Coating dielectric substrates by plasma-reduction of metallic ions in solvents

Isaschar Genisha,a,⁎, Alexander Irzhb, Aharon Gedankenc, Assaf Andere, Arie Zabanc, Lior Kleinad
a Department of Physics, Nano-magnetism Research Center, Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel
b Department of Chemistry, Nano-magnetism Research Center, Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel

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A B S T R A C T
We demonstrate herein the coating of dielectric surfaces with metallic thin films using the plasma-reduction of metallic ions such as HAuCl4, AgNO3, H2PtCl6, PdCl2, Ni(NO3)2 and Co(NO3)2 in solutions. Stable plasma was formed using 12 MHz/18 W and 2.45 GHz/900 W plasma generators and was confined in a Pyrex vacuum chamber with an inert gas environment. Depending on the controlled parameters, the fabricated films are either continuous or granular with grains of nano-size dimensions. All samples were chemically analyzed using X-ray diffraction analysis, and were morphologically observed using High Resolution Electron Beam microscopy. As an example of their electrical conductivity, Van der Pauw resistivity measurements were carried out for a gold layer at a wide temperature range. The smooth resistivity signal spreading at this range indicates that the conductive layer is stable and electrically continuous. An estimation of the adhesion of the deposited films was conducted by resistance measurements, followed by an ultrasonic bath treatment. Our results indicate no change in the resistance after this treatment, namely, a good adhesion of metallic particles to the glass surface has been achieved. The fact that this method is fast, simple, and low in cost (compared to other methods like sputtering or cvd), and can be applied for coating flat, rough, and porous surfaces can indicate its importance in future applications.

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1. Introduction

Among the various methods used for film deposition, wet coating by electrochemistry is particularly attractive for its relative simplicity and low cost. However, this method cannot be applied in all cases, and especially not when the surface for deposition is dielectric. In such cases, other wet coating methods are used, including sonication [1,2] and microwave heating [3].

We demonstrate herein plasma wet coating by covering a surface (dielectric or non-dielectric) with a solution and using plasma to reduce the wet layer to a pure metallic film. This method extends previous methods of film deposition that use plasma, [4–6] and its main advantage is the possibility to offer fast, simple, and low cost coating over a wide range of surfaces.

Plasma is created by accelerating free electric charge using an electromagnetic field. Collisions between the free accelerated charges and atoms in the system lead to an increase in the total amount of free charge. The collective behaviour of these particles is known as plasma [7–9].

The use of plasma for the reduction of metallic precursors has been discussed previously [10,11]. In the current work plasma is generated inside a vacuum chamber using an electric coil or magnetron. A free electric charge, [7] (electrons and ions that are heavier and move with a smaller velocity) originally from the inserted, controlled gas and partly from the outgassing of the solution, is accelerated and collides with other gas atoms, creating plasma. The mean free path between collisions is determined by the pressure. Since electrons are excited and drop back again to lower levels, a constant glow is observed while the plasma exists. The plasma's free electrons, the heavier ions and the increasing temperature are used to reduce the metallic ions of the solution, creating particles that can (at high solution concentration or at sufficient reduction time) form continuous layers.

In this paper, the new method is introduced and we demonstrate the coating of dielectric substrates with gold, silver, platinum, palladium, nickel and cobalt. X-ray analysis of the deposited films indicates their high purity. In addition, we explore the morphology of the deposited film, its relation to deposition parameters, and its adhesion.

