Electrochemical reduction of gold nanoparticles using scanning electrochemical microscope (SECM) technique

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Abstract:
A thin film of gold–ions doped microscope slides was synthesized by using the sol-gel method. Firstly, tetraethyl orthosilane (TEOS) incorporated with AuCl3 was hydrolyzed and then conduced. Microscope slides have been immersed in silica solution for a few minutes to form a thin layer of silica on the slides. Then, the scanning electrochemical microscope (SECM) technique was used for electro reduction of gold ions. Many techniques have been used to characterize the microscope slides before and after the reduction such as scanning electron microscope (SEM), x-ray photoelectron spectroscopy (XPS), optical microscopy, and x-ray diffraction (XRD) calculations.
Keywords: Electrochemical reduction, gold nanoparticles, SECM.

التحضير الكهروكيميائي لجزيئات الذهب النانوية باستخدام تقنية المجهر الكهروكيميائي الماسح

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الخلاصة :
تم تصنيع طبقة رقيقة من الشرائح المضاف إليها أيونات الذهب باستخدام طريقة السول–جل. أولاً، تم تحليل رباعي إيثيل اورثوسيلان بوجود كلوريد الذهب. تم غمر شرائح المجهر في محلول السيليكا لبضع دقائق لتكوين طبقة رقيقة من السيليكا على الشرائح. بعد ذلك، تم استخدام تقنية المجهر الكهروكيميائي الماسح للاختزال الكهربائي لأيونات الذهب الموجودة على سطح الشرائح. تم استخدام العديد من التقنيات لتوصيف شرائح المجهرالمستخدمة قبل وبعد الاختزال: المجهر الإلكتروني الماسح، وجهاز حيود الاشعة السينية، والمجهر الضوئي، وحسابات مطيافية الأشعة السينية للفوتون الإلكتروني.
الكلمات المفتاحية: الاختزال الكهروكيميائي, جزيئات الذهب النانوية, تقنية المجهر الكهروكيميائي الماسح

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Introduction

Many efforts have been made in the microelectronics sector to substitute metals with Ultrafine Metal Powder [1], when it comes to developing a Conductive paste for printing printed thin film circuits [2]. Metal particles are mixed with glass powder in the thick film technology [3], which is finely divided. The mixture shall then be screened or otherwise applied to the ceramic substrate. The paste will adhere to the substrate when the substrate is fired at a given temperature. Thus, metal nanoparticles in glass matrices are likely to be useful materials for potential applications.

The properties of the designed metal silica particles are dependent on the type of desired application. The main parameters which influence the electrical performance of a complete matrix are particle size, mass distribution and particle shape characteristics in combination with electrical conductivity [4].

Sol-gel is a process for the synthesis of chemicals which was widely applied to the preparation of thin films, inorganic glass, ceramics precursors and powders in relatively low temperatures. Sol-gel is an interesting technique that can be used in combination with other techniques, particularly for the preparation of ceramics and glass materials [5-7]. It is possible to control the distribution of components, as well as the porosity and size of particles.

Powderless processing of glasses, ceramics and thin films or fibres directly from the solution is enabled by the Sol-gel method [8-10]. The precursors are mixed and variously shaped materials can be formed at lower temperatures than those used for traditional methods of preparation.

It's more than 150 years since the Sol-gel method has been taught. The formation of a transparent material by slow hydrolysis of an ester of silicic acid was the first to be reported by Ebelman.

During his work on silica sols, Graham first came up with the term Sol-gel in 1864[11]. This technique has been developed and used in a variety of fields over the course of several decades of research. The material chemistry process is done by the hydrolysis and condensation of metal and nonmetal alkoxide precursors that lead to the formation of solid networks [12-14].

Materials which have been prepared using the sol-gel method yield an excellent mean for the incorporation of various particles such as biomolecules, organic molecules or metal ions for potential application [15-18]. Because of the high purity of obtained materials, silica has been used as a supporting material. During gel formation, the incorporation of species on the glass matrix may be carried out [19-21].

Materials and methods

Materials

All reagents were purchased from Sigma-Aldrich (USA): sulfuric acid, potassium chloride, hydrogen peroxide, tetraethyl orthosilicate (TEOS), p-benzoquinone, potassium tetrachloroaurate, ethanol and hydrochloric acid. Ultra-pure water was used to prepare all solutions.

