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News & Views

Driving dislocation motion in ZnS single-crystalline semiconductor for extraordinary mechano-electro-optical properties

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Dislocations, which are topological line defects within a crystal lattice, play a dominant role in crystal plasticity and thus affect various mechanical, electronic, magnetic and optical properties of crystals. These dislocations also play a crucial role in the structural hardening and material processing [1]. In general, mechanical stress is believed to be the fundamental driving force for the movement of dislocations in a crystal. Under the mechanical action, the dislocations glide, multiply, or interact with each other while they traverse the crystal lattice, resulting a change in shape, commonly referred to as deformation or yield. During this process, the dislocations motion directly determines the deformation behavior of the crystal. Dislocations motion becomes critical on how to regulate their mechanical and functional properties based on the generation, motion, interaction, storage, annihilation of dislocations in crystalline materials under the action of driving forces. Since the proposal of dislocation theory in the 1930s, the dislocation dynamics, i.e., the laws of motion, multiplication and interaction of dislocations in a crystal have been thoroughly studied under the action of external field [2]. However, many processes are responsible for the dynamic properties of dislocations, which occur simultaneously in a crystal with motion of a number of dislocations. Besides, their motion strongly depends on the intrinsic properties of the crystal and the external field conditions. The study of dislocation dynamics in various materials is a complex and challenging field that has garnered significant attention in materials science. The comprehension of the interplay between dislocation motion dynamics and material behavior under diverse driving forces holds crucial significance in the field of materials science and engineering.

In recent years, remarkable advancements have been achieved in the field of dislocation dynamics, owing to progress in dislocation theory and experimental techniques, despite their inherent complexity. Particularly noteworthy is the increasing proficiency of electron microscopes, such as scanning or transmission electron microscopy (STEM or TEM), in facilitating the observation of dislocation motion. Furthermore, with the aid of more advanced *in-situ* technology, extensive studies on dislocation dynamics have been carried out. For example, the quantity and mobility of dislocation in metals & alloy (Al, Au and Ti-Pt, etc.), dielectrics (LiF, $BaTiO_3$ and Si_3N_4 etc.), graphene, and semiconductors (InSe, diamond, halide perovskites and sphalerite (ZnS) etc.) have been studied in details under the action of external fields (even including other additional stimulus besides mechanical stress) [3–7]. Banerjee et al. [3] reported an unprecedented phenomenon on an ultra-large, fully reversible elastic deformation of nanoscale (~300 nm) single-crystalline and polycrystalline diamond needles. Up to 9% maximum tensile strains (approaching the theoretical elastic limit) was achieved for the single-crystalline diamond with maximum tensile stress reaching ~89 to 98 GPa. Li et al. [6] reported an exceptional plastic deformation of $CsPbX_3$ (X = Cl, Br or I) single crystal, which can be facilely morphed into distinct geometries without localized cleavage or cracks by *in-situ* compression. Wei et al. [7] reported the super-plastic deformability in van der Waals inorganic semiconductors (the bulk single-crystalline InSe), which can be compressed by orders of magnitude and morphed into a Möbius strip or a simple origami at room temperature. Based on further research, a combinatory deformability indicator has been proposed to prescreen candidate bulk semiconductors with super-plastic deformability.

Some important results of these studies, especially the elastic and plastic deformability study on inorganic semiconductors in recent years, show that the dislocation dynamics of ionic and covalent crystals can be influenced by an electric field (known as electro-plasticity), photon irradiation (known as photo-plasticity) etc., when subjected to mechanical loading. Oshima et al. [8] observed that the ZnS single crystal with sphalerite structure can plastically deform up to ε = 45% in complete darkness without fracture even at room temperature (Fig. 1a, b). It is notable that the optical bandgap of the specimen deformed up to ε_t = 35% plastic strain in complete darkness lowered by 0.6 eV compared with the undeformed specimen. While ZnS single crystal immediately fractured when it deformed under light irradiation is most likely due to the suppressed plastic deformation by photoexcited charge carriers around the dislocations, where they become trapped and pinned through electrostatic effects. As shown in Fig. 1c–g, the difference

