Journal of Physics: Conference Series **764** (2016) 012019 doi:10.1088/1742-6596/764/1/012019

Characterization of nanostructured TiO_2:Ag films: structural and optical properties

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Abstract.TiO_2:Ag nanocomposites have been prepared by sol-gel method with varying silver concentration. Different technological approaches are employed to study the formation of Ag nanoparticles in titanium dioxide matrix. The obtained thin films are either thermally treated at temperatures from 300 to 600°C or UV irradiated for 15 minutes between layer deposition**.** XRD and FTIR studies reveal that Ag is incorporated in TiO_2 films as nanoparticles and no Ag oxide phases are detected. Optical characterization performed by UV-VIS spectroscopy confirms the formation of silver nanoparticles. The influence of thermal treatment and UV radiation on the optical and structural properties is studied.

1. Introduction

Titanium oxide is one of the most widely studied metal oxide semiconductors for various applications due to its interesting chemical, electrical and optical properties, chemical stability, non toxicity, high transparency and high refractive index, cheapness and commercial availability, antibacterial and hydrophilic ability [1]. TiO_2 has many uses such as solar energy conversion, photocatalyst, photoelectrochemical splitting of water, purification and treatment of polluted water and air and can be found in multitude of applications: gas sensors, photochromic, electrochromic and optoelectronics devices, ceramics [2]. Titanium oxide can exist in different titania polymorphs such as rutile, anatase and brookite. These three polymorphs are structurally similar: the Ti atom is octahedrally coordinated, but differs in the way the TiO_6 octahedra are linked within anatase, rutile and brookite. The anatase tetragonal crystal structure is made of distorted TiO_6 octahedral sites sharing four corners. The brookite (orthorhombic, the structure with the lowest symmetry among the polymorphs) is also made of distorted octahedral sites elongated along the c-axis, and each octahedron shares three edges with adjacent octahedra. The rutile structure (tetragonal, thermodynamically stable phase) is made of chains of TiO_6 octahedra that share a vertex along the c-axis. The anatase transforms into rutile upon heating, exothermally and irreversibly over a certain range of temperatures [3]. The brookite phase is the rarest of the TiO_2 polymorphs. Anatase TiO_2 has a band gap of 3.2 eV (385 nm), while the rutile phase has a smaller band gap of 3.0 eV (410 nm) [4].

Ag presents numerous interesting properties, such as high catalityc efficiency, low cost compared to other noble metals, and high oxygen adsorption reactivity. TiO_2 thin films doped with Ag have

shown many interesting characteristics. Moreover, Ag metallic ion is known as a high mobility cation, which has been used in resistive switching devices [5]. In this sense, TiO_2 thin films doped with Ag NPs are attractive material for applications in sensors, photocatalysis, as plasmonic colors, hot spots, thermal phototherapy, plasmon assisted solar energy conversion, information storage devices, displays, smart windows and switches. Silver nanoparticles embedded in dielectric films exhibit optical responses arising from the excitation of surface plasmons in the metal nanoparticles (NPs) that induces optical absorption. The frequency and shape of the surface plasmon resonance (SPR) depends on the size, shape and volume fraction of Ag NPs.

In this work, TiO_2:Ag nanocomposites are prepared by sol-gel method with varying silver concentration. Different technological approaches are employed to study the formation of Ag nanoparticles in titania matrix. The obtained thin films are either thermally treated at temperatures from 300 to 600°C or UV irradiated for 15 minutes.

2. Experimental

The details of sol solution preparation for TiO_2 have been previously reported [6]. It must be noted that the sol solution is proven to be stable more than 2 years, maintaining its excellent film forming properties. The Ag precursor used was silver nitrate as it was added 0.1, 0.5 and 1% wt $AgNO_3$ in titanium sol solution. The thin films were deposited by spin-coating procedure at 8000 rpm. For the first group of samples, the spin coated procedure was followed by low temperature firing (150°C/30 min) and repeating the layer deposition 5 times in order to increase the film thickness. For the second group, UV treatment for 15 min. was applied between layers. The TiO_2 and TiO_2:Ag films have been thermally treated at 300, 400, 500 and 600°C in oxygen for 1 hour. The film thickness was in the range of 240 to 200 nm depending on the annealing temperatures. The substrates used were Si wafers and quartz. XRD spectra of the films were recorded by means of XRD diffractometer Bruker D8, at the grazing angle 2°, step time of 8 s and step of 0.1°. FTIR measurements were performed in the spectral region 350-1200 cm^{-1} by Shimadzu FTIR Spectrophotometer IRPrestige-21. Optical measurements were performed using UV-3600 Shimadzu spectrophotometer.

