

Deposition and Photocatalytic Activity of Ag:V₂O₅ Thin Films

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ABSTRACT

In this work, the deposition and photocatalytic response of V₂O₅ thin films modified with different amounts of Ag (Ag:V₂O₅) is reported. Films were deposited on glass and silicon substrates (100), using the pulsed laser deposition (PLD) technique. A high purity vanadium target, with a different number of silver pellets attached on it were used. Thin films were characterized by energy dispersive spectroscopy (EDS) to determine the elemental chemical composition; structural changes due to the addition of Ag were monitored by Raman spectroscopy; Optical microscopy was used to observe the surface morphology and UV-Vis spectroscopy was employed to determine optical properties. Photocatalytic response of the prepared films was studied through the degradation of a malachite green solution using a solar irradiation source.

INTRODUCTION

There have been various approaches of wastewater treatment for the removal of organic pollutants, such as pesticides, dyes or organic compounds present in the aqueous phase [1]. The most widely studied are based on the use of semiconductors as photocatalyst materials. The photocatalytic process is currently recognized as an efficient method to carry out the oxidation of organic matter to a high degree of mineralization using solar light. However, the applications of most of semiconductors for this purpose have been limited by their relatively high band gap which requires UV light for their activation and in some cases their low quantum yield due to a higher recombination rate [2]. Therefore, the study of modification of semiconductors with metals has been an important strategy towards the improvement of their photocatalytic response. In general terms, the incorporation of metals into a semiconductor can result in doping, coupling of semiconductors and formation of ternary materials depending on the metal load. In particular, for photocatalytic applications using solar light it is crucial the narrowing of the band gap in order to extend their absorption to longer wavelengths [3]. Much work is still necessary in order to control the amount of the modifying element because the properties of the obtained materials depend strongly on the metal concentration incorporated into the semiconductor. Therefore, a lot

of work has been devoted in the last years to investigate deposition techniques capable to prepare semiconductor films modified with metals with controlled composition.

From a chemical point of view, V_2O_5 is an excellent catalyst because of its rich and diverse chemical configuration that is based on two factors: the variety of vanadium oxidation states, ranging from 2^+ to 5^+ and the variability of the oxygen coordination geometries. This structural diversity allows the existence of a wide variety of different coordination with oxygen ions that provide an important control of the physical and chemical surface properties [4].

In the last few years, laser ablation has been extensively used to produce a wide variety of materials in thin film form due to its advantages over other deposition techniques due to the intrinsic characteristics of the laser ablation plasma, i. e. species with high kinetic energy and high plasma density [5]. Additionally, the versatility of this technique has allowed the implementation of different variants in order to improve some characteristics of the deposits [6, 7]. In this work it is reported the preparation of V_2O_5 modified with different amounts of silver in which the alternant sequential ablation of two different targets in vacuum is performed in order to control the silver content in the film.

EXPERIMENTAL

Thin films were deposited by alternating the ablation of a vanadium and a silver targets sequentially. For this purpose a composed target in which the ratio of the ablation areas of both targets was varied. The target was prepared by attaching silver disks (4.5 mm diameter, 2 mm thick) onto the surface of a high purity vanadium target (25.4 mm diameter, 2 mm thick); by changing the number of Ag disks allows to vary the amount of Ag atoms arriving to the substrate. The V and Ag plasmas were produced by laser ablation using a Nd:YAG laser with emission at the fundamental line (1064 nm) and 5ns pulse duration. The films were deposited at base pressure close to 2×10^{-4} Torr on glass and Si (100) substrates located 5 cm away in front of the targets. The laser fluence on both targets was kept constant at 18 J/cm^2 while the deposition time was 60 min. Therefore, during the experiments the vanadium and the silver plasmas are produced in an alternated way and combined on the substrate depositing the Ag: V_2O_5 film.

Elemental chemical composition of the thin films was determined by Energy dispersive X-ray spectroscopy (EDS) using an Oxford EDX probe coupled to a JEOL JSM 6510LV microscope. Raman spectroscopy was used to study the microstructural features of the films. The Raman spectra were acquired using an HR LabRam 800 system equipped with an Olympus BX40 confocal microscope. A Nd:YAG laser beam (532 nm) was focused by a 100x objective onto the sample surface ($\approx 1 \mu\text{m}$ diameter spot). All spectra were calibrated using the 521 cm^{-1} line of a silicon wafer. Optical properties were measured using UV-Vis spectroscopy on a Perkin Elmer lambda 35 spectrophotometer. Optical images of the film surface were obtained using the optical microscope of the Raman system. Photocatalytic activity of the Ag: V_2O_5 thin films (1 x 1 cm) was evaluated by using 25 ml of a $10 \mu\text{mol/l}$ of malachite green dye (MG) solution. The reaction system was irradiated using a solar simulator at power levels of 30 mW/cm^2 under continuous stirring. Degradation was followed by the decrease in the characteristic absorption band of the MG peaking at 619 nm taking an aliquot each 15 minutes of reaction time.

