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研究課題名（和文）ウルツ鉱型半導体の力学特性に及ぼす光環境効果の実験的計測とメカニズム解明

研究課題名（英文）Experimental evaluation and mechanism elucidation of light environment effects on mechanical properties of wurtzite semiconductors

研究代表者
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研究成果の概要（和文）：無機半導体材料は通常、室温で脆く壊れやすいと考えられてきたが、最近そうした無機半導体結晶の可塑性が光環境に敏感であることが発見された。しかし、光環境が無機半導体材料の力学的性質に及ぼす影響は未だに理解が不十分である。そこで本研究では、結晶塑性の支配する転位のナノスケール挙動を評価するために、光環境制御下でのナノインデンテーション試験を実施した。その結果、硫化亜鉛結晶に対する実験からは、光照射下と暗闇下の両方で転位生成がひずみ速度に依存しないことが分かった。また、酸化亜鉛結晶に対する実験では、光照射が転位のすべり運動に顕著な影響を及ぼすことが分かった。

研究成果の学術的意義や社会的意義
材料がどのように変形し、破壊していくのかという基本的な現象を解明することは、材料を利用する分野において重要な課題である。最近では光環境が材料の強度特性に影響を及ぼすことが発見され、注目されている。しかし、その現象の理解は未だ不十分であり、メカニズムを解明することが期待されている。本研究では、異なる光環境下で硫化亜鉛および酸化亜鉛の転位挙動をナノスケールで評価し、これらの材料の室温塑性変形挙動の一端を解明することに成功した。これらの成果は無機半導体材料のよりよい材料加工技術の開発に貢献すると考えられる。

研究成果の概要（英文）：Inorganic semiconductor compounds are typically brittle at room temperature, which has limited their applications nowadays. Since 2018, research has shown that ZnS crystals exhibit brittle fracture under white light, but show notable plasticity in darkness. However, the impact of light on the mechanical properties of such materials is not fully understood. In this study, in-situ nanoindentation experiments with a controllable lighting system were adopted to evaluate the mechanical responses at the nanoscale under varying light conditions. Tests on ZnS single crystals demonstrated that the dislocation nucleation in ZnS nanoindentation is strain-rate insensitive both in light and in darkness. Experiments on ZnO revealed that light slightly affects the dislocation nucleation in ZnO, but significantly influences dislocation motion.

研究分野：結晶欠陥工学

キーワード：転位　無機化合物

１．研究開始当初の背景

Crystalline inorganic compounds have high strength, high chemical stability, and unique electromagnetic properties, so they are expected to be applied to various industrial fields. However, their “brittleness” poses a significant challenge to broadening their applications. These materials typically show little or no plastic deformation at room temperature, and are prone to fracture along specific crystal planes and grain boundaries upon external mechanical loading. Consequently, their safety and reliability must be rigorously evaluated before they can be used as both structural and functional materials. The “brittleness” of crystalline inorganic compounds originates from the strong ionic and covalent chemical bonding, as well as from the complex crystal structure. So far, numerous efforts have been made to overcome the brittleness.

The role of the external light environment in affecting the room temperature plasticity of inorganic compounds has been recognized since 2018. It was reported that ionic ZnS single crystals exhibit brittle fracture under the environmental white light, but demonstrate extraordinary compression plasticity in darkness [Oshima et al., Science, (2018)]. Such a difference in deformability under different light conditions is attributed to the interaction between “dislocations” and “light”. One possible mechanism pointed out, the photo-excited carriers (electrons and holes) will interact with the electrostatic fields near dislocations, then change the atomic-scale structure of dislocations, and finally affect the plasticity of materials [Matsunaga et al., Acta Mater., (2020)]. Yet, the understanding of how light influences the plasticity of many other crystalline inorganic compounds remains lacking. Advancing the knowledge of the interaction mechanisms between light and mechanical properties is thus of significant importance.