2. Material and methods

Ethanol solutions of HAuCl4, AgNO3, H2PtCl6, PdCl2, Ni(NO3)2 and Co(NO3)2 (Aldrich Co.) are used, mostly with a 0.1 and 0.05 M concentrations. To fabricate a film from these solutions, we wet the substrate with few drops (one to three) of any of these solutions and place the substrate in a plasma chamber for 1 to 3 min (depending on the plasma generator). The plasma systems used for this work are: a) A 12 MHz/18 W commercially-available plasma machine (Harrick Plasma, Model PDC-32G-2, used originally to clean samples from organic material). This plasma system has an ∼7.7 cm × ∼16.5 cm cylindrical chamber with a removable cover. The system applies a maximum...
power of 18 W to the radio frequency (RF) coil, with no RF emission.

b) A domestic 2.45 GHz/900 W modified microwave oven (Crystal), in which we installed an ∼13.5 cm long cylindrical Pyrex vacuum chamber with an ∼5.1 cm diameter. Both systems were connected to vacuum pumps that can achieve a pressure of ∼10^{-2} Torr.

The wet substrates that were inserted inside the 12 MHz/18 W or the 2.45 GHz/900 W plasma systems were under a low pressure inert environment before the reaction started. For the 12 MHz/18 W system a preliminary flow of helium gas was used as an inlet for 1 min, at a constant flow rate of 50 cc/min, in order to achieve the inert environment. At this system the reaction itself was carried out for 3 min under a constant flow of He at a rate of 30 cc/min. In the case of the 2.45 GHz/900 W plasma system, we used argon to achieve an inert environment at a flow of 5 l/min, while during the reaction, of only 1 min, no gas flowed through the system. In both cases the samples lay in the center of the chamber and remained static during the reaction. In Table 1 we summarize the experimental conditions.

The films fabricated by this method were characterized by X-ray diffraction analysis (XRD, Bruker AXS D*, Cu Kα radiation = 1.5418 Å), and a high resolution scanning electron microscope (HR-SEM, Jeol JSM-7000F field emission electron microscope). For some of the films electrical resistively measurements were performed, when the electric connections were made by using a wire bonder (West Bond 7476E) with 25 µm diameter aluminum wires. In these cases the measurements were carried out using a Quantum Design Physical Property Measurement System (PPMS). This system was used for the characterization of the temperature dependence of the electrical resistivity and for room temperature measurements. In order to analyze the thickness of some of the films, we used an atomic force microscope, AFM, (Digital Instruments NanoScope IV) after removing small parts of these layers by mechanical or chemical means (nitric acid). In addition, we have demonstrated the good adhesion of one of these layers after an ultrasonic bath treatment (Elma Trammsonic T310 with a vibration frequency of 35 kHz and a 70 HF peak/W).

All the data presented here are on films deposited on a glass substrate (Yancheng Rongkang Glassware Co., Ltd., China, Cat. No. 7102). However, we also used this method to coat a wide variety of substrates, including: plastic, copper slides and carbon mesh.

<table>
<thead>
<tr>
<th>Plasma source</th>
<th>Solution</th>
<th>Concentration (M)</th>
<th>Reaction time</th>
<th>Iterations</th>
<th>Substrate size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 MHz/18 W</td>
<td>HAuCl₄</td>
<td>0.1</td>
<td>3</td>
<td>5</td>
<td>5×5</td>
</tr>
<tr>
<td></td>
<td>HAuCl₄</td>
<td>0.1</td>
<td>3</td>
<td>2</td>
<td>5×5</td>
</tr>
<tr>
<td></td>
<td>HAuCl₄</td>
<td>0.08</td>
<td>3</td>
<td>1</td>
<td>7×</td>
</tr>
<tr>
<td></td>
<td>HAuCl₄</td>
<td>0.06</td>
<td>3</td>
<td>1</td>
<td>7×7</td>
</tr>
<tr>
<td></td>
<td>HAuCl₄</td>
<td>0.04</td>
<td>3</td>
<td>1</td>
<td>7×7</td>
</tr>
<tr>
<td></td>
<td>HAuCl₄</td>
<td>0.01</td>
<td>3</td>
<td>1</td>
<td>7×</td>
</tr>
<tr>
<td></td>
<td>AgNO₃</td>
<td>0.1</td>
<td>3</td>
<td>5</td>
<td>5×5</td>
</tr>
<tr>
<td></td>
<td>AgNO₃</td>
<td>0.1</td>
<td>3</td>
<td>2</td>
<td>5×5</td>
</tr>
<tr>
<td></td>
<td>H₂PtCl₆</td>
<td>0.1</td>
<td>3</td>
<td>5</td>
<td>5×5</td>
</tr>
<tr>
<td></td>
<td>H₂PtCl₆</td>
<td>0.1</td>
<td>3</td>
<td>2</td>
<td>5×5</td>
</tr>
<tr>
<td></td>
<td>PtCl₄</td>
<td>0.1</td>
<td>3</td>
<td>5</td>
<td>5×5</td>
</tr>
<tr>
<td></td>
<td>PtCl₄</td>
<td>0.1</td>
<td>3</td>
<td>2</td>
<td>5×5</td>
</tr>
<tr>
<td>2.45 GHz/900 W</td>
<td>Ni(NO₃)₂</td>
<td>0.5</td>
<td>1</td>
<td>7</td>
<td>25×25</td>
</tr>
<tr>
<td></td>
<td>Ni(NO₃)₂</td>
<td>0.5</td>
<td>1</td>
<td>7</td>
<td>25×25</td>
</tr>
</tbody>
</table>

