

Preparation of Iridium and Platinum Films by MOCVD and their Properties(MOCVD法によるIrおよびPt膜の合成と諸性質)

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号	1715
発行年	1994
URL	http://hdl.handle.net/10097/6988

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授 与 学 位	博 士 (工 学)		
学位授与年月日	平成 7 年 3 月 24 日		
学位授与の根拠法規	学位規則第 4 条第 1 項		
研究科, 専攻の名称	東北大学大学院工学研究科 (博士課程) 材料物性学専攻		
学 位 論 文 題 目	Preparation of Iridium and Platinum Films by MOCVD and their Properties (MOCVD 法による Ir および Pt 膜の合成と諸性質)		
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論 文 内 容 要 旨

Chapter 1. Introduction

Platinum group metals, such as iridium (Ir) and platinum (Pt), have high electrical conductivity and catalytic activity, which enable them as conducting electrodes. For electronic device applications, epitaxially grown electrode films on semiconductors or insulating substrates (such as Si, MgO and sapphire) are demanded. For the applications to solid state electrolytes such as gas sensors and fuel cells, in contrast, porous and catalytic electrodes are needed. These metals also have high melting point and high chemical stability that make them promising as protective films for high temperature usage, in which thick and microcrack-free films should be prepared. Therefore, the appropriate morphology for these films should be controlled depending on their applications.

Metalorganic chemical vapor deposition (MOCVD) enables one to control the films morphology with the additional advantages of conformal coverage and radiation damage-free and low-temperature depositions. MOCVD might be advantageous to prepare electrode films as well as protective films. So far, Ir and Pt films have been prepared by MOCVD. Impurity-free films of good crystalline quality have been obtained. However, epitaxial growth has been

achieved only for Pt films. There are no reports on electrochemical properties of MOCVD Ir or Pt films as catalytic porous electrodes. Only MOCVD Ir films have been investigated to provide oxidation protection for graphite, C-C composites and refractory metals at high temperatures.

The purpose of this study is to achieve the appropriate morphology of Ir and Pt films that is required for their applications. (1) Epitaxial electrode films. (2) Porous and catalytic electrode films. (3) Thick and dense protective films. Films are prepared by MOCVD. Films are examined according to the applications. (1) Crystal structure. (2) Electrochemical properties. (3) Corrosion resistance.

Chapter 2. Preparation

The preparation of Ir and Pt films by MOCVD has been investigated for the last three decades. So far, a variety of organometallic precursors have been examined. These include Ir- and Pt-acetylacetonates, Ir- and Pt-allyl compounds, Ir-cyclooctadiene and Ir-cyclopentadienyl compounds, Pt-methylcyclopentadienyl compounds, Pt (CO)₂ Cl₂ and Pt (PF₃)₄. With the exception of Ir- and Pt-acetylacetonates, there are no commercial available precursors. In general, Ir- and Pt-acetylacetonates require higher deposition temperature (300-750°C) than that required (120-600°C) for other precursors. While all precursors have yield amorphous or polycrystalline films, there is only one precursor (Pt-acetylacetonate) that has produced epitaxial films. Ir-acetylacetonate has shown the highest deposition rate (25 μm/h). A problem with organometallic precursors is the carbon contamination of the films. Carbon content up to 80 at% has been reported. To overcome this problem the addition of H₂ gas to the precursor vapor has been extensively used. O₂ gas has been used in a less extension. Most of the precursors can produce carbon-free Ir and Pt films by the addition of H₂ or O₂ gas.

In this study, Ir- and Pt-acetylacetonates were used as precursors. They are commercial available and the higher temperature required for deposition could be appropriate to achieve epitaxial growth. Ir-acetylacetonate exhibits the highest deposition rate, which is advantageous to prepare thick films. O₂ gas was used to prevent carbon contamination. The effects of deposition conditions and oxygen gas addition on deposition rates, composition and microstructure were studied and the optimum conditions were determined.

A horizontal hot-wall MOCVD apparatus was used. Oxygen gas was added to the source vapor around the substrates (FR_{O₂} = 0-12 cm³/min). Quartz glass substrates were used. Argon gas was used as the carrier gas (FR_{Ar} = 50 cm³/min). The precursor temperature was kept constant (T_{prec} = 180°C). Deposition temperature (T_{dep}) was varied from 400 to 800°C and total pressure (P_{tot}) was controlled from 2 to 100 Torr. Depositions were performed for 20 min.

