

Conference paper

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Synthesis by successive ionic layer deposition (SILD) methodology and characterization of gold nanoclusters on the surface of tin and indium oxide films

Abstract: The ability of successive ionic layer deposition (SILD) technology to synthesize gold clusters on the surface of tin(IV) oxide and indium(III) oxide films is discussed. It was shown that during the process, concentration of active sites that are capable of absorbing gold ions, and the size of the gold particles thus formed, may be controlled by both concentration of the solutions used and the number of SILD cycles. Thus, SILD methodology, employing separate and multiple stages of adsorption and reduction of adsorbed species, has considerable potential for customizing the properties of the deposited metal nanoparticles. In particular, it is shown that during the deposition of gold nanoparticles on the surface of tin(IV) oxide and indium(III) oxide films by SILD methodology, conditions can be realized under which the size of gold nanoclusters may be controllably varied between 1–3 nm and 50 nm. A model is proposed for the formation of gold clusters during the SILD process.

Keywords: absorption; Au nanoparticles; characterization; chemical synthesis; deposition; gold; In_2O_3 ; NMS-IX; particles; scanning electron microscopy (SEM); SnO_2 ; successive ionic layer deposition (SILD); surface modification.

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Article note: A collection of invited papers based on presentations at the 9th International Conference on Novel Materials and their Synthesis (NMS-IX) and the 23rd International Symposium on Fine Chemistry and Functional Polymers (FCFP-XXIII), Shanghai, China, 17–22 October 2013.

Introduction

Gold nanoparticles synthesized on the surface of metal oxides attract attention of many researchers because of their unique properties and opportunities to be used in various applications [1–8]. It is known [9–11] that gold nanoparticles (AuNPs) supported by metal oxides become very catalytically active at certain cluster sizes. In particular, for gold nanoparticles deposited on the titanium dioxide surface the sharp increase in reactivity takes place if gold clusters have a size of ~2.5–3 nm [10]. In this case, for example, reaction of carbon monoxide oxidation occurs at an increased rate at significantly lower temperatures than while using conventional catalysts. The nature of this effect in the case of gold is still not clear, but gold nanoparticles have already found

applications in heterogeneous catalysis [12–14] and in bio- and chemical sensors, including gas sensors [15–17]. However, it was established that catalytic activity of gold clusters drops dramatically if the clusters size deviates from optimal one. This suggests that the success of gold clusters using in catalysis and sensor design would be largely determined by the possibilities of technology to form clusters of optimal size on desired surfaces.

Many protocols have been developed for synthesis of different types of gold nanoparticles, varying in size, shape and ligand shell composition. For example, gold nanoparticles can be prepared using various physical deposition methods such as evaporation, sputtering, laser ablation, and discharge plasma synthesis [12, 18]. In particular, these methods were used in the experiments, where gold nanoclusters supported by metal oxides showed high catalytic activity. Methods of deposition from the gas phase such as chemical vapor deposition (CVD) [19], and chemical vapor infiltration (CVI) [20] can be also used for the gold nanoclusters (AuNPs) forming. However, majority physical methods as well as CVD and CVI methods are rather expensive. In addition, they have significant limitations in the formation of clusters on the developed surfaces. Wet chemical methods have no such limitations and that is why they started attracting greater attention. Many of chemical and physical methods, applicable for synthesis and deposition of gold nanoparticles (clusters) with average diameters from 5 to 150 nm, were discussed by Saha et al. [15].

Currently, the method of gold nanoparticles deposition from solutions based on the classic citrate reduction of gold (III) derivatives is the most widely used method of chemical synthesis of gold nanoparticles (Turkevich-Frens method [21]). The Brust–Schiffrin method [22] is another popular method for AuNPs synthesis; the gold (III) derivatives are reduced by sodium borohydride (NaBH_4) in an organic solvent using either a two-phase liquid/liquid system or a suitable single-phase solvent. Hydrophobic gold nanoparticles can be prepared using this method.

However, analysis of the literature showed that as a rule, while using only gold containing salt and reducing agent, only large gold colloidal nanoparticles with size varying in the range from 10 to 150 nm could be reproducibly synthesized [21]. The AuNPs size in this range can be controlled by the ratio between the reducing agents and gold (III) derivatives [the hydrogen/sodium tetrachloroaurate (III)] [23]. During subsequent studies it was found that the reduction of the gold nanoparticles size can be achieved by using physical methods of the particle size control [24–26], including the control of hydrothermal synthesis conditions [27], or by using surface-active additives, which allow controlling the nanoparticles growth process in solution [22, 28, 29]. In particular, for reducing the gold nanoparticles size up to 1–5 nm, one can introduce into solution various ligand molecules, which form self-assembled (SA) monolayers on the nanoparticle surface and thus stabilize nanoparticles. Typical ligand molecules for gold nanoparticles are phosphines, amines, thiolates and other sulfur-containing organic reagents. Among them thiolates are the most investigated ligand molecules. They provide stronger binding of thiol to gold compared with phosphines and amines [8]. Based on these approaches a variety of wet chemical methods have been developed. Many of them are listed in Table 1. From Table 1 it is seen that in the AuNPs synthesis, a chloroauric acid (HAuCl_4) and sodium borohydride (NaBH_4) are the most commonly used reagents.

However, it was found that additives used for the AuNPs size stabilization were the source of sulfur and other impurities. These impurities together with chlorine ions from common precursor HAuCl_4 can be incorporated in the synthesized gold nanoparticles and adversely affect their functional properties. For example, it was established that the presence of chlorine, due to the AuCl_{4-x} complex forming, facilitates surface migration of gold especially during heat treatments [30]. As a result, relatively large gold particles are being formed during synthesis. In other words, if one needed small gold clusters, required for applications in catalysts and gas sensors, the presence of chlorine ions in AuNPs is undesirable. However, in real situation chlorine can be removed only during additional thermal treatment ($T > 300\text{ }^\circ\text{C}$), when gold clusters are already formed. It should be noted that heat treatment at temperatures above $300\text{ }^\circ\text{C}$ is also often required for a complete reduction of gold ions to metal. Ko et al. [31] have shown that the reduction of gold during heat treatment is a typical process for all systems containing gold precipitated from solutions.