２．研究の目的

Based on the above background, the project aims to elucidate the effects of light illumination on the mechanical properties of advanced inorganic compounds. By conducting nano-scale mechanical experiments and transmission electron microscopy observations, the influence of light on the dislocation-mediated plasticity in several inorganic compounds can be systematically investigated. By comprehensively manipulating the external light environment, we can hopefully enhance the deformability of crystalline inorganic compounds and contribute to the development of advanced structural and functional devices.

３．研究の方法

Nanoindentation under controllable light environment was adopted to evaluate the influence of light irradiation on the plasticity and dislocation behaviors in ZnS and ZnO. Regarding sphalerite ZnS single crystals, indentation tests were conducted on the (001) plane under two light conditions: in darkness and in 365 nm light. The sample was loaded to the maximum load of 60 μN at three different strain rates (0.637 /s, 0.193 /s, 0.064 /s), followed by 0.5 s load holding and then unloading to a load of zero. Regarding wurtzite ZnO single crystals, indentation tests were performed on the (0001) 45^{o} off plane under two light conditions: in darkness and in 405 nm light. This orientation was specially designed to activate the most preferred slip system in ZnO. Three types of indentation tests were performed using a Berkovich diamond indenter: (i) low-load nanoindentation tests, the sample was loaded up to 60 μN; (ii) high-load nanoindentation tests, which were conducted with a maximum load of 500 μN; and (iii) nanoindentation creep tests, 300 μN load was maintained for 100 s. All indentation tests were performed by the load-control mode.

After the nanoindentation tests, the cross-sections containing the local areas beneath the indentation imprints were extracted by a focused ion beam (FIB). Typical cross-sectional morphology and substructures beneath the indents were then imaged with a transmission electron microscope (TEM).

4．研究成果

(1) Light influence on the strain-rate dependence in ZnS

Fig. 1(a) displays representative load-depth curves during nanoindentation tests under various strain rates in darkness. All three curves exhibit clear pop-ins (green arrow), i.e., the sudden depth bursts at a certain load in the load-depth curves. The occurrence of pop-in in ZnS single crystals were verified to result from the onset of plasticity. Prior to pop-in, the material beneath the indenter underwent pure elastic deformation. The overlap between the elastic portions at different strain rates suggests no obvious influence of strain rate on the material’s elastic constants. Following the pop-in, elasto-plastic deformation occurred. Fig. 1(b) shows the curves at three strain rates in 365 nm light. As well, the elastic segments at different strain rates overlap with each other, indicating no significant influence of strain rate on the elastic constants under illumination. Comparing the curves at the same strain rate in Fig. 1(a) and (b), there is no obvious difference between the elastic portion in light and that in darkness.

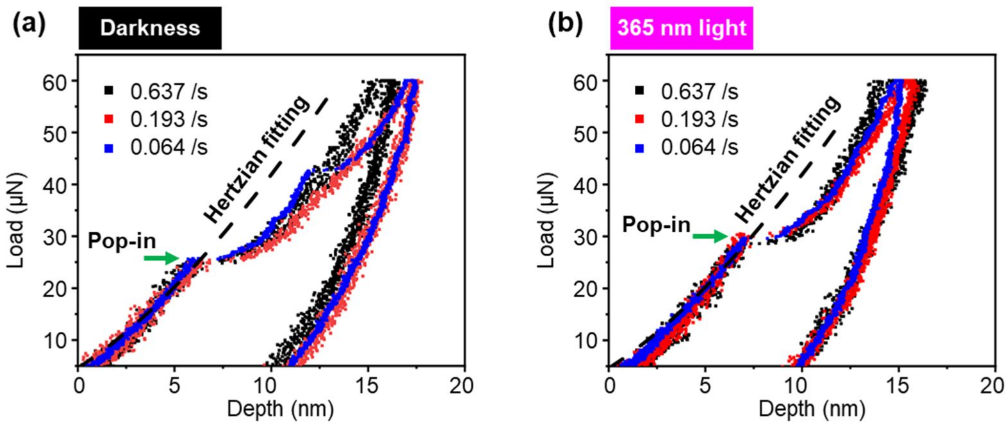

Fig. 1 Representative nanoindentation load-depth curves obtained at a peak load of 60 μN under varying strain rates in (a) darkness and (b) 365 nm light.

