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Optimized Electroless Silver Coating for Optical and Plasmonic Applications

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Abstract Electroless metal deposition is a simple and convenient technique to fabricate metallic films and to provide isotropic metal functionalization of 3D structures with complex geometries. In this work, we describe the synthesis of silver coatings by means of a modified Tollens reaction and their use as optical coating. The chemical composition of the metallization bath is here addressed to optimize the metal coating deposition. The synthesis parameters have been tailored in order to deposit very smooth films which were characterized by scanning electron microscopy, atomic force microscopy, and optical spectroscopy. 2D diffraction gratings and sinusoidal plasmonic gratings were produced with the proposed method. Optical characterization confirmed the plasmonic activities of the resultant structures, proving the efficiency of the described method for optical applications. Thermal annealing was found to improve the surface roughness of the coating and therefore the optical properties of the plasmonic gratings.

Keywords Silver coating · Electroless · Plasmonic · Grating

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Introduction

Electroless metallization is a wet chemical process where a metal salt is reduced to form a metal layer on a surface [1–7]. When compared to the chemical vapor deposition or sputtering techniques, this method possesses peculiar advantages such as straightforward procedures, low-cost equipment, short coating time, high degree of flexibility for processing optimization, and potentiality to coat substrates of different materials, ranging from macroscopic flat surfaces to micron-sized ones with complex 3D geometries. Therefore, electroless plating is an effective alternative to vacuum deposition techniques, and it has been utilized with successes in a number of different applications [8–10].

The most popular method for the electroless deposition of silver coating is based on the Tollens reaction [11–16]. In this procedure, $Ag(NO)_3$ is first mixed with $NH_3(OH)$ to form a silver ammoniacal complex which is subsequently reduced by weak reductants, such as the aldehyde groups contained in sugars. The reduction takes place in alkaline media, and a strong base is also added to catalyze the reaction. A wide range of optimized procedures have been reported in which the Tollens reaction has been optimized by changing the type of precursors or by activating the substrate [17, 18].

In this work, we describe a reproducible method to obtain thin and smooth silver layers on flat substrates, and the optimized coating technique has been applied to multi-dimensional microstructures. Smooth silver layers have

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been obtained by slowing the reaction kinetics introducing an extra chemical agent, Arabic Gum, capable of strongly complexing silver ions in solution. The use of Arabic Gum was found to affect significantly the deposition rate, allowing fabricating thin films with reproducible thickness and good smoothness with respect to coatings realized through to the traditional Tollens reaction. In order to prove the effectiveness of the developed process for optical and plasmonic applications, two 2D diffraction gratings have been coated with a thin silver layer, and their optical and plasmonic properties have been demonstrated.

Experimental

Silver Deposition

The deposition method is derived from the Tollens reaction. This reaction is well known and is described in standard chemistry textbooks. The general pathway of silver ions reduction by aldehydes in alkaline condition can be described as follows:

$$2Ag(NH_3)_2^+ + RCHO + 2OH^- \rightarrow 2Ag + RCOOH + 4NH_3 + H_2O$$

where $Ag(NH_3)^{2+}$ is the diammine silver complex formed between the ammonia and silver nitrate. RCHO, the aldehyde group, is oxidized to $RCOO^-$, the carboxylic group. Glucose has been used in this work as the source of aldehyde groups as it is a commonly employed chemical in the Tollens reaction. Arabic Gum has been introduced in the abovementioned reaction system because it is known to complex silver ions in solution inducing a slower reduction rate [19, 20].

All chemicals have been purchased from Aldrich and used without any further purification. The silver deposition solution is obtained by mixing a 42.5-g/L $Ag(NO_3)$ (97%) aqueous solution with a 30 % weight ammonia solution. A 32-g/L NaOH solution and a 50-g/L Arabic Gum solution are added next, and a 45-g/L glucose solution is finally introduced.