One should also take into account that many of indicated above additives such as thiols and others are toxic. Another problem with AuNPs synthesis, which appears when approaches mentioned above are used, is the removal of organic molecules of surfactants from the layer of gold nanoparticles. As a result, there are

Table 1 Brief characterization of wet chemical methods used for synthesis of gold nanoparticles.

No.	Method	Reagents	Comment	References
Gold nanoparticles in solution (colloidal particles)				
1	Turkevich method	HAuCl ₄ ; Na ₃ Cit.	10–150 nm AuNPs. Citrate reduction of gold (III) derivatives	[21]
2	Brust method	HAuCl ₄ ; NaBH ₄ ; dodecanethiol (C ₁₂ H ₂₅ SH); tetraoctylammonium bromide as the phase-transfer reagent	1–8 nm gold NPs. Au reduction in two phase (water-toluene) solution.	[22]
3	Reduction in solution	HAuCl ₄ ; NaBH ₄ ; ascorbic acid; cetyltrimethylammonium bromide (CTAB)	Gold NRods have an aspect ratio of 3.4 with a diameter of 11 nm.	[32]
		HAuCl ₄ ; NaBH ₄	11–80 nm AuNPs	[28]
		HAuCl ₄ ; NaBH ₄ ; and cysteine or cysteamine or cysteamine/PEG-SH for particles stabilization	6–15 nm spherical AuNPs	[29]
4	Schlenk line techniques	HAuCl ₄ ; NaBH ₄ ; octadecylamine; tri-nocetylphosphineoxide (TOPO)	8.5 nm spherical AuNPs	[27]
5	Radiolytic method	HAuCl ₄ ; NaBH ₄	5–10 nm spherical gold NPs	[24]
6	UV irradiation techniques	HAuCl ₄ ; hexadecyltrimethylammonium chloride (HTAC)	10 nm spherical AuNPs or rod-like AuNPs, depending UV irradiation time	[25]
7	Sonochemical method	NaAuCl ₄ ; 2-propanol; ultrasonic irradiation	30–70 nm AuNPs depending on the conditions of synthesis.	[26]
Gold nanoparticles on the surface				
1	Layer-by-Layer self-assembly	Colloid particles by the Brust method	AuNPs on the surface of glass	[33]
		HAuCl ₄ ; NaBH ₄ ; dithiols; and tetraoctylammonium bromide for particle stabilization	6 nm AuNPs (1–8 cycles of deposition) (glass substrate)	[34]
2	Particle self-assembly on Si by Pulling method (one cycle)	HAuCl ₄ (H ₂ O) ₄ ; NaBH ₄ ; cetyltrimethylammonium bromide (CTAB)	3,5 nm AuNPs after one cycle (Si substrate)	[35]
3	Langmuir-Blodgett (LB) deposition	Colloid particles by the Schlenk method	Monolayer of 10 nm AuNPs (SiO ₂ @Si substrate)	[36]
		Gold nanoparticles stabilized by alkanethiolates, alkaneselenides, and alkanetellurides	Monolayer of 2 nm AuNPs (mica)	[37]
4	AuNPs immobilization	Colloid particles by the Turkevich method	60 nm AuNPs (Si substrate)	[38]
5	Sonochemical deposition	HAuCl ₄ ; NH ₄ OH; silica,	5 nm gold NPs (SiO ₂ spheres).	[39]

difficulties with controlling both the cluster size, and the adhesion of coatings formed. In addition, capping agents can also hinder the surface modification for achievement a required functionality of particles for particular applications [40].

With regard to the formation of gold nanoparticles (nanoclusters) on the surface of various substrates, the most application found techniques involving transfer on the substrate of nanoparticles formed in a colloidal solution. For these purposes methods such as self-assembly [33–35], Langmuir–Blodgett [36, 37], and other variations of deposition techniques [38, 39, 41, 42] can be used. Brief description of the methods listed above is given in Table 1. Co-precipitation and impregnation methods can also be used for forming clusters on the surface of metal oxide powders [42–44].

Successive Ionic Layer Deposition (SILD) technology, described in the present article, also refers to the chemical deposition methods and therefore this technique has all advantages of wet chemical methods designed for AuNPs synthesis. In addition, SILD methodology, because of its specificity, has a distinctive feature – the ability to control the particle size; SILD methodology is a multi-step process, wherein the size control of deposited particles can be achieved by multiple repetitions of chemical treatments. Detailed descriptions of this method have been reported [45, 46].

One should note that a similar approach based on separation of nucleation and growth in the particles formation was used by Slot and Geuze [47] and by van Bergen en Henegouwen and Leunissen [48] for the formation of colloidal gold nanoparticles. In particular, van Bergen en Henegouwen and Leunissen [48] have demonstrated that repetitive cycles of chloroauric acid reduction by white phosphorous in the presence of gold particles lead to a controlled growth of the particles in the range of 5–12 nm. It was assumed that the preexisting gold particles acted as nuclei for further condensation of the newly added gold, leading to the observed particle diameter growth.

Thus, the task of present research was to evaluate the capabilities of successive ionic layer deposition methodology to synthesize gold clusters on the surface of metal oxides and control their size. We believe that this problem is of interest, because in spite of the large number of publications, deposition of gold nanoparticles with controlled size on the required surface still represents a great challenge.

