The Study of Near-Band-Edge Property in Oxygen-Incorporated ZnS for Acting as an Efficient Crystal Photocatalyst

Min-Han Lin, Perumalswamy Sekar Parasuraman, and Ching-Hwa Ho*

Abstract: A wide gap semiconductor material has attracted attention as a heterophotocatalyst because of its light harvesting nature to be used in alternative energy production for the next generation. We, herein, grow and synthesize ZnS_{1−x}O_x series compounds using the chemical vapor transport (CVT) method with I_2 serving as the transport agent. Different crystals, such as undoped ZnS and oxygen-doped ZnS_{0.04}O_{0.08} and ZnS_{0.08}O_{0.12}, revealed different bright palette emissions that were presented in photoluminescence spectra in our previous report. To study the electron–hole pair interaction of this sample series, the near-band-edge transitions of the sample series were characterized in detail by photoconductivity (PC) experiments. Additional results from surface photovoltage (SPV) spectra also detected the surface and defect-edge transitions from the higher oxygen-doped ZnS crystals. PC measurement results showed a red-shift in the bandgap with increasing incorporation of oxygen on ZnS. Consequently, the samples were subjected to photoirradiation by xenon lamp for the degradation of methylene blue (MB) by acting as heterophotocatalysts. Undoped ZnS emerged as the best photocatalyst candidate with the fastest rate constant value of 0.0277 min^{-1}. In cubic {111} ZnS, the polarized Zn^2+ → S^− ions may play a vital role as a photocatalyst because of their strong electron–hole polarization, which leads to the mechanism for degradation of the MB solution.

Introduction

Recently, natural energy conversion has received greater attention because of the current generation’s interest in an ecofriendly life. Specifically, wide bandgap semiconductor photocatalysts have played vital role in broad applications, such as solar cells, water splitting, hydrogen evolution reactions, and pollutant degradation. The major criteria for good photocatalytic reaction is based on photon absorption, photogenerated electron–hole pairs, migration and recombination of the photogenerated electron–hole pairs, adsorption–desorption of reactants–products, and also redox reactions on the surface of photocatalysts. Furthermore, geometry (size, shape, and structure) of the materials could also tune properties and their possible applications. The interface reaction controlled the surface energy and reactivity, which were dependent on various parameters, such as spatial conformation, structural state of atoms, and molecules. In particular, single crystals were directly connected to specific crystallographic faces that exhibited dissimilar surface and atomic configurations to the polycrystalline and amorphous thin films. Therefore, facet effect had become an ideal character for a heterogeneous photocatalyst that was highly sensitive to its surface orientation and crystallinity. This also intrinsically decided the mechanism pathway of semiconductor in the photocatalytic reaction, which were well satisfied aforementioned criteria. TiO_2 and ZnO are well-known example of photocatalysts because of their abundant availability, nontoxicity, and stability. They are only sensitive to ultraviolet region because their bandgap is 3.2 eV in anatase-phase TiO_2. On the other hand, ZnO acts as an alternative photocatalyst because of its direct gap (3.37 eV) and larger exciton binding energy of 60 meV. Morphology, geometry, crystallinity, and oxygen defects mark them as efficient photocatalysts. Their major drawback is the fast recombination of electron hole pair, which hindered superficial diffusion of charge carriers and decreased the photo-degradation of dye. However, zinc sulfide was a prime candidate because of its environment friendly nature and also its theoretical ability to generate more photocarriers than selenide and bromide. The direct bandgap of ZnS semiconductor (~3.7 eV and exciton binding energy ~39 meV) is larger than that of the ZnO semiconductor (~3.37 eV and exciton binding energy ~60 meV). The gap states and band edge of ZnS would also facilitate the zinc sulfide acting as a UV–visible photocatalyst. These materials have two polymorphic phases, such as major sphalerite and...
minor wurtzite,\textsuperscript{16} which were similar to that of zinc oxide. The preparation process was easy, and structural defects, such as sulfur vacancies, twins, and stacking faults, were used in the crystal for irradiating defect emissions.\textsuperscript{17} Despite the advantages of ZnS described above, it still has the disadvantage of being active only in the UV region. To overcome this issue, C or N doping of a hierarchical porous microsphere of ZnS demonstrated the ability to harvest visible light, which in turn degraded organic pollutants to greater extend.\textsuperscript{18} Furthermore, it has been reported that ternary crystals of Zn\textsubscript{\(x\)}Cd\textsubscript{\(1-x\)}S performed as excellent photocatalysts for the degradation environmental pollutants because of the strong visible light absorption properties of CdS and tunable band gap, achieved by changing mole ratio of Zn.\textsuperscript{19} ZnS/CuS nanospheres decorated on reduced graphene oxide nanocomposite are highly efficient photocatalysts for dye degradation under simulated sunlight.\textsuperscript{20} In our latest literature survey, only one study focused on sampling for ZnS(1−\(x\))O\textsubscript{x} by annealing at 400 °C, but this study lacked an explanation of the optical measurement.\textsuperscript{21} Our group previously reported the color palette emission in ZnS(1−\(x\))O\textsubscript{x} (\(x\) = 0, 0.06, 0.12) series grown by chemical vapor transport (CVT) method using I\textsubscript{2} as transport agent.\textsuperscript{22} These sample series emitted UV, purple, blue and green emission from photoluminescence spectra due to its defect state and also free exciton. Moreover, the cubic zinc sulfide (c-ZnS) can also act as heterogeneous photocatalysts for methyl blue degradation.\textsuperscript{23} In spite of that, they were still lacking evidence about its photoconductivity (PC) capability as well as minor photogenerated carriers could stimulate the surface voltaic output through surface photovoltage (SPV) experiment. As a consequence, it would assist to predict for reasoning interaction between the electron–hole pair in the photodegradation of methylene blue (MNB) by the ZnS(1−\(x\))O\textsubscript{x} (\(x\) = 0, 0.06, 0.12) series crystals.