By comparing the maximum shear stress at the first pop-in, there is a weak strain-rate dependence in ZnS. Regardless of the strain rates and light conditions, the values of average maximum shear stresses are close to the theoretical strength of μ/2π. Such a high level of stress implies a homogeneous dislocation nucleation at the onset of pop-in. The average maximum shear stresses at three strain rates are very close for both in darkness and in light. The difference is almost within the standard deviation and therefore within the systematic error. Overall, the strain rate shows a very limited influence on the dislocation nucleation in ZnS.

To interpret the rate insensitivity of the dislocation nucleation in ZnS, the classical dislocation theory was adopted to estimate the activation energy ΔG required for the formation of a circular dislocation loop. The ΔG is plotted as a function of loop radius r and is shown by the blue line in Fig. 2. For dislocation nucleation to occur, the activation energy must overcome the energy barrier. In the present results, the value of ΔG is below zero in most cases. This indicates that dislocation nucleation could almost occur only with external stresses and without any assistance of thermal energy. Therefore, the dislocation nucleation process in ZnS shows a weak dependence on the strain rate. During indentation tests, plastic deformation is always accompanied by the motion of nucleated dislocations from the sample surface to deeper regions. Dislocation motion in crystals requires a local stress to overcome the Peierls barrier. In this study, the maximum shear stress at the first pop-in (≈μ/2π) is several times higher than the Peierls stress of ZnS. The local shear stress when a pop-in event occurs is much greater than those required for dislocation motion. Hence, dislocation motion could also occur only with external stresses and without assistance of thermal energy.

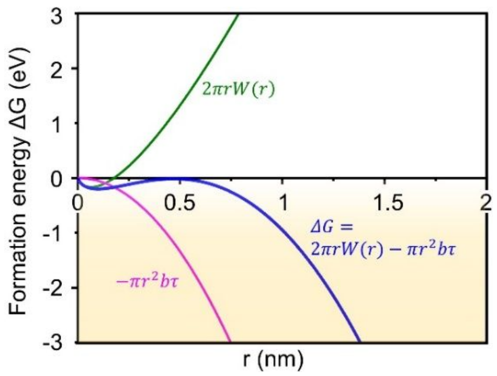

Fig. 2 Free energy of dislocation nucleation (ΔG) as a function of dislocation loop radius (r) for ZnS single crystals.

(2) Light influence on ZnO nanoindentation

The effects of light illumination on the dislocation-mediated plasticity in ZnO were studied by nanoindentation tests under different light conditions. The experimental platform was schematized in Fig. 3(a). Clear pop-in events were detected both in light and in darkness, as shown in Fig. 3(b). The maximum shear stresses at pop-in were found to approximate the theoretical shear strength regardless of the light conditions. The activation volume at pop-ins was calculated to be larger in light than in darkness. Cross-sectional transmission electron microscope images taken from beneath the indentation imprints were displayed in Fig. 3(c-d). It was found that all indentation-induced dislocations were located beneath the indentation imprint in a thin-plate shape along one basal slip plane. These indentation-induced dislocations could spread deeper in darkness than in light, revealing the suppressive effect of light on dislocation behavior. It was found that dislocation glide ceased at a higher stress level in light, indicating the increase in the Peierls barrier under light illumination. Furthermore, nanoindentation creep tests showed the suppression of both indentation depth and creep rate by light.