Experimental

Synthesis

The main problem of the noble metals synthesis by successive ionic layer deposition methodology, compared with the synthesis of metal sulfide and metal oxide [45, 46], is that the applied layer consists of only one kind of atoms and therefore it is difficult to select conditions for their irreversible adsorption on the second and subsequent cycles of ion layering. However, experiment showed that this problem can be successfully solved by using a water solution of sodium borohydride (NaBH_4) as a reducing agent of gold ions (HAuCl_4). It is known that, upon being mixed, these reagents interact with each other, forming gold nanoparticles by reaction



In Table 1 it is seen that this reaction is used in almost all methods applied for the gold clusters deposition. One of the main advantages of the reducing agent used is that the hydrolysis of sodium borohydride forms products that can also act as strong reducing agents [49]. As a result, the reaction (1) is irreversible and has high reaction rate at room temperature. This means that the reduction of HAuCl_4 with NaBH_4 can take place at room temperature, while the citrate reduction requires boiling of the solution.

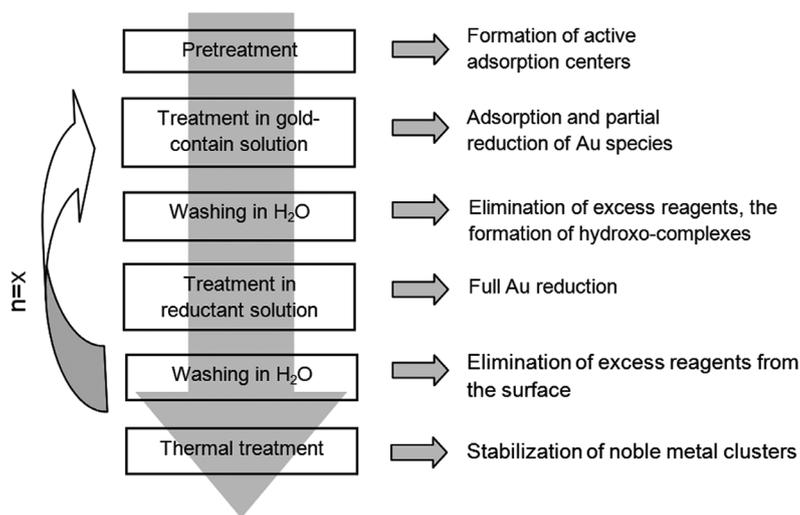


Fig. 1 Schematic illustration of successive ionic layer deposition technology used for Au clusters deposition.

Synthesis of gold nanoparticles on the substrates by SILD technology was conducted using the route presented in Fig. 1. For these purposes we used a special automatic plant described [46]. It contains chemical cups with different reagents, an electro-mechanical drive with a holder for the samples and a control unit on the base of personal computer. Synthesis was attained by the consistent dipping of the sample into the reagents solutions in accordance with a program shown in Fig. 1. In the first SILD cycle a support was treated in a metal salt solution (HAuCl_4) and then samples were washed with distilled water to remove the non-reacted reagents, treated with water solution of NaBH_4 , and again washed in distilled water. Such treatments represent one deposition cycle. For synthesis of gold nanoparticles we used 1–16 SILD cycles.

Gold clusters synthesized by successive ionic layer deposition methodology were deposited on the surface of the tin and indium oxide films. SnO_2 and In_2O_3 are conductive metal oxides promising for gas sensor application [50, 51]. The tin and indium oxide films used in present experiments were deposited at temperatures $T_{\text{pyr}} \sim 350\text{--}550$ °C by spray pyrolysis method using SnCl_4 or InCl_3 water solutions. The features of this process, as well as the SnO_2 and In_2O_3 films characterization were described in [52–54]. Single-crystal silicon wafers (Si:B(100), $10 \Omega\cdot\text{cm}$) were used as substrates for deposition of metal oxides. Immediately prior to synthesis of gold nanoparticles by SILD methodology, a single-crystal silicon substrate with a layer of metal oxides was treated during 15 min in KOH solution (pH ~ 8.0) in order to reach the surface wettability (maximum concentration of the hydroxyl groups).

As the reactants for AuNPs synthesis we have used $\text{HAuCl}_4\cdot n\text{H}_2\text{O}$ with a gold mass content of 49.47 % obtained from Ltd. Aurat (Russia), and NaBH_4 and Na_3Cit obtained from Vekton (Russia). Working water solutions with required concentration of chloroauric acid and sodium borohydride were prepared immediately before synthesis. For preparation of solutions as well as for washing procedure, Milli-Q high pure water with resistivity exceeding 18 M Ω was used.

The choice of precursor concentrations in solutions prepared for the AuNPs synthesis was based on our experience obtained while designing the technology of metal oxides and the noble metal synthesis [45, 46, 55, 56]. In particular, in preliminary experiments concentration of reagents varied in the range of 0.0001 M–0.01 M solution for gold and of 0.001–0.1 M for the reducing agent. Significantly higher concentrations of the reducing agent are required for complete reduction of adsorbed gold ions. Further increase in concentration is undesirable since at higher concentration of reagent a solution has too high pH. Later we have come to the conclusion that in our case 0.001 M for HAuCl_4 solution and 0.02 M for NaBH_4 solution were optimal concentrations of reactants. It has been found that indicated concentrations provided an acceptable process duration required for the formation of gold nanoparticles with desired size. Experiment showed [55] that the treatment time in each solution should be in the range of 0.5–2 min. In particular, in our initial experiments, time of treatment in a solution of a reducing agent equaled 2 min. Duration of the subsequent washing with water and treatment in the gold-contain solution equaled 1 min.

Structure and morphology characterization

Synthesized layers were studied by using scanning electron microscopy (SEM), scanning ion microscopy (SIM), as well as by using X-ray photoelectron spectroscopy (XPS).

Morphology of the films was monitored by using a Philips XL30 ESEM and FEI Nova Nanolab SEM/FIB scanning electron microscopes. SIM investigations were performed with scanning helium ion microscope (HIM) Zeiss Orion. All SEM and HIM images were obtained in a secondary electron detection mode using acceleration voltage 10–30 kV.

