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## 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Cul薄膜
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 著者(和文)	
Author(English)	Masatake Tsuji
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Photoelectric conversion devices are composed of a stacking structure of functional materials. Thin film fabrication by optimal deposition methods for each layer is crucial for practical optoelectronic applications. This thesis demonstrated thin film fabrication and elucidation of defect formation mechanism in CuI-based materials and CaZn<sub>2</sub>N<sub>2</sub> with abundant and environmentally benign constituents toward next-generation optoelectronics.

The device applicability of CuI-based materials was presented for hole transport layers in photovoltaic and EL devices, and photodetectors. The hole concentration in CuI could be controlled from 10<sup>18</sup>–10<sup>14</sup> cm<sup>-3</sup> by the Zn doping on CuI. First-principles calculations revealed that this mechanism is not due to simple electron doping, but due to the preferential formation of new tetragonal Cu<sub>1-2x</sub>Zn<sub>x</sub>I solid solution phases with the formation of V<sub>Cu</sub>+Zn<sub>Cu</sub> complex defects. In addition, the author found the direct reaction between CuI and CsI and demonstrated that CsCu<sub>2</sub>I<sub>3</sub> and Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> are formed by the room-temperature solid-state reaction. A possible origin of the unique local structure of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> was elucidated in terms of unique and efficient defect formation: CsI possess interstitial and antisite where Cu<sup>+</sup> and I<sup>-</sup> ions can occupy, respectively, and consequently formed are  $\mathrm{Cu_i}$  and  $\mathrm{I_{Cs}}$  complex defects which can be the basis of unique  $Cs_3Cu_2I_5$  and  $CsCu_2I_3$  phases. Such a defect formation originates from unique elemental characters, the size flexibility of iodine, and the ease of cation diffusion of Cu<sup>+</sup> ions. Unique local structure formation based on fast cation diffusion to intrinsic crystallographic void provides a novel possibility in materials design for electron-active functionality.

Finally, a very wide-range bandgap tuning and epitaxial thin film growth of CaZn<sub>2</sub>N<sub>2</sub> were realized by a high-pressure synthesis and an MBE technique with an active N-radical source, respectively. These demonstrations will pave the way to the next-generation green LEDs.