values of K_{I0} (Table I), which were calculated from six cracks measured for each light condition, we conclude that the crack tip opening in darkness was approximately 45% larger. The underlying mechanism for the increased toughness is attributed to the dislocation behavior about the crack tip, as will be discussed later. It is also worth mentioning that no time-dependent sub-critical crack growth for this material is observed after the 24-h waiting time, as evidenced by the comparison of the COD measurement of the cracks stored for one month (Figs. S1 and S2 in the supplementary material) and one day. This rules out sub-critical crack growth that might affect the measurement on K_{I0} as in the case for glasses.[25]

A proper interpretation of the change in the crack tip toughness resides in the understanding of the dislocation behavior, including dislocation nucleation, multiplication, and mobility at the crack tip under different light conditions.

First of all, our load optimization procedure (Fig. S3 in the supplementary material) clearly demonstrates that dislocations are generated prior to crack formation. Our most recent work using nanoindentation pop-in studies under different light irradiation further suggests that dislocation nucleation is not strongly affected by light. Therefore, it is reasonable to exclude the light effect on the crack-tip dislocation nucleation.

Second, we can rule out the effect of dislocation density based on the ECCI observation for both light conditions shown in Fig. 3. The dislocations near the surface region are visualized by the white tailing features, based on which the dislocation density under different light conditions is estimated, showing no significant difference (Table S1 in the supplementary material, showing a line density of about 2×10^6/m

TABLE I. Crack tip toughness and the traveling distance of the slip traces under different light conditions.

Light condition	Darkness	UV light (365 nm)
Crack tip toughness, K_{I0} (MPa·m$^{0.5}$)	0.26	0.18
Traveling distance of slip traces (μm)	46.86 ± 3.01	36.74 ± 4.54

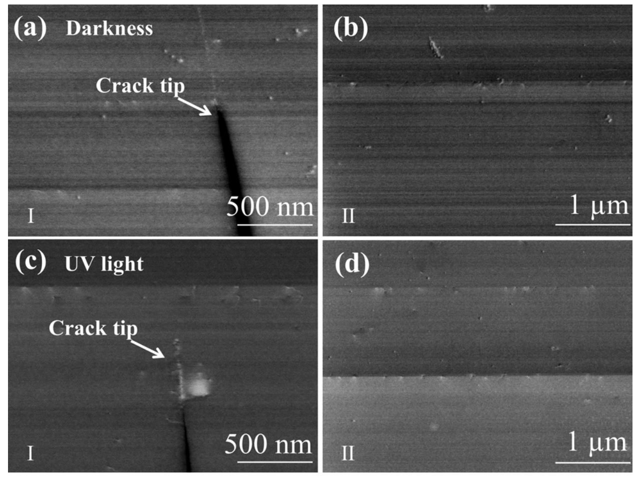

FIG. 3. ECCI results from Vickers indentation with a load of 0.98 N in darkness [(a) and (b)] and under UV light [(c) and (d)].

for all cases in Fig. 3), as also confirmed by the TEM observation in ZnS after Vickers indentation.[14]

Third, we quantified the dislocation mobility by analyzing the slip traces. As a direct visualization of the dislocation mobility, the surface slip patterns induced by the Vickers indentation in the two different light conditions were compared further. Figure 4 shows amplitude error images obtained using AFM. Note that the main crack is along the $[1\bar{1}0]$ direction [see Fig. 1(a)], while the slip traces of the main crack are along the $[\bar{1}\bar{1}0]$ direction, which is perpendicular to the crack plane. The traveling distance for the slip traces along $[1\bar{1}0]$ is much longer in darkness [Fig. 4(b)] than in UV light [Fig. 4(c)]. Four indents for each light condition were scanned. On average, in darkness, the slip traveling distance is about 30% larger than in that UV light (Table I). The much larger plastic zone size in darkness (hence lower hardness) is consistent with the previous study by Koubaïti *et al.*,[14] who showed that the propagation distance of dislocations is much larger in darkness by using TEM observation.