Preparation of gold ions -doped silica matrix

The hydrolysis of tetraethyl orthosilicate with the presence of gold salt is the most important step for a silica synthesis film treated with gold nanoparticles. A solution of 5 ml of TEOS, 1 mL of water, and 10 mL of ethanol was prepared and 2 mg of potassium tetrachloroaurate (III) was added. Then 0.2 ml of hydrochloric acid (concentrated) was added and the solution was stirred for 6 h. The mixture was left overnight to reach a pre-hydrolysis reaction under lab temperature.

Coating films on microscope slides have been done using a dip coating process. The pre-cleaned microscope slides were immersed in the prepared mixture, withdrawn and rinsed with ultra-pure water.

The cleaning treatment involved first immerse in acetone to remove organic impurities. Then immerse with ethanol and rinse with ultra-pure water.

Then, the microscope slides were immersed in a Piranha solution which consist of (75 ml of sulfuric acid and 25 ml of hydrogen peroxide) to activate the microscope slide surface and assure a good adherence of gold-doped silica into the microscope slide surface. The coated microscope slide surfaces were rinsed with

ultra-pure water and dried in oven using 110°C for 90 min.

The electrochemical reduction of aurate ions

The ultramicroelectrode tip (UME) was moved near the silica-doped film at about 2-3 µm using the approach curve method. 5mM of p-benzoquinone (Q) has been prepared by dissolving 0.135gm in the 250 ml deionized water as the oxidized form of the redox couple. Potassium chloride was used as the supporting electrolyte and hydrochloric acid was added to acidify the medium. The cyclic voltammogram showed that the potential reduction is at -0.25V as shown in figure 1. The UME tip has been biased at a cathodic potential (-0.4 V) vs silver wire and two different biasing times (2 min and 5 min) have been used for reducing gold salt on the microscope slide surface. The p-benzoquinone molecule diffuses toward the surface of the working UME tip as it undergoes electrochemical reduction to generate the reduced form of the redox couple (hydroquinone). The latter, in turn, attacks the gold-doped silica film surface and reduces gold ions to fine nanoparticles as shown in the equations below:

at the UME tip: $3Q + 6H^+ + 6e^- \rightarrow 3QH_2$ 1

at the silica surface : $3QH_2 + 2Au^{3+} \rightarrow 2Au + 3Q$ 2

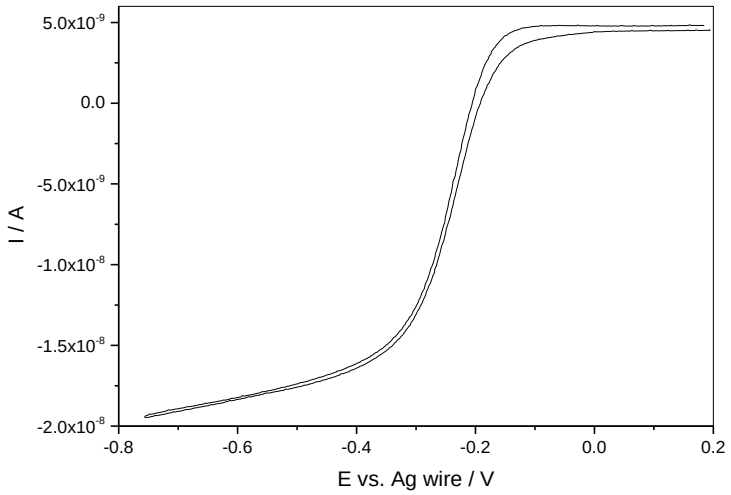

Figure 1. Cyclic voltammogram in acidic aqueous solution containing 5mM of p-benzoquinone in 0.1M KCl at 10µm Pt UME. Scan rate: 50 mV/s.

Characterization

After the electrochemical reduction of the gold ions-doped silica matrix, microscopic and spectroscopic techniques were used to characterize the films to ensure the reduction process was achieved successfully.

Results Microscopic measurements

Hitachi High-Tech's scanning electron microscopes (SEM) model SU3800 and optical microscope (Leica, model MZ10 F) techniques were used to characterize the morphology of gold ion doped-silica film surface which was reduced by electrochemical generation of hydroquinone at the tip of the UME which in turn diffused toward the doped silica film surface. The scanning electron microscope and optical microscope analysis showed the presence of gold spots on the silica film as shown in Figure 2. On the other hand, increasing the time of electrolysis led to generating a high concentration of gold nanoparticles spot.

