

화학적 방법을 이용한 TiO₂ 박막제조 및 응용

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Formation of TiO₂ thin film using chemical methods and the application

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ABSTRACT

PEC전지 전극으로 사용될 수 있는 CdSe는 수용액상에서 광부식이 심하기 때문에 투명한 보호막이 필요하다. TiO₂는 광부식이 심한 광전극의 보호막으로 적합하며 이 논문에서 화학적 방법(전기증착과 화학조증착)을 이용하여 산성용액이나 알칼리용액에서 TiO₂ 박막을 제조하여 광흡수나 광전류를 측정하였다. XRD를 이용해서 제조된 TiO₂ 박막의 결정성을 확인하였으며 막의 표면특성은 SEM으로 측정하였으며 광흡수 특성이 관찰되었다. 제조된 TiO₂ 박막의 광전류는 100 mW/cm²의 광세기를 가지는 제논 램프를 이용하여 측정하였다. CdSe에 TiO₂박막을 코팅했을 때의 CdSe막의 광흡수와 광전류를 측정하여 TiO₂ 코팅효과를 관찰하였다.

Key words : TiO₂ thin film(TiO₂ 박막), Electronic deposition(전기증착), Chemical bath deposition(화학조증착), Photo electrochemical cell(PEC전지)

1. Introduction

TiO₂ has been one of the most extensively studied oxides because of its remarkable optical and electronic properties. TiO₂ film in anatase phase could accomplish the photocatalytic degradation of organic compounds under the

radiation of UV. It has been application prospects in the field of environmental protection such as sterilization and sewage disposal. A recent interest is focused on an amphiphilic TiO₂ surface induced by UV irradiation, which is expected to be applicable to a windshield and a mirror for vehicles¹⁾. On the other hand in the field of alternative energy, a dye-sensitized solar cell is now a hot topic due to its high conversion

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efficiency produced with a porous TiO₂ electrode that is composed of few tenths of nanometer-sized particles²⁻³). TiO₂ with rutile phase is known as a good blood compatibility material and can be used as artificial heart valves.

From the point of view of practical use, the fixation of TiO₂ onto a substrate is very important and some methods to fix the TiO₂ particles have been developed. Consequently, a low cost preparation and fixation of the TiO₂ photocatalyst with nanosized particle is necessary for practical applications. Many deposition methods such as thermal and anodic oxidation of titanium, electron beam evaporation, chemical vapor deposition, plasma enhanced chemical vapor deposition, reactive sputtering, sol-gel, spray pyrolysis etc have been reported to prepare nanometersized particle powder or thin films⁴).

Recently, much emphasis has been put on the soft solution chemical processes for the preparation of advanced inorganic materials such as perovskite-type oxides, spinel-type oxides, superlattices and nanodots with quantum size effects. These low cost processes have been used environmentally benign conditions. Therefore, these soft solution chemical processes are important for the preparation and fixation of the TiO₂ particles. Such processes include sol-gel, atomic layer deposition, electrochemical deposition, spray pyrolysis, dip coating, solution hydrolysis etc.

The TiO₂ nanoparticles have been prepared by chemical method using hydrolysis of TiCl₄, Ti(SO₄)₂, and TiL₄⁴⁻⁷). The TiCl₄ was slowly dropped in deionized water at 273 K to get TiO₂ particles. Whereas, Ti(SO₄)₂ solution was dropped in aqueous ammonia solution under stirring to get TiO₂ powder. Barringer and Bowen⁸) prepared submicron TiO₂ powders by controlled hydrolysis

of an alcoholic solution of Ti(OC₂H₅)₄ or Ti(i-OC₃H₇)₄, and showed that these powders gave sintered bodies with fine-grained microstructure and high density of a low sintering temperature. Kato et al⁹) synthesized spherical TiO₂ powder from an aqueous solution of TiO(SO₄)₂ by homogeneous precipitation using urea as the precipitating agent at 343-363 K. The reports to produce TiO₂ films from chemical hydrolysis method are scanty in the literature. Transparent nanocrystalline anatase TiO₂ films were deposited on to conducting glass substrates from titanium tetraisopropoxide colloidal solution¹⁰⁻¹¹). In order to increase film thickness, the anatase TiO₂ films were treated with TiCl₄ solution for few hours and annealed at high temperature. The TiO₂ film thickness was typically 4 to 8 micron. For photosensitization studies, the TiO₂ coated glass was heated at 623 K for 30 mins. Vigil et al¹²) have deposited TiO₂ films using microwave heating on glass and fluorine doped tin oxide coated glass substrates.