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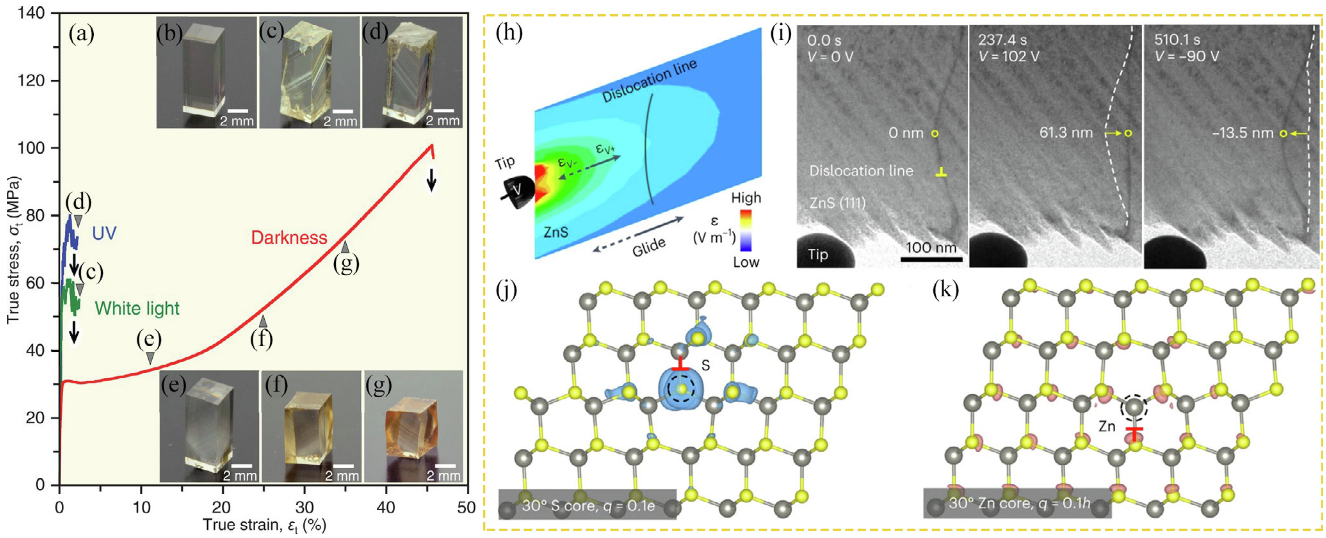

Fig. 1. (Color online) Characterizations of plastic deformation and dislocation motion driven by an external electric field in single-crystalline ZnS. (a) Stress–strain curves of ZnS single crystals under white or UV light (365 nm) or in complete darkness. (b) An undeformed specimen. The specimens deformed under (c) white light-emitting diode (LED) light and (d) UV LED light (365 nm). The specimens deformed up to (e) ε_t = 11%, (f) ε_t = 25%, and (g) ε_t = 35% in complete darkness. (a–g) Reproduced with permission from Ref. [8], Copyright © 2018, American Association for the Advancement of Science. (h) Schematic of the experimental set-up in TEM. (i) Chronological bright-field TEM images show the positions of a dislocation as a variable voltage is applied. The net charge distributions (q) of the 0.1e-charged 30° S core (j) and the 0.1h-charged 30° Zn core (k, where h is the charge of a hole). (h–k) Reproduced with permission from Ref. [9], Copyright © 2023, Nature Publishing Group.

in the surface morphologies, i.e., distinct slip lines and an evidence of deformation twinning in Fig. 1c and d under white and UV light whereas faint fine slip lines in Fig. 1e–g under darkness, indicates that the deformation mechanism is different depending on the light condition. These two different plastic deformation behaviors with or without light irradiation are closely related to the characters of dislocation. Without light, dislocations are more mobile and multiply easily. The density functional theory calculations show that the band-gap of the dislocation-core region is lower by 0.84 eV than that in the perfect crystal. It is found that the presence of dislocations can narrow the band-gap by formation of extra energy levels at the band-gap edge. Thus, the dislocation multiplication further results in the band-gap shift and the shape change in the band-gap edge with rising strain as the observed color changes in Fig. 1c–g. While with light, the electrons or holes excited by light irradiation can be trapped at extra energy levels around the band-gap edge of the dislocation cores. Consequently, the partial dislocations can be negatively or positively charged by electrons or holes. These findings highlight the substantial influence of photon irradiation on dislocation behavior, leading to significant alterations in both mechanical and optical properties of functional semiconductors. Notably, it becomes evident that mechanical action plays a vital role in shaping the dynamics of dislocation motion in single-crystalline ZnS semiconductors. Furthermore, the application of mechanical forces can induce colossal crystal deformations, subsequently the local electronic field within the ZnS material would be generated. The localized electric field, in turn, exerts a driving force on charged dislocations, influencing their motion and overall behavior.