Without the addition of oxygen, black-colored films were obtained. Auger electron spectro-

scopy (AES) revealed carbon contamination in these films. High-resolution electron microscopy (HREM) indicated that they consisted in aggregated crystalline metal particles (1 – 3 nm in diameter) surrounded by amorphous carbon. When a small amount of oxygen gas was added, silver-colored films that strongly adhered to the substrate were obtained. No impurity carbon was observed in these films by AES. Good crystalline quality was revealed by x-ray diffraction (XRD). Pt deposition rates were higher than those of Ir, because of a higher vapor pressure and a higher metal content of Pt-acetylacetonate. The addition of oxygen gas decreased Ir and Pt deposition rates due to the formation of denser films and volatile metal oxide species.

Appropriate deposition conditions for silver-colored films with good crystalline quality were determined as follows : $P_{tot} = 2 - 5$ Torr, $T_{dep} = 500-600^{\circ}\text{C}$, $T_{prec} = 180^{\circ}\text{C}$. The addition of oxygen gas to the source vapor was effective in obtaining carbon-free films : $FR_{O_2} = 3 \text{ cm}^3/\text{min}$ (for Ir) and $FR_{O_2} = 12 \text{ cm}^3/\text{min}$ (for Pt). Without the addition of oxygen gas, films consisted in aggregated metal particles 1 – 3 nm in diameter surrounded by amorphous carbon.

Chapter 3. Epitaxial Growth

Epitaxially grown electrode films on semiconductors or insulating substrates are used under-electrodes for functional ceramic films (i. e. ferroelectric, superconducting, piezoelectric films, etc.), which also epitaxially grow on the electrically conducting films. Ir and Pt metals are promising for the electrodes because of their high electrical conductivity. As under-electrode films, they provide the opportunity to grow functional ceramics films requiring a high temperature processing and to prevent the chemical interaction with the substrate material because of their high melting temperature and high chemical stability. So far, amorphous or randomly oriented polycrystalline Ir or Pt films have been prepared by MOCVD on amorphous or single-crystal substrates. There is only one report of epitaxial MOCVD (100)-oriented Pt films on KTaO_3 and SrTiO_3 substrates. In this study, Ir and Pt films were grown on MgO, sapphire and Si single-crystals. AlN (piezoelectric) films were grown on the Ir and Pt films.

Films were grown under the appropriate deposition conditions determined in Chapter 2. Oxygen gas was added to the source vapor. Sapphire (0001), $(11\bar{2}0)$ and $(01\bar{1}2)$, MgO (100) and Si (111) single-crystals were used as substrates. AlN films were grown by electron cyclotron resonance plasma-assisted CVD. The films orientation and epitaxial relationships between films and substrates were determined by XRD and x-ray pole figures.

Epitaxial growth of Ir and Pt films was achieved on MgO and sapphire substrates by adding oxygen gas to the precursor vapor. No epitaxial growth of films was observed on Si substrates because SiO_2 layer was formed on the surface due to oxidation. Ir and Pt films grow in $[100]$ orientation on MgO (100). Ir and Pt films grow in $[111]$ orientation on sapphire $(01\bar{1}2)$ and

(0001). Only Ir films grow in $[100]$ orientation on sapphire $(\bar{1}1\bar{2}0)$. Pt films orientation on sapphire $(\bar{1}1\bar{2}0)$ could change as the growth proceeds with predominance of $[111]$ orientation as the film grows. Epitaxial Pt films with only one in-plane orientation on sapphire (001) were obtained for the first time. So far, epitaxial Pt films containing two in-plane orientations grown by PVD methods on sapphire (0001) have been reported. Epitaxial growth of AlN films was achieved on Ir-and Pt-coated sapphire (0001) substrates.

Chapter 4 . Electrochemical Properties

The catalytic activity of Ir and Pt metals and their high electrical conductivity enable them as electrodes for solid electrolytes. An oxygen concentration cell that utilizes ZrO_2 solid electrolyte requires porous metal electrodes to allow absorption and liberation of oxygen gas. Moreover, catalytic metal electrodes are needed for the charge transfer reactions at the interface between electrode-solid electrolyte. Noble or platinum group metal pastes are commonly used to prepare the porous electrodes. ZrO_2 oxygen concentration cell operates at temperatures between 500 and 1000°C. Some problems associated with the charge transfer at the interfacial region between the electrode and electrolyte may limit the utility of ZrO_2 cells at lower temperatures.