Among the various methods in use for the production of porous as well as compact titanium oxide thin films, the electrodeposition appears to be a simple and low cost method. The main advantage is the easy control of film thickness, morphology, composition etc. through electrical quantities such as deposition current and applied potential. Relatively few reports are available on the electrodeposition of TiO₂ film. Both the types; cathodic and anodic electrodeposition have been reported in the literature. Natarajan and Nogami¹³) and Zhitomirsky¹⁴⁻¹⁶) have reported on cathodic deposition of TiO₂ film. Kavan et al¹⁷) have reported on deposition of TiO₂ film on F-doped tin oxide glass and metallic (Pt, Au Ti) electrodes by anodic oxidative hydrolysis of acidic TiCl₃ solution. Matsumoto et al¹⁸) have reported the

TiO₂ deposition from (NH₄)₂[TiO(C₂O₄)₂] solution onto alumite, followed by pulsed deposition from TiCl₃ solution. Flood et al.¹⁹⁾ have prepared transparent nanocrystalline semiconductor sandwich electrodes of configurations CdS/TiO₂ and TiO₂/CdS on F-doped tin oxide glass, where TiO₂ was deposited from TiCl₃ solution at room temperature.

In all the above electrodeposition experiments, the solution of titanium salts is used in the acidic PH range of 1 to 3 only^{14~18)}. The titanium ions are not complexed and the deposition baths are unstable due to precipitation of titanium hydroxide. The hydrogen peroxide is used as an oxidizing agent. The TiO₂ thin films obtained are porous and of anatase phase.

In the present work, thin films of titanium oxide have been deposited on ITO substrate by 1) anodic electrodeposition from acidic bath, 2) cathodic galvanostatic deposition from alkaline bath, and 3) chemical deposition. The deposition and characterization of these TiO₂ films are reported.

2. Experimental

2.1 Electrodeposition of TiO₂ films from acidic bath

TiO₂ thin films are electrodeposited from acidic and alkaline baths containing Ti(III)Cl₃ solution at room temperature. For deposition from aqueous acidic bath, 0.05 M TiCl₃ solution was made by mixing TiCl₃ in conc. HCl in 1 : 2 ratio and its pH was adjusted between 2-5 using 7% NaHCO₃ solution with constant stirring. Deposition of TiO₂ film was carried out onto ITO substrate. Anodic potential of + 1.0 V vs Ag/AgCl was applied for the time of 30 min.

2.2 Electrodeposition of TiO₂ films from alkaline bath

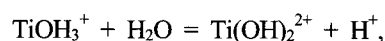
For deposition of TiO₂ from alkaline bath, the 0.05 M TiCl₃ solution was mixed with 0.1 M EDTA into 1 : 1 ratio. To this, a solution of ammonium hydroxide (28%) was added with constant stirring. At pH equal to 10.0, a whitish-grayish precipitate was formed in the solution. A pH equal to 12.20 was obtained by further addition of ammonia solution. A constant current of 1 mA/cm² was passed between ITO cathode and platinum anode.

2.3 Chemical bath deposition of TiO₂ films

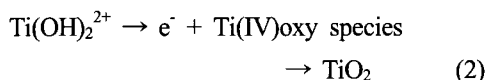
Chemical bath deposition of TiO₂ films at room temperature was carried out from titanium(III) chloride, TiCl₃ (Aldrich, USA) solution. As received TiCl₃ (20-30 wt% in HCl) solution was taken into beaker and its pH was adjusted between 2-5 using 7% NaHCO₃ solutions with constant stirring. Deposition of TiO₂ films was carried out onto previously cleaned ITO coated glass substrates. The substrates were cleaned with detergent solution and ultrasonically, before use. The TiO₂ films were taken out of the bath after deposition period of 1-6 hrs, washed with water and dried under argon flow. The TiO₂ films were heat treated in air at 723 K for 1-12 hrs.

3. Results and discussion

The reaction mechanism for electrodeposition of TiO₂, from acidic TiCl₃ solution under anodic bias, has been reported in the literature^{17, 20~21)}. Under anodic bias and in acidic solution, the deposition mechanism of TiO₂ has been proposed as

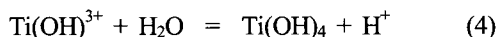
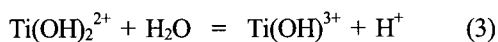


$$Kp = (2-7.7) \quad (1)$$

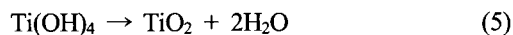


Ti(OH)_2^{2+} will be produced by the hydrolysis of Ti^{3+} on the dilution and pH adjusting process of TiCl_3 solution. Ti(OH)_2^{2+} will then be oxidized to Ti(IV)oxy species. According to Kavan et al¹⁷⁾, the Ti(IV)oxy species is an intermediate between TiO^{2+} and TiO_2 , consisting of partly dehydrated polymeric Ti(IV) hydroxide, which will be finally converted into TiO_2 by dehydration during electrolysis.

