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# Structural analysis of $TiO_2$ and $TiO_2$-Ag thin films and their antibacterial behaviors

# Structural analysis of $TiO_2$ and $TiO_2$-Ag thin films and their antibacterial behaviors

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**Abstract.** $TiO_2$ (rutile and anatase) thin films was first prepared using reactive sputtering, in an Ar+$O_2$ plasma. In the 2nd stage of the experiment, various amounts (3, 7, and 10 at. %) of Ag was doped into the rutile film in order to form $TiO_2$-Ag thin films. These films were annealed for one hour in Ar atmosphere, at 300, 400, and 500 $^oC$. The films' structures were then examined using X-ray diffractometry. FESEM (field-emission scaning electron microscopy) was used to investigate the surface emergence of Ag particles. As for the examination of optical band gaps and absorption of these films, UV-Vis-NIR photometer was used. The results show that, in as-deposited condition, the addition of Ag might disrupt the growth of crystalline structure and cause the formation of amorphous films. After annealing, it is found that the structure tends to become anatase phase which is a metastable phase between amorphous titanium oxide and rutile. More importantly, the absorption of the Ag-doped films would be enhanced in the visible-light range. Some of the enhancement is clearly due to plasmon resonance effect. The Ag-doped samples have shown some antibacterial effect in dark. When irradiated with light, the samples show a synergistic behavior combining the bactericidal effect of Ag ions and photocatalytic effect of $TiO_2$.

## 1. Introduction

$TiO_2$ attracts many researchers due to its interesting properties that include chemical stability, good optical transparency, high refractive-index, etc. Moreover, $TiO_2$ by far is the most popular photocatalytic material. Therefore, it can be used as an optical coating [1] as well as a good photocatalyst [2]. Unfortunately, $TiO_2$, although is an inexpensive and stable photocatalyst, the wide band gap nature makes the material only works under UV light irradiation. Hence, the development of highly efficient $TiO_2$-based photocatalysts is still a much interesting topic.

$TiO_2$ thin films can be prepared using various techniques that include sol-gel method [3], chemical vapor deposition [4], and physical vapor deposition [5]. Although three polymorphous phases can exist, one can normally find rutile (band gap=3.0 eV) and/or anatase (band gap=3.2 eV) phases in a thin film state. Due to the difference in band gap, anatase $TiO_2$ requires an irradiation light with wave length shorter than 380 nm, in order to function, while rutile phase require a wave length shorter than 413 nm. However, while researchers are still debating which phase (or a mixed phase) can be a more efficient photocatalyst, many researchers agree that it is necessary to extends $TiO_2$'s absorption edge into visible light range. In order to make it work under visible light irradiation, many studies doped $TiO_2$ with N, C, F, and P elements or some transition metals. A thorough review in this regard can be found in Ref. [6]. Depending on the concentrations of various dopants, many studies show that the efficiency of the doped $TiO_2$ can be improved under visible light irradiation. Recently, more and more studies are focusing on embedding Ag nanoparticles into semiconductive oxide films. Ag is a nontoxic precious metal with remarkable catalytic activity [7, 8].

In addition, Ag particles may have promising size- and shape-dependent optical properties under visible light irradiation [9, 10].

In sum, adding Ag into an oxide-based photocatalyst may have many advantages, as described in the following:

1. The band gap may be narrowed [11].
2. Ag can be an efficient antibacterial material with or without light irradiation [12]
3. Ag doping may increase the absorption of visible light due to plasmonic effect [13]
4. Ag can serve as electron trapping sites (avoid recombination) due to Schottky barrier effect [14, 15]. It can also facilitate electron excitation by creating a local electric field.

The present study is aiming at preparing $TiO_2$ and Ag-doped $TiO_2$ thin films, and studying their structural changes as well as the variations of optical properties, before and after annealing, as functions of Ag doping and annealing temperature. The processing conditions for producing anatase and rutile films were first determined. Following this, $TiO_2$-Ag films were prepared and characterized. Finally, the antibacterial behavior is examined.