To further address the photodegradation mechanism in zinc oxysulfide, the present work would accurately categorize the oxygen-doped ZnS series as a p-type semiconductor by hot-probe measurement using metal–semiconductor-metal (MSM) configuration. These oxygen-incorporated ZnS series showed good ohmic contact and, further, reduced dark resistivity as the oxygen content increased. These sample series were sharply characterized by PC and SPV measurements, which clearly showed absorption-band movement, as well as the appearance of defect and surface-state edge transitions for the identification of successful doping of oxygen in the ZnS(1−\(x\))O\textsubscript{x} series. These sample series, such as undoped ZnS, ZnS\textsubscript{0.94}O\textsubscript{0.06}, and Zn\textsubscript{0.88}O\textsubscript{0.12} may be better hetero photocatalysts. However, among them, the \{111\} c-ZnS crystal was the better candidate for photodegradation of 50-μM MNB with a rapid rate constant of \(k = 0.0277 \text{ min}^{-1}\). In optical measurements, several SPV and PC features, such as surface states, band edge, and valence sites, of the zinc oxysulfide significantly affect the photodegradation of the MNB solution. Hence, ZnS(1−\(x\))O\textsubscript{x} series may be suitable candidates for

Figure 1. (a) Measured temperature of the hot-probe source using soldering iron. (b) Measurement configuration of the hot-probe experiment for a semiconductor. (c–e) Measured thermoelectric motive force (thermal voltage) from (c) undoped ZnS, (d) ZnS\textsubscript{0.94}O\textsubscript{0.06} and (e) Zn\textsubscript{0.88}O\textsubscript{0.12}. The sample morphology and background voltage are also shown in their respective inset photos.
organic devices as photocatalysts and applied in, for example, dye-sensitive solar cells (DSSCs) in the near future.