DISCUSSION

Compositional characterization

Figure 1 shows the Ag content in the films as a function of the silver/vanadium ablated areas. It is clearly observed that as the ablated area of the silver target is increased, the Ag content increases from 0.7 to 9.0 at. %, suggesting that the silver content in the prepared thin films was varied in a controlled way. This behavior seems reasonable, because a higher ablated area of the Ag target corresponds to a higher ablation rate and consequently more Ag species arriving to the substrate available to be incorporated into the growing film.

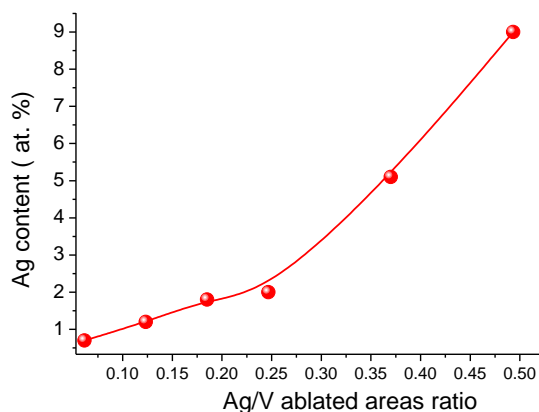


Figure 1. Silver content as a function of the silver/vanadium ablated areas

Raman characterization

The Raman spectra of films with Ag content lower than 1.6 at. % show peaks at 144, 194, 284, 303, 404, 484, 702 and 994 cm^{-1} as is shown in figure 2. These Raman features are characteristic of V_2O_5 [8]. As the content of Ag was increased in the films, new features appears at 218, 300, 380, 429 and 487 cm^{-1} which correspond to AgO. It is noticed that at the highest Ag content in the film the corresponding Raman spectrum show peaks at 234, 432, 489, 560, 943 and 963 attributed to the formation of AgO_2 [9]. The Raman results suggest that as the Ag is incorporated into the deposited material, a mixture of vanadium oxide (V_2O_5) and silver oxides (AgO and AgO_2) compose the film.

Optical microscopy

The optical images of the films surface deposited with different Ag contents are shown in figure 3. It is observed that the film surface became covered with a large number of quasi spherical particles as the silver content was increased. The film deposited without Ag showed a very smooth surface without particles. The number of these particles increases with increasing the amount of silver in the film and could be attributed to coalescence of Ag species. EDS measurements showed that such particles are composed of silver suggesting the formation of Ag nanoparticles.

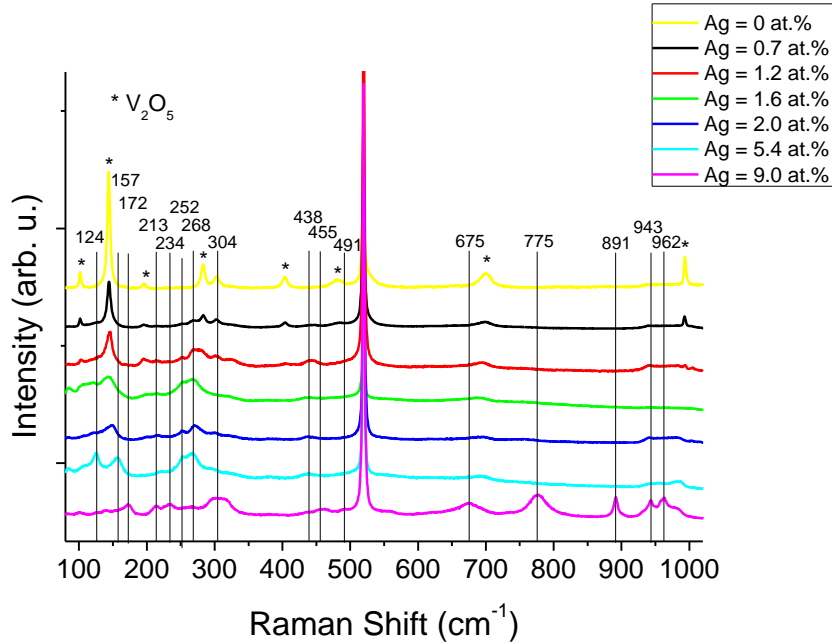


Figure 2. Raman spectra of films with different silver atomic content.