The Arabic Gum content is varied to evaluate its effect on the silver deposition. The used concentrations are 0, 6.5, 13, and 20 g/L. The respective compositions will be referred to as A, B, C, and D, respectively. The concentrations of the other chemicals are held constant ($Ag(NO_3)$, 11 g/L; $NH_3(OH)$, 0.04 g/L; NaOH, 3.1 g/L; Glucose, 5.8 g/L).

Borosilicate glass slides were used as substrates for the silver coating. They were first cleaned in a $H_2O_2/NH_3(OH)$ 3:1 *v/v* mixture and then treated in oxygen plasma cleaner.

The substrate is dipped vertically in the freshly prepared solution. Every 4 min, the substrate is extracted from the solution and rinsed with water in order to remove bigger aggregates and assure a homogeneous coating. This process is continued for a total deposition time of about 30 min. The resulting coating is rinsed with water and ethanol and finally dried in a convection oven at 80 °C. The silver-coated samples have been annealed at 200 °C a furnace under Ar/H_2 atmosphere, to avoid silver oxidation.

Morphological characterizations were performed by scanning electron microscopy (SEM, Philips XL30) and atomic force microscopy (AFM, NT-MDT Solver Pro in tapping mode). UV–vis total transmittance and reflectance spectra were taken with a UV–vis–NIR spectrophotometer (JASCO V-570) equipped with an integrating sphere (model ISV-469, internally coated with barium sulfate).

X-ray diffraction (XRD) analysis of the silver coatings was performed with a diffractometer (Philips PW1710) equipped with grazing incidence optics. The analysis was performed at 0.5° incidence, using CuKα Ni-filtered radiation at 30 kV and 40 mA. The average crystallite size was calculated from the Scherrer equation after fitting the experimental profiles with Lorentzian curves.

Transmittance at normal incidence and ellipsometry quantities Ψ and Δ were measured using a J.A. Woollam V-VASE Spectroscopic Ellipsometer in vertical configuration, at three different angles of incidence (60°, 65°, and 70°) in the wavelength range 300–1,000 nm. Optical constants n and k were evaluated from Ψ, Δ and transmittance data using WVASE32 ellipsometry data analysis software. The same instrument has been used also for measuring the reflectance of the plasmonic grating.

Silver-Coated Gratings

Two optical 2D structures were fabricated both involving the fabrication of a dielectric grating and the electroless deposition of a silver layer on top. The first one consists of linear dielectric rods on a flat substrate to create a diffraction grating. This was fabricated by using the two-photon polymerization technique [21] using the IPL resist (Nanoscribe GmbH) coated with a silver layer. Each grating consists of 20 parallel lines, and each line is 150 μm long. The grating periods are 5 and 10 μm, and the width of each line is about 800 nm. The second optical structure was obtained through the deposition of a silver layer on a sinusoidal grating fabricated by soft nanoimprint lithography on an organic/inorganic hybrid sol–gel film.

A polydimethylsiloxane (PDMS; Sylgard 184, Dow Corning) replica of a silicon master, presenting the sinusoidal nanostructures to be transferred on the film, was obtained by replica molding. The elastomeric mold was gently pressed on the freshly deposited hybrid films, and