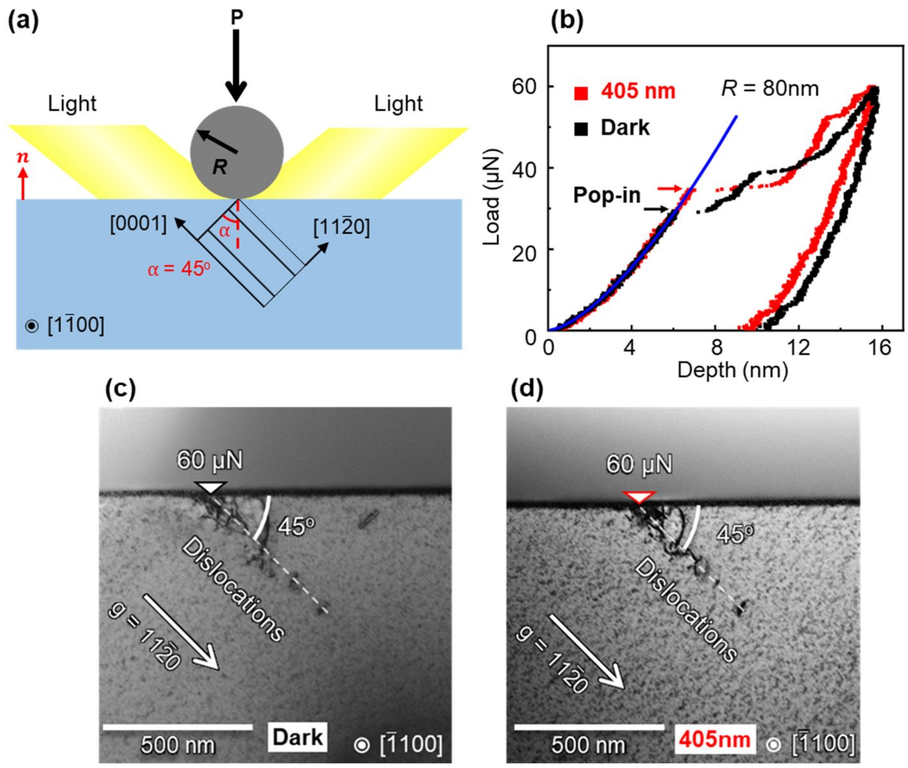

Fig. 3 (a) A schematic of photoindentation tests.(b) Representative indentation load-depth curves obtained at a maximum load of 60 μN, in darkness and 405 nm light. Typical bright-field cross-sectional TEM images taken from beneath the indentation imprints: (c) 60 μN test in darkness; (d) 60 μN test in light.

５．主な発表論文等

〔雑誌論文〕　計4件（うち査読付論文　4件／うち国際共著　4件／うちオープンアクセス　1件）

１．著者名 Li Yan、Oguri Hiroto、Matsubara Ayaka、Tochigi Eita、Fang Xufei、Ogura Yu、Matsunaga Katsuyuki、Nakamura Atsutomo	４．巻 131
２．論文標題 Strain-rate insensitive photoindentation pop-in behavior in ZnS single crystals at room temperature	５．発行年 2023年
３．雑誌名 Journal of the Ceramic Society of Japan	６．最初と最後の頁 685～689
掲載論文のDOI（デジタルオブジェクト識別子） 10.2109/jcersj2.23064	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Oguri Hiroto、Li Yan、Tochigi Eita、Fang Xufei、Tanigaki Kenichi、Ogura Yu、Matsunaga Katsuyuki、Nakamura Atsutomo	４．巻 44
２．論文標題 Bringing the photoplastic effect in ZnO to light: A photoindentation study on pyramidal slip	５．発行年 2024年
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jeurceramsoc.2023.09.060	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

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掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jmst.2023.02.017	査読の有無 有
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３．雑誌名 Journal of the American Ceramic Society	６．最初と最後の頁 7030～7035
掲載論文のDOI（デジタルオブジェクト識別子） 10.1111/jace.18686	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

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2．発表標題 Effects of Light Illumination on the Dislocation-mediated Plasticity in Single-crystalline ZnO
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1．発表者名 Yan Li, Xufei Fang, Eita Tochigi, Yu Oshima, Sena Hoshino, Hiroto Oguri, Yuichi Ikuhara, Katsuyuki Matsunaga, Atsutomo Nakamura
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〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関