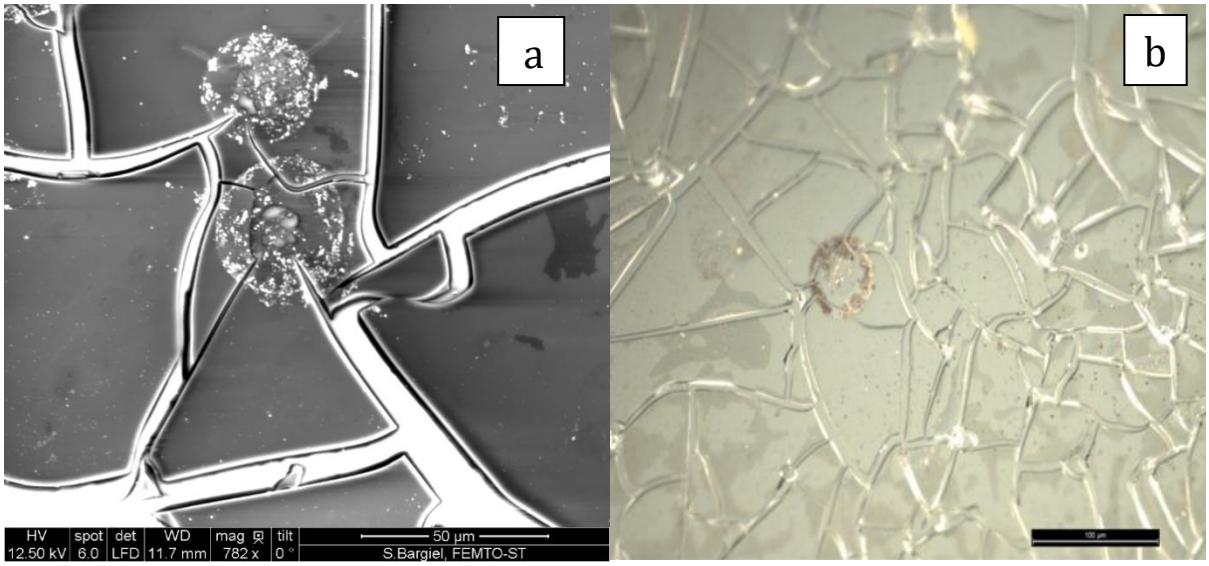

Figure 2. (a) electronic observation (by SEM) and optical (b) for the gold spots obtained by the SECM tip.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron Spectroscopy is a powerful surface analysis technique used to characterize thin films and to determine the atomic composition of gold-doped thin films.

The spectroscopic analysis by using x-ray photoelectron spectroscopy (XPS) Shimadzu Amicus, (Model: ESCA 3400) was able to detect the gold nanoparticles in the range 83-90 eV which corresponds to the 4f peak (Figure 3). In addition, the photoelectron peak of Si has also been observed.