3. Results and discussions

Figure 1 present XRD spectra of TiO_2:Ag films, obtained by sol B (0.5 wt% Ag precursor) annealed at temperatures from 300 to 600°C. The lowest annealing temperature results in amorphous film structure and increasing the annealing temperature induces crystallization.

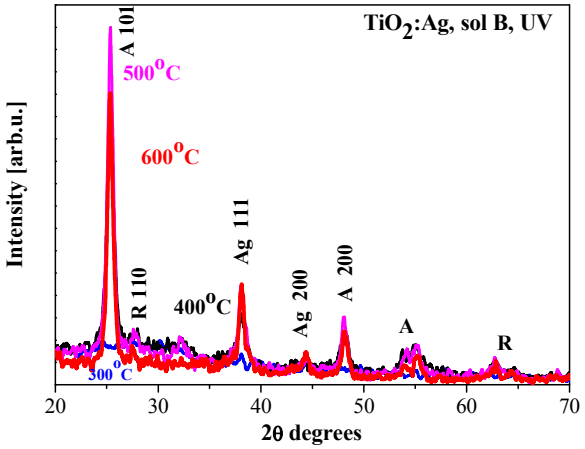

Figure 1. XRD spectra of sol-gel TiO_2:Ag films, obtained by sol B (0.5 wt% Ag precursor) annealed at temperatures from 300 to 600°C. The marks A and R denote anatase and rutile phase, respectively.

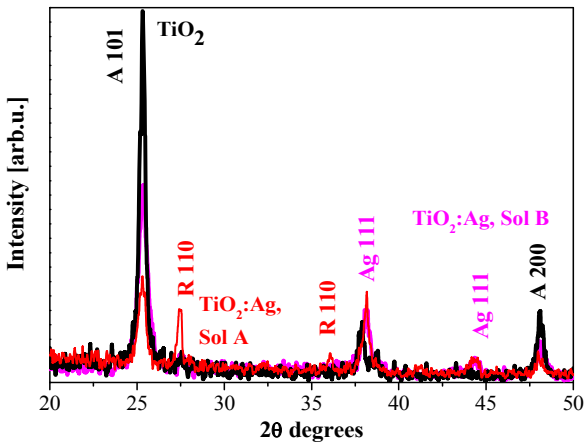

Figure 2. Comparison of XRD spectra of pure TiO_2 and TiO_2:Ag films, obtained by sol A (1 wt% $AgNO_3$) and sol B (0.5 wt% $AgNO_3$). The TiO_2:Ag films were UV treated between layers. The samples are finally annealed at 600°C.

The two crystal phases – anatase (PDF card №00-004-0477), and rutile (JCPDS №21-1276) are clearly presented in the XRD spectra of 400 to 600°C annealed films. The previous study of sol-gel undoped TiO_2 [6] films showed that the rutile phase begins to form after high temperature annealing (at and above 800°C). The spectra manifest a diffraction reflection due to presence of Ag (cubic structure, PDF card №00-004-0783), indicative that silver is incorporated in the film structure as metallic nanoparticles. For annealed at 600°C film, two strong lines Ag 111 and Ag 200 attributed to metallic Ag are detected. Similar results had been previously reported for XRD study of thermally treated TiO_2:Ag films, obtained by sol A (1 wt% Ag precursor) [7]. Figure 2 shows the comparison of XRD spectra of TiO_2:Ag films with different silver incorporation. It is clearly seen that higher Ag content results in better crystallinity with stronger lines related to rutile TiO_2 and metallic cubic Ag. The spectrum of undoped TiO_2 film reveals that the film is fully crystallized in anatase phase (see figure 2, black line).