A.C. impedance spectroscopy is a powerful technique to investigate electrode processes. It allows one to distinguish the dispersions from bulk, grain boundary and the electrode-electrolyte interface effect. D.C. measurements give global information on the kinetics of the electrochemical process at the electrodes. In this study, Ir and Pt films were prepared as electrodes for ZrO_2 solid electrolyte.

Porous films containing carbon, Ir (C) and Pt (C) (i.e. films prepared without the addition of oxygen) were deposited on stabilized (Y_2O_3 -8 mol%) ZrO_2 pellets. For comparison, carbon-free Ir and Pt films, sputtered Ir and Pt films, and Pt paste electrodes were also prepared on the ZrO_2 pellets. Their electrochemical properties were investigated at temperatures between 230 and 800°C by A.C. spectroscopy and D.C. measurements.

A.C. impedance spectroscopy indicated very difficult charge transfer at the interface Pt (C) / ZrO_2 , on the contrary, an easy interfacial reaction for Ir (C) films. Ir (C) films exhibit the highest conductivity associated to the electrode process below 600°C. D.C. measurements revealed no polarization effect for Ir (C) films. Pt paste electrodes showed almost the same electrode conductivity as the Pt (C-free) films. A ZrO_2 oxygen cell that utilizes Ir (C) films as electrodes obeys the Nernst equation at temperatures as low as 300°C. Ir (C) films may have the most promising properties as the electrode for ZrO_2 electrolyte at temperatures below 600°C.

Chapter 5 . Corrosion Resistance

Materials used as protective coatings for high temperature require chemical stability, high melting point and thermal shock resistance. Ceramic films (SiC, TiC and TiN) have been proposed to improve the corrosion resistance of structural materials such as stainless steels. These ceramic films could be satisfactory under an isothermal corrosion but not under severe dynamic (cyclic change of temperature) corrosion due to large thermal expansion mismatch. Metallic films with the appropriate properties could be applicable to the dynamic corrosion. Ir and Pt metals are good candidates for protective films as they have these advantageous properties. Although Ir films have been investigated to provide oxidation protection for graphite, C-C composites and refractory metals at very high temperatures ($\sim 2000^{\circ}\text{C}$), there have been no reports of corrosion in halogen containing atmosphere.

H_2 is expected to be a new energy source. "UT-3" is a promising process for H_2 production. In this process, high temperature corrosion of structural materials is an important problem because of highly corrosive gases (bromine, oxygen, hydrogen bromide, etc.) should be used at around 800°C . Stainless steels are widely used as construction materials in high temperature oxidizing environments as they combine the required physical properties with reasonable corrosion resistance. In this study, Ir and Pt films were prepared on stainless steel as a candidate structural material for "UT-3" process. Their corrosion resistance was investigated in a $\text{Br}_2\text{-O}_2\text{-Ar}$ atmosphere at 800°C .

Ir and Pt films were prepared under the appropriate deposition conditions determined in Chapter 2. Oxygen was added to the source vapor. Stainless steel (SUS304) plates were used as substrates. Depositions were performed for 40 to 180min.

Corrosion resistance was evaluated by mass change measurements. The corrosive atmosphere was prepared by flowing an $\text{O}_2\text{-Ar}$ mixture through liquid bromine. Gases flowed from the top of a reaction tube and exhausted from the bottom. Partial pressure of bromine was kept constant at 70 Torr. The oxygen partial pressure was controlled between 34 and 690 Torr. Total pressure inside the reaction tube was 760 Torr.

Films exhibit rough surface due to a columnar-grain growth as observed by SEM. A denser layer was observed at the film/substrate interface. No impurities were detected in as-deposited films by EPMA. Films well adhered to the substrates. Ir and Pt films were obtained up to $2.5\ \mu\text{m}$ and $25\ \mu\text{m}$ thick, respectively. After 6 h of exposure to the corrosion gases ($P_{\text{Br}_2} = 70$ Torr, $P_{\text{O}_2} = 690$ Torr), $25\ \mu\text{m}$ thick Pt-coated SUS304 showed a scale-free surface while $2.5\ \mu\text{m}$ thick Ir-coated SUS304 showed a surface scale identified as IrO_2 by XRD. For the same corrosion conditions, Cr_2O_3 and an unknown product were formed on $6\ \mu\text{m}$ thick Pt-coated SUS304. EPMA results indicated the reaction between Cr_2O_3 and Pt. For thick enough Pt films ($25\ \mu\text{m}$ thick) the formation of Cr_2O_3 could be delayed. IrO_2 and Cr_2O_3 were formed on 1