RESULTS AND DISCUSSION

Hot-Probe Measurement of ZnS\(_{(1-x)}\)O\(_x\) Series. The typical semiconductors were easily categorized as n- or p-type by the MSM model using hot-probe experiment. The contact ends of the sample were prepared by using conductive paste (Ag) and metal wire. Once the voltmeter was fixed on these sample series (ZnS, ZnS\(_{0.94}\)O\(_{0.06}\), ZnS\(_{0.88}\)O\(_{0.12}\)), the heated end (soldering iron heat source) became positive, while the cool end became negative at room temperature (see Figure 1b). It created thermal gradient and generated high-density carriers that diffused to the lower-temperature end of low carrier density. For a p-type semiconductor, holes are excited and diffused out from the hot end to the cold end, generating negative voltage at hot end compared to that of the cold end. On the other hand, for an n-type semiconductor, the electrons diffuse out by concentration gradient, which creates positive voltage. For the hot-probe experiment of the ZnS\(_{(1-x)}\)O\(_x\) series, the soldering iron probe was heated to 170 °C (see Figure 1a). The soldering iron probe was kept in contact with the hot end of the sample series, and the thermoelectric power (ΔV), with the background subtracted, yielded −0.964 V for pure ZnS, −0.620 V for ZnS\(_{0.94}\)O\(_{0.06}\), and −0.518 V for ZnS\(_{0.88}\)O\(_{0.12}\). The results are displayed in Figure 1c–e. The series samples are obviously p-type semiconductor distinguished by the sign of thermal electromotive force (Seebeck voltage) ΔV by thermal gradient. The carriers’ diffusion current could be dominated by the concentration of excited carriers, that is, \(Δp = (p_{\text{excited}} - p_0)\) for the thermally excited holes in a p-type semiconductor, which expressed as \(^2\)^2

\[
I_p = (q) \cdot \Delta p \cdot \mu_h \cdot P_h \cdot \Delta T / \Delta x
\]  

where \(P_h = \Delta V / \Delta T\) is the differential thermoelectric power (Seebeck coefficient) and \(\Delta T / \Delta x\) is temperature gradient between hot and cold probes. The sizes of the samples ZnS, ZnS\(_{0.94}\)O\(_{0.06}\), and ZnS\(_{0.88}\)O\(_{0.12}\) are similar (i.e., see insets of Figure 1c–e and the geometric information are shown in Figure 3c), and the cold-end temperature is ∼25 °C. The measured magnitudes of Seebeck coefficient (\(|\Delta V / \Delta T|\)) are determined to be 6.65, 4.27, and 3.57 mV/K for the ZnS, ZnS\(_{0.94}\)O\(_{0.06}\), and ZnS\(_{0.88}\)O\(_{0.12}\), respectively. The relatively lower value of Seebeck coefficient of the ZnS\(_{0.88}\)O\(_{0.12}\) sample maybe correlates with a lower resistivity of the higher oxygen-contained ZnS. We will verify this result by resistivity measurement. Moreover, the p-type conductivity of the CVT-grown chalcogenides with ICl\(_3\) or I\(_2\) as the transport agent...
agent is usually a result of the crystal growth, owing to the formation of sulfur–halogen complex acceptor level, for example, (SCl)_{2−} in FeS_{2}. The p-type conductivity of the ZnS_{x−x_0}O x (0 ≤ x ≤ 0.12) grown by iodine transport is maybe also caused by a sulfur–iodine complex acceptor level, noted as (SI)_A, that existed in the crystals.