Consider that the UV light intensity is low (~510 μW/cm^2) in the current experiment, the surface energy of the material under UV light and darkness is expected to be unchanged. The preceding analyses narrow it down that the higher fracture toughness in darkness is most likely caused by the dislocation mobility. As briefly introduced before, the light effect on the dislocation mobility has been widely studied and recognized. Osip'yan *et al.*[10] proposed that the light excites the electron and hole pairs leading to the change in the charge of dislocations, resulting in the change in the electrostatic interaction and, hence, the decrease in the dislocation mobility. The most recent compelling evidence on the decrease in dislocation mobility in light is presented by Oshima *et al.*,[19] who conducted a room temperature creep study on bulk ZnS under various light conditions. By switching on the UV light (365 nm), a decrease in the creep strain rate of a factor of about four hundred was achieved in comparison to that in darkness. According to the DFT (density functional theory) calculations, such reduced dislocation mobility under light irradiation can be ascribed to the trapping of electrons (at the Zn core) or holes (at the S core) at the charged dislocations, which induce atomic reconstructions at their cores.[29]

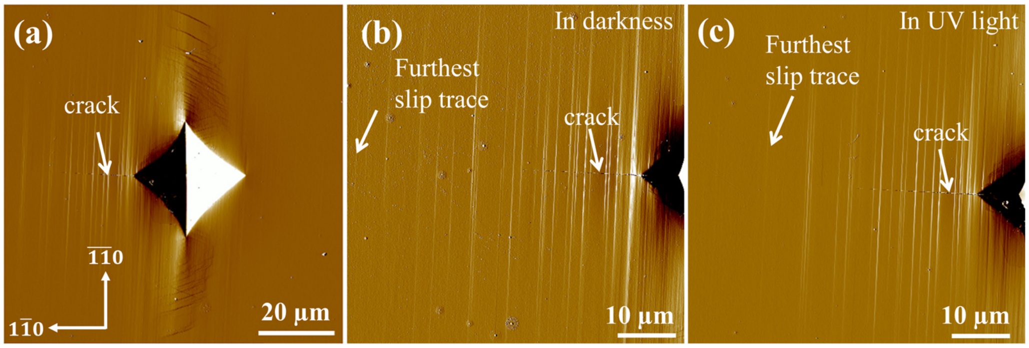

FIG. 4. AFM amplitude error images of Vickers indentations obtained with a load of 0.98 N: (a) overview of one representative indent imprint with slip patterns and crack formation; (b) slip patterns and crack in darkness; (c) slip patterns and crack in UV light. AFM parameters: tapping mode; scan speed, 15 μm/s; and setpoint amplitude, 50%.

According to the dislocation crack tip shielding theory,[15,17,18,30] we write the dislocation-free local stress intensity factor K_e as

$$K_e = K_A - K_{shield}, \tag{2a}$$
$$K_A = K_e + K_{shield}. \tag{2b}$$

Due to the low UV light intensity and identical elastic parameters as discussed above, it is reasonable to assume an identical K_e for both darkness and UV light conditions. K_A is the applied stress intensity factor, in this case, the measured crack tip toughness K_{I0}. In addition, K_{shield} is the sum of the shielding effect from the dislocations, which were emitted and moved away from the crack tip. For simplicity, the shielding term takes the form of[15]

$$K_{shield} = A \sum_i \frac{\mu b}{\sqrt{2\pi x_i}}, \tag{3}$$

where A is a pre-factor accounting for geometry and x_i refers to the position of the ith dislocation with respect to the crack tip.

Hirsch *et al.*[15] assumed that nucleated dislocation loops from the source at the crack tip move away from the tip if the stress at a critical distance x_c from the tip is sufficient to expand the loop. In darkness, the higher dislocation mobility is equivalent to a lower friction stress, which further gives a smaller critical distance x_c in darkness. In this case, more dislocations beyond the critical distance will contribute to the effective shielding, giving a higher toughening effect as evidenced by the higher crack tip toughness in darkness. This argument is further supported by the calculations by Zhu *et al.*,[31] who demonstrated a larger crack tip shielding effect with lower friction stress.

Note that in Eq. (1), the elastic stress field is assumed, which may be violated by the presence of the dislocations at the crack tip. However, due to the non-significant (in comparison to metals) shielding effect of the dislocations in ZnS, the crack tip stress field is assumed not to be strongly modified by the dislocations. Therefore, Eq. (1) can still be used for approximation in order to quantify the light effect on the fracture toughness, which may lead to a disturbance of the absolute values of the measured crack tip toughness.

In summary, we compared the crack tip toughness K_{I0} in complete darkness and UV light (365 nm) on single-crystal (001) ZnS using the near-tip crack opening displacement method. We found that the crack tip toughness for the single major crack along the $[1\bar{1}0]$ direction increased from 0.18 MPa m$^{0.5}$ under UV light to 0.26 MPa m$^{0.5}$ in darkness. The switch of the crack tip toughness under different light conditions is proposed to be caused by the significant change in dislocation mobility, which has been experimentally evidenced by the traveling distance of the slip traces along $[1\bar{1}0]$. Our result suggests a promising route to actively controlling the fracture toughness of photoplastic semiconductors with UV light.

See the supplementary material for details of the experimental protocol, waiting time effect on the crack opening displacement, and load optimization.

The authors declare that they have no conflict of interest.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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