Thermal properties of lattice defects formed in ZnO and their contribution to n-type conduction

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Thermal properties of lattice defects formed in ZnO and their contribution to *n*-type conduction

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Abstract: The effects of the following lattice defects on the *n*-type electric conduction in hydrothermally grown ZnO single crystals were investigated by means of $^{1}H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction analysis (NRA), positron annihilation lifetime spectrometry (PALS), and electric conductivity measurements: oxygen vacancies (V_O), interstitial zinc atoms (Zn_i), and impurity hydrogen atoms (H). The results of NRA and PALS suggest that H take three different bound states in the lattice: two types are loosely bound to the lattice and the other is a strongly bound H existing as (zinc vacancy)-hydrogen complexes. It was found that H concentration and electric conductivity of ZnO are not simply correlated.

For the samples heat-treated at temperatures between 1073 K and 1273 K, defect-induced conduction was observed by sample warming (thermal excitation) and light irradiation (photoexcitation), which suggests that V_O and Zn_i as deep and shallow donors, respectively, were formed by the high-temperature treatments. After heat treatment at 1373 K, however, the conductivity arises only from thermal excitation, demonstrating that only Zn_i contribute to the conductivity but V_O do not. Taking into account the results of PALS measurements as well, the author proposes a mechanism of the defect-induced *n*-type conduction in ZnO that carrier electrons are generated from Zn_i as a result of charge cancellation between zinc vacancies and V_O.

Zinc oxide (ZnO) has received expectation as an alternative material replacing semiconductors which can be applied to electric devices being essential in the modern society. For the application of ZnO, intrinsic *n*-type conduction has been known to be a very important physical property of the material. Although interstitial zinc atoms (Zn_i), oxygen vacancies (V_O), and impurity hydrogen atoms (H) generated or incorporated in the matrix during the crystal growth processes and heat treatments are regarded as the origin of the conduction, the mechanism of carrier generation is still not clearly understood. Accordingly, it is of great importance to obtain information on the physical and/or chemical state and thermal behavior of lattice defects contributing to the *n*-type conduction of the undoped ZnO. In order to reveal the origin of the conduction, in this work, $^{1}H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction analysis (NRA), positron annihilation lifetime spectrometry (PALS), and electric conductivity measurements were performed to investigate their state of being in hydrothermally grown ZnO single crystals.

The NRA results suggest that H in the as-grown sample take three different bound states: two types are loosely bound to the lattice (LBH1 and LBH2) and the other is a strongly bound H (SBH). Figure 1 shows heat-treatment temperature dependence of the concentrations of H taking different bound states. It is found that LBH1 and LBH2 are removed out of the nuclear reaction sites at 393 K and 773 K, respectively, but SBH survive with their average concentration of 0.10(3) at.% even at 973 K. Compared with the PALS results and theoretical calculations, it is suggested that SBH exist as (zinc vacancy)-H complexes. As shown in Fig. 2, the electric conductivity increases at 393 K but decreases stepwisely in the temperature range of 473-973 K; this tendency demonstrates that the electric conductivity does not simply correlate with the concentration of H.

The electric conductivity of the ZnO samples increased dramatically with rise in the heat-treatment temperature up to 1473 K as shown in Fig. 2, which indicates that the intrinsic lattice defects are formed. From the electric conductivity measurements with the photoexcitation and thermal excitation, the electric conduction originated from shallow (Zn_i) and deep donors (V_O) was observed in the samples heat-treated at 1073-1273 K. At 1373 K, however, the conductivity increased only when the sample was thermally excited as shown in Fig. 3, signifying that V_O become inactive electrically but only Zn_i contribute to the conduction. From the observed variation of the conductivity in the samples heat-treated under different oxygen partial pressures, the author proposes a new conduction mechanism that free electrons are generated from Zn_i through charge cancellation between zinc vacancies (V_{Zn}) and V_O when Zn_i and V_{Zn} are formed simultaneously in the presence of V_O.

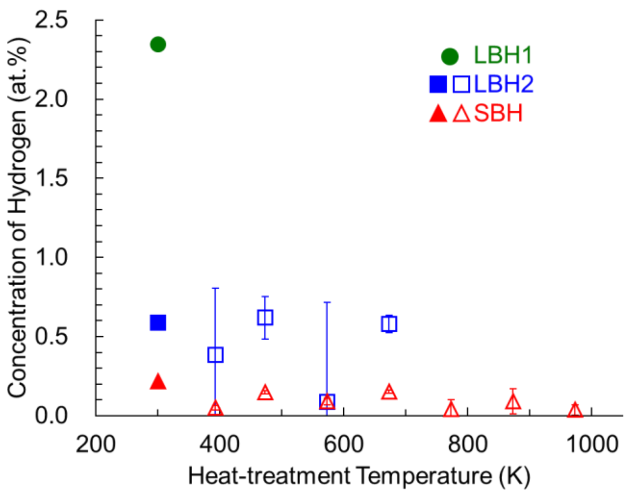

Fig. 1 Heat-treatment temperature dependence of the concentration of impurity hydrogen atoms in hydrothermally grown ZnO single crystals. The solid symbols represent the data for the as-grown sample.