Fig. 1. (a) XRD analysis of a gold layer. Inset: normalized resistivity vs. temperature of a gold layer. (b) AFM image of a gold layer after two reduction iterations. By removing a small part of the layer an estimation of the layer thickness could be done.

Fig. 2. HR-SEM images of a gold layer obtained by two reduction iterations using each time one drop of H₂AuCl₄ ethanol solution on a 5 mm × 5 mm glass substrate. a) A general view (∗10000) of the gold layer; large polyhedron (some almost rectangular) shaped grains and small particles in between and on the grains. Inset: image (∗10,000) taken after tilting the sample 68° relative to its normal. The image shows a crystalline structure covered by smaller particles. b) Small particles observed with magnification of ∗100,000.
3. Results and discussion

3.1. 12 MHz/18 W plasma generator

Using the 12 MHz/18 W plasma generator we deposited a gold film on a 5 mm × 5 mm glass substrate. Fig. 1a presents the XRD pattern of this film. To obtain a strong XRD signal it is preferable to use thick films. Therefore, the film whose XRD data are presented was fabricated by repeating the reduction process 5 times (each time the sample was irradiated by plasma for 3 min), adding one drop (≈0.017 ml) of the solution (0.1 M) at each iteration. The XRD pattern shows clear peaks of gold (Powder Diffraction File: 03-065-2870). No impurity peaks are detected, indicating that a pure gold layer is formed. Using the Scherrer formula [12,13] the average size of the gold crystallites was found to be 18 nm.

Fig. 1a shows also the resistivity measurements as a function of temperature obtained for a gold layer fabricated using two iterations of plasma reduction procedures with solution concentration of 0.1 M. The resistivity measurements performed using the Van der Pauw technique, [14,15] with a PPMS system, reveal a behavior typical for gold [16] that was found to be, in this case, above the percolation threshold. The smooth electric signal over this wide range of temperatures indicates that the gold layer is electrically continuous. In order to analyze the samples’ structure a small part of the gold coating was mechanically removed. Using AFM imaging, at the coating edge, the thickness of the particle layer was found to be ~1 µm (see Fig. 1b).

Fig. 2a shows the morphology of this thick gold film using HR-SEM. This sample consists of large polyhedrons (some almost rectangular) gold grains, as can be also seen from the inset image obtained after tilting the sample 68° with respect to its normal. The geometries obtained here are consistent with some previous work on the growth of gold crystals. [17–22] For a quantitative estimate of the particles’ size, we used Scion Image software. The size of the large polyhedrons is 3.2 ± 0.8 µm. On the large grains there are particles with a calculated size of 34 ± 18 nm. In addition there are smaller particles of 12 ± 5 nm between the polyhedron grains (Fig. 2b).