The effect of changing pH of the TiCl_3 solution from acidic to alkaline medium on titanium species is seen from following reaction mechanism. When the pH is less than 2.45, the solution contains the Ti(OH)_2^{2+} species in TiCl_3 solution. However, if the pH is greater than 2.45, the Ti(OH)_4 species are present in the solution as per following reactions²⁰⁻²¹⁾.



The Ti(OH)_4 species are soluble in aqueous solution and remains soluble in bath in the alkaline pH region (pH. > 7.0). From this solution, chemical precipitation of TiO_2 occurs as



The cathodic deposition condition depends upon bath temperature, nature of substrate, metal ion concentration, complexing agent and its concentration etc.

3.1 Electrodeposition of TiO_2 films Acidic bath

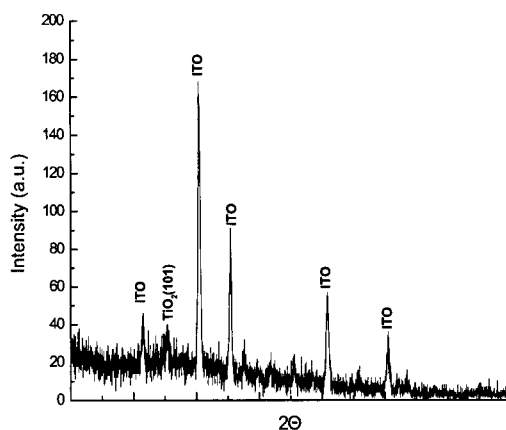


Fig. 1 (a) The XRD pattern of TiO_2 film deposited on ITO substrate (acidic bath)

TiO_2 exists in three different phases: anatase, rutile and brookite. However, only anatase, rutile and amorphous films of TiO_2 have been reported²²⁾. The TiO_2 film with different structures varied in optical and photocatalytic properties. It is found that TiO_2 film consisting of anatase and rutile phases with an appropriate ratio has the best photocatalytic activity. So, it is important to optimize preparative process to obtain TiO_2 film with appropriate film composition. The influence of annealing temperature on the properties of magnetron sputtered TiO_2 film has studied. The phase transformation temperature from anatase to rutile was between 973 and 1173 K. Annealing temperatures until 773 K showed weak peaks due to anatase phase.

The XRD pattern of TiO_2 is shown in Fig. 1 (a). It shows strong diffraction peaks due to ITO glass substrate. The weak diffraction peak at 25.3° corresponds to anatase phase of TiO_2 ²⁶⁾. This shows that electrodeposited TiO_2 consists of amorphous and fine grains; similar to the observations reported for magneto sputtered, sol gelcoated and electrodeposited TiO_2 films^{17,23)}.

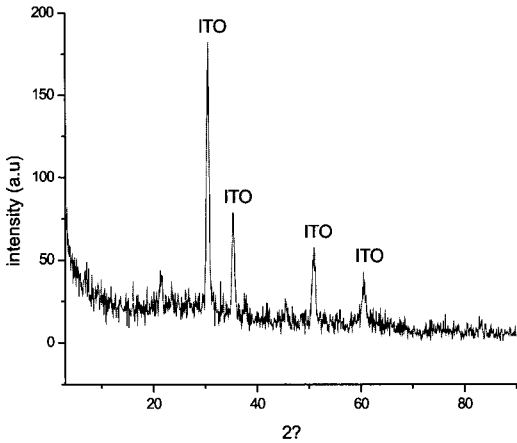


Fig. 1 (b) The XRD pattern of TiO₂ film deposited on ITO substrate (alkaline bath)

Scanning electron micrographs of TiO₂ film are shown at two different magnifications (20,000 × and 50,000 ×) in Fig. 2 (a, b). At 20,000 × magnification, a compact nanostructure of TiO₂ film is well seen; in contrast to the highly porous,

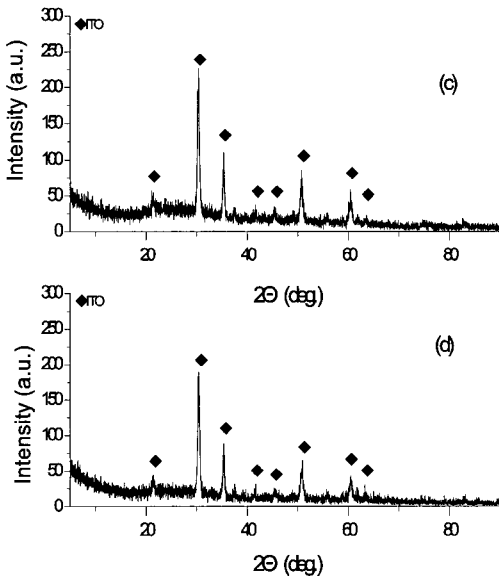


Fig. 1 (c, d) The XRD patterns of TiO₂ films (Chemical bath) deposited on ITO substrates at two different thicknesses (c) 10 nm, and (d) 50 nm. The films were heat treated at 623 K for 12 hrs

granular and flat textured TiO₂ film usually obtained with sol-gel method²⁴). The average grain size estimated from Fig. 2 (b) was 50-60 nm, which is comparable to sol-gel deposited TiO₂ film.