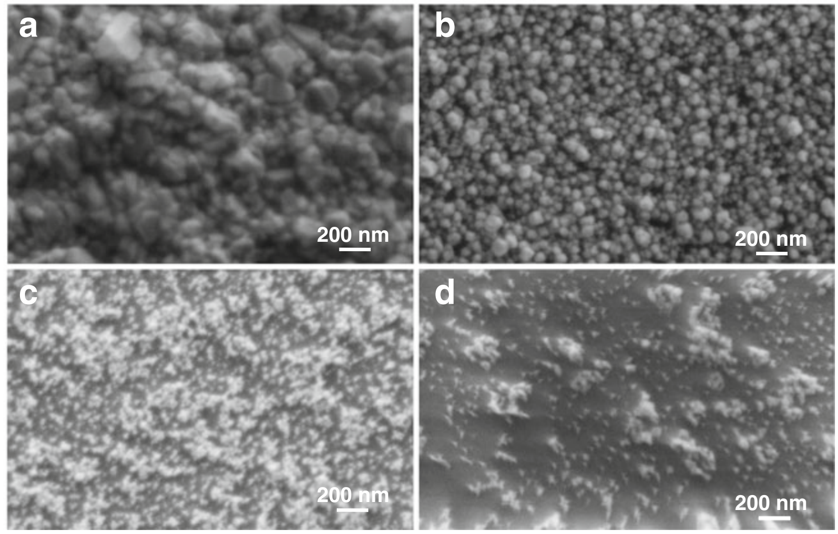

Fig. 1 SEM images of silver coatings on the flat glass substrates. The content of Arabic Gum in the electroless deposition bath is increased from **a** to **d**, following compositions A to D, respectively

the assembly was cured in a convection oven at 80 °C for 30 min to peel PDMS off the sample. The realized photonic crystal presents sinusoidal features of 500 nm period and 40 nm peak-to-peak amplitude. The near-field coupling of the nanostructured dielectric substrate with a metallic layer has demonstrated to excite surface plasmon polaritons at