## 2. Experimental methods

$TiO_2$ thin films were first deposited on fused quartz glass substrates by reactive DC magnetron sputtering of a metallic Ti target. The target had a diameter of 50 mm and was tilted by 30$^o$ to the substrate holder. The distance of target-to-substrate was 100 mm. For deposition, the sputtering system was first pumped down to $7x10^{-4}$ Pa and then Ar gas (35 sccm) was introduced to fill the chamber up to 0.65 Pa. The substrates were ultrasonically cleaned in acetone (5 min) and isopropanol (5 min), then, blown dry. Prior to film deposition, the target was sputter-cleaned in Ar plasma at a pressure of 0.65 Pa for 10 min, with shutter closed. At the same time, the substrates were cleaned in Ar plasma for 10 min. by applying a bias of 100 W (RF).

The deposition time was around 30 min, while the film thickness was controlled nearby 500 nm. Film thickness was determined by a surface profiler (Kosaka Surfcoder). After the processing conditions for producing anatase and rutile $TiO_2$ films were determined, $TiO_2$–Ag thin films were prepared using reactive co-sputtering with Ti and Ag targets. In this case, the contents of Ag was controlled around 3, 7, and 10 at.% in the $TiO_2$-Ag films. Following the deposition, Some of the deposited films were then annealed for one hour at 300, 400, and 500 $^o$C using a rapid thermal annealing (RTA) system (SJ, ARTS-150) in an argon atmosphere, with ramping rate set at 100 $^o$C/sec.

The phases of the deposited films, before and after annealing, were examined by X-ray diffractometry (XRD). For the optical properties, the film's absoption (Absorption= 100%-Transmission-Reflection) was measured by a UV-VIS-NIR double beam spectrophotometer (JASCO-V750). For the investigation of the surface emergence of Ag particles, the films were examined using field-emission scanning electron microscopy (JEOL 6700F).

For the antibacterial testing, the coated and uncoated samples were cut and placed on a tray and then incubated with a calibrated bacterial suspension of E. coli. The samples were then incubated at 37 $^o$C for various times up to 24 hours. After incubation, the antibacterial property could be evaluated according to the value of Antibacterial Efficiency (E) which was calculated according the following equation:

$$E\ (\%) = [(A-B)/A] \times 100\% \qquad (1)$$

where A=number of viable bacteria with uncoated (standard) sample in the tray; B=number of viable bacteria with coated sample in the tray.

## 3. Results and discussions

### *3.1 Structural analysis*

Figure 1 shows the X-ray diffraction patterns of as-deposited samples. It is found that the rutile pattern is slowly destructed and replaced by Ag pattern when the amount of Ag is increased from 3 at.% to 10 at.%. Apparently, the doping of Ag during deposition would disrupt the growth of crystalline rutile structure. This is known as the second element effect [16]. Figures 2 show the

comparison of X-ray diffraction patterns of $TiO_2$-10%Ag with and without annealing, as functions of annealing temperature and Ag contents. It is observed that the addition of Ag can enhance the formation of anatase phase after annealing. This can be explained as the following: The incorporation of Ag first disrupt the structure of rutile and cause the formation of amorphous state, as observed in Figure 1. During annealing, the metastable anatase phse can nucleate easier than rutile phase. This has become more obvious when the contents of Ag reach 7 at.% and higher. When the starting phase is an anatase phase, the observed result is similar to that of the rutile phase. The annealed $TiO_2$ phase tends to become anatase if Ag is doped into the films.

Figure 3 shows the surface SEM micrographs of the sample with 7at.% Ag, and was annealed at 400 $^oC$. The emergence of Ag particles on films' surface is observed on all the Ag-doped samples.