Recently, the manipulation of the dislocation dynamics solely controlled by a non-mechanical stimulus has been successfully demonstrated by Li et al. [9]. Aided by *in-situ* TEM, the authors can observe in real time the motion behavior of an individual dislocation line in a ZnS single crystal sample under an external electric field via a tungsten tip (Fig. 1h). Interestingly, its direction of movement depends on the direction of electric field: it moves away from the tip under a positive voltage bias while reversing the original direction and moving towards the tip as the electric field is reversely loaded (Fig. 1i). Combined with the atomically resolved high-angle annular dark-field (HAADF) imaging and DFT calculations, they found that the dislocation core of the 30° S is negatively charged (Fig. 1j) while which of the 30° Zn is positively charged (Fig. 1k). And the minimum energy paths (MEPs) analysis of the dislocation glide shows that their glide barriers could be reduced by the electric field. All these results further reveal the reason on manipulation of the backward and forward dislocation motion under an external electric field possible as shown in Fig. 1i.

In this experiment, a reversible movement, direct probing and controlling of the dislocation are realized by using an electric field alone, which is another important breakthrough in this field. This method opens up the possibility of modulating dislocation-related behaviors and other photoelectrical properties (such as catalysis, luminescence and even superconductivity etc.) without contacting the samples.

So far, it could be reasonably inferred that the dislocation motion dynamics solely controlled by electric field in single-crystalline ZnS are originated from the chargeability of the dislocations. Additionally, since motion of a charged dislocation corresponds to local charge transportation, the dislocation mobility may be limited by dragging of the surrounding charge cloud compensating the dislocation charge. Therefore, different charge states of the dislocations (such as the 30° S and the 30° Zn) in ZnS can cause a large difference in their mobilities, resulting in the observed deformation twinning (Fig. 1c and d). Take effects of the photo-plasticity into consideration, Nakamura et al. [10] speculated that the extraordinary plasticity behavior could be mainly due to the interaction of the dislocations with the photoexcited electrons and/or holes. Therefore, they proposed an "photo-indentation" technique to verify this conjecture by combining nanoscale indentation tests with a fully controlled lighting system (inset in Fig. 2a(i)) [10]. They clearly observed increased pop-in stress (indicates dislocation nucleation near the surface of ZnS single crystal) under light irradiation (Fig. 2a(i)). In addition, the dislocation mobility significantly decreased by 15% under the light irradiation. Based on further investigation, it has been observed that the pop-in stress has the highest value when the material is subjected to light irradiation at a wavelength of 365 nm (Fig. 2a(ii), (iii)), in comparison to other wavelengths such as 300 or 550 nm. This phenomenon