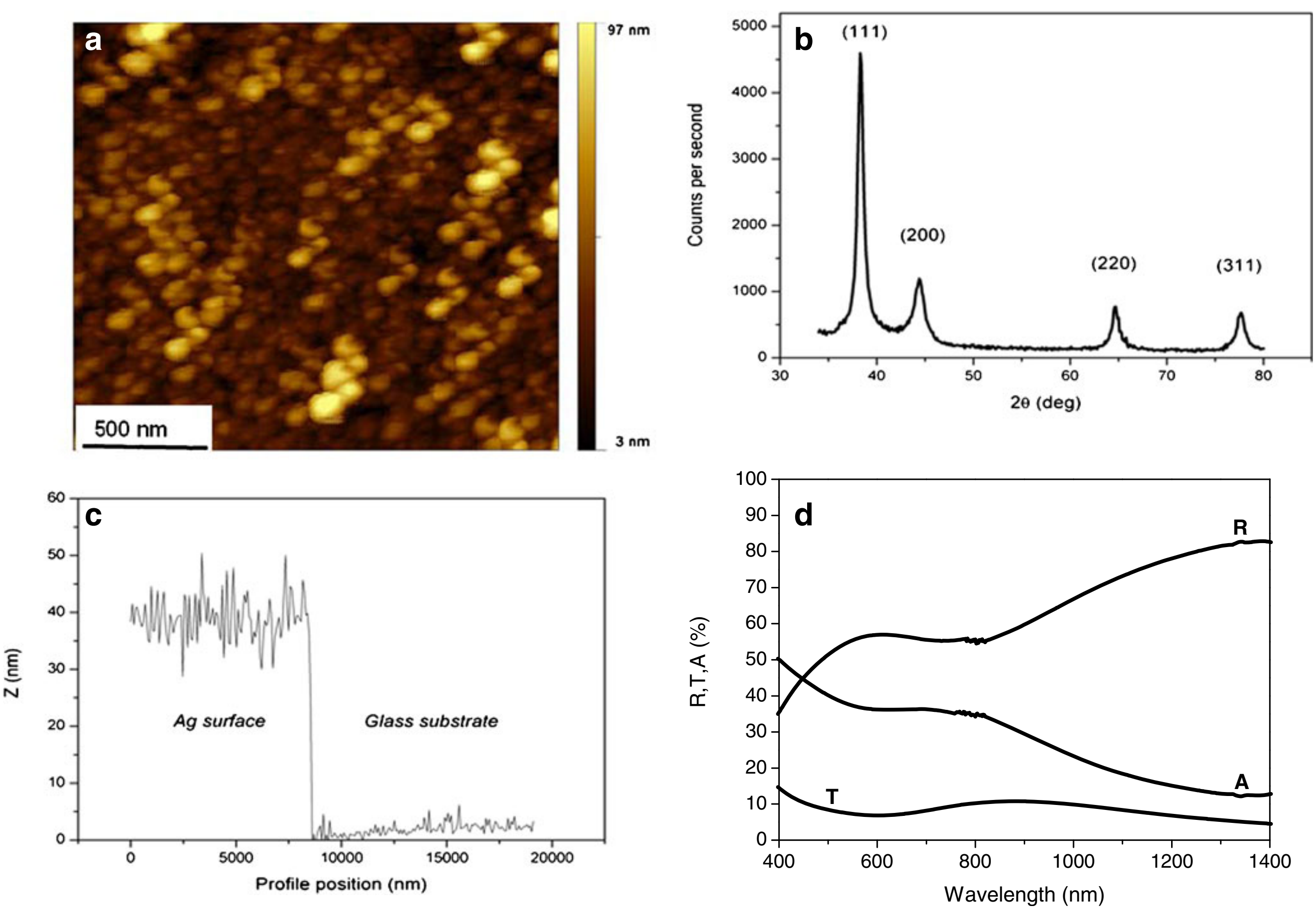

Fig. 2 Silver coating from composition B: **a** AFM image, **b** XRD pattern of a silver coating and diffraction indexes of metallic silver (JCPDS No. 87-0720), **c** AFM profile across a scratch on the silver coating, **d** reflectance (*R*), transmittance (*T*), and absorptance (*A*) spectra

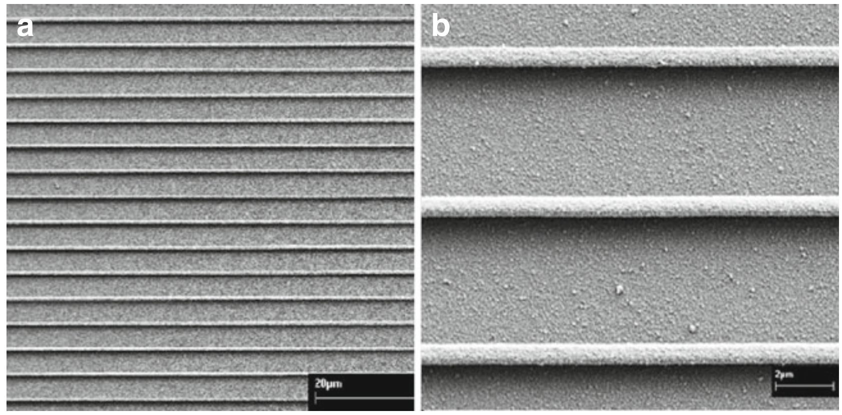

Fig. 3 Silver coated grating (period=5 μm) **a** low magnification view showing the long-range uniformity of the grating and of the silver coating, **b** magnified image of three coated rods

certain wavelengths, according to the light polarization and the incidence angle.

Results and Discussions

Silver Coating

The effect of Arabic Gum on the film morphology is evident from the SEM images of the silver coatings reported in Fig. 1. If no Arabic Gum is used (composition A, Fig. 1a), the deposition of silver is very fast and a rough surface is obtained. In addition, the control over thickness is limited and thin films with reproducible thickness are difficult to obtain.

As soon as Arabic Gum is added, the silver deposition is slowed down and a thin, smooth silver film is obtained (composition B, Fig. 1b). On the other hand, if the Arabic Gum content is raised, the silver reduction rate is too slow and a complete coverage of the substrate cannot be achieved (compositions C and D, Figs. 1c and d, respectively) in the adopted deposition time. Isolated silver clusters are in fact seen in this case.

The effect of Arabic Gum on the silver growth kinetics is evident also in the silver bath. The rapid production of a blackish silver powder is seen if no Arabic Gum is used (as obtained by XRD measurements on the precipitated powder), while silver nanoparticles are formed as an intermediate step in the other cases because a transparent yellow solution showing a plasmon band is observed.

