氏　名（本　籍）	DANIEL, Shipwiisho Likius（Namibia）
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論 文 審 査 委 員	主査　佐　藤　光　史
	副査　小　野　幸　子
	大　倉　利　典
	鷹　野　一　朗
	大　石　知　司（芝浦工業大学教授）

論文要旨

CONTENTS

SCOPE

The fabrication of Ag-NP/TiO_2 composite nanostructured thin films, enhancement of its electrical conductivity, and their potential applications due to the visible-light-driven plasmon, where by large amounts nano-scale Ag particles up to 80 mol% can be incorporated in titania matrix using a chemical processes, are the main subjects studied in this thesis. Titanium dioxide (titania or TiO_2) as a semiconductor displays photo-responsive behavior under ultraviolet (UV) light irradiation, thereby severely limiting its practical applications. It is highly desirable to develop a new visible-light-driven TiO_2 based thin film that can use visible light under sunlight irradiation. In another scientific field, it is well understood that the excitation of localized plasmon on the surface of silver-nanoparticles (Ag-NP) causes a tremendous shifting of plasmon resonance peak at well-defined wavelengths near UV and in the visible region. Moreover, incorporating more amount of nano-scaled size Ag particle is necessary for decreasing of the electrical resistance of TiO_2 from $10^{12}\,\Omega$.

Ag-NP, as a guest has been introduced into (or onto) TiO_2 using various methods. Many of these different methods are used to synthesize nanoparticles directly on semiconductor supports. Physical vapor deposition (PVD) and chemical vapor deposition (CVD) are the two most common types of thin film formation methods. Ag-NP/TiO_2 films from PVD methods such as sputtering or vapor deposition require sophisticated equipment. CVD methods can be employed to synthesize nanoparticles of controlled size and shape in solutions and on supports. The most widely applied chemical technique for the preparation of Ag-NP/TiO_2 composite materials is the sol-gel process, which has been applied to the fabrication of the most Ag-NP/TiO_2 system. The prepared solution for fabricating the Ag-NP/TiO_2 composite thin films available in literatures and obtained by mixing a sol-gel solution of titania for thin film fabrication with a silver solution having a concentration of up to only 18 mol% due to Ag particles coalesce with each other into huge particles during sintering.

Recently, the molecular precursor method (MPM) has been demonstrated to offer excellent miscibility of the solutions, which has also been observed in several precursor solutions during the fabrication of ceramic films by the method developed by our laboratory. Based on the study in our laboratory an excellent perovskite-type $SrTiO_3$ thin film was fabricated using a mixed precursor solution from a titania precursor solution containing a Ti complex of ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) and a SrO precursor solution containing a Sr complex of EDTA prepared using MPM. It was found that mixed precursor solution containing exactly equal amounts of Ti and Sr can be easily prepared due to the excellent miscibility of the solutions. The stability, homogeneity, miscibility, and other characteristics of the precursor solutions, which are adequate to various coating methods, are practical advantages, as compared with the conventional sol-gel method. This thesis is therefore, intended to develop systematic method where by more amounts nano-scaled size Ag particle up to 80 mol% can be incorporated in titania matrix using MPM. We expected that the more amount of Ag-NP introduced into (or onto) TiO_2 matrix would be greatly boosted electrical conductivity and simultaneously may enhance visible-light-driven plasmonic property of Ag-NP/TiO_2 heterostructure if it gets assisted by the enhanced near-field amplitudes of localized surface plasmon associated with metallic silver.

I therefore, herein, try to fabricate Ag nanoparticles/titania (Ag-NP/TiO_2) composite thin films consist of large quantity of Ag nanoparticles (Ag-NP) and evaluating their conductivity, plasmonic and photoresponse properties using the new method, MPM. A coating molecular precursor solution can be prepared by a reaction of $Ti(O^iPr)_4$ with EDTA under the presence of dibutylamine and hydrogen peroxide. Consecutively, the Ag acetate ethanol solution was developed in this thesis, simply dissolving the silver salt in ethanol. The two precursor solutions can be then mixed at different molar concentration to form composite solution. On the basis of these considerations, Ag-NP/TiO_2 composite thin films can be fabricated by employing various Ag molar concentrations (10-80mol%). Specifically, the following topics have been investigated in details in the present thesis.

