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Materials Design and Development of Copper(I) Iodide-Based Compounds for Optoelectronics

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本論文の概要

Opto-electronic devices are one of the essential components supporting our daily lives, such as display, solar cell, smart window and so on. Especially, n-type transparent amorphous oxide semiconductors (TAOS) have been widely investigated and are already applied to drive pixels of FPDs represented by organic light emitting diode (OLED) displays. However, developing next generation displays is hampered by the lack of p-type TAOS arising from the nature of ionic oxides. Conventional organic luminescent materials have several serious issues, i.e., chemical instability in the ambient condition and short lifetimes originating from the intrinsic nature of organic materials. To resolve these issues, I propose a materials design concept and develop the copper(I) iodide-based compounds that possess promising opto-electrical properties such as high mobility p-type semiconducting nature or highly efficient luminescence. Copper(I) iodide (CuI) is already known as a simple binary compound consisting of two abundant and non-toxic elements. Cuprous ion (Cu^+) has a closed (i.e., $d^{10}s^0$) shell configuration whose energy is almost comparable to those of the iodine 5p orbital. I 5p has much larger orbital radius (>200pm) than O 2p orbital (~126pm). As a result, CuI exhibits a high hole mobility (~40cm^2/Vs in single crystal) with a direct band gap (~3.1eV). Moreover, its crystallographic dimensionality of [Cu-I] tetrahedral site is easily controllable by introducing Cs ion, resulting in the adjustment of opto-electrical properties, such as PLQY, bandgap, mobility and carrier concentration. This thesis describes opto-electrical properties for application to next generation optoelectronics by design of copper (I) iodide-based compounds.

各章の概要

Chapter 1. "General Introduction"

Chapter 1 is a brief review of the background of the components of display, such as semiconductor and luminescent materials. Then, the issues of the components in current display are addressed, and the motivations and objectives of this thesis are described.

Chapter 2. "Material Design of p-Type Transparent Amorphous Semiconductor, a-CuSnI"

In order to obtain p-type transparent amorphous semiconductor (TAS), a material design concept for p-type TAS materials is proposed utilizing the pseudo s-orbital nature of spatially spreading iodine 5p orbitals and amorphous Sn-containing CuI (a-CuSnI) thin film is reported as an example. The resulting a-CuSnI thin films fabricated by spin coating at low temperature (140°C) have a smooth surface. The Hall mobility increases with the hole concentration and the largest mobility of ~ 9 $cm^2V^{-1}s^{-1}$ is obtained, which is comparable with that of conventional n-type TAOS.

Chapter 3. "Control of Opto-Electrical Properties Through Dimensionality: 1D $CsCu_2I_3$"

This chapter describes a new strategy for p-type transparent semiconductor (TS) with low carrier concentration and new luminescent material with unique optical properties. $CsCu_2I_3$ with one dimensionally connected CuI_4 unit has smaller dispersion of VBM than CuI, whereas the formation energy for Cu-vacancy has higher than CuI. Thus, I expected low carrier concentration suitable for semiconductor application would be realized. The material synthesized by inverse temperature crystallization (ITC) method showed ~ $2.34\times10^{13}cm^{-3}$ with Hall mobility of ~$0.34cm^2V^{-1}s^{-1}$. Furthermore, novel optical properties, such as broadband and large Stokes shift luminescent material with PLQY of ~8% was obtained.

Chapter 4. "Lead-Free Efficient Blue-Emitting $Cs_3Cu_2I_5$ with 0D Bulk Core/shell Structure"