The best results in terms of smoothness and substrate coverage are obtained with composition B. In Fig. 2, AFM images of the coating and XRD analysis are presented. The structure of the film is consistent with a closely packed arrangement of silver nanoparticles with 40–50 nm diameter, as evident from the AFM image. The thickness is in the 40–50-nm range, resulting in a semitransparent silver film with good reflectivity. The surface roughness, as estimated from AFM measurement, is in the 10–15-nm range, assessing a good surface quality. XRD analysis confirms the

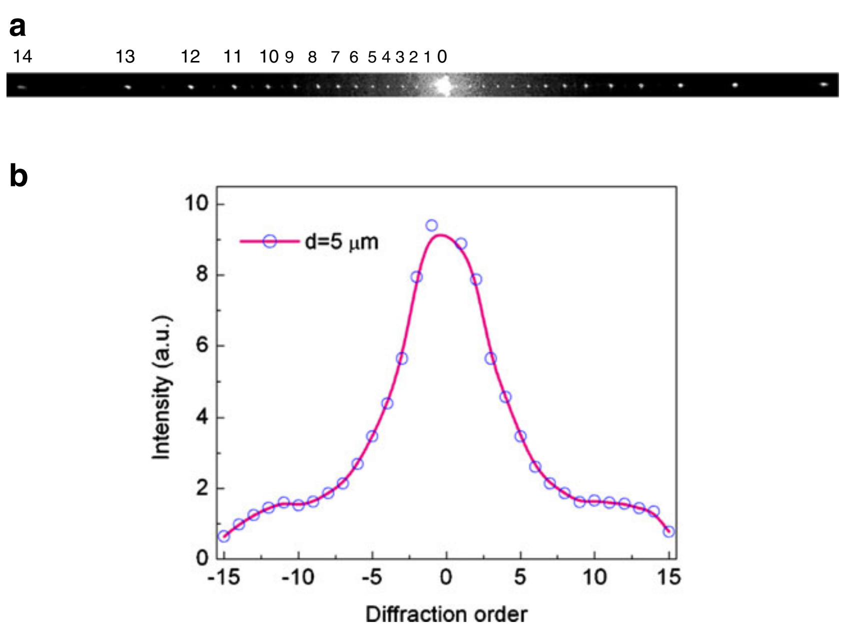

Fig. 4 **a** Diffraction image of the silver coated 2D grating (d=5 μm). **b** Measured power for each diffraction orders of the 5-μm period 2D grating

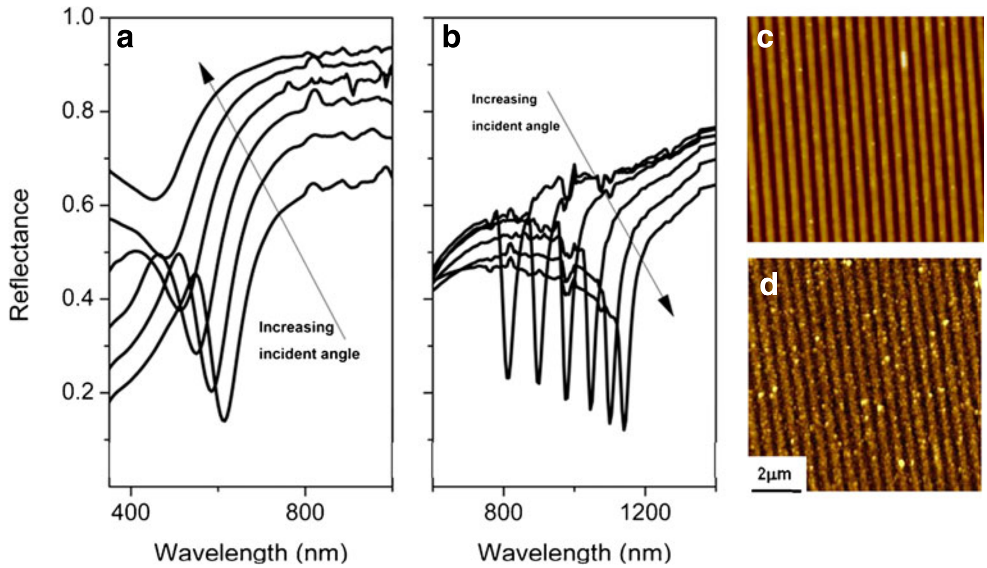

Fig. 5 Reflectance spectra of electroless silver-coated grating at 20°, 30°, 40°, 50°, and 60° incident angle using the s-polarized light (**a**) and the p-polarized light (**b**); AFM images of the bare (**c**) and of the silver-coated sol–gel hybrid photonic crystal (**d**)

presence of crystalline silver and the absence of silver oxide phases. The mean crystallite diameter evaluated with the Scherrer formula was 43 nm, in agreement with the AFM measurements.