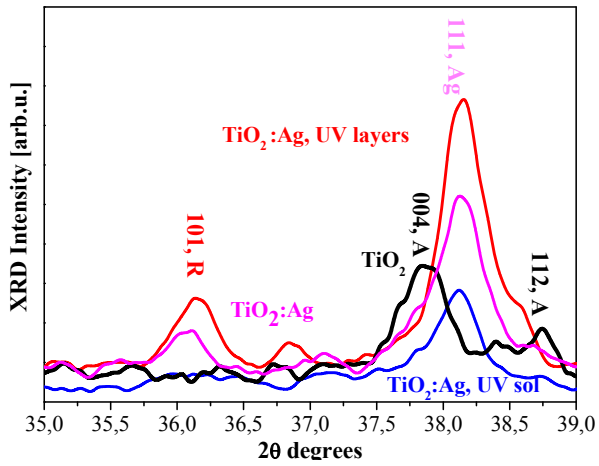

Figure 3. XRD spectra of sol-gel TiO_2 and TiO_2:Ag films. TiO_2:Ag films are obtained by sol A (1 wt% Ag precursor) in three types: thermal treatment (150°C/10 min) between layers, UV treatment of sol before film deposition and UV treatment between layers. The samples are finally annealed at 600°C.

Figure 3 shows XRD spectra of undoped TiO_2 and TiO_2:Ag films, obtained by sol A (1 wt% Ag precursor), undergone three different treatments: thermal treatment (150°C/10 min) between layers, UV treatment of sol before the film deposition and UV treatment between layers. All the samples are finally annealed at 600°C. The films with incorporated Ag nanoparticles present a fraction of rutile titania and metallic silver. The UV treatment of films leads to strongest XRD lines of silver. The crystallite sizes have been determined for the existing crystal phases in film structure (see table 1). It is very interesting that the biggest Ag crystallites are found out for TiO_2:Ag from sol A, treated at 600°C. For UV treated films, it is determined that silver nanoparticles grew bigger, when the sol has been preliminary UV radiated. The crystallite sizes for anatase and rutile phase are also determined.

Table 1. Estimated crystallite sizes of TiO_2:Ag films.

	TiO_2	TiO_2:Ag sol A, thermally treated films	TiO_2:Ag sol B, thermally treated films	TiO_2:Ag sol A, UV treated films	TiO_2:Ag sol A, UV treated sol
Anatase	12.4 nm	10.9 nm	17.7 nm	8.2 nm	12.1 nm
Rutile		18.4 nm	8.8 nm	25.1	15.4 nm
Ag		80.2 nm	8.3 nm	19.7 nm	25.0 nm

XRD analysis reveals diffraction features characteristic for metallic state of silver with no Ag-O phases detected. Another conclusion is that Ag NPs induce anatase-rutile phase transformation at lower annealing temperatures than it appeares for undoped TiO_2 films. UV treatment results in better

expressed rutile phase compared to only thermally treated films. The lower Ag concentrations the smaller Ag NPs crystallites are grown.

FTIR study has been performed in details for thermally and UV treated films, but there is presented only the spectra of sol-gel TiO_2:Ag films, obtained by sol A and sol B. The Ag doped films have been either annealed at 150°C or UV treated between layers. The samples are finally annealed at 600°C (see figure 4). The weak IR band at 1058 cm^{-1} is assigned to Si-O bonding (due to Si substrate).

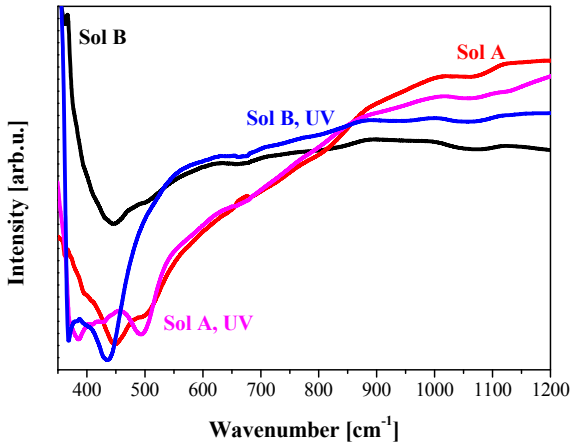

Figure 4. FTIR spectra of sol-gel TiO_2:Ag films, obtained by sol A (1 wt% Ag precursor) and sol B (0.5wt% Ag precursor). The Ag doped films have been either annealed at 150°C or UV treated between layers. The samples are finally annealed at 600°C.