**Optical Characterization of Absorption Band, Defect Edge, and Surface States.** The series samples’ (named as ZnS_{1−x}O_x) bright palette visible emissions upon laser illumination in photoluminescence due to defect sites and band edge were previously illustrated. The ZnS_{1−x}O_x crystals were shown to contain defects of sulfur (V_S) and oxygen vacancies (V_O) because of the deficiency of chalcogen and oxygen atoms in the crystals. Detailed characterizations of defect and band-edge states can also be implemented directly by using PC and SPV measurements from different axial orientations to identify exact relationship of these samples with photon. For PC measurements, the [111]-face sample was cut down in rectangle shape, the electric field ε was applied in the (111) direction, and the incident photons were impinged on the [111] plane. Frequency-dependent PC measurements were carried out to identify various transition features by defects, imperfections, and band edges in ZnS_{1−x}O_x. The results are shown in Figure S1. From the relative peak-intensity changes of the frequency-dependent PC spectra in ZnS, ZnS_{0.94}O_{0.06} and ZnS_{0.88}O_{0.12}, some of the peak features, such as sulfur vacancy (V_S), sulfur–iodine complex acceptor level (SI)_A, and main absorption band, are detected. Essentially, the intensity of each PC feature decreases with chopped frequency as the incident light increases. Figure 2a shows the selective PC spectra of ZnS, ZnS_{0.94}O_{0.06}, and ZnS_{0.88}O_{0.12} at 25 Hz, which are more relevant to show all the defect and imperfection-related transitions. The main absorption band is marked in the yellow-highlighted region, where the PC peak positions of the ZnS, ZnS_{0.94}O_{0.06}, and ZnS_{0.88}O_{0.12} series crystal were determined to be 3.801, 3.798, and 3.767 eV at 300 K. As the oxygen content is increased, the main PC peak is also red-shifted. On the other hand, the PC intensity is also decreased when the oxygen content is increased evident from the magnification scale in Figure 2a. It may be related to both resistivity and photosensitivity of ZnS_{1−x}O_x being decreased. For ZnS, there is a PC peak feature present at 3.64 eV below band edge. It is inferred to come from the acceptor level (SI)_A in the p-type ZnS. This (SI)_A defect feature can also be found in the SPV spectra of ZnS_{1−x}O_x [e.g., ZnS and ZnS_{0.88}O_{0.12}] below main band edge displayed in Figure 2b. The SPV spectra of the ZnS_{1−x}O_x in Figure 2b are detected by a surface Schottky solar-cell structure of Cu/ZnS_{1−x}O_x (x = 0, 0.06, and 0.12). The SPV measurement configuration can measure and enhance the imperfection states of ZnS_{1−x}O_x coming from the surface states. For the x = 0.12 sample in Figure 2b, two obvious transition features coming from sulfur vacancy V_S (∼2.8 eV) and ZnO (E_g ZnO ∼3.2 eV) can be detected by the SPV spectrum. The occurrence of V_S also indicated that incorporation of oxygen was successfully grown on the sulfur vacant site in these sample series. Furthermore, the PC spectra in Figure 2a can also detect the main band feature of the ZnO (E_g ZnO) in the highest oxygen-incorporated ZnS_{0.88}O_{0.12} sample owing to the existence of separated phases. The result was also evident in previous thermorelectance measurement. Figure 2c shows the representative band scheme for the band edge, defect, and imperfection states detected by above optical and thermoelectric experiments. Essentially, the band-edge transition of [111] c-ZnS is about 3.77 eV. The separated phase of ZnO can exist in the ZnS_{1−x}O_x of higher oxygen content. The transition energy of valence-band edge (E_V) to the sulfur vacancy V_S is about 2.8 eV. The existence of (SI)_A acceptor near E_V can render a p-type conductivity of the ZnS_{1−x}O_x, which verified by hot-probe experiment. The band scheme in Figure 2c could further

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**Figure 3.** (a) V−I measurement of the ZnS_{1−x}O_x series crystals. (b) Dark resistivity of the oxygen-incorporated ZnS series crystals. (c) Tabulated values for the resistance, area, and length of pure ZnS and oxygen-doped ZnS. The left inset shows the geometric information for calculation of sample resistivity.
facilitate the analysis of photocatalytic behavior of the ZnS(1-x)O_x crystal photocatalyst in the dye degradation.