I found 1D $CsCu_2I_3$ as a yellow luminescent material. However, 1D $CsCu_2I_3$ is still insufficient phosphor due to low PLQY in solid state. To resolve this problem, I thought copper (I) iodide-based compound with zero-dimensional photoactive site, $Cs_3Cu_2I_5$, would be a new luminescent material with high PLQY. $Cs_3Cu_2I_5$ synthesized by slow vapor saturation of an antisolvent (VSA) method showed a high PLQY of 90% and good air-stability. Each Cu-I photoactive site is separated by Cs ions; this arrangement may be considered a host-guest system. An embedded core/shell structure is effective for enhancing the PL by confining the exciton into the photoactive site; this accounts for the large exciton binding energy (~490 meV). For practical applications, blue electroluminescence of Pb-free halides was demonstrated using solution-derived 0D $Cs_3Cu_2I_5$ thin film. Furthermore, I succeeded in fabricating a white luminescent thin film by one-step spin-coating method using the mixed precursor solution of 1D $CsCu_2I_3$ (yellow) and 0D $Cs_3Cu_2I_5$(blue) to achieve full coverage in the visible range of the spectrum.

Chapter 5. "General Conclusion"

In this last chapter, I summarize this thesis about copper (I) iodide-based compounds for next generation optoelectronics.

Publication List

Papers Included in the Thesis

1. **Taehwan Jun,** Junghwan Kim, Masato Sasase, and Hideo Hosono

   "Material Design of p-Type Transparent Amorphous Semiconductor, Cu–Sn–I"

   Adv. Mater. 30,1706573, (2018).

2. **Taehwan Jun,** Kihyung Sim, Soshi Iimura, Masato Sasase, Hayato Kamioka, Junghwan Kim, and Hideo Hosono

   "Lead-Free Highly Efficient Blue-Emitting $Cs_3Cu_2I_5$ with 0D Electronic Structure"

   Adv. Mater. 30, 1804547, (2018).

Other Papers

1. Kihyung Sim, **Taehwan Jun**, Joonho Bang, Hayato Kamioka, Junghwan Kim, Hidenori Hiramatsu, Hideo Hosono

   "Performance Boosting Strategy for Perovskite Light-emitting Diodes"

   Appl. Phys. Rev. 6, 031402, (2019).

International Presentations and Proceedings

1. Junghwan Kim, **Taehwan Jun**, Hideo Hosono (**Oral**)

   "New P-type Amorphous Semiconductor with High Transparency and High Mobility of 9 cm^2/Vs for Next-Generation Displays"

   2018 SID Meeting, Los Angeles, USA, May 20-25,

   SID Symposium Digest of Technical Papers, 49, 236 (2018).

2. **Taehwan Jun**, Kota Aoyama, Joonho Bang, Junghwan Kim, Hideo Hosono (**Oral**)

   "Solution-Processable P-type Transparent Amorphous Semiconductor for Flexible Electronics"

   2018 AMFPD, Kyoto, Japan, July 3-6,

   25th International Workshop on Active-Matrix Flat panel Displays and Devices

3. **Taehwan Jun**, Kihyung Sim, Soshi Iimura, Masato Sasase, Hayato Kamioka, Junghwan Kim, Hideo Hosono (**Oral**)

   "Pb-Free Blue-Emitting 0D $Cs_3Cu_2I_5$ with High PLQY of ~90%"

   2019 SID Meeting, San Jose, USA, May 13-17,

   SID Symposium Digest of Technical Papers, 50, 1176, (2019).

Domestic Presentations

1. **Taehwan Jun**, Junghwan Kim, Hideo Hosono（**Oral**）

   " Transparent Amorphous p-type Semiconductor with High Mobility (~9 cm^2/Vs), Cu-Sn-I: Utilization of I 5p orbital as Pseudo Extended s-orbital"

   The 65th JSAP Spring Meeting, 19p-F202-5, (2018).

2. **Taehwan Jun**, Soshi Iimura, Junghwan Kim, Hideo Hosono (**Oral**）

   "Zero-dimensional Blue Emitting Lead-Free Halide with High PLQY Exceeding 90%"

   日本学術振興会, 第 166 委員会, 第 82 回研究会, 東京, (2019).

3. 青山皓太、**全泰桓**、金正煥、細野秀雄 (**Oral)**

   "Development of New p-type Semiconductor and its Application to Flexible Electronics"

   The 66th JSAP Spring Meeting, 11p-W834-10, (2019)

Awards

1. AMFPD'18-ECS Japan Section Young Researcher Award (2019 年 7 月)