Optical absorption spectrum of TiO₂ film is shown in Fig. 3 (a). The film shows sharp decrease in absorption at 300 nm, indicating that the grain size of TiO₂ film particle is independent of film thickness. A tailing absorbance in visible region of 400 to 500 nm was observed. A similar absorbance has been observed for the TiO₂ produced by hydrolysis of TiCl₄^{17,25}. Serpone

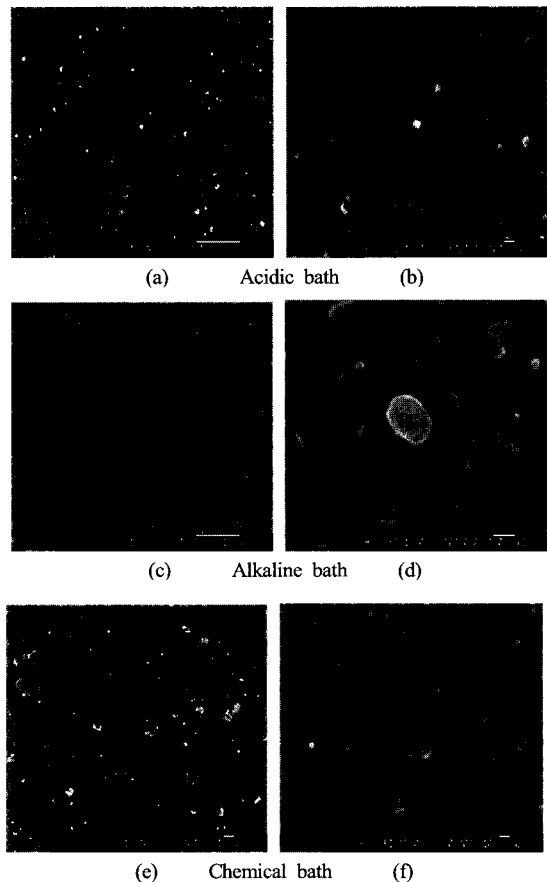


Fig. 2 (a-f) The SEM pictures of TiO₂ films at different magnifications: (a, b) acidic bath, (c, d) alkaline bath and (e, f) chemical bath

suggested that the visible absorption is attributed to the charge-transfer transition from Cl^- to $Ti(IV)^{25}$. The same phenomena will occur in present case as TiO_2 film is prepared from $TiCl_3$ solution.

Application of TiO_2 in photocatalysis is well known. Dye-sensitized photoelectrochemical cell systems based on highly porous nanocrystalline films of TiO_2 are of considerable interest because of their demonstrated highpower conversion efficiency (7-9%), potential low cost, and high

semiconductor stability. The most extensively studied system consists of a monolayer of a Ru-bipyridyl based charge transfer dye adsorbed onto the surface of a thin nanocrystalline TiO_2

