N_2-COMPATIBLE NICKEL PRECURSOR AND HIGHLY ACTIVE WATER-OXIDATION IRIDIUM CATALYST PREPARED BY MOCVD

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論 文 名　：N_2-COMPATIBLE NICKEL PRECURSOR AND HIGHLY ACTIVE WATER-OXIDATION IRIDIUM CATALYST PREPARED BY MOCVD
(窒素雰囲気下で使用可能な MOCVD 用ニッケル前駆体と MOCVD 法により調整される高活性な水酸化イリジウム触媒の開発)

区　　分　：　甲

論 文 内 容 の 要 旨

The metal and metal-based thin films on a substrate have been of interest because of their potential applications in many fields containing electronic and catalyst. Among the deposition methods, metal organic chemical vapor deposition (MOCVD) is one of the most convenient ways providing films with good coverage and fine structure. However, the success of this method strongly depends on the available of precursors having high volatility, reasonable thermal stability and clean decomposition to deposit desired film. Therefore, the synthesis of new precursors or selection of suitable available precursors is remarkably important and challenging to the chemists.

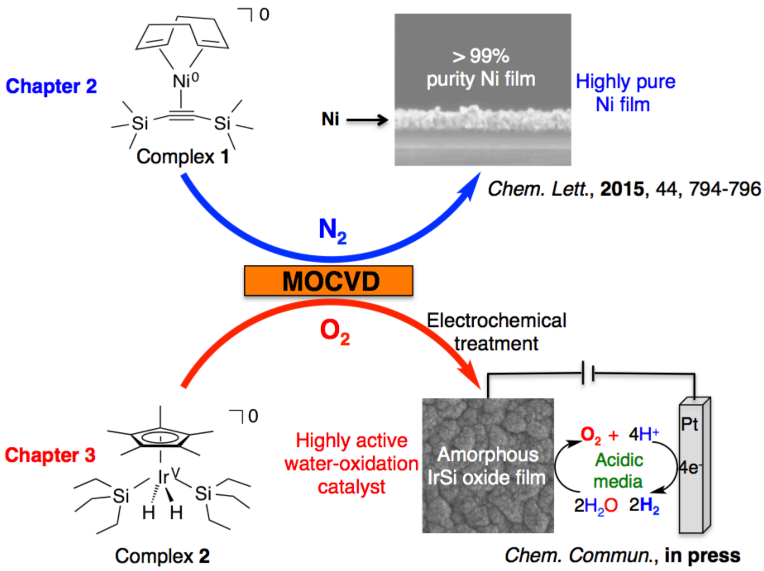

Fig. 1 A schematic description and arrangement of the dissertation.

In this dissertation, the author gives two examples, one is synthesis and another is selection of suitable MOCVD precursors. Those are able to deposit metal film or metal-based film for the specific applications. The description and arrangement of this work are depicted in Fig. 1.

In chapter 1, the author describes the general introduction of this dissertation.

In chapter 2, the author describes the synthesis of a novel Ni complex that serves as MOCVD precursor to deposit highly pure nickel film using nitrogen (N_2) as the carrier gas.

Ni film is important in several fields especially in microelectronic devices. Because of some critical requirements such as conformal and uniform deposition in high aspect ratio, such Ni films have been deposited by MOCVD. However, there has not yet been any MOCVD precursor that can form highly pure Ni film using cheap and safe N_2 as the carrier gas, so far. In this chapter, the author reports a novel Ni^0 complex **1** (Fig. 1) that serves as MOCVD precursor to deposit a highly pure Ni film using N_2 as the carrier gas. Complex **1** was synthesized conveniently in high yield (83 %) from commercial available reagents of bis(1,5-cyclooctadien)nickel $Ni(COD)_2$ and 1,2-bis(trimethylsilyl)acetylene. ^1H, ^{13}C NMR spectroscopies, elemental analysis and X-ray crystallography were performed, those confirmed the proposed structure. Sublimation test of **1** gives a vapor pressure of 90.7 Pa at 45 ^oC. This is one of the highest values for known Ni MOCVD precursors. The thermalgravimetry differential thermal analysis (TG-DTA) measurement demonstrated that **1** is suitable for MOCVD. The Ni film was obtained by MOCVD of **1** at relative low temperature using a cheap and safe N_2 gas as the carrier gas. The X-ray photon spectroscopy (XPS) results revealed a highly pure Ni film (> 99%). A fairly smooth and conformal Ni film with multiform crystalline grains was determined by scanning electron microscopy (SEM) atomic force microscopy (AFM) and X-ray diffraction (XRD) spectroscopy. The author believes that this novel zero-valent Ni organometallic compound will be a promising new MOCVD precursor for deposition of Ni film.

In chapter 3, the author describes the selection of an iridium complex serving as a MOCVD precursor to deposit iridium-based film, which possesses high catalytic activity for electrochemical water-oxidation.

Ir oxide is the best catalyst for electrochemical water-oxidation in acidic media in terms of high catalytic activity and long-term stability. But Ir is very expensive and scarce, which hinder Ir from its application. Many efforts have been made to reduce Ir contents in anode and improve the catalytic activity via two approaches. First is developing new preparation methods that provide novel morphologies and structures with higher active area to enhance the catalytic activity. Second is doping other components such as Ta and Sn oxide into Ir oxide to reduce the Ir loading in anode as well as improve catalytic ability and stability due to the synergistic interaction of multicomponent by forming solid solution of mixed metal oxides. In this chapter, a novel IrSi oxide film has been prepared by MOCVD using an iridium-silly complex **2** (Fig.1) as a single precursor and successive electrochemical oxidization. The film was characterized by several methods: X-ray photoelectron spectroscopy (XPS), scanning transmission electron microscopy (STEM) equipped energy dispersive X-ray spectroscopy (EDS) mappings, scanning electron microscopy (SEM) and X-ray diffraction (XRD) spectroscopy. Those determined an amorphous structure of IrSi oxide film with homogeneously distribution of Ir and Si element in the solid phase. The IrSi oxide film on fluorine doped tin oxide (FTO) substrate exhibited high catalytic activity and stability for water oxidation. The turnover frequency (TOF) of 7.2 s^{-1} at 1.76 V vs NHE was determined for water oxidation in acidic media. This value is higher value than those reported for Si oxide-doped Ir oxide and higher even than pure Ir oxide. This work has succeeded doping Si oxide into Ir oxide to reduce Ir contents as well as enhance catalytic activity and stability using a novel preparation strategy. The author believes the analogous organometallic compounds with direct metal-silyl bonds will be promising single MOCVD precursor that is able to form highly homogeneous Si oxide-doped metal oxide film for applications not only in catalyst but also other fields.

In conclusion, the author has succeeded in synthesis of a novel zero-valent Ni complex. This is the first example of a Ni MOCVD precursor that provides a highly pure Ni film using N_2 as the carrier gas. The author also succeeded in utilization of an Iridium complex with Ir-Si direct bonds as a precursor to make Si oxide-doped Ir oxide film by MOCVD method. This film functions as a high activity and stability water oxidation catalyst in acidic regime. This is the first example of doping Si oxide into Ir oxide to reduce Ir contents as well as enhance catalytic activity and stability for water oxidation in acidic media.