Electrical-Resistivity Measurement of ZnS(1-x)O_x. For the evaluation of electrical conductivity of the ZnS (1-x)O_x series crystals, voltage–current (V–I) measurements of the three samples investigated by hot-probe experiments are also carried out under dark condition. Figure 3a depicts the V–I measurement results measured with MSM configuration for the ZnS(1-x)O_x series plates with Ag coating two ends of the samples. The experiments were done under dark condition, and voltage scanning range was from -200 to +200 V. It is clear that the dark resistance is very high owing to the high purity and wide bandgap of the ZnS(1-x)O_x series crystals. The values of dark resistivity (5.51 MΩ cm for ZnS, 4.96 MΩ cm for ZnS0.94O0.06, and 4.43 MΩ cm for ZnS0.88O0.12) are much higher than that of an N-doped p-ZnS thin film grown by metalorganic vapor phase epitaxy. It shows the high purity of the ZnS(1-x)O_x series samples. From Figure 3a, it also displays good ohmic-contact behavior after applying a linear fitting equation to its linearity. Figure 3b shows the values of dark resistivity of ZnS, ZnS 0.94O0.06, and ZnS0.88O0.12. The dark resistances are tabulated in Figure 3c for comparison together with the dimensions of the three ZnS(1-x)O_x samples are also included. The value of resistivity decreases as the oxygen content is increased in the ZnS(1-x)O_x series. It is maybe owing to the higher defect and surface-state density existed in the higher oxygen-incorporated ZnS.

Ideal II–VI Crystal Photocatalyst for Methylene Blue Degradation. On the basis of the defect and imperfection-state study described above, ZnS(1-x)O_x series crystals used for photocatalytic degradation of organic pollutants were evaluated. A 50 µM methylene blue (MNB, C16H18ClN3S) solution was used for simulation of the degradation target. The area of sample size was about 3 x 2 mm² and the volume of the MNB solution is about 4 mL. Figure 4a–d show the normalized absorbance spectra of the solutions’ photocatalytic degradation of 50 µM MNB with and without ZnS(1-x)O_x series crystals as the photocatalyst. The Xe-arc lamp’s white light (consists of mixed wavelength from ultra to visible and infrared region) was irradiated on MNB, ZnS + MNB, ZnS0.94O0.06 + MNB, and ZnS0.88O0.12 + MNB, and the spectra were recorded at time intervals of 0, 10, 20, 30, 40, 50, and 60 min. The absorbance spectra of MNB have generally the largest absorption peak close to 660 nm, maximum absorption intensities of the MNB solutions were in the region of 550–700 nm, where at least two absorption peaks of 610 and 660 nm could be clearly observed. As photoillumination time was increased, the speed of the MNB degradation occurred in the order of pure {111} c-ZnS > ZnS0.94O0.06 > ZnS0.88O0.12 > MNB. The results were directly shown by absorption intensity at 660 nm and with decreasing tendency shown in Figure 4a–d. The photoreaction decay of the MNB degradation with time can be analyzed using normalized rate equation as:

\[ C/C_0 = \exp\{-k\cdot t\} \]  

(2)