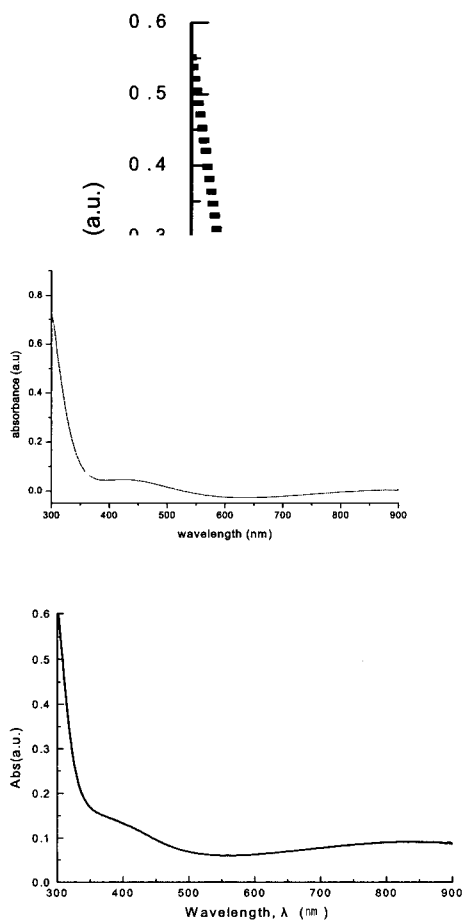
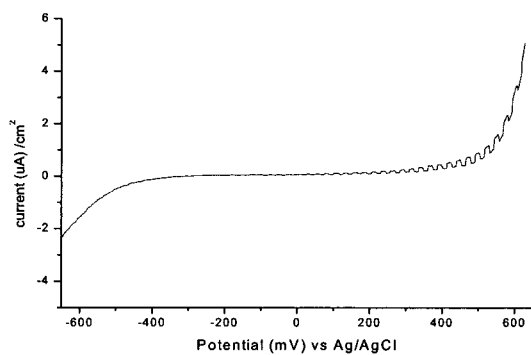
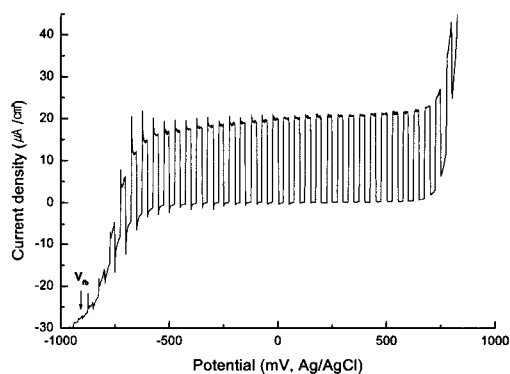


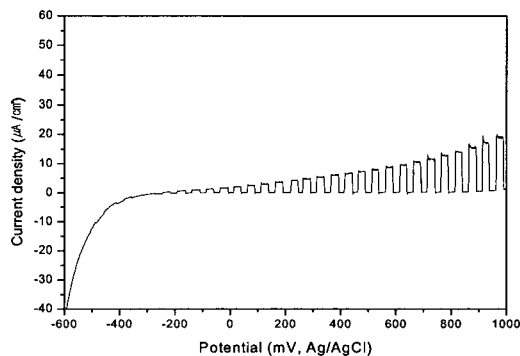
Fig. 3 (a-c) Optical absorption of TiO_2 films (a) acidic, (b) alkaline, and (c) chemical baths



(a) Acidic bath



(b) Alkaline bath



(c) Chemical bath

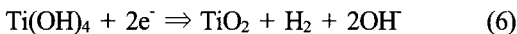
Fig. 4 (a-c) The I-V characteristics of $TiO_2/NaOH/Pt$ cell: (a) acidic, (b) alkaline, and (c) Chemical bath

thin film supported on ITO coated glass. The TiO₂ is stable in many electrolytes and TiO₂ based photoelectrochemical and photoelectrolysis cells in different electrolytes such as KOH, NaOH, KCl, Na₂SO₄-NaI, H₂SO₄, K₃FeCN₆, etc^{26~28} have been studied.

In the present investigation, we have studied I-V characteristic of TiO₂ thin film in 1 M NaOH electrolyte. Fig. 4 (a) shows I-V characteristic for TiO₂ film. The film exhibits photo activity in NaOH electrolyte with n-type behavior. The dark current is nearly equal to zero. The photocurrent obtained was of the order of microamp/cm². The low magnitude of photocurrent may be due to high band gap (> 3.2 eV) and nanocrystallinity (as evidenced by XRD study) of TiO₂ film. The flat band potential, "V_{fb}" was found to -900 mV, Ag/AgCl. Similar V_{fb} value has reported by earlier worker²⁸.

3.2 Electrodeposition of TiO₂ films Alkaline bath

Under normal deposition conditions, when concentration of Ti species is greater than 10⁻⁵M, the TiO₂ forms a stable insoluble phase which is in equilibrium with soluble Ti(OH)₄ phase^{20~21}. From such bath, containing Ti(OH)₄ and TiO₂ phases in equilibrium, the cathodic deposition of TiO₂ on substrate is possible as per the reaction



The addition of EDTA as a complexing agent was found to be advantageous as it stabilized deposition bath for days, without forming precipitation. The thick TiO₂ film (2.5 micron) was deposited from EDTA complexed bath. The deposition current density was varied in the range

of 0.5 to 25 mA/cm² to control film thickness. The pH range of 7~12 is allowed the control of film morphology and thickness.

The crystallinity of TiO₂ film was analysed using X-ray diffraction patterns. Fig. 1(b) shows a typical XRD pattern of TiO₂ film on ITO substrate. Practically, no difference was observed between XRD patterns corresponding to ITO coated glass and corresponding to the as-deposited TiO₂ film on ITO coated glass substrate, which indicates amorphous character of TiO₂ film. Deposition of amorphous TiO₂ film from acidic baths containing H₂O₂ as an oxidizing agent, has been reported by Zhitomirsky^{14~16} and Karuppuchamy et al²⁹. These films showed crystalline anatase phase after annealing above 723 K. However, in the present case, the TiO₂ film remained amorphous and compact after annealing at 723 K in air for 24 hrs.