μm thick Ir-coated SUS304. Ir or IrO_2 did not react with Cr_2O_3 . For thick enough Ir films ($2.5 \mu\text{m}$ thick) the formation of Cr_2O_3 could be further delayed by IrO_2 . $25 \mu\text{m}$ thick Pt and $2.5 \mu\text{m}$ thick Ir films prevent the corrosion of SUS304 at $P_{\text{Br}_2} = 70$ Torr and $P_{\text{O}_2} = 34\text{-}690$ Torr.

Chapter 6 . Conclusions

Ir and Pt films were prepared by MOCVD. The physicochemical properties of Ir and Pt metals enable them as conductive electrode films as well as protective films. These applications require a specific appropriate morphology. (1) Epitaxial electrode films. (2) Porous and catalytic electrode films. (3) Thick and dense protective films. This study was aimed to achieve that morphology. The results of this study are summarized as follows.

- (1) Epitaxial Ir and Pt electrode films were achieved on MgO and sapphire single-crystal substrates. Films could epitaxially grow by the addition of oxygen gas to the source vapor.
- (2) Porous and catalytic Ir electrode films were achieved. Ir (C) composites (Ir particles 1 – 3 nm in diameter surrounded by amorphous carbon) showed superior electrochemical properties as the electrode for ZrO_2 electrolytes at temperatures as low as 300°C .
- (3) Thick Ir and Pt protective films were achieved. $2.5 \mu\text{m}$ thick Ir and $25 \mu\text{m}$ thick films prevent the corrosion of stainless steel (SUS304) in a $\text{Br}_2\text{-O}_2\text{-Ar}$ atmosphere at 800°C , $P_{\text{Br}_2} = 70$ Torr and $P_{\text{O}_2} = 34\text{-}690$ Torr.

審査結果の要旨

イリジウムや白金などの貴金属は導電性が高く、触媒活性を有し、高温で化学的に安定であることなどから、各種電子デバイスや固体電解質用電極や耐食コーティング用の材料として用いられている。従来、これらの貴金属膜は、粉体の塗布や真空蒸着によって作製されていたが、本論文では、有機金属化合物を原料として化学気相析出（MOCVD）法によりイリジウムおよび白金の膜を合成し、得られた膜の電子デバイス用電極、固体電解質用電極、耐熱金属の耐食コーティングとしての有効性を明らかにしたもので、全編6章よりなる。

第1章は緒論で、本研究の背景と目的について述べている。

第2章では、原料にイリジウムおよび白金のアセチルアセトネートを用い、酸素ガスを原料ガス中に添加して、合成温度500~600°C、全ガス圧力2~5 Torr、原料温度180°Cで、各種非晶質および多結晶基板上に不純物を含まない鏡面のイリジウムおよび白金膜が得られることを明らかにしている。

第3章では、Si, MgO および Al₂O₃ 単結晶基板上にイリジウムおよび白金膜がエピタキシャル成長することを示し、膜と基板との結晶学的な方位関係、エピタキシャル成長機構、イリジウムと白金膜のエピタキシャル成長の相違を明らかにするとともに、一方向に面内配向した単結晶白金膜を Al₂O₃ 単結晶基板上に作製することに初めて成功している。

第4章では、イリジウムと炭素の複合膜（Ir-C）の電気化学的性質を A. C. インピーダンス法、濃淡セル法、カレントインタラプション法などを用いて調べることにより、Ir-C膜が ZrO₂ 固体電解質用電極として、300°Cもの低温でも極めて触媒活性の高い優れた電極であることを明らかにしている。

第5章では、SUS304 鋼にイリジウムおよび白金膜を被覆することにより、800°Cの高温下、臭素を含む高腐食性ガス中でも十分な耐食性が達成されることを示している。

第6章では総括である。

以上要するに本論文では、MOCVD 法により作製されたイリジウムおよび白金膜の合成条件と組織、構造、電気化学的性質および耐食性の関係を調べ、これらの貴金属膜の電子デバイス用電極、固体電解質用電極および耐食被覆材としての有用性を明らかにし、MOCVD 貴金属膜の実用化の可能性を示したもので、材料物性学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。