A weak band at 668 cm^{-1} can be observed in all spectra, which some authors assigned to integrated anatase and rutile structure [8]. The FTIR spectra of thermally treated films show a broad and strong absorption band near to 445 cm^{-1} and a weak band at 504 cm^{-1}. UV treatmeant results in splitting of the strong band in two separate lines at 385 and 430 cm^{-1} (UV, Sol A) and at 370 and 435 cm^{-1} (UV, Sol B). Similar behaviour was previuosly detected [9] and it is caused by the formation of rutile fraction. The bands located in the range 430 -435 cm^{-1} are attributed to Ti-O bonds of crystalline anatase titania, on the other hand the 445 cm^{-1} is assigned to rutile phase. The band at 385 cm^{-1} is also referred to rutile phase. No lines, assigned to Ag-O bonds are detected.

FTIR analysis reveals that the silver incorporation reflects on shapes and intensity of absorption bands with no traces of Ag-O bonds. Characteristic absorption bands assigned to rutile titanium dioxide are observed for samples annealed at 600°C and for TiO_2:Ag films after UV radiation. The structure of films consists of mixture of antase and rutile phase and UV treatment leads to well prounnced absorption bands due to rutile TiO_2 in comparison with thermally treated films. FTIR investigation confirms the conclusions derived from XRD analysis that no Ag-O bonding is observed and the silver incorporation induces anatase-rutile transformation.

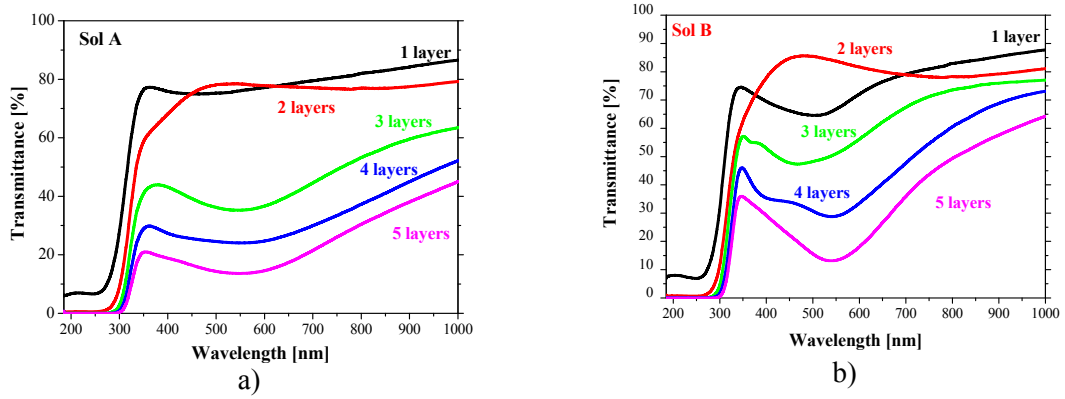

Figure 5. Transmittance spectra of sol-gel TiO_2:Ag films from sol A (1 wt% Ag precursor) and sol B (0.5 wt% $AgNO_3$) (b) depending on number of layers and UV radiated for 15 minutes between layers.

For optical characterization, the thin films were deposited on quartz substrates. Optical properties of nanocomposite layers of TiO_2:Ag films are studied by transmittance measurements as a function of number of layers, silver concentrations, thermal and UV treatment.

Figure 5 shows the transmittance spectra of sol-gel UV treated TiO_2:Ag films from sol A (1 wt% Ag precursor) and sol B (0.5 wt% $AgNO_3$) with varying number of layers. As can be observed the treansparency is decreased with increasing the layers and the shape of the absorption bands is changed. The samples from sol A manifest very broad bands in the spectral range of 510-550 nm, which can be due to the plasmonic features induced by larger Ag nanoparticles or/and overlapping of higher order plasmon modes [10]. It is very interesting to observe that better expressed surface plasmon resonance (SPR) bands are observed for UV treated TiO_2:Ag films from sol B, the lower silver concentration. The one layered film possesses a strong band at 506 nm. For three layered film the plasmonic bands are located at 363 and 470 nm, where the 363 nm feature can be related to the quasispherical Ag nanoparticles or Ag oligomers with different sizes [11] and the other band is also connected with SPR of near spherical size Ag NPs. The four layered film manifest two absorptions at 400 and at 540 nm and the thickest film has a very deep feature at 540 nm. The SPR at 400 nm is characteristical sign for presence of spherical Ag NPs [12]. The manifestation of the SPR bands is a proof for the formation of silver nanoparticles and the broadness of these bands is also indicative for Ag NPs with broad size distribution and various shapes [12].