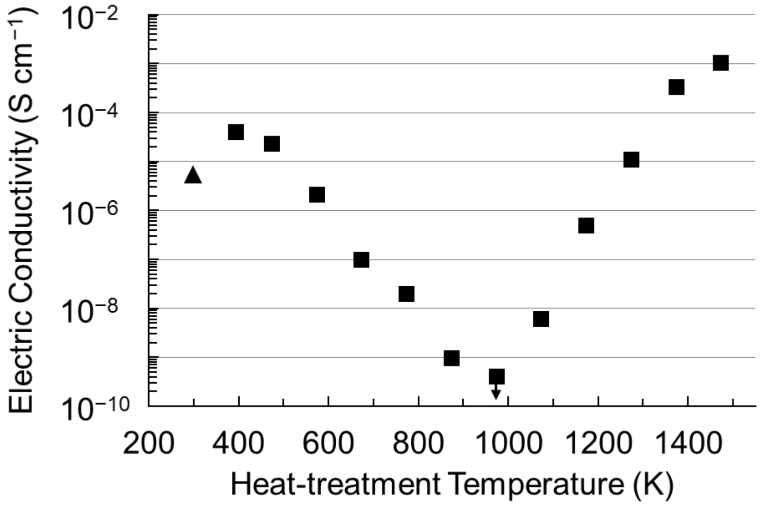

Fig. 2 Heat-treatment temperature dependence of the electric conductivity in hydrothermally grown ZnO single crystals. The triangle symbol represents the data for the as-grown ZnO sample. The upper limit is shown for the electric conductivity in the sample heat-treated at 973 K.

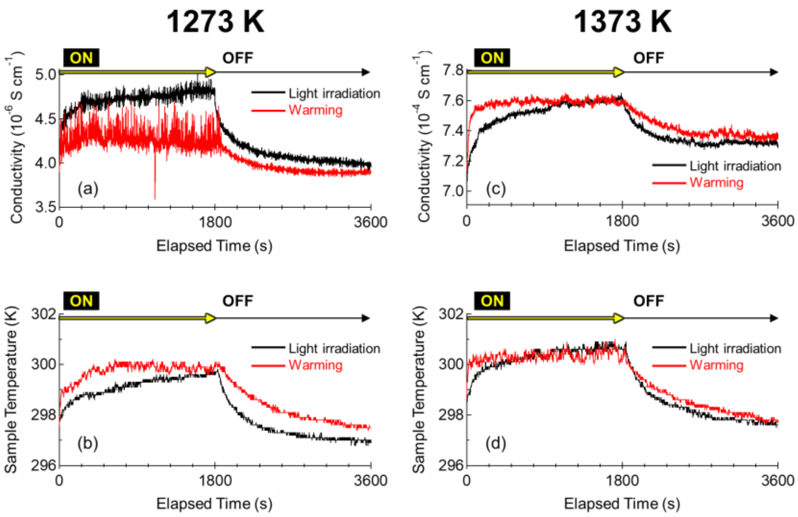

Fig. 3 Time variations of the conductivities ((a) and (c)) and sample temperatures ((b) and (d)) for the samples heat-treated at 1273 K (left) and 1373 K (right) as a functions of elapsed time of light irradiation (black lines) and of sample warming (red lines).

令和２年１月２８日

学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Thermal properties of lattice defects formed in ZnO and their contribution to *n*-type conduction

（酸化亜鉛中に形成された格子欠陥の熱的性質と *n* 型電気伝導性への寄与）

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３．審査結果の要旨（600～650 字）

標記学位論文を各審査委員が個別に審査した後、全委員によって提出者の口頭説明に対する予備審査を行った。その後、公聴会を令和 2 年 1 月 28 日に開催し、終了後に審査委員会において本論文を審査した。審査結果を以下に記す。酸化亜鉛（ZnO）は 3.4 eV のバンドギャップを有するため、化学量論組成に近い結晶では絶縁体としての性質を示すと思われるが、その合成過程において混入・生成する不純物や酸素空孔（V_O）等がドナー準位を形成して *n* 型電気伝導性が発現すると考えられている。特に水熱合成法によって育成された ZnO 中には多量の水素（H）が不純物として混入しており、H の電気伝導性への寄与が指摘されてきた。しかし、固体中の微量 H を定量することは極めて困難であり、H 濃度と電気伝導度との相関を議論するには至っていないのが現状である。そこで本研究では、$^{1}H(^{15}N,\alpha\gamma)^{12}C$ の核反応分析法によって ZnO 中の H 濃度を定量し、電気伝導度と H 濃度は単純な相関関係にはないことを指摘した。さらに、H は ZnO 格子中で３種類の束縛状態をとっており、異なる熱安定性をもつことを見出した。一方、電気伝導に寄与する H を除去した ZnO 中では、熱処理の過程で生じる V_O が亜鉛空孔のアクセプターとしての活性を抑制する効果を発見し、格子間 Zn による *n* 型伝導の発現機構を説明することに成功した。これまで独立に議論されていた個々の格子欠陥の伝導性への寄与を、それらの相互作用の観点から明らかにしたことは、今後の ZnO の半導体材料の開発に資するものである。従って、本博士論文は博士（理学）の学位に値すると判断した。

４．審査結果　　(1) 判　　定（いずれかに○印）　（合　格）・　不合格

(2) 授与学位　　博　士（　理　学　）