In Fig. 2, the transmittance T, the reflectance R, and the absorptance A ($A=100-R-T$) curves are also presented. An average reflectance of about 70 % is retrieved, and a broad absorption band below 800 nm is observed. This behavior can be attributable to the localized plasmon resonance coming from the particle-like nature of the coating or to scattering [22, 23]. Even if the observed reflectance in the whole visible range is proper of metallic film behavior, it is likely that the constituting particles are not perfectly joined to form a continuous film, thus inducing localized surface plasmon resonance. Voids or other type of discontinuities might also be responsible for such absorption features.

Silver-Coated Gratings

SEM images of the 2D diffraction grating after silver coating are reported in Fig. 3. It can be clearly seen that the polymer rods are straight and the silver coating is uniform on a large spatial range. The quality of the silver coating can be examined looking at the optical property measurement of the 2D grating. The diffraction image of the grating illuminated with a helium–neon laser beam is presented in Fig. 4a. Fifteen diffraction orders, which match the theoretically predicted maximum orders, can be clearly seen from the

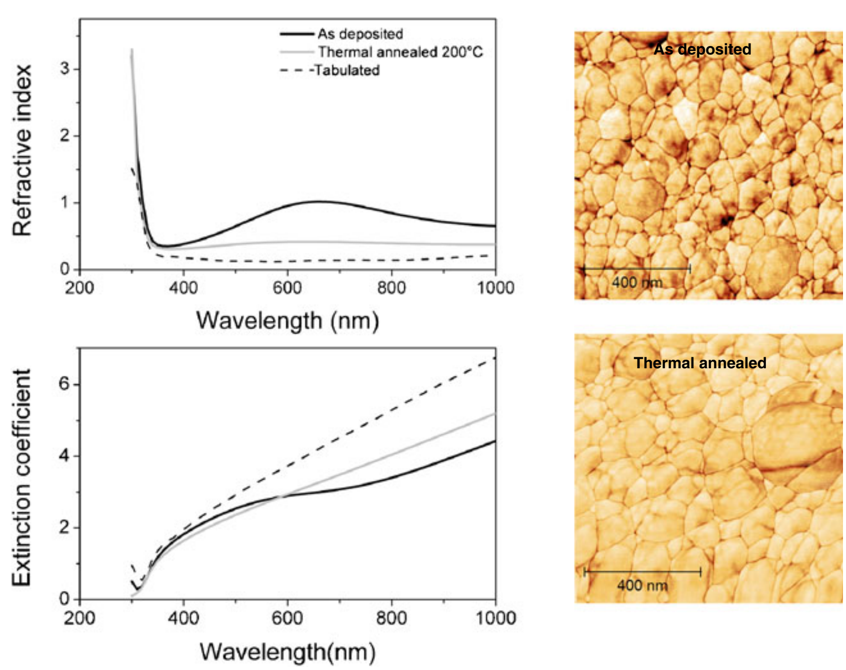

Fig. 6 Refractive index and extinction coefficient curves for as-deposited and thermally annealed samples. Tabulated dielectric constant is also included for silver [25]. Corresponding AFM phase images are also shown

image, demonstrating the high quality of the hybrid grating as well as the smoothness of the silver coating. The measured diffraction power for each order is presented in Fig. 4b. An almost symmetric distribution can be clearly observed.

Surface plasmon polaritons can be excited on metal-coated dielectric substrates using sinusoidal diffraction gratings [24]. The plasmon resonance can be detected as a dip in the reflectivity curve, at certain wavelengths of the incident light, for different values of the incidence angle. As known from the theory, light polarization must be orthogonal to the grating pattern to excite plasmons propagating on the surface of the metallic film.