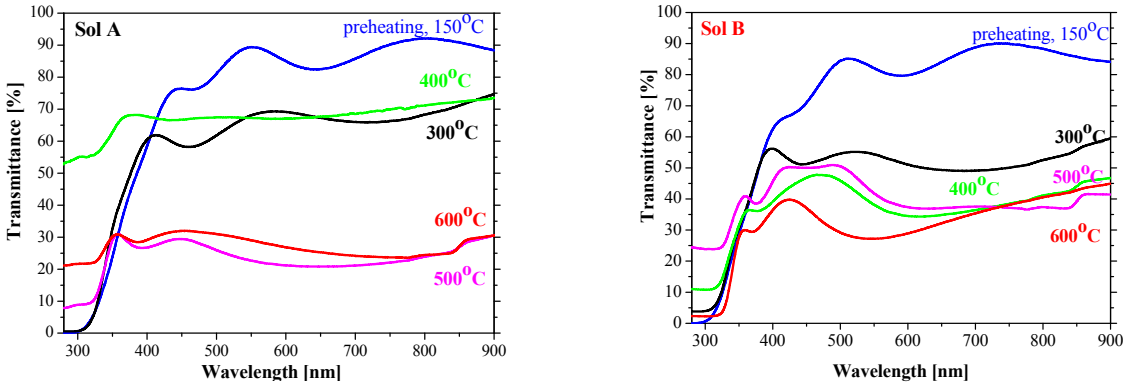

Figure 6. Transmittance spectra of sol-gel TiO_2:Ag films (5 layers) from sol A and sol B, thermally treated at different temperatures.

Figure 6 presents the optical spectra of TiO_2:Ag films (5 layers) from sol A and sol B, thermally treated at different temperatures. All the films show plasmonic absorption but the position and intensity depends significantly on the annealing temperatures. For all samples a band near 400 nm can be observed – an SPR due to spherical Ag NPs but there are also broader bands at higher wavelengths which can be related to bigger nanoparticles, to non spherical shapes and to higher plasmonic modes.

Comparison of the optical absorption of low temperature annealed undoped TiO_2, TiO_2:Ag films (150°C, preheating temperature) and only UV treated films is given in figure 7. The low absorption of undoped TiO_2 indicates its high transparency. The only thermally treated films with Ag NPs also reveal relatively low absorption and the UV treatment drastically increases the absorption in the visible spectral range. The transmittance studies prove that Ag is embedded in TiO_2 films as nanoparticles as plasmon absorptions are clearly exhibited in the visible spectral range. Absorption peaks, a sign for spherical Ag nanoparticles are observed along with broader absorption bands that can be assigned to bigger nanoparticles or to different more complex shapes of Ag NPs. Plasmonic nanostructured thin films with increased absorption can be useful in thin-film solar cells through efficient scattering of the incident light in semiconductor absorber [13].

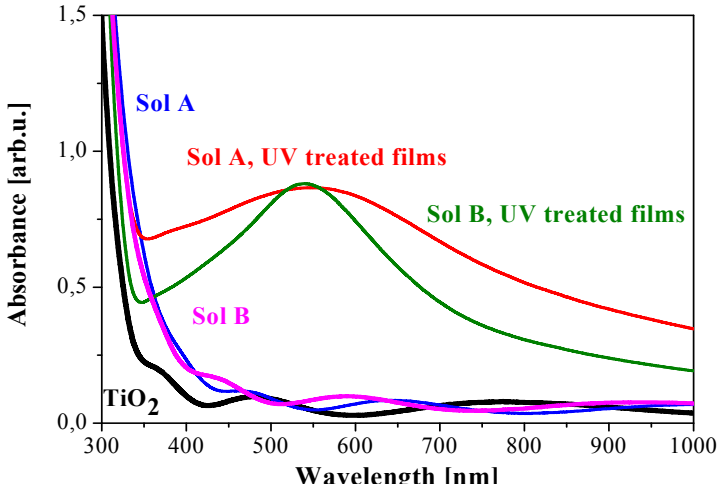

Figure 7. Optical absorbance of sol-gel TiO_2 and TiO_2:Ag films (5 layers) from sol A and sol B, preheated at 150°C or UV treatment.