Scanning electron microscope Zeiss Merlin equipped with Oxford instruments Inca X-act EDX (energy-dispersive X-ray) detector for X-ray microanalysis was used for characterization of a surface composition. X-ray photoelectron spectra were collected from an ultrahigh vacuum system equipped with the hemispherical electrostatic analyzer Omicron EA125 with the $\text{MgK}\alpha$ line ($h\nu = 1253.6$ eV) for excitation. The O, Sn, In, Au, Cl, and C lines were recorded in detail with band pass energy of 20 eV.

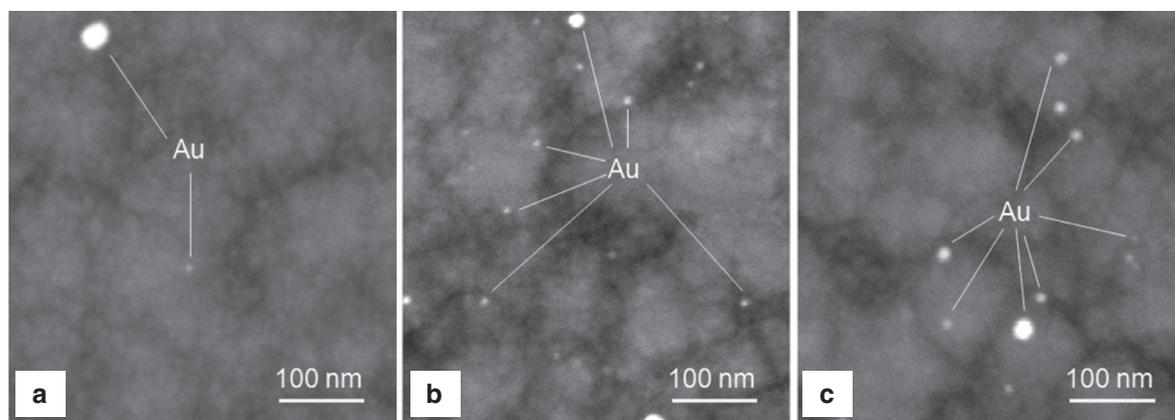


Fig. 2 Micrographs of gold nanoparticles synthesized on the surface of $\text{SnO}_2 @ \text{Si}$ films as a result of one SILD cycles, using different aqueous solutions of reagents: (a) HAuCl_4 and NaBH_4 ; (b) HAuCl_4 and NaBH_4 . Before synthesis substrate was treated in the NaBH_4 solution for 2 min, followed by washing with water; (c) $\text{HAuCl}_4 + \text{Na}_3\text{Cit}$ and $\text{NaBH}_4 + \text{Na}_3\text{Cit}$. Before synthesis substrate was treated in the NaBH_4 solution for 2 min, followed by washing with water. The grain size in the SnO_2 films, used as support for gold nanoparticles, varied in the range 8–10 nm.

Results and discussion

Au clusters characterization

First experiments related to AuNPs synthesis showed that after standard surface treatment of substrates in dilute KOH solution, the deposition of gold, consisting of adsorption procedure from HAuCl_4 solution, washing with water, treatment with a solution of NaBH_4 and washing with water, was not uniform, and the density of gold clusters was small (see Fig. 2a). On the surface of the films we have been observing only a few gold clusters with non-reproducible sizes.

For this effect explanation one can assume that the synthesis of gold nanoparticles was conducted in conditions when the pH of the equilibrium HAuCl_4 solution (about 2.0) was actually near pH of the isoelectric point (the points of zero charge) of the tin dioxide surface, which, according to [57, 58], is equal to 3.5–4.5. We believe that in these conditions the electrical charge density on a surface has a relatively small value, and this leads to a relatively low adsorption of gold ions. In addition, the amount of adsorption can also be affected by the cation-anion composition of HAuCl_4 solution. Hydro-chemical equilibria in solutions (Fig. 3) were estimated using simulation program HYDRA [<https://sites.google.com/site/chemdiagr/> or <http://www.kth.se/che/medusa>]. From these calculations one can conclude that in HAuCl_4 solution situated in the hydro-chemical equilibrium, only some part of gold ions is in an ionic form and is capable to be adsorbed on the surface. It has been reported [58, 59] that in the HAuCl_4 solution there exist neutral or negatively

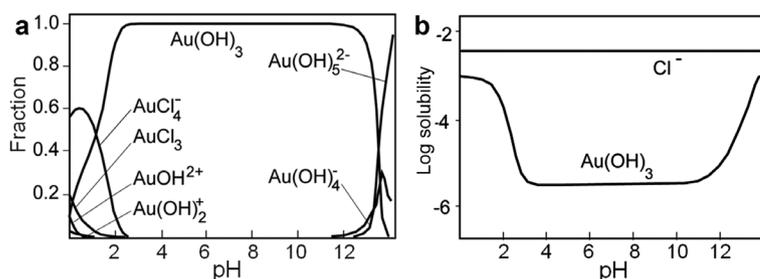
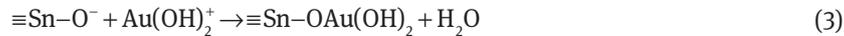


Fig. 3 (a) Relative equilibrium concentration of gold complexes, and (b) log solubility of $\text{Au}(\text{OH})_3$ as a function of the pH of the solution ($[\text{Au}^{3+}] = 0.001 \text{ M}$, $[\text{Cl}^-] = 0.004$).

charged gold complexes of the general formula $\text{AuCl}_x(\text{H}_2\text{O}_y(\text{OH})_z)$, namely, $\text{AuCl}_3(\text{H}_2\text{O})$, $\text{AuCl}_3(\text{OH})$, $\text{AuCl}_2(\text{H}_2\text{O})(\text{OH})$, $\text{AuCl}_2(\text{H}_2\text{O})(\text{OH})$, $[\text{AuCl}_2(\text{OH})_2]^-$, $[\text{AuCl}(\text{OH})_3]^-$, $[\text{Au}(\text{OH})_4]^-$, $[\text{AuCl}_3(\text{OH})]^-$, $[\text{AuCl}_2(\text{OH})_2]^-$, $[\text{AuCl}(\text{OH})_3]^-$, and $[\text{AuCl}(\text{OH})_3]^-$.