Scanning electron micrographs of TiO₂ film on ITO coated glass substrate (Fig. 2 (c, d)) at two magnifications (20,000 × and 100,000 ×) were observed. A well covering, compact and non-porous TiO₂ coating surface was observed at the magnification of 20,000 ×. At high magnification, elongated grains of 100~200 nm sizes are well seen. However, careful observation of SEM picture finds each grain is made up with an aggregate of amorphous particles. Such morphology remained unchanged even after annealing above 723 K. Karuppuchamy et al²⁹ have reported open porous structure morphology for cathodically deposited TiO₂ film from acidic bath. The difference in deposition bath conditions might be responsible for this structural difference.

For the purpose of optical absorption study, TiO₂ film of small thickness was deposited. Fig. 3 (b) shows variation of optical absorption with wavelength for TiO₂ film. The optical absorption

spectrum of TiO₂ film on ITO coated glass showed sharp increase in absorption below 350-nanometer wavelength. The high optical absorption coefficient (104 cm⁻¹) indicates direct band gap transition. A tailing absorbance in visible region of 400 to 500 nm was observed.

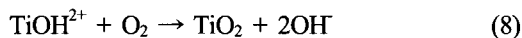
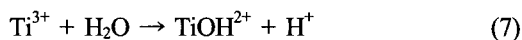
In the present investigation, we have studied I-V characteristic of TiO₂ thin film in 1 M NaOH electrolyte. Fig. 4 (b) shows I-V characteristic for TiO₂ film. The film exhibits photo activity in NaOH electrolyte with n-type behavior. The dark current is nearly equal to zero. The photocurrent obtained was of the order of microamp/cm². The low magnitude of photocurrent may be due to high band gap (> 3.2 eV) and amorphous structure (as evidenced by XRD studies) of TiO₂ film and series resistance offered by ITO substrate.

A distinct advantage in using the alkaline solution bath complexed with EDTA is to obtain amorphous, compact, pinhole free and adherent titanium oxide film. Because the bath contains soluble Ti(OH)₄ and insoluble TiO₂ phases in equilibrium, the concentration of Ti(OH)₄ remains same during deposition. This allows us to get reproducible results. Also as there is no reaction in the electrolyte due to EDTA complex, when current is not passing through the solution, the electrolyte solution can be used many times and many days. A coating of compact coating of TiO₂ is useful for arresting photo-decomposition of low band gap semiconductor and as a buffer layer in solid-state and dye-sensitive solar cells.

3.3 Chemical deposition of TiO₂ films

In the present case, TiO₂ films have been deposited on ITO coated glass substrate by slow hydrolysis of TiCl₃ solution. Rotzinger and

Gratzel²¹⁾ have reported on the kinetics of decomposition of TiCl₃ solution. Reaction of Ti(III) with O₂ is rate determining step in TiO₂ formation. The TiOH²⁺ is the only reactive species as per the reactions;



The reaction (1) should have rapid pre-equilibrium.

The pH of TiCl₃ was varied between 2-5 with addition of NaHCO₃ solution. It was found that with increasing pH, rate of hydrolysis was increased resulting into TiO₂ precipitate formation in bulk of solution without film formation on the substrates. The suitable pH range was found to be 3-3.5. The TiO₂ film formation started within about 30 mins and completed within 6 hrs at room temperature (296 K). The solution color changed from violet-blackish to whitish after six hrs and further dipping of substrate into bath resulted in to dissolution of deposited TiO₂ and ITO coating on the substrate in the solution. The TiO₂ film thickness was typically between 10 to 50 nm, depending upon solution pH and deposition time. The TiO₂ films were thin, specularly reflecting, and well adherent to the ITO coated glass substrate.

Film crystallinity was analysed using X-ray diffraction. Practically no difference was observed between XRD corresponding to ITO coated glass and corresponding to the as-deposited TiO₂ film on ITO coated glass substrate, which indicates very low crystallinity and amorphous characters. The TiO₂ films were heat treated at 623 K for 12 hrs. In Fig. 1 (c, d), spectra are shown corresponding to the heat-treated TiO₂ films on ITO coated glass at two

different thickness (10 and 50 nm). The similarity between them shows that amorphous character practically does not change. Only peak intensity of ITO material was reduced with thick TiO₂ film. Similar results have been reported for TiO₂ films deposited from microwave-activated solutions¹²⁾.