To explore the dependence of the film morphology on the concentration of the solvent, we put one drop of a HAuCl₄ solution of various concentrations on a 7 mm × 7 mm glass substrate. The concentrations of the solutions were: 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 M.

Fig. 3 shows HR-SEM images of the layers produced with various concentrations. We noted the evolution of isolated small gold particles of 20 nm from a 0.01 M solution (Fig. 3a) to aggregated gold particles of several microns (Fig. 3f) when the concentration is 0.1 M. It appears that by changing the concentration of the solute one can achieve good control over the grain size. This possibility is important for future applications of this method. When comparing the surface structure, as presented in Fig. 3, it seems that by increasing the concentration of the solute, clusters are formed. These clusters are

![Fig. 3. HR-SEM images of gold layers produced by wetting a 7 mm × 7 mm glass substrate with one drop of H₂AuCl₄ dissolved with ethanol with increasing concentrations (a) 0.01 M, (b) 0.02 M, (c) 0.04 M (d) 0.06 M, (e) 0.08 M, (f) 0.1 M. All HR-SEM images refer to the same magnification (×10,000).](image-url)
connected to each other and their size increases with concentration. At sufficient concentration these clusters are partially “broken” into distinguishable polyhedrons that are still connected by smaller particles, as also observed in Fig. 2a.

The same method was employed to fabricate layers of silver, platinum and palladium on glass substrates. Fig. 4 shows XRD analysis of these films (with 5 reduction iterations). The XRD pattern illustrates the expected peaks for silver (Fig. 4a, Powder Diffraction File: 00-003-0921), platinum (Fig. 4b, Powder Diffraction File: 00-004-0802) and palladium (Fig. 4c, Powder Diffraction File: 01-087-0638), with no indication of impurity phases. Using the Scherrer formula, an estimation of the average crystal size was \( \sim 55 \) nm for silver, \( \sim 7 \) nm for platinum, and \( \sim 9 \) nm for palladium. Using scion image the average particle size for 5 reduction iteration was found to be: 66 \( \pm \) 27 for Ag, 14 \( \pm \) 3 for Pt and 7 \( \pm \) 2 nm for Pd.

Fig. 5 shows HR-SEM images of films deposited using 0.1 M solutions on a 5 mm \( \times \) 5 mm glass substrate with only two iterations. For these images particle size analysis using Scion imaging yielded 13 \( \pm \) 3 nm for platinum and 13 \( \pm \) 4 nm for palladium (Figs. 5b and c, respectively). The same analysis was done for silver layers and shows a large deviation from the size of platinum and palladium, giving an average particle size of 45 \( \pm \) 17 nm (Fig. 5a). These particles aggregate to plate-like structures. The large deviation of the particle size of silver is probably related to its positive reduction potential (0.7991 V) which is smaller than those of platinum and palladium. The relatively high positive potential of platinum and palladium lead to the formation of large amount of seeds at the first stage of the reaction that grow to smaller particles in comparison to silver. We note that in addition to the reduction potential there are other factors that influence the way seeds continue to crystallize, including solubility of the precursors and interactions between the solution and the substrate.

The correlation between the particle size obtained from HR-SEM images and from the Scherrer formula indicates that repeating the iteration procedure on an already coated substrate with the same reduced material does not change the particle size significantly, although it increases the layer thickness.

3.2. 2.45 GHz/900 W plasma generator

Attempts to reduce other metallic ions having lower standard reduction potentials by using the same procedure did not yield a
metallic layer. The 12 MHz/18 W plasma generator is able to reduce metallic ions with only high, positive, reduction potentials such as silver, gold, platinum, and palladium.