where \( k \) is the rate constant for the photodegraded reaction. The normalized concentration change (\( C/C_0 \)) versus degradation time for the ZnS(1-x)O_x series was shown in Figure 5.
determine the rate constant $k$ for all these samples series the exponential decay of the MNB degradation using eq 2 is analyzed. The best fit was remarked in red solid lines displayed in Figure 5. The photodegradation rate constants $k$ of MNB for the pure ZnS, ZnS$_{0.94}$O$_{0.06}$, ZnS$_{0.88}$O$_{0.12}$, and MNB samples were determined to be 0.0277, 0.0242, 0.0113, and 0.005 min$^{-1}$, respectively. The $k$ value for photodegradation of pure [111] c-ZnS sample is the greatest among them. On comparison, pure ZnS is about 1.14 times higher than ZnS$_{0.94}$O$_{0.06}$ ($x$ = 0.06), 2.45 times higher than ZnS$_{0.88}$O$_{0.12}$ ($x$ = 0.12), and 5.26 times higher than pure MNB. It is a well-known fact that pure MNB complete degradation occurs at slower interval (approximately 200 min), which also reflects same behavior when they were exposed to visible light. The complete degradation time of MNB itself in Figure 5 is still much longer than that in the presence of the ZnS$_{1-x}$O$_x$ crystal photocatalysts. A well-known phenomenon is that a highest $k$ value would have a maximum photodegradation ratio. 29 Scheme 1a represents a simple mechanism of photocatalytic degradation of MNB using [111] c-ZnS as the photocatalyst. It is known that the zinc-blende [111] face has the same atomic arrangement as that of wurtzite {0001} excepting that the stacking sequence of the zinc-blende phase is in ABCABC stacking along the (111) direction, while that of the wurtzite ZnS is stacking with ABAB order along the (0001) direction. 30,31 Both the two ZnS phases of zinc-blende {111} and wurtzite {0001} have the same ZnS$_4$ tetrahedron, where the wurtzite structure has certain deformation to cause the separation of centers of the positive and negative charges of Zn$^+$ and S$^-$. The distortion of ZnS$_4$ unit in wurtzite {0001} results in dipole moments and internal electrical field, which benefits to the transfer and separation of photogenerated electrons and holes. For a perfect zinc-blende {111} plane, there is no distortion in the ZnS$_4$ unit. However, the defects (e.g., V$_{Zn}$, etc.) in c-ZnS should have slightly deformed ZnS$_4$ units to create dipole and internal field in the [111] c-ZnS. That is the reason why the undoped [111] c-ZnS has the fastest degradation rate in the ZnS$_{1-x}$O$_x$ series, as shown in Figure 5. As shown in Scheme 1a, with the [111] c-ZnS crystal was irradiated by Xe-arc lamp, electrons in the valence band (VB) were transited to the conduction band (CB) for production electronic–hole pairs. In the indirect oxidation process of dyes, the hydroxyl reactive radicals (•OH = OH$^-$ + h$^+$) were formed by combination of holes with water molecules or hydroxide anions. 32,33 This reaction also generates hydroperoxyl radicals (O$_2$ + e$^-$ → O$_2^-$ and *O$_2^-$ + H$^+$ → •HO$_2$) and hydroxyl radicals (•OH) to degrade organic pollutants. 34 The valence-band potential (h$^+$) is positive enough to generate hydroxyl radicals on the ZnS surface, and the conduction-band potential (e$^-$) was significantly negative to reduce molecular oxygen near the environment. 29 More hydroxyl radicals and photocarriers will be generated because of the high population of electron–hole pairs, which makes [111] c-ZnS a powerful oxidizing agent. Such a powerful photocatalytic mechanism attacks the MNB solution on or near the surface of ZnS to remove the organic pollutants. Whereas the oxygen-doped ZnS series crystals (e.g., ZnS$_{0.88}$O$_{0.12}$) also generate reactive hydroxyl radicals, but electrons are easy to get trapped in between the bands. In addition, the ZnO phase existed in the oxygen-doped samples and promoted fast recombination of electron–hole pair by the ZnO crystal phase. The fast recombination (less carrier lifetime) of the ZnO band edge will significantly increase the degradation time of the MNB solution. 11,29,35,36 The detailed photodegradation mechanisms

Figure 5. Analysis of photodegradation ability for ZnS$_{0.88}$O$_{0.12}$, ZnS$_{0.94}$O$_{0.06}$, and ZnS photocatalysts in 50-μM MNB solution under the illumination of xenon-arc white light. The solid lines are the fitting results by using rate constant ($k$) of degradation speed within 1 h.

Scheme 1. Representative Mechanism Pathways of (a) ZnS and (b) ZnS$_{(1-x)}$O$_x$ as the Crystal Photocatalysts for Methylene Blue Degradation
of the oxygen-incorporated ZnS are demonstrated in Scheme 1b for comparison.