Chapter 1 introduces the importance and some basic knowledge of nanomaterials, fabrication processes, and plasmonic properties of Ag-NP/TiO_2. The specific properties of molecular precursor method have been presented thereafter. The understanding of the background of light harvesting phenomena will make one appreciate the progress of light harvesting technology, therefore the preparation methods for various Ag-NP/TiO_2 heterostructures and the modern applications of Ag-NP/TiO_2 based nanomaterials have been extensively reviewed in **Chapter 2**.

Chapter 3 outlines general experimental procedure and the designation for the preparing Ag-NP/TiO_2 composite thin films using molecular precursor method. The principles of each characterization method (XRD, TEM, FE-SEM, XPS, four probe techniques, photocurrent measurement etc.) are briefly discussed and the experimental conditions usually used are also given.

Using the two precursor solutions of titania and silver prepared using MPM, the resultant composite solution with a 1 : 1 mixed molar ratio was used to fabricate Ag-NP/TiO_2 composite thin films heat treated at different temperature (250-800℃) have been achieved (**Chapter 4**). All the fabrication processes are accompanied by investigating the nanostructure behavior of the produced thin films, with the aim to find the optimal heat-treatment temperature for constructing Ag nanoparticles/titania composite nano-level structure in air. X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), and X-ray photoelectron spectroscopy (XPS) evaluation of the effect of the morphology and the nanostructures of the Ag nanoparticles in the composite thin films revealed that heat treatment temperature of 600℃ is suitable for the fabrication of titania (mixture of rutile and anatase) composites doped with metallic Ag-NP nanostructure.

In **Chapter 5**, metallic Ag-nanoparticles/titania (Ag-NP/TiO_2) composite thin films with different Ag molar concentrations ($10 \leq$ Ag mol% ≤ 80) were prepared on a quartz glass substrate at 600℃, in order to find the percolation threshold for the electrical resistivity of Ag-NP/TiO_2 composite thin films. The composite sample is non-conductive, until the volume fraction of the conducting phase reaches the so-called percolation threshold. The percolation threshold for the Ag-NP/TiO_2 composite thin film was identified at an Ag fraction φ_{Ag} value of 0.30. The lowest electrical resistivity of $10^{-5}\,\Omega\cdot$cm was recorded, at φ_{Ag} of 0.55. XRD, FE-SEM and transmission electron microscopic (TEM) evaluation of the effects of the morphologies and nanostructures of the Ag nanoparticles in the composite thin films on the electrical resistivity of the film revealed that the films consist of metallic Ag nanoparticles homogeneously distributed in the titania matrix.

In **Chapter 6**, the titania, a semiconductor was replaced by zirconia, an insulator and the electrical resistivity of Ag-NP/ZrO_2 composite thin film was also investigated using the identical procedures as those reported in chapter 5. The shortening of the distances between the metallic Ag particles and the agglomeration of metallic Ag particles lead to the formation of the conducting paths. So, the electrical resistance of Ag-NP/ZrO_2 film deceases greatly once metallic Ag is incorporated. The lowest electrical resistivity of 10^{-3} $\Omega\cdot$cm was recorded, at φ_{Ag} of 0.44.

