論文 / 著書情報
Article / Book Information

題目(和文)	オプトエレクトロニクス用 CaZn2N2およびCuI薄膜
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種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料 系 材料 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 工学 ）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

While the optoelectronics to date has been based on Si and III–V group alloy-based semiconductors, various functions, that cannot be achieved with single-crystal based semiconductors, are expected for next-generation devices: e.g., flexible displays, wearable devices, transparent devices have been demonstrated based on organic electronics. In particular, materials which are constituted by non-toxic, environmental-friendly, earth-abundant and inexpensive elements are required for sustainable society. In recent years, halide-perovskite based optoelectronics has also attracted significant attention. Halide materials are unstable as solid crystals due to their low melting point, defect intolerance, and ionic conductivity. While they seem to be unsuitable for optoelectronics, but their affinity with low-temperature solution processes has led to the development of solar cells, EL devices, quantum dots, and single crystalline laser that exhibit high performance. On the other hand, as seen in the GaN and its alloy based blue-LEDs that first established with the success of the p-type doping, semiconductor devices cannot be resulted in practical use simply by good bulk performance, but can only be realized through the optimal doping methods, film formation processes, and device structures. Although ionic semiconductors can make the new markets with fabrication process that differ from those of Si and III–V group semiconductors, complexity of the systems hinder control of carrier doping. Namely, doping control and process development based on understanding of the material properties are essential to achieve the expected performance.

The general objective of thesis is to fabricate thin films of candidate materials based on non-toxic elements toward next-generation optoelectronics and to understand the defect formation mechanism for exploring novel functional materials.

In Chapter 2, the hole concentration in CuI was successfully controlled continuously from 10^{18} to 10^{14} cm^{-3} by Zn substitution into Cu site for the fabrication of HTL and TFT devices. The low formation energy and shallow acceptor level of V_{Cu} in CuI inhibit the suppression of the hole carrier generation. However, we found that hole carrier generation is suppressed by the Zn addition. First-principles calculations revealed that this mechanism is not due to simple electron doping, but due to the preferential formation of new tetragonal $Cu_{1-2x}Zn_xI$ solid solution phases with the formation of V_{Cu}+Zn_{Cu} complex defects. It is also found that the energy band alignment in $Cu_{1-2x}Zn_xI$ is simultaneously modulated by the deepening of the CBM composed of Zn-4s and the deepening of the VBM due to the decrease in the contribution of Cu-3d. Note that $x \sim 0.1$ and $x = 0.2$ were suitable for TFT and HTL applications, respectively. Especially in the $x = 0.2$ composition, the hole injection barrier to halide perovskite is small, and this material can be used for HTL with balanced carrier injection with ZSO used for ETL. In addition, although the crystal structure of $Cu_{1-2x}Zn_xI$ is two-dimensional, the band structure remains three-dimensional. This is because the spatially dispersed I-5p orbital is maintained, which strongly reflects the characteristics of iodides.

In Chapter 3, we demonstrated the direct reaction between CuI and CsI by the room-temperature solid-state reaction and observed the reaction process in order to prepare high quality thin films of $Cs_3Cu_2I_5$ and to elucidate the origin of its unique crystal structure. The proposed reaction mechanism is completely novel: the diffusion of Cu^+ and I^- into CsI crystals are accompanied by the formation of I_{Cs} antisites and Cu_i interstitial defects to form a local structure of $Cs_3Cu_2I_5$. This unique reaction occurs due to the low packing density of the CsCl-type structure of CsI and the diffusivity of Cu^+ ions. Although the use of voids in crystals as a reaction field has been reported in the catalysis, these findings provide a new perspective on ionic crystals: $Cs_3Cu_2I_5$ and $CsCu_2I_3$ can be regarded as systems with ultrahigh concentrations of complex defects in the CsI lattice, and the low packing density of the framework, which facilitates chemical reactions even at low temperatures. This chapter proposes a new material design concept for CsCl-type crystals, which have been considered unsuitable as semiconductors due to their too high ionicity and low chemical durability, i.e., weak defect tolerance, and opens up new possibilities for ionic semiconductors.

In Chapters 3 and 4, we synthesized and fabricated thin films of a novel nitride materials for the LEDs.

$CaZn_2N_2$ is a candidate for red light-emitting semiconductor because of its defect tolerance, which prevents the formation of defect levels in the mid-gap that inhibit luminescence. However, due to the difficulty of synthesis and the lack of demand for red emitting materials, high-quality thin films and the band gap tuning into the green-light region are essential for practical use. In this chapter, we have realized the world's first epitaxial growth of $CaZn_2N_2$ by using N* with high nitridation power, and modulated the bandgap continuously from red to UV region by substituting Zn sites with Mg.