In Fig. 5a, the reflectance spectra detected with linearly polarized light, with the electric field vector lying in the sample plane and orthogonal to the grating direction, are shown. A reflectivity minimum related to plasmon absorption is observed, whose position shifts to lower wavelengths for increasing incidence angle.

Similar results are obtained using linearly polarized light with the electric field vector lying in the plane of incidence (Fig. 5b). The sample must be rotated by 90° with respect to the previous case in order to have a light component orthogonal to the pattern direction. The plasmon resonances are at higher wavelengths, and their position is shifted to higher wavelengths when the incidence angle is increased, as expected from the theory.

In Fig. 5c, d, AFM images of the patterned sol–gel hybrid film before and after the application of a silver coating are shown. The quality of the silver coating was found to be improved by thermal annealing at 200 °C. In Fig. 6, the dielectric constants (refractive index and extinction coefficient) measured with spectroscopic ellipsometry for as-deposited and thermally annealed samples are shown along with tabulated values for silver. In the as-deposited sample, the presence of an absorption band was evidenced in the extinction coefficient curve and in the dispersion curve. These features disappeared in the thermally annealed sample, whose dielectric constants approach the tabulated values for silver. In addition, the contact between silver particles composing the film is improved as seen from the AFM images.

AFM phase images of both samples are shown in the same figure, where the boundaries of silver particles composing the film are clearly evident. After thermal annealing, the dimensions of the silver particles increase significantly, suggesting sintering and coarsening processes. As a result, the improved welding of the particles and disappearance of discontinuities or voids responsible for the undesired plasmon resonances or scattering determine an overall film quality refinement. This is likely due to the improved contact between particles promoted by the thermal annealing resulting in a better metallic behavior of the coating. The reflectivity of the flat coating increases significantly (Fig. 7a), and the plasmonic resonance of the grating becomes much more narrow and sharper, enhancing the quality of the plasmon response of the grating (Fig. 7b and c).

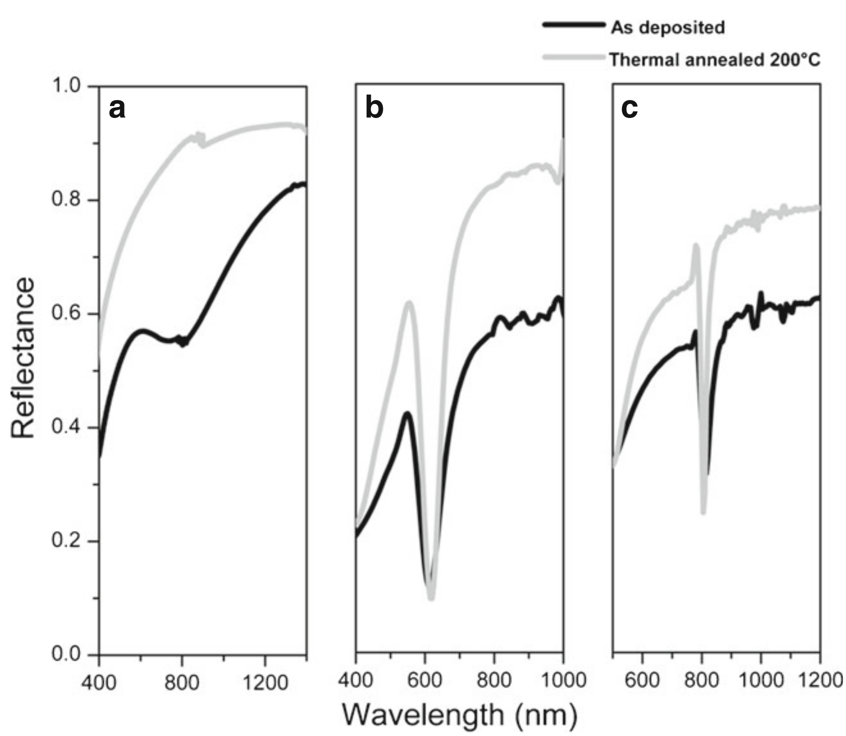

Fig. 7 Reflectance spectra of a flat silver coating (**a**) and of the plasmonic grating (**b**, **c**) as deposited and after a thermal annealing at 200 °C. For the plasmonic grating, the spectra are acquired at 20° incidence angle, for s-polarized incident light (**b**), and for p-polarized incident light (**c**), in the same conditions of the measurements reported in Fig. 5