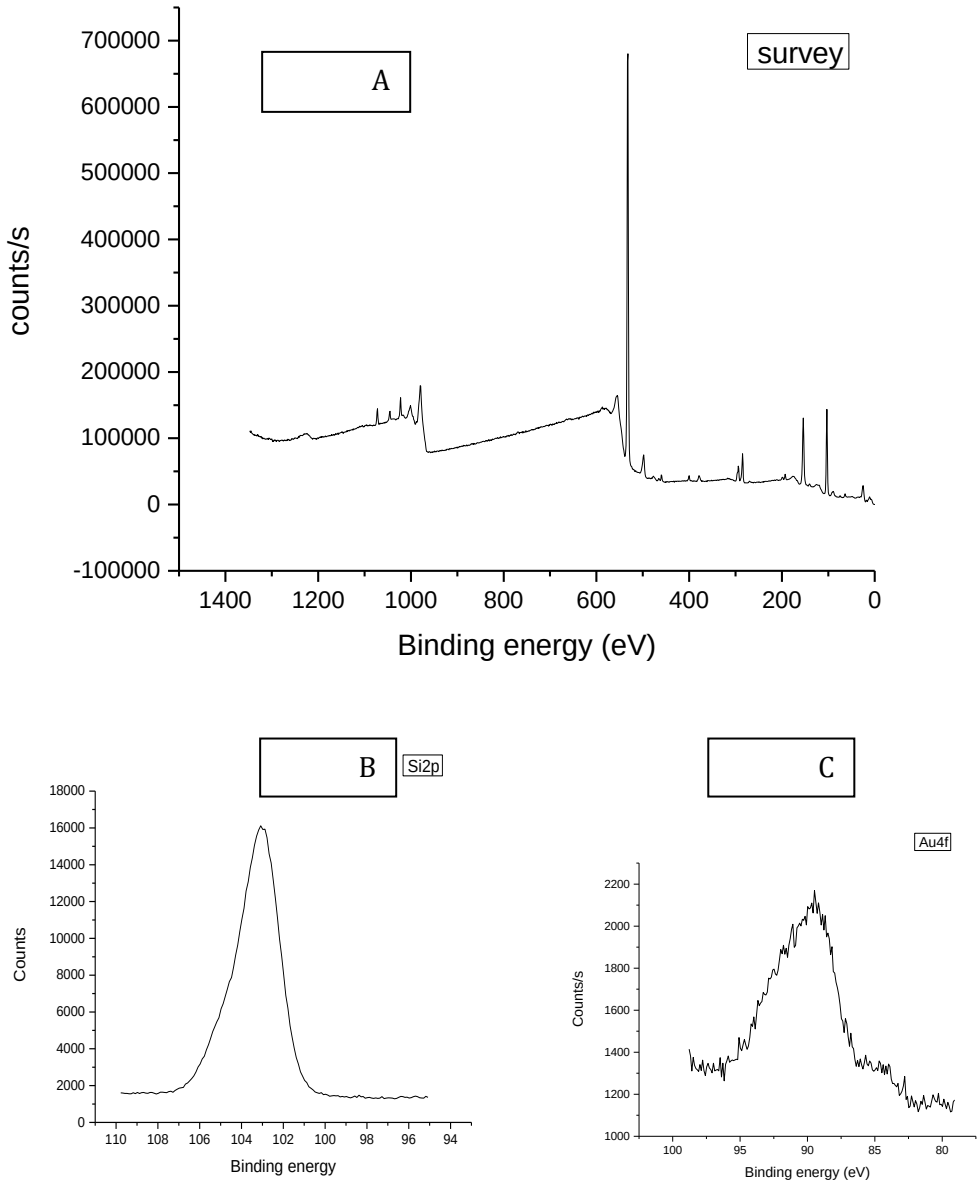

Figure 3. XPS spectrum for gold-doped silica film (a) ,(b) gold photoelectron peak and (c) silicon photoelectron peak.

X-Ray diffraction (XRD)

X-Ray diffraction (XRD) measurements were carried out in the 2□ □range of 30°-100° by using Shimadzu diffractometer employing CuKα radiation.

The X-ray diffraction pattern (Figure 4) has showed clearly the presence of gold nanoparticles at two theta positions 38.2°, 44.4° and 64.7° which derived from the (111), (200) and (220) planes, respectively. The crystallite size of generated gold nanoparticles has been calculated based on XRD peak width and it found to be around 20nm using Scherrer's equation.

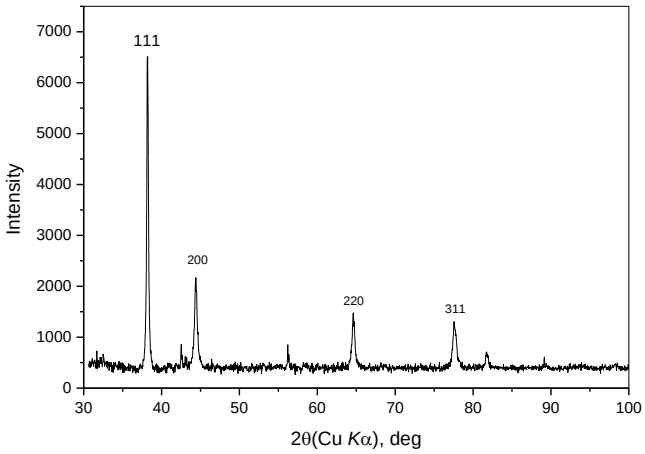

Figure 4. XRD pattern of side doped with gold after cathodic reduction for gold ions.

Conclusion

Composite materials formed by gold ions embedded in microscope slides were achieved by the sol-gel method using an acidic condition. The doped gold ions have been reduced using SECM by using the feedback mode which was recognized as a valuable way for local modification of solid state surfaces. Hydroquinone species were generated at the tip of UME as the reducing agent of gold ions. The pH effect on the reduction of gold ions is an important factor because the protons are involved in the reduction reaction of benzoquinone.

This method has many important advantages. For instance, simple and easy operation, the short time required for reducing the gold ions, and mild working conditions. The size and shape of generated spots depend on the active area and electrolysis time.

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