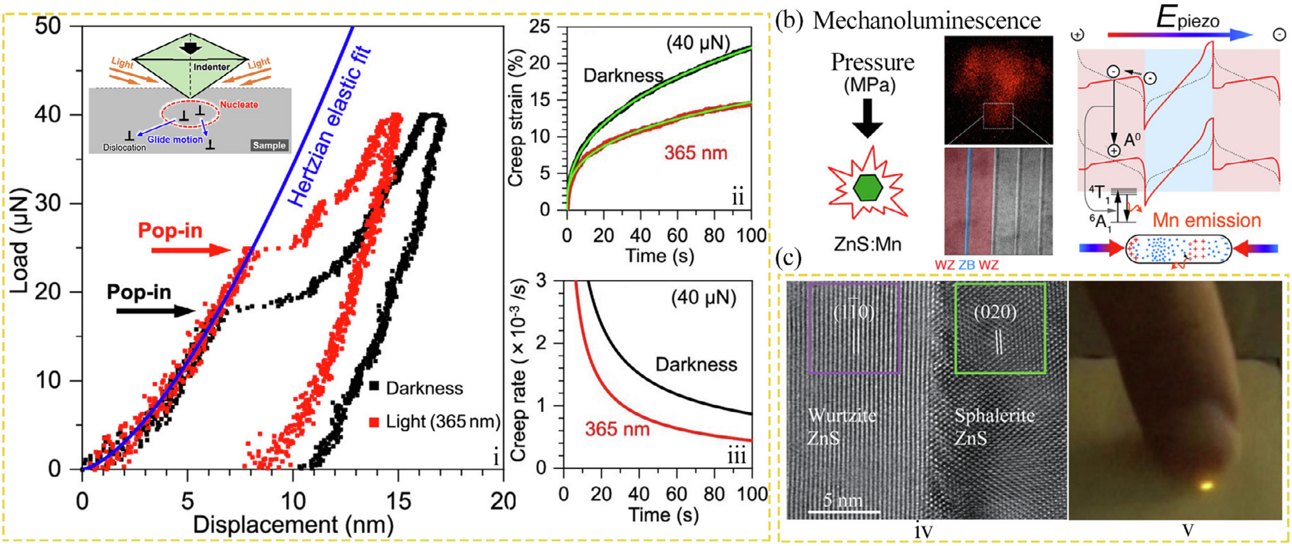

Fig. 2. (Color online) (a) Schematic of an indented sample with light irradiation (inset) and representative indentation load–displacement curves on the (001) surface in ZnS (i), indentation creep strain (ii) and the corresponding creep strain rate (iii) under 40 μN. Reproduced with permission from Ref. [10], Copyright © 2021, American Chemical Society. (b) Schematic of the ML related mechanisms relying on the interplay and between WZ/ZB hybrid crystal lattices and its defects. Reproduced with permission from Ref. [11], Copyright © 2021, American Chemical Society. (c) High-resolution TEM image of a bi-phase ZnS junction (iv) and ML photograph from Mn^{2+}-doped ZnS-based heterostructure (v). Reproduced with permission from Ref. [12] Copyright © 2022, Springer and Ref. [13] Copyright © 2020, Wiley-VCH, respectively.

can be attributed to the production of a larger number of photoexcited carriers, which subsequently interact more strongly with dislocations. The preferred wavelength of 365 nm closely aligns with the bandgap of ZnS, which ranges from 3.5 to 3.7 eV, corresponding to a wavelength range of 335 to 354 nm.

Accordingly, it may inspire investigations on *in-situ* real-time observations of dislocation motion driven by coupling electric field with photon even solely controlled by light to explore the underlying fundamentals between microstructures and photo-physics in materials, since understanding the interaction between light and a material is extremely important. For instance, the effects of light on the electronic and optical properties of solar cells, photo-electro-catalysis, luminescent materials (LED/Phosphors) and even superconductors. Taking the structure–property-performance concept into consideration, the research on dislocation dynamics of piezoelectric wurtzite (WZ) structure ZnS may bring more new and unexpected findings because most studies still focuse on its zinc blende (ZB) structure. Furthermore, the investigations on effects and relationship between dislocation dynamics and ions doped ZnS with single even hybrid phase of WZ and ZB structure would also be interesting due to their excellent photophysical properties such as mechanoluminescence (ML) and electroluminescence (EL) [11–13].

On the ML related research, Mukhina et al. [11] studied the ML of Mn^{2+} activated single ZnS microparticles from a microscopic perspective. The result shows that the ML properties of these particles result from interplay between a non-centrosymmetric crystal lattice and its defects, viz., dislocations and stacking faults (Fig. 2b). And under elastic low-force, the recoverable ML (hundreds of thousands of repeated luminescence in doped ZnS) is dependent on the special electrical properties of the interfaces between WZ and ZB crystal phases within the microparticle. Among these interfaces some are electron-depleted, which will result in the local enhancement of the piezoelectric field (E_{piezo}) generated under the external stress. Hence, it can be speculated that the revisable motion of dislocations is correlated to the recoverable ML as the observed reversibility of dislocation under electronic field [9]. Besides, the motion of dislocation generally involves electron-transfer during bond breaking and rebuilding, which could be one of the reasons resulting in the recoverable ML in doped ZnS. And this conjecture could be further investigated via *in-situ* real time experiments by combination of TEM/STEM (or atomic force microscope (AFM)) and super-resolution optical microscopy coupling with ultra-fast single photon detection system.

Ma et al. [12] also demonstrated that the ML properties can be greatly enhanced by the Mn^{2+} activated WZ and ZB crystal hybrid phase of ZnS (Fig. 2c(iv)) as well as the high brightness ML mediated by Mn^{2+}-doped ZnS-based heterostructure (Fig. 2c(v)) [13]. All these studies further indicate the importance and necessity of research on relationships between the dislocation behaviors related mechano-electro-optical properties and the ions doping semiconductors as well as their hybrid phases. The interactions of the dislocation behaviors and photons can be observed at the atomic-scale in real time owing to the unique mechanoluminescent phenomenon with real-time conversion capability of mechanical energy into light, which will refresh our understanding of the fundamentals in between ML and material structures from both experimental and theoretical perspectives. Given that the light is a wave composed of coupled electric and magnetic fields, we could go out on a limb and assume that the light or the magnetic field would be the next one who solely controls the dislocations motion in compounds as the electric field does in ZnS sphalerite single crystal. All these foreseeable results will help guide the development of outstanding ML materials and related applications in smart sensing and lighting devices.