In **Chapter 7**, the plasmonic properties of Ag-NP/TiO_2 composite thin film were investigated. These composite thin films of ca. 100 nm thickness were fabricated by the MPM at 600℃ in air. Usually, a problem is that Ag-NP, which are chemically very reactive, would be oxidized at direct contact with TiO_2. To prevent this oxidation, Ag core have to be coated with a passive material, such as SiO_2 shells and Al_2O_3 nanomasking to separate them from TiO_2. In this thesis, we employed UV-Vis spetroscopic technigues, whereby the diffuse reflectance spectra (DRS) derived from Kubelka-Munk equation were investigated. It was found that the Ag-NP/TiO_2 composite thin films exhibit size- and shape-dependent plasmon resonances that obtained without masking nor shelling the Ag core. XPS spectra of the resultant composite thin films, demostrated that MPM is capable to fabricate the metallic Ag-NP in titania instead of AgO_x, a neccesity for exhibition of plasmon resonance bands under UV-Vis absorption spectra.

With the main emphasis on lower electrical resistivity and plasmonic properties associated with Ag-NP/TiO_2 composite thin films reported in chapters 5 and 7 respectively. It is necessary to consider that there are different technologies of solar energy conversion and this energy is used in different forms for different production, public, and household purposes. As a result, either solar energy in some forms (electricity, heat, or cold) or different energy products or energy services (hot gas, air, water, dried products, special ceramic materials) can be generated as the final product supplied to the consumer. Therefore, **Chapters 8 and 9** investigated the photoelectrochemical and photocatalytic properties of the fabricated composite thin films respectively; a route toward the industrial applications. The composite thin films show a very intense localized surface plasmon resonance (LSPR) absorption band in the Vis-light region. This is associated with a considerable enhancement of the electric near-field in the vicinity of the Ag-NP. We therefore, hypothesized that this enhancement in the visible-light region could boost the excitation of electron-hole pairs in TiO_2, hence, increase the efficiency of the photoresponse.

The enhancement effects are believed to be based on LSPR of Ag-NP on the basis of both the photo-excited electron transfer from Ag-NP to the conduction band of TiO_2, and the lower electrical conductivity of the COMP-Ag*n*. Here I show that this is true indeed. Moreover, we have obtained for the first time using a chemical process, novel kind nano-sized Ag-NP/TiO_2 composite thin films with a unique property: the conversion of the originally anodic photocurrent Ag-nano particle-titania thin film to the cathodic one was clearly observed by means of photocurrent.

Finally, **Chapter 10** makes a brief conclusion on the major results on the present studies related to Ag-NP/TiO_2 composite thin films. Moreover, some suggestions for future works in this area such as photovoltaic and antibacterial studies are also provided.

論文審査要旨

本論文は，化学的湿式法の分子プレカーサー法（MPM）により，前例のない広範囲な濃度の銀ナノ粒子をチタニアに均一分散した銀ナノ粒子/チタニア（Ag-NP/TiO_2）複合薄膜についての研究を，全10章にまとめたものである．

第1章は，太陽光の有効利用に半導体を活用する研究の背景と目的を記載した．第2章では，可視光の波長より小さい銀ナノ粒子とチタニア薄膜の形成に関する物理的および化学的方法を調査し，銀ナノ粒子と半導体であ

るチタニアとの相互作用に関する先行研究を基に，これらの系を活用して可視光を有効利用する理論と研究の具体的な意義を述べた．

第3章は，全編に関わる実験方法や各種機器測定の原理と方法について，詳細に記載した．この中で，銀ナノ粒子とチタニア薄膜形成用の各プレカーサー溶液は，各々銀塩とエチレンジアミン四酢酸（EDTA）のチタン錯体から調製し，百～数百nmの厚さをもつAg-NP/TiO_2複合薄膜（COMP-Agn（10 mol%≤n≤80 mol%））が得られることを示した．成膜にはスピンコート法が有効で，石英基板上での熱処理で均一な薄膜が得られることを示した．

第4章は，分子プレカーサー法によってAg-NP/TiO_2複合薄膜を形成するために，先ずAg/Ti物質量比が1のプレカーサー膜の熱処理を70～800℃の温度範囲で探索し，薄膜のXRDやXPSから，安定で光反応活性を期待できるアナターゼ/ルチル混合系を得るために600℃の熱処理が適切で，かつ銀の酸化物が共存しないことを明らかにした．TG-DTAによる熱分析，FE-SEMによる表面観察，UV-Visスペクトル，電気抵抗率や力学的強度の温度依存性を詳細に検討し，決定した熱処理温度の合理性を確認した．