Conclusions

An improved method for the electroless deposition of silver coatings has been proposed. Smooth and thin silver layers have been obtained by modifying the standard Tollens reaction, slowing the silver reduction kinetics by the addition of Arabic Gum, a complexing agent for silver. In addition, thermal annealing has been shown to further improve the optical properties of the coating.

This procedure could be successfully used for silver functionalization of 2D diffraction and sinusoidal plasmonic gratings, showing the potential application in optics and plasmonics. Due to the facile procedure and isotropic nature of electroless coating, we believe this method can be effectively used in a number of optical and photonic applications.

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References

1. Yun-Sheng C, Tal A, Kuebler SM (2007) Chem Mater 19:3858
2. Malureanu R, Zalkovskij M, Andryieuski A, Lavrinenko AV (2010) J Electrochem Soc 12:157
3. Henry AC, McCarley RL (2001) J Phys Chem B 105:8755
4. Koo HC, Kim SY, Cho SK, Kim JJ (2008) J Electrochem Soc 9:155
5. Buckley F, Hope G (2006) IEEE Proc. Int. Conf. Nanoscience and Nanotechnology 528
6. Brejna PR, Griffiths PR (2010) Appl Spectrosc 64:493
7. Wul D, Zhang T, Wang WC, Zhang L, Jin R (2008) Polym Adv Technol 19:335–341
8. Kaneko K, Yamamoto K, Kawata S, Xia H, Song JF, Sun HB (2008) Opt Lett 33:1999
9. Zhang J, Zhan P, Liu H, Wang Z, Ming N (2006) Mater Lett 60:280
10. Tian C, Wang E, Kang Z, Mao B, Zhang C, Lan Y, Wang C, Song Y (2006) J Solid State Chem 179:3270
11. Barsegova I, Lewis A, Khatchatouriants A, Manevitch A, Sukenik C (2002) Appl Phys Lett 81:2461
12. Malvadkar NA, Demirel G, Poss M, Javed A, Dressick WJ, Demirel MC (2010) J Phys Chem C 114:10730
13. Bois L, Chassagneux F, Desroches C, Battie Y, Destouches N, Gilon N, Parola S, Stephan O (2010) Langmuir 26:8729
14. Yin Y, Li ZY, Zhong Z, Gates B, Xia Y, Venkateswaran S (2002) J Mater Chem 12:522
15. Qi H, Alexson D, Glembocki O, Prokes SM (2010) Nanotechnology 21:085705
16. Schaefers S, Rast L, Stanishevsky A (2006) Mater Lett 60:706
17. Textor T, Fouda MMG, Mahltig B (2010) Appl Surf Sci 256:2337
18. Formanek F, Takeyasu N, Tanaka T, Chiyoda K, Ishikawa A, Kawata S (2006) Appl Phys Lett 88:083110
19. Chen Y-S, Tal A, Torrance DB, Kuebler SM (2006) Adv Funct Mater 16:1739
20. Li J, Hossain M, Jia B, Buso D, Gu M (2010) Opt Express 18:4491
21. Jia B, Li J, Gu M (2007) Aust J Chem 60:484
22. Da Silva A, Andraud C, Lafait J, Dakka AJ (2000) Phys Cond Matter 12:4125
23. de Vries AJ, Kooij ES, Wormeester H, Mewe AA, Poelsema B (2007) J Appl Phys 101:053703
24. Romanato F, Hong Lk, Kang HK, Wong CC, Yun Z, Knoll W (2008) Phys Rev B 77:245435
25. Palik ED (1985) Handbook of optical constants of solids. Academic, New York