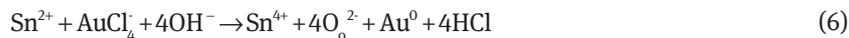
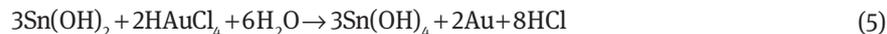
In general, the reactions of gold adsorption (immobilization) at the surface of tin dioxide in water solution at equilibrium pH can be of several types. Some of these reactions with participation of protonated OH-group, negatively charged $\equiv\text{Sn}-\text{O}^-$ -groups, and hydroxyl $\equiv\text{Sn}-\text{OH}$ -groups are shown in (2), (3) and (4), correspondingly.



It has been found [60–62] that point defects such as oxygen vacancies, appearing during partial reduction of titanium dioxide ($\text{Ti}^{4+} \rightarrow \text{Ti}^{2+}$) [62], were the main adsorption centers for gold deposition at the titanium dioxide surface. For example, according to Wahlstrom et al. [60], a single oxygen vacancy at the titanium dioxide surface can bind three gold atoms on average. This means that oxygen vacancy array plays a key role in the binding of gold atoms and small clusters to the surface during the initial stages of adsorption.

SnO_2 can be considered as an analogue of TiO_2 . Therefore, for increasing gold ions adsorption on the metal oxides surface it was suggested to conduct an additional treatment in a solution of NaBH_4 before the first substrate treatment in the HAuCl_4 solution. Sodium borohydride is a reducing agent, and therefore treatment in this solution, due to partial reduction of metal oxides (e.g., to $\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}$), should facilitate an increase in concentration of adsorption centers. The time of treatment in the NaBH_4 solution was 2 min. After this treatment it was applied a substrate washing in water for 1 min. Subsequent studies showed that after treatment in sodium borohydride the number of active centers for the gold sorption really increased. As one can see from SEM images shown in Fig. 2b, in this case the number of gold nanoparticles on the tin dioxide surface, appearing after one SILD cycle, greatly increased. The homogeneity of the gold clusters distribution was also significantly improved. Therefore, this sequence of treatments during successive ionic layer deposition was accepted as an optimal one, and further this sequence of treatments was used for the synthesizing gold particles on the surface of metal oxides (SnO_2 and In_2O_3).

Assuming that a partial reduction of the metal oxide surface really occurs, one can state that in this case the precipitation of gold, for example on the tin dioxide surface after treatment by NaBH_4 , may take place already at the stage of treatment in the HAuCl_4 solution due to a partial reduction of HAuCl_4 by tin ions (II), using reactions (5) or (6):



In the reaction (6) O_0^{2-} corresponds to oxygen incorporated into the tin dioxide lattice.

However, it is quite possible that after metal oxides treatment in the NaBH_4 solution and removal of excess by washing with water, the part of reducing agent remains on the surface in adsorbed form, and then reacts with anions of HAuCl_4 to form gold nanoparticles. This means that after pretreating substrate in the NaBH_4 solution, the reaction of HAuCl_4 reduction, regardless of a mechanism of this process, may occur even when the substrate immerse in a solution of chloroauric acid. It should be noted that the XPS data confirm that gold, precipitated by SILD technology, is in the neutral form (Au^0), i.e., the reduction of gold ions really does not require an additional heat treatment. It is seen in Fig. 4 that binding energies for $\text{Au}4f$ lie in the energy ranges of 84.0–84.2 eV and 87.7–87.9 eV, which correspond to Au^0 [64, 65].

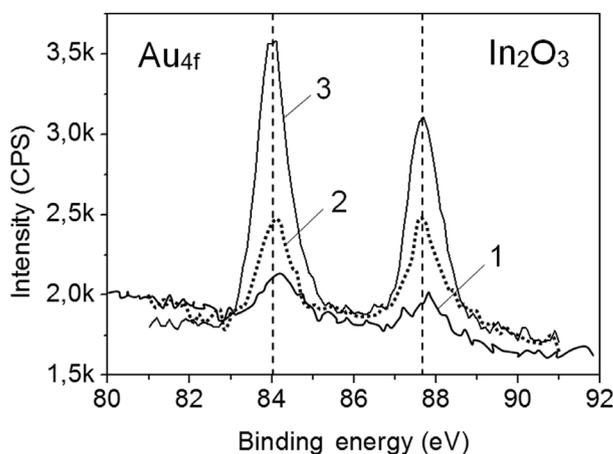


Fig. 4 XPS Au4f core level spectra of the indium oxide films with surface modified by gold clusters deposited by SILD methods: 1- 0.5 deposition cycle; 2- 2 deposition cycles; 3- 4 deposition cycles. (0.5 cycle means that the time of treatments in the HAuCl_4 and NaBH_4 solutions was reduced 2-fold in comparison with usual route.)

Furthermore, X-ray photoelectron spectroscopy (Fig. 5) as well as data of energy-dispersive X-ray (EDX) spectroscopy (Fig. 6) indicated that the surface of samples contained only gold, tin, oxygen and carbon elements. This means that gold clusters do not contain chlorine and sodium, which present in the solutions used. The absence of chlorine is a good indication of the effectiveness of the washing procedure used in SILD process. This feature is a great advantage of successive ionic layer deposition method, because the removal of the reactants excess and the reaction products takes place already during deposition, in contrast to other methods of chemical deposition discussed in the Introduction.