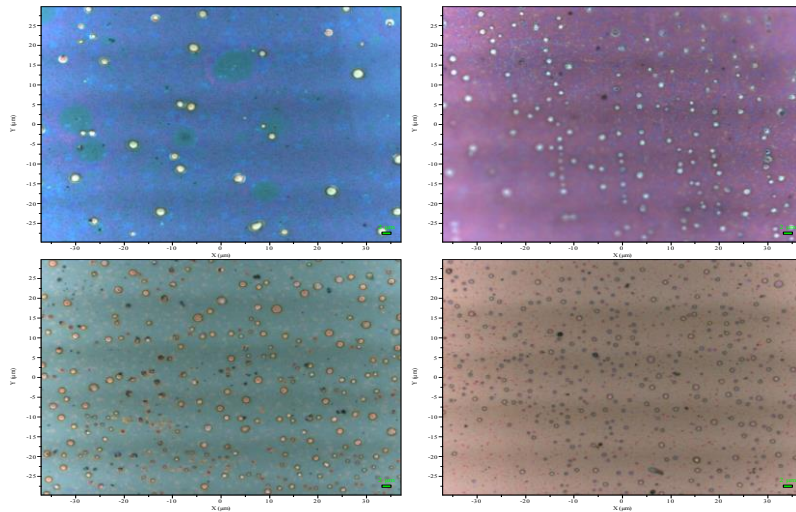


Figure 3. Optical images of thin films at different silver content

UV-Vis spectroscopy

The optical absorption spectra, in the reflectance mode, of the prepared films as a function of the silver content are shown in figure 4. An absorption band around 600 nm is observed, characteristic of nanometer sized silver particles surface plasmon [10]. It is observed a blue shift of the maximum as the silver content increases indicating a reduction in the particle size. This is in good agreement with the previous results in which is observed the formation of smaller Ag particles as the silver content increases. The presence of a single band suggests that the nanoparticles are spherical in shape.

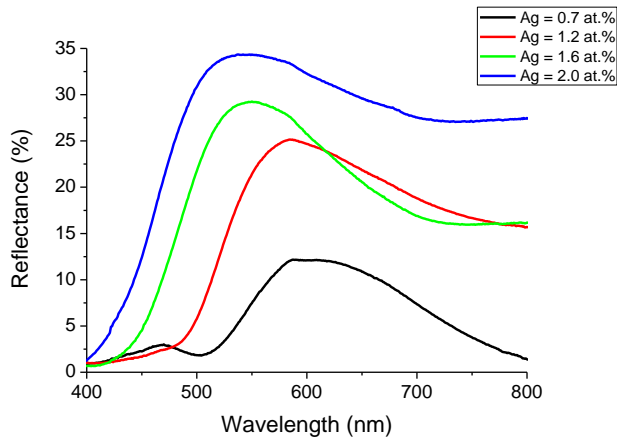


Figure 4. UV-Vis spectra of the thin films with different atomic contents of silver.

Photocatalytic characterization

Figure 5 shows the degree of degradation of the malachite green dye as a function of the reaction time. The catalyst were activated using visible light from a solar simulator. It is observed that the sample without silver degrades approximately 25% of the MG solution whereas the films containing silver exhibit a better photocatalytic activity than the V_2O_5 . Silver addition to the catalytic formulation until 1.6 at % shows the best degradation degree, reaching 60% in 180 minutes of time reaction, almost 240% higher than the catalysts without Ag; this behavior could be explained in terms of the optical coupling of the semiconductors present in the films, because the material is composed by a mixture of vanadium oxide and silver oxides; particularly, at 1.6 at. % of silver content, the film consist of a mixture of V_2O_5 and AgO which result in a synergistic effect on the catalytic activity; the formation of Ag_2O at higher Ag contents has a detrimental effect on the photocatalytic response. It is worth noting that additional peaks were not observed in the UV-Vis spectra, suggesting that there are not intermediary's organic compounds and indicative of the complete mineralization of the malachite green dye.

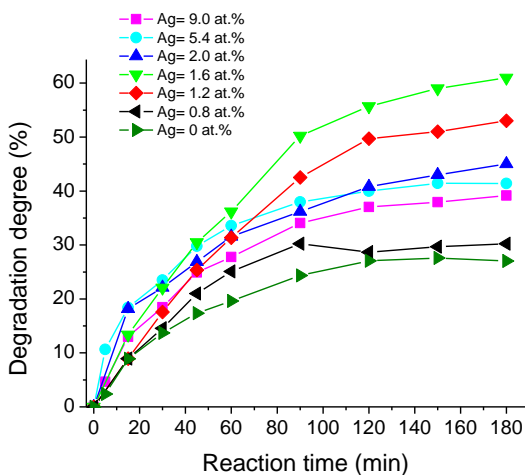


Figure 5. Degradation degree of a solution of MG dye using Ag: V_2O_5 catalysts under solar irradiation

CONCLUSIONS

A deposition configuration using multiple targets was successfully employed to prepare Ag:V₂O₅ thin films with different contents of silver. Depending on the Ag load incorporated in the film a mixture of vanadium oxide (V₂O₅) and silver oxides (AgO and Ag₂O) compose the film. There is no evidence of the formation of silver vanadates even at the highest Ag content. Additionally, as more silver is incorporated in the film a greater number of Ag nanoparticles is formed on the film surface. Thin films containing silver exhibit a better photocatalytic performance than V₂O₅ films. This result could be attributed to the optical coupling of the semiconductors present in the prepared thin films.

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