Advancements in *in-situ* electron microscopy and computer simulations have significantly facilitated the accurate visualization of crystalline defects and the exploration of dislocation dynamics in crystalline materials. To enhance our comprehension of the intricate relationship between dislocation dynamics and materials, it is imperative to delve deeper into various aspects that warrant further scrutiny. Though not exhaustive, the following areas merit special attention in future research endeavors aimed at expanding our understanding of this relationship: (1) the coupling effects on dislocations and semiconductors of non-mechanical fields such as light, electron wind force, electron beam irradiation, electric and magnetic field, etc.; (2) the related dislocation behaviors on photo-electro-mechanical properties of materials such as metal halide perovskites, catalytic agents in energy and catalysis, high temperature superconducting transition in superconductors and dislocation induced enhancement on dielectric and piezoelectric properties in ferroelectrics [14] as well as the dislocation related dynamics of crystal growth [15]; (3) the research on dislocation dynamics over local barriers in crystal that further expands to twin crystal (or hybrid phase), polycrystals and grain boundaries is necessary. And the relationship between fracture and dislocation dynamics needs further study, since current studies focused on the ductile region [16]. The further findings may throw new light on the underlying knowledge of dissociation dynamics and their roles on materials in the future.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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References

[1] Lee C, Kim G, Chou Y, et al. Temperature dependence of elastic and plastic deformation behavior of a refractory high-entropy alloy. Sci Adv 2020;6:eaaz4748.
[2] Zhao B, Zhang Q, Fu X, et al. Brittle-to-ductile transition in Ti–Pt intermetallic compounds. Sci Bull 2021;66:2281–7.
[3] Banerjee A, Bernoulli D, Zhang H, et al. Ultralarge elastic deformation of nanoscale diamond. Science 2018;360:300–2.
[4] Zhang J, Liu G, Cui W, et al. Plastic deformation in silicon nitride ceramics via bond switching at coherent interfaces. Science 2022;378:371–6.
[5] Dong J, Li Y, Zhou Y, et al. Giant and controllable photoplasticity and photoelasticity in compound semiconductors. Phys Rev Lett 2022;129:065501.
[6] Li X, Meng Y, Li W, et al. Multislip-enabled morphing of all-inorganic perovskites. Nat Mater 2023;22:1175–81.
[7] Wei TR, Jin M, Wang Y, et al. Exceptional plasticity in the bulk single-crystalline van der Waals semiconductor InSe. Science 2020;369:542–5.
[8] Oshima Y, Nakamura A, Matsunaga K. Extraordinary plasticity of an inorganic semiconductor in darkness. Science 2018;360:772–4.
[9] Li M, Shen Y, Luo K, et al. Harnessing dislocation motion using an electric field. Nat Mater 2023;22:958–63.
[10] Nakamura A, Fang X, Matsubara A, et al. Photoindentation: a new route to understanding dislocation behavior in light. Nano Lett 2021;21:1962–7.
[11] Mukhina MV, Tresback J, Ondry JC, et al. Single-particle studies reveal a nanoscale mechanism for elastic, bright, and repeatable ZnS: Mn mechanoluminescence in a low-pressure regime. ACS Nano 2021;15:4115–33.
[12] Ma R, Wang C, Yan W, et al. Interface synergistic effects induced multi-mode luminescence. Nano Res 2022;15:4457–65.
[13] Peng D, Jiang Y, Huang B, et al. A ZnS/CaZnOS heterojunction for efficient mechanical-to-optical energy conversion by conduction band offset. Adv Mater 2020;32:1907747.
[14] Höfling M, Zhou X, Riemer LM, et al. Control of polarization in bulk ferroelectrics by mechanical dislocation imprint. Science 2021;372:961–4.
[15] Zhao H, Zhu Y, Ye H, et al. Atomic-scale structure dynamics of nanocrystals revealed by in situ and environmental transmission electron microscopy. Adv Mater 2022;35:2206911.
[16] Hu X, Liu N, Jambur V, et al. Amorphous shear bands in crystalline materials as drivers of plasticity. Nat Mater 2023;22:1071–7.

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