Regarding the effect of heat treatment at 400 °C on gold clusters synthesized by SILD methodology, the SEM study showed that after such treatment in the air for 30 min the particle size almost did not change; only the contour of the particles became clearer and agglomeration of contacted clusters took place (see Fig. 7). This means that major changes in the structure of gold clusters occur already at the stage of deposition; and subsequent heat treatment has no significant effect on the structure of the already formed gold nanoparticles.

The influence of the number of deposition cycles on the XPS spectra and images of gold nanoparticles is shown in Figs. 4 and 8a, correspondingly. X-ray photoelectron spectra presented in Fig. 4 testify that repetition of deposition cycles is being accompanied by an increase of the gold content at the metal oxide surface. Moreover, the change in the intensity of the Au4f peaks corresponds to the variation of the number of SILD

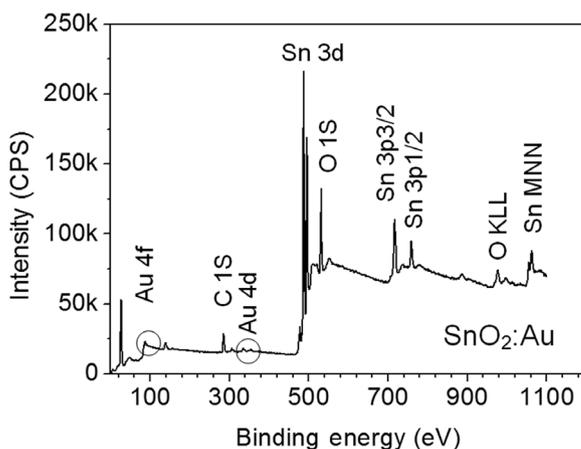


Fig. 5 Full-range XPS spectra of the tin dioxide films modified by gold clusters deposited by SILD method (8 deposition cycles).

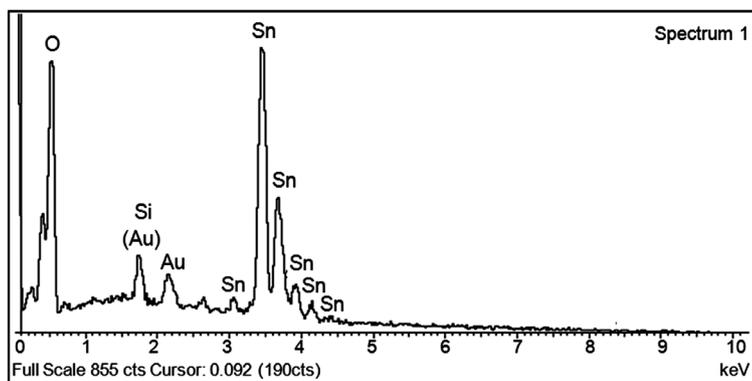


Fig. 6 EDX spectra of SnO_2/Si modified by gold nanoparticles using 3 SILD cycles.

cycles. However, this dependence is somewhat different from linear one. The growth of the intensity of the Au4f peaks is enhanced with increasing number of deposition cycles.

Comparison of images shown in Figs. 2 and 8 also indicates that the size of gold clusters on the surface of the tin and indium oxide films increases with the number of deposition cycles. This proves that at one hand, the growth of coatings takes place through the growth of clusters, and, on the other hand, that successive ionic layer deposition technology is capable to control the size of gold clusters. For example, if, after one cycle of deposition, when treatments in the HAuCl_4 and NaBH_4 solutions were used, the cluster size was up to 8 nm, then after three deposition cycles the size of biggest gold clusters was 20 nm or more (see Fig. 8a). Although, as is seen from the cluster size distribution shown in Fig. 9a, even after three deposition cycles the main part of gold clusters had the size in the range of 3–5 nm. But unfortunately, it should be noted that synthesized particles had a large variation in their size, and along with small clusters, clusters with a substantially bigger size presented on the surface. This is a major disadvantage of the method, because clusters with various sizes have different functional properties. However, this situation is typical for almost all methods of the AuNPs synthesis [19], including wet chemical methods. Regardless of the reagents used, polydispersed nanoparticles are being formed.

We have also established that while using proposed technological route for the AuNPs synthesis, the size of gold clusters has been increasing too fast with the number of deposition cycles. Such behavior of gold nanoparticles is not optimal for using in catalysis and gas sensors design. To resolve this problem it was proposed an approach based on the use of chemicals, covering the growing gold particles and preventing their growth [66]. In our experiments, we evaluated the efficiency of this approach for using in SILD technology.

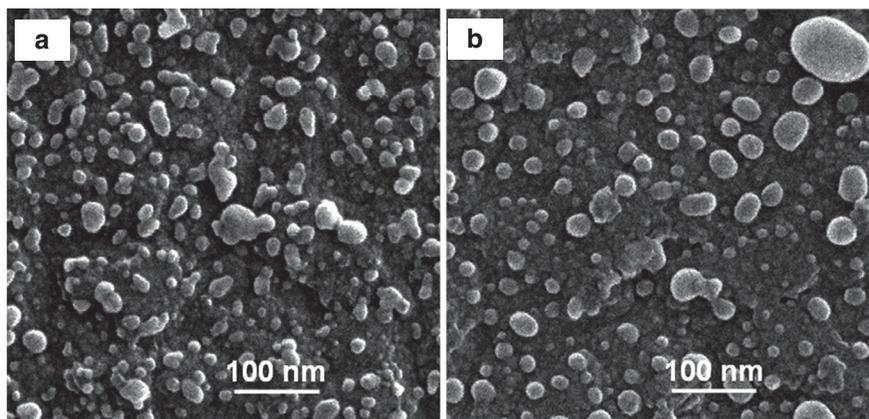


Fig. 7 Micrographs of gold nanoparticles synthesized from water solutions of HAuCl_4 and NaBH_4 on the surface of the SnO_2/Si substrate using 3 SILD cycles: (a) before and (b) after annealing at 400 °C during 30 min.