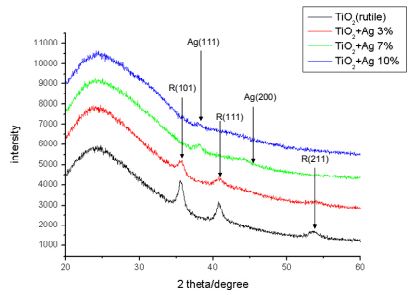


**Figure 1.** X-ray diffraction patterns of $TiO_2$(rutile) and $TiO_2$-Ag thin films in as-deposited states.

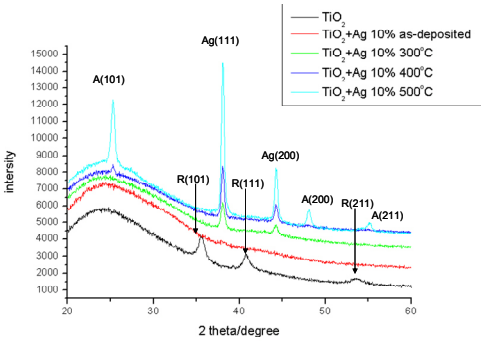


**Figure 2.** X-ray diffraction patterns of $TiO_2$-Ag (10 at.%) with and without annealing (Annealing temperature: 300$^oC$, 400$^oC$ and 500$^oC$)

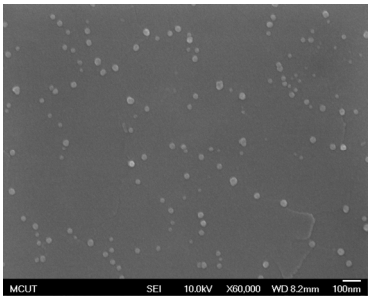


**Figure 3.** Surface SEM micrograph of the sample with 7at.% Ag, after being annealed at 400 $^oC$.

*3.2 Optical properties*

Figure 4 shows the absorption spectra for all the as-deposited films. It is found that the sample with 7 at.% Ag has a strong and wide absorption peak between 400-550 nm. This is known due to plasmon resonance absorption. Awazu et al. [13] recently proposed a new term based on plasmon-enhanced photocatalytic effect. The new term was named "plasmonic photocatalysis". The idea of plasmonic photocatalysis utilizes the assistance of plasmon resonance that is known to enhance light absorption. For anatase $TiO_2$ phase to be activated, a UV irradiation with wavelength shorter than 380 nm is required to generate electron-hole pairs. In the case of Ag-doped $TiO_2$, the embedded Ag nano-particles could show a very intense absorption band within 400-500 nm due to the influence of plasmon resonance [17]. This is associated with a considerable enhancement of the electric near-field in the vicinity of the Ag nanoparticles. It is thought that this near-field enhancement could boost the excitation of electron-hole pairs in $TiO_2$ and therefore increase the efficiency of the photocatalysts. Similar related ideas were already outlined in the past [18, 19]. It is known that the resonance

wavelength depends on the size and shape of the Ag nano-particles, as well as the particle-forming material. Therefore, the extended absorption peak is not observed on some other samples. Figure 5 shows the absorption spectra for the annealed $TiO_2$-10%Ag with the variation of annealing temperature. For most of the samples, the plasmon effect is still obvious. For the samples with 10 at.% Ag, high annealing temperature (i.e. 500 $^oC$) can cause a full range absorption. This could be due to the formation of large Ag metal particles. From the calculation using Tauc formula, $(\alpha E)^{1/2}=(E-E_g)$, and Lambert-Beer law, it is found that the addition of Ag into $TiO_2$ could decrease the value of band gap form 3.2 to 2.9 eV, at maximum.