第5章では，前章の検討を踏まえ，広範囲な銀濃度のAg-NP/TiO_2複合薄膜について，四探針法による25℃における電気抵抗率を測定し，パーコレーション閾値の存在を詳細に探索した．その結果，銀ナノ粒子の体積分率（φ_{Ag}）の電気抵抗率に対する依存性から，パーコレーション閾値が$\varphi_{Ag}=0.30$であることを見出した．また，$\varphi_{Ag}=0.55$の薄膜が最低抵抗率の10^{-5} Ω・cmに達することを実証した．また，XRDとTEM測定により，アナターゼ/ルチルの含有率によらず，均一分散している銀ナノ粒子の形状と大きさ，および分離距離がAg-NP/TiO_2複合薄膜の電気抵抗率に強く影響することを明らかとした．

また，第6章ではマトリックスとして絶縁性のZrO_2を用い，チタニア系と同様に広範囲な銀濃度のAg-NP/ZrO_2複合薄膜を形成した．これらの複合薄膜形成においても分子プレカーサー法が有効なことを示し，それらの電気抵抗率からパーコレーション閾値を検討し，チタニア系との相違について理論的に考察した．

第7章で，Ag-NP/TiO_2複合薄膜のUV-vis吸収スペクトルを詳細に検討した．その結果，銀ナノ粒子に起因する表面プラズモン共鳴（SPR）吸収が約410 nmにピークとして，また局在化表面プラズモン共鳴（LSPR）吸収が可視光領域の広範囲な吸収帯として観察される一方，チタニアの光学的バンド端は変化しないことを明らかとした．

第8章では，Ag-NP/TiO_2複合薄膜の光電流密度を測定し，先行論文で報告されたアノード光電流ではなく，カソード光電流が発生することを見出した．また，光電流密度値が銀ナノ粒子の含有量に依存することやZrO_2系との比較から，分子プレカーサー法が銀ナノ粒子をチタニア半導体中に高度に分散できる現在唯一の方法で，電気化学的に特異な性質を有する安定な薄膜を与えることを示した．

第9章では，銀ナノ粒子/チタニア複合薄膜の光触媒としての機能を検討した．複合薄膜の光触媒活性は，紫外光または可視光照射下でのメチレンブルー水溶液の脱色率変化から評価した．その結果，銀ナノ粒子の含有量によって，銀ナノ粒子/チタニア複合薄膜の光触媒活性が照射光の波長に強く依存することを見出した．すなわち，銀量が40 mol%より少ない複合薄膜は，紫外光照射下のみで光触媒として作用すること，またこの範囲までの銀量の場合，複合薄膜の紫外光感度は銀量の増加に伴って，同一条件下で形成したチタニア薄膜の約半分まで段階的に減少することを先ず見出した．一方，50 mol%以上の銀含有量の複合薄膜は可視光にも応答し，その程度は減少した紫外光感度よりわずかに低いことを明らかにした．複合薄膜の拡散反射スペクトル（DRS）の解析によって，可視光応答性が銀ナノ粒子のSPRとLSPRによることを示した．このように，銀ナノ粒子の表面プラズモン吸収と脱色率増加の間に明確な関係があり，銀ナノ粒子プラズモンが薄膜の導電率を増幅し，かつ光触媒反応の活性化に寄与することを実証した．

第10章で研究結果をまとめ，優れた混和性をもつ分子プレカーサー法による薄膜材料形成の将来性について議論し，研究全体を総括した．

以上のように，本論文は太陽光の有効利用に展開可能な薄膜材料創成において，分子プレカーサー法を活用した独創的な研究成果をまとめており，工学の分野において大きな成果を得たことが認められ，博士（工学）の学位を授与するに十分値するものである．