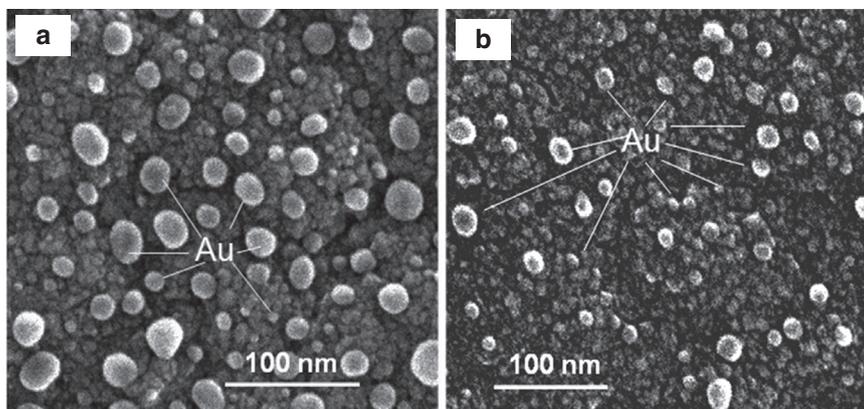


Fig. 8 Micrographs of gold nanoparticles synthesized on the surface of the $\text{SnO}_2@\text{Si}$ substrate after 3 SILD cycles using water solutions of the following reagents: (a) HAuCl_4 и NaBH_4 ; (b) $\text{HAuCl}_4 + \text{Na}_3\text{Cit}$ и $\text{NaBH}_4 + \text{Na}_3\text{Cit}$.

In order to reduce the size of gold particles, we have added trisodium citrate (Na_3Cit) to the solution used for the AuNPs deposition. Na_3Cit ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) was previously used for the same purpose [66]. It was assumed that citrate anions could be adsorbed on the surface of small gold nanoparticles and inhibit their growth during the subsequent deposition cycles. The Na_3Cit concentration in the solution was adjusted to a concentration exceeding in 2 times the concentration of the reagent: 0.002 M in the solution of HAuCl_4 and 0.04 M in the solution of NaBH_4 .

SEM study of the tin dioxide films, modified with Na_3Cit , showed that the addition of Na_3Cit did not provide a significant optimizing effect for gold nanoparticles synthesized during one deposition cycle (see Fig. 2c). Moreover there was deterioration in the uniformity of the clusters distribution on the film surface. Only in the case of increasing the number of deposition cycles, one can observe the expected decrease in the size of clusters synthesized using solutions containing trisodium citrate (see Fig. 8a and b). As it is seen in the size distribution shown in Fig. 9b, a slight increase in the number of clusters with size of 2–5 nm and a strong decrease in the number of large clusters with size exceeding 20 nm were observed while using Na_3Cit during gold nanoparticles deposition. This indicates that the approach developed for the colloidal AuNPs preparation may also be used in SILD technology for forming gold nanoparticles on the surface of substrates. However, as it is shown in Fig. 2c, the uniformity of the clusters distribution on the surface of metal oxides is being deteriorated. In addition, it was found that the morphology of a film, obtained while using surfactants (Na_3Cit), was being strongly changed after heat treatment. Perhaps, the presence of surfactants reduces the interaction of the clusters with substrate (see Fig. 10), and thereby increases their mobility, i.e., promotes the aggregation of growing clusters. Therefore, we decided not to use this approach in our following experiments. In addition, one should take into account that the citrate, which acts as a passivation layer on the surface of

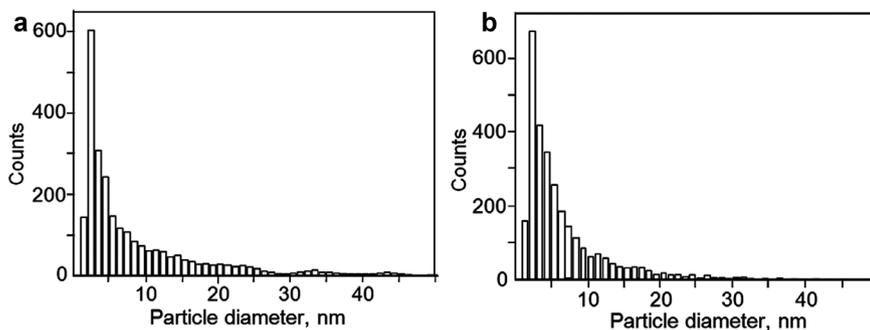


Fig. 9 Histogram of a size distribution of Au^0 clusters on the surface of the $\text{SnO}_2@\text{Si}$ substrate after 3 deposition cycles when using water solutions of the following reagents: (a) HAuCl_4 and NaBH_4 ; (b) $\text{HAuCl}_4 + \text{Na}_3\text{Cit}$ and $\text{NaBH}_4 + \text{Na}_3\text{Cit}$.

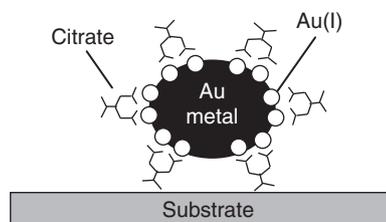


Fig. 10 Schematic view of gold micelle formed in citrate containing solution. When AuNPs are formed, some citrate ions remain strongly attached to Au(I), which is present in Au^0 . (Idea from Stendroff and Herschbach [67]).

nanoparticles, can reduce the effectiveness of the surface functionalization of metal oxides, especially for biomedical applications.