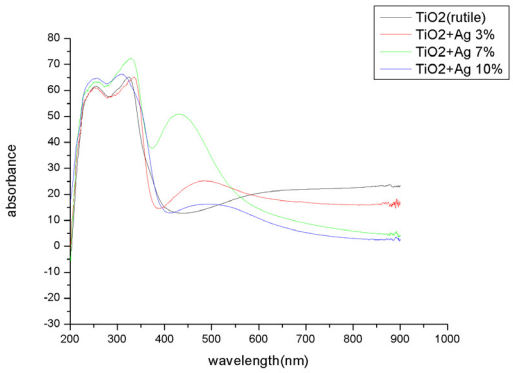


**Figure 4.** The absorption spectra of $TiO_2$ (rutile) and $TiO_2$-Ag thin films in as-deposited state.

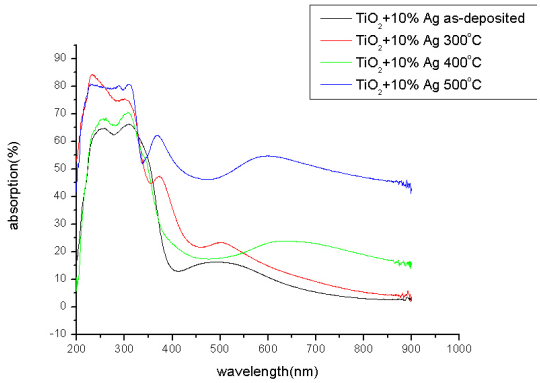


**Figure 5.** The absorption spectra of $TiO_2$-Ag (10 at.%) with and without annealing (Annealing temperature: 300$^o$C, 400$^o$C and 500$^o$C)

Figure 6 shows the antibacterial efficiency of $TiO_2$ and $TiO_2$-Ag thin films tested in dark. It is obvious that the surfaced Ag can dissolve and cause the damage of E.coli. Figure 7 shows the same group of samples tested under the irradiation of visible light with peak intensity at 500 nm. According to the results, it can be observed that a synergistic effect combining Ag and photocatalytic characteristics of $TiO_2$ is observed. Clearly, the doped Ag can help extending the effective light absorption of $TiO_2$.

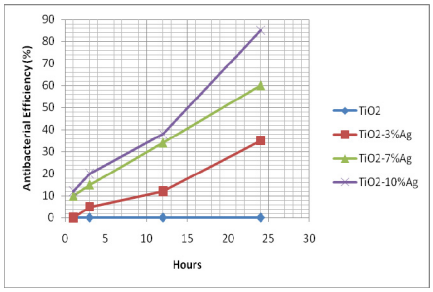


**Figure 6**. Antibacterial effecncy of $TiO_2$ and $TiO_2$-Ag thin films after being annealed at 500 $^o$C for one hour. (Tested in dark)

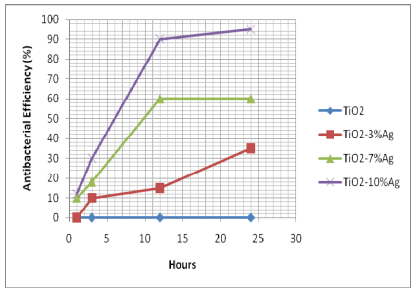


**Figure 7.** Antibacterial effecncy of $TiO_2$ and $TiO_2$-Ag thin films after being annealed at 500 $^o$C for one hour. (Tested in visible light)

## 4. Conclusions

$TiO_2$ (rutile and anatase) and $TiO_2$-Ag thin films were prepared by reactive co-sputtering processes. The structure and optical properties were examined and analyzed as functions of annealing

temperature and Ag contents. The results show that, in an as-deposited condition, the addition of Ag might disrupt the growth of crystalline structure and cause the formation of amorphous films. After annealing, it is found that the structure tends to become anatase phase, particularly when the Ag content is increased. This is due to that anatase phase is considered to be a metastable phase between amorphous state and rutile structure. More importantly, the absorption of the Ag-doped films would be enhanced in the visible-light range. Some of the enhancement is clearly due to plasmon resonance effect. This makes plasmonic photocatalysis possible. The Ag-doped samples have shown some antibacterial effect in dark. When irradiated with light, the samples show a synergistic behavior combining the effect of Ag ions and photocatalytic effect of $TiO_2$.

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