**CONCLUSION**

In conclusion, the transition states, vacant sites, near band-edge properties, and photocatalytic behavior of II–VI oxygen-incorporated ZnS and ZnS(1−x)Ox (x = 0, 0.06, and 0.12) have been evaluated in detail. These series crystals were grown by CVT method with I2 as the transport agent. The possible incorporation of iodine into the ZnS(1−x)Ox series results in p-type conductivity, which is evident by hot-probe experiment. From the comparison of optical measurements, including PC and SPV measurements, possible defects, such as sulfur vacancy V_S, p-type acceptor level (Si)_A, and a ZnO second phase are observed to exist in the ZnS(1−x)Ox. A xenon-arc white light and 50 μM MNB solution are used for testing the photodegradation ability of organic pollutants by the crystal photocatalysts. The undoped [111] c-ZnS shows the fastest photodegradation rate owing to the existence of dipole moment and internal electric field created by defect deformed {111} cubic ZnS. Whereas more imperfection states and the occurrence of ZnO second phase in the higher oxygen-incorporated ZnS(1−x)Ox significantly decrease the photodegradation ability of the crystal photocatalyst. The [111] c-ZnS emerges out as the best heterophotocatalyst without any adsorption of methylene blue. It can be an efficient crystal photocatalyst for application in energy and environment use.

**EXPERIMENTAL SECTION**

Preparation of ZnS(1−x)Ox Series Single Crystals by CVT Method. ZnS(1−x)Ox series, such as pure ZnS, ZnS(0.94)O(0.06) and ZnS(0.88)O(0.12) crystals, were grown by the chemical vapor transport (CVT) method using I2 as transport agent. Detailed procedure for the CVT growth of doped and undoped ZnS(1−x)Ox series was described elsewhere. The growth temperature was setting as 1000 °C (heating zone) → 950 °C (growth zone) with gradient ~2.5 °C/cm to the quartz ampules. The reaction keeps 300 h for production large single crystals. With increasing oxygen content, the color changed, fresh pale yellowish color, a dark yellow color, and pure white color in the as-grown ZnS(0.98)O(0.02), ZnS(0.96)O(0.04) and pure ZnS crystals, respectively. 

**Preparation of ZnS(1−x)Ox Series Single Crystals by CVT Method.**

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Chemical Reagent and Materials Prepared. Methylenedioxime (C_6H_6O_2N_2) was purchased from Kojima Chemical Co., Ltd. Deionized water, magnetic stirrer, copper plate, and Xenon-arc lamp (with LPS-250 power supply) were from Photonics Technology International (PTI).

Hot Probe and I–V Measurements. A hot point probe for ZnS(1−x)Ox series was constructed using MSM model, which was a simple and rapid method to classify conductivity type of semiconductors. The experiment used KEITHLEY 182 voltmeter attached to the sample, where the positive end had been heated (soldering iron as the heating source) and the negative end was maintained at room temperature. The temperature was measured using a TES 1310 TYPE-K thermometer. Heat sources could increase the number of carriers in the semiconductor. The main carriers will move from the high temperature end to the room temperature end by the carriers’ diffusion mechanism. The sign of thermal electromotive force measured from the voltmeter could reveal conductivity type of the semiconductor. The I–V measurements of the ZnS(1−x)Ox series were performed by the auxiliary of a Keithley 2614B source measure unit. The voltage scanning range was set at −200 to 200 V.

Photoconductivity (PC) and Surface Photovoltage (SPV) Measurements. The PC and SPV experiments do not require any optical sensor because photodetector is the sample itself. For SPV measurement, a ZnS(1−x)Ox plate was attached on a copper sample holder by silver paste; the holder acts as the bottom electrode of the measurements. The top surface of sample can be micropatterned and coated with either golden or copper mesh on the sample plane. This was the top electrode of the SPV measurement. The photoexcited electron transfer from the high temperature end to the room temperature end carriers in the semiconductor. The main carriers will move from the high temperature end to the room temperature end by the carriers’ diffusion mechanism. The sign of thermal electromotive force measured from the voltmeter could reveal conductivity type of the semiconductor. The I–V measurements of the ZnS(1−x)Ox series were performed by the auxiliary of a Keithley 2614B source measure unit. The voltage scanning range was set at −200 to 200 V.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00260.

Frequency-dependent photoconductivity spectra to show defect and near-band-edge transitions in ZnS(1−x)O, with x = 0, 0.06, and 0.12 (PDF)

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Notes

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