In order to initiate much more energetic plasma that can reduce metal ions with lower reduction potentials, we have modified a domestic 2.45 GHz/900 W microwave oven. The modification of the microwave included the insertion of a Pyrex vacuum chamber (∼5.1 cm wide and ∼13.5 cm long) and a cylindrical opening (∼2.5 cm diameter and ∼15 cm long [23,24]) that allowed the injection and pumping of argon gas into and from the vacuum chamber. Fig. 6 shows the XRD data of films fabricated by reducing Ni(NO₃)₂ and Co(NO₃)₂ on 2.5 cm × 2.5 cm glass substrates. In each reduction iteration 3 drops (∼0.023 ml each drop) with solution concentration of 0.05 M were used. This reduction procedure was repeated 7 times for each sample. The XRD analysis for cobalt (Powder Diffraction File: 01-089-7093) shows the existence of fcc polycrystals, and for nickel we find that the hexagonal phase (Powder Diffraction File: 00-045-1027) as well as the fcc phases were formed (Powder Diffraction File: 01-070-1849). The use of the Scherrer formula has yielded a particle size of 17 nm for nickel and 25 nm for cobalt.

Fig. 7 presents an HR-SEM image of nickel (a) and cobalt (b) layers obtained with only one reduction iteration. Using Scion imaging we find the particle size of nickel in this case to be 26 ± 9 nm. Both layers seem to be homogenous, but while the particle shape and size characteristics of nickel are obvious, cobalt particles are almost indistinguishable, forming a continuous layer.

In order to demonstrate the relatively good adhesion of these samples, the glass substrate coated with cobalt fabricated with only one reduction iteration was dipped into a beaker that consists of ethanol. The beaker with the sample was then vibrated using an ultrasonic bath [25,26]. By monitoring the resistance, which depends on the film’s geometrical factors, an estimation of the samples’ mechanical stability was carried out. After vibrating the sample for different time periods (1 min at the first 5 vibration tests and 5 min at the rest of the vibration tests) the sample was electrically connected using a wire bonder with a four point configuration and plugged into the PPMS system for room temperature measurements. The results given in Fig. 8 show the normalized resistance with respect to the measurements before the adhesion check (R/Rₜ₀); each point in the graph is an average resistivity result over 1 min. The reduced resistance is approximately constant with maximum resistivity change of 2.4% between the initial measurements, done before putting it into the ultrasonic bath, to the most diverted one. The difference between the initial point at t = 0 to the last one (t = 30 min) is of 0.14%. The relatively small changes in the samples’ resistance are probably due to small changes in the electrical connections and the samples’ temperature. The fact that there is almost no change in the resistivity measurements indicates that the sonication didn’t cause any mechanical change in the sample, and the fabricated film remained the same. In order to measure the layers’ thickness, part of the sample was coated using positive photoresist (Shipley Microposit S1813) that was then hardened by baking at 120 °C for 15 min. After baking, the sample was inserted into a concentrated nitric acid (10 M) for 1 min in order to remove the cobalt layer from the unprotected area. The positive photoresist was then removed using acetone and dried with a flow of nitrogen gas. The AFM image taken from the edge of the remaining layer shows a relatively uniform layer with a thickness of ∼30 nm (see Fig. 8).

4. Conclusion

In conclusion, the plasma-induced reduction of metallic solutions reported in the current manuscript is applicable to a wide range of metallic solutions. In this paper the technique was used to create layers composed of small metallic particles of Au, Ag, Pt and Pd using 12 MHz/18 W plasma system and of Co and Ni with 2.45 GHz/900 W plasma system. Using the 12 MHz/18 W system metallic particles of nanometric scale and also metallic particles of Au with micron scale...
were fabricated. The size of these particles is controlled by the solution's concentration as demonstrated in the case of Au particles. For a sufficient solution concentration, an electrically continues layer is formed.

We note, however, that solution reduction of Co and Ni didn’t occur in the chamber with a 12 MHz source, and only by using plasma source of higher frequency and power (2.45 GHz/900 W) efficient reduction was achieved. For the case of Co that was reduced with a 2.45 GHz/900 W generator, the layer was found to have very good adhesion.

This method is fast, simple, and low-cost, and can be applied to coat flat, rough and porous surfaces.

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References