From transmittance measurements it can be estimated the optical band gap (see figure8). The estimated optical band gaps (E_g) for TiO_2 films are higher than those reported for bulk anatase TiO_2 - 3.2 eV and bulk rutile 3.03 eV [7]. The widening of the band gap is due to the nanocrystalline nature of the films, grain size, variation of the crystal structure.

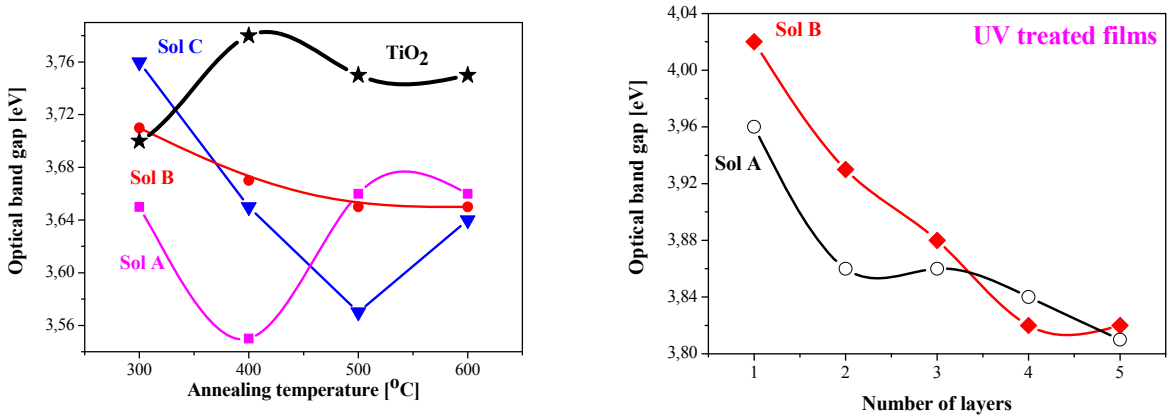

Figure 8. Optical band gap of sol-gel TiO_2:Ag films from sol A (1 wt% $AgNO_3$), B (0.5 wt% Ag NO_3)and C (0.1 wt% $AgNO_3$) (5 layers) thermally treated at different temperatures compared to undoped TiO_2 and optical band gap values of UV treated TiO_2:Ag films from sol A and B depending on number of layers.

The optical band gap of thermally treated TiO_2:Ag films are smaller than those of pure titania due to effect of Ag nanoparticles. The observed decrease of E_g with silver addition is reported by other authors [14]. The UV radiated films show very different optical behavior. They possess optical band gaps ranging from 3.80 to 4.04 eV depending on the number of layers and silver concentration. Many authors reported a relation between the optical band gap and crystallites sizes, which can be related to quantum confinement [16], the presence of the two crystal phases of TiO_2 and Ag nanoparticles.

4. Conclusions

The sol-gel approach offers a facile deposition method of Ag nanoparticles TiO_2 films. The results indicate that the silver incorporation and its concentration affect the crystallinity and the optical

properties of TiO_2:Ag thin films. The annealing temperatures and UV treatment influence greatly on the structural and optical behaviour of TiO_2:Ag nanostructured thin films. XRD analysis reveals that the silver is crystallized in metallic state. It has been found that Ag presence facilitates the anatase to rutile transformation and the UV treatment results in better expressed rutile phase compared to only thermally treated films. FTIR investigation show no absorption bands related to Ag-O bondings and IR lines characteristic for anatase and rutile phase of TiO_2 are observed. Optical characterization reveals that Ag nanoparticles are successfully formed in titanium dioxide matrix as surface plasmon resonance effect is detected. Optical absorption in the visible spectral range exhibits plasmonic features characteristic for spherical Ag nanoparticles and broader absorption bands that can be assigned to bigger nanoparticles or higher plasmonic modes.

Acknowledgements
Financial support from the project INERA under the contract REGPOT 316309 for the paper presentation at the INERA Conference 2016 "Vapor Phase Technologies for Metal Oxide and Carbon Nanostructures" is gratefully acknowledged

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