Scanning electron micrographs of TiO₂ film on ITO coated glass substrate at two different magnifications (5,000 × and 50,000 ×) are shown in Fig. 2 (e, f). At 5,000 × magnification, a well covering and rough TiO₂ film surface is seen. At high magnification, a TiO₂ film with porous structure is clearly visible, similar to those of other chemical methods such as sol-gel, spray pyrolysis, dip coating etc.

Optical absorption spectrum of TiO₂ film on ITO coated glass is shown in Fig. 3 (c). The TiO₂ film show sharp increase in absorption below 350 nm. A tailing absorbance in visible region of 400 to 500 nm was observed. A similar absorbance has been observed for the TiO₂ films obtained from electrodeposited TiO₂ films.

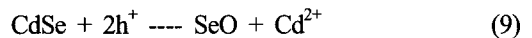
The photoactivity of TiO₂ thin film in electrolyte such as 1 M NaOH electrolyte was studied. Fig. 4 (c) shows I-V characteristics for TiO₂ film deposited on ITO coated glass substrate under chopped light condition. The film showed photoactivity with n-type behavior. The flatband potential, "V_{fb}" was found to be ~-500 mV, (Ag/AgCl).

TiO₂ thin films have been grown onto ITO coated glass substrates using room temperature chemical deposition method from TiCl₃ solution. The samples obtained are well adherent and amorphous. The following advantages have been found for the method described: it is simple, it uses low temperatures (less than 300 K), layers are grown in a relatively short time, thickness

control is possible through pH of solution and deposition time. The TiO₂ films are porous and exhibit photoactivity. These widen the technological uses of chemically deposited TiO₂ films.

3.4 Photoelectrochemical (PEC) studies of CdSe/TiO₂ films

CdSe film has been extensively used in photoelectrochemical (PEC) cells with different electrolytes. However, CdSe is not stable in aqueous electrolytes. In case of CdSe, the decomposition of CdSe is observed under illumination of PEC cell due to the location of valence band edge of CdSe below water oxidation level. The holes reaching to the surface of CdSe are not removed from the surface due to poor solution kinetics and hence decomposition of CdSe occurs as



On the other hand, n-type TiO₂, shows sufficient stability as not to decompose during photo-oxidation of water³⁰⁾. However, it has band gap greater than 3.0 eV so it utilizes only a small percentage of the solar spectrum, resulting in poor conversion efficiency. Many attempts have been made to improve the PEC conversion efficiency of TiO₂ by selective surface treatments such as surface chelation, surface derivatization, platinization and selective metal ion doping on the surface of n-TiO₂³¹⁾. Different types of composite coating films such as TiO₂/CdS, TiO₂/ITO, TiO₂-Al₂O₃, Cd₃P₂-TiO₂ etc have been studied for photocatalytic work and development of photoelectrochemical devices^{32~34)}. The nanostructured TiO₂ possess very high effective surface area and the incident

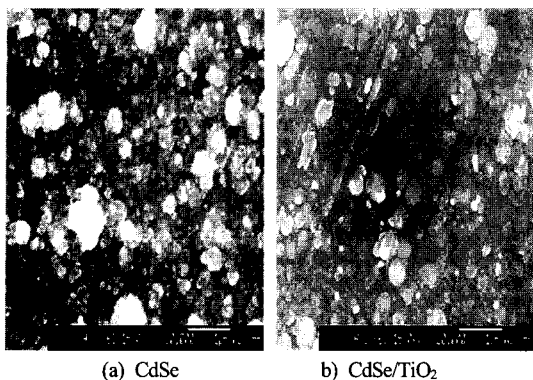


Fig. 5 (a, b) The SEM pictures of electrodeposited CdSe and CdSe/TiO₂ films

photon-to-current conversion efficiency is found to be in excess of 80 %.

In the present work, decomposition of CdSe film electrode in photoelectrochemical cell is avoided by depositing a compact and thin (20-50 nm) layer of nanocrystalline TiO₂ on CdSe. Electrodeposition of CdSe was carried out on ITO substrate. Over CdSe film surface, the TiO₂ film is deposited from acidic bath at + 0.1 V vs Ag/AgCl for 10 min. The SEMs of CdSe and CdSe/TiO₂ films are shown in Fig. 5 (a, b). There is no significant difference in morphologies of CdSe and CdSe/TiO₂ film surfaces. This indicates

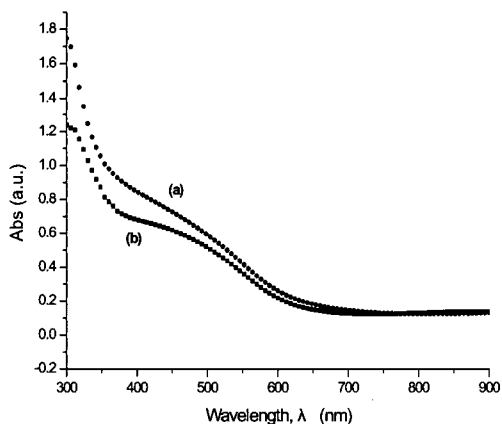


Fig. 6 (a, b) Optical absorption of electrodeposited (a) CdSe and (b) CdSe/TiO₂ films

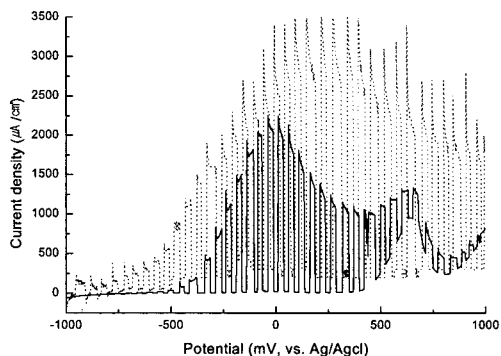


Fig. 7 The current voltage (I-V) characteristics of (a) {- solid line} CdSe, and {- dashed line} CdSe-TiO₂ based PEC cells

that TiO₂ film with 20-50 nm thickness covers the CdSe surface well, without altering original morphology of CdSe film.

The optical absorption of CdSe/TiO₂ spectrum shows increased absorption at all wavelengths in visible region compared to CdSe film; indicating TiO₂ film with uniform thickness can be coated on CdSe film surface (Fig. 6 (a, b)). Similar observation has been reported for TiO₂/CdS sandwich film prepared by electrodeposition and electrostatic interaction³⁵⁾ methods.

The photoelectrochemical cells were formed with CdSe and CdSe/TiO₂ electrodes for the study

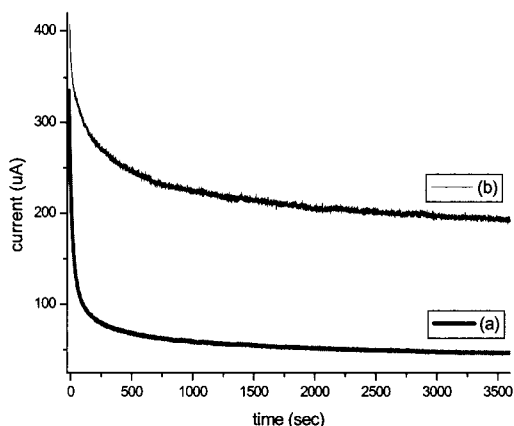


Fig. 8 Stability studies of electrodeposited (a) CdSe and (b) CdSe/TiO₂ based PEC cells

of PEC properties in 1 M NaOH electrolyte. The current-voltage (I-V) characteristic of CdSe electrode is shown in Fig. 7 (- solid line). The film exhibited photo activity in NaOH electrolyte with n-type behavior. Fig. 7 (-- dashed line) shows the I-V characteristic of CdSe/TiO₂ electrode. It shows that the photocurrent is improved significantly with CdSe/TiO₂ electrode. This improvement can be attributed to increased spectral absorption of CdSe/TiO₂ film during applied potential³⁵.

In order to use CdSe/TiO₂ electrode for PEC applications, a long-term stability of CdSe/TiO₂ electrode is warranted. In preliminary study, we have carried out a short-term stability test of CdSe/TiO₂ film. Fig. 8 (a, b) show the variation of short circuit photocurrents (I_{sc}) with time, for CdSe and CdSe/TiO₂ electrodes. The photocurrent stability was improved for CdSe/TiO₂ electrode³⁶.

4. Conclusions

산용액에서 전기증착 후 450도에서 열처리할 경우 아나타제 상의 TiO₂ 박막이 얻어지며 이 막은 표면밀도가 높아서 CdSe의 보호막으로 적당하였다. 알칼리 용액에서 전기증착을 할 경우 450도에서 열처리 후에도 무정형의 TiO₂로 존재하며 표면에 기공이 없기 때문에 보호막으로 적절하였다. 화학조 증착으로 얻어진 TiO₂ 박막은 20 nm 보다 작은 입자로 구성된 기공성의 막을 구성하여 보호막으로는 적절하지 않지만 표면적이 넓어서 다른 용도로 활용이 가능할 것으로 판단된다. CdSe에 TiO₂를 코팅할 경우 광흡수량이 증가하였으며 CdSe의 광전류도 증가하였고 수용액에서의 안정성도 증가하는 것을 관찰하였다. TiO₂막을 코팅했을 때 광흡수나 광전류가 증가하는 것은 CdSe에 코팅된 TiO₂가 빛의 반사특성에 영향을 주었기 때문으로 판단되며 수용액에서 CdSe가 물과 접촉하는 것을 방지하여 안정성을 증가

시킨 것으로 판단된다.

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