In order to improve the control of the size of gold clusters synthesized by successive ionic layer deposition methodology we decided to reduce the duration of treatment of the substrates with the tin and indium oxide films in the NaBH_4 solution from 2 min to 1 min and in the HAuCl_4 solution from 1 min to 30 sec. In our opinion, these changes should reduce the amount of gold adsorbed during one cycle of deposition, and thus create better conditions for the AuNPs' size control during successive ionic layer deposition process. The last one should be achieved by reducing both the concentration of sites for gold adsorption and the amount of gold involved in the reduction reaction. For these experiments we have used the tin and indium oxide films with a large crystallite size. We believe that while using such films, opportunities of electron microscopy to observe the growth of gold clusters on the metal oxides surface can be realized to a greater extent. SEM images of these films after different treatments, obtained using the instrument (Nova Nanolab SEM/FIB) with better resolution, are shown in Figs. 11 and 12. The results shown in these Figures confirmed our assumptions. The clusters size was being decreased, and we needed more deposition cycles for forming gold nanoparticles with indicated above sizes.

As for clusters with abnormally large size, which are shown on the images in Figs. 12c and 13c, their number is noticeably less than the number of grains. Therefore, those clusters should not have a significant effect on the functional properties of the modified films. Moreover, their appearance and the growth take place especially intensively when the large number of deposition cycles was used. Further research, related to the study of gas-sensitive properties of the tin and indium oxide films, showed that modification by gold, when a large number of deposition cycles were used, is not optimal for achieving high gas sensitivity.

Analysis of the SEM images presented in Figs. 11 and 12 shows that the cluster growth occurs mainly near the tops of the crystallites, as well as within the cavities formed by several crystallites of the base material. This regularity coincides with regularities established for clusters formed on smooth surfaces, where the growth or accumulation of gold clusters first at all takes place at the step edges [11, 68, 69]. It is known that in these places the substrate atoms have the largest number of uncoordinated bonds. In particular, according

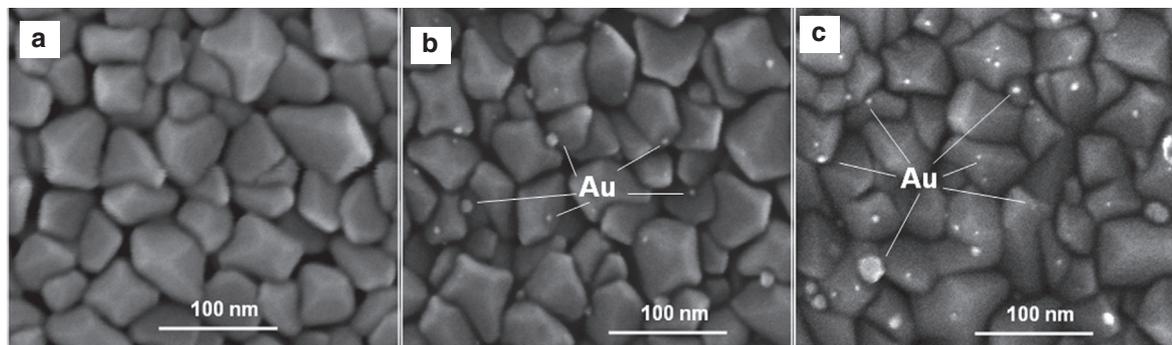


Fig. 11 SEM images of the indium oxide films modified by gold clusters deposited by SILD methods: (a) – initial; (b) – 2 deposition cycles; (c) – 4- deposition cycles.

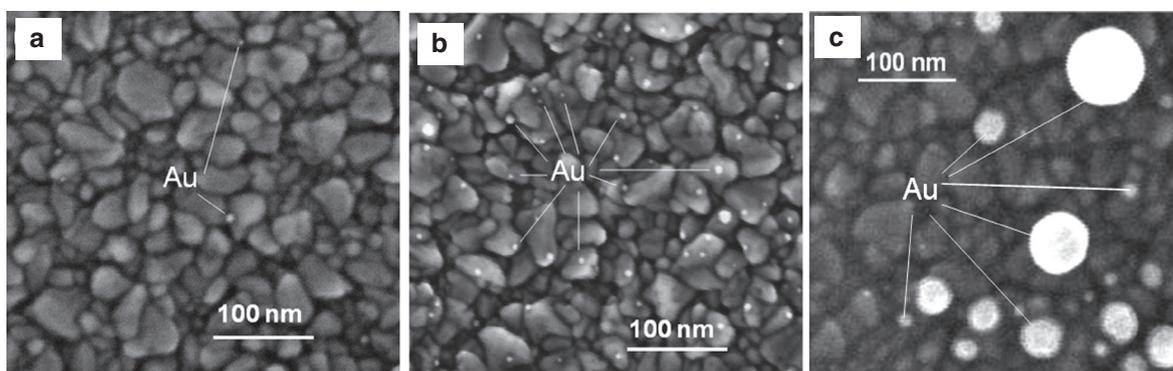


Fig. 12 SEM image of the SnO_2 films deposited by spray pyrolysis and gold-modified by SILD method: (a) – 1 deposition cycle; (b) – 4 deposition cycles; (c) – 8 deposition cycles.

to Wahlstrom et al. [60], the step edges of oxide surfaces can be considered as a collection of oxygen vacancies. However, the average size of the clusters formed at the top of crystallites is less than inside the cavities. Apparently, gold nanoparticles in cavities are being formed by aggregating smaller clusters from contiguous crystallites.

In the SEM images it is also seen that after 4 deposition cycles almost each crystallite contains 1–2 gold clusters. This confirms our assumption that the formation of 3D clusters occurs by aggregating 1D clusters from the whole surface of crystallographic planes, facing the crystallite. The average sizes of gold clusters, formed on the surface of the tin and indium oxide films (Figs. 11 and 12) are given in Table 2.

On the X-ray photoelectron spectra of the films after modification using 0.5 deposition cycles one can see that gold presents on the surface of the films (see Fig. 4). However, we observe nothing on the SEM images. This indicates that the size of gold clusters formed on the grain surface is less than resolution of the microscope used. According to our estimations, in this case the 1D gold clusters should have a size $<2\text{--}3$ nm. One should note that gold clusters at initial stages of growth on a flat TiO_2 surface during thermal evaporation have a size in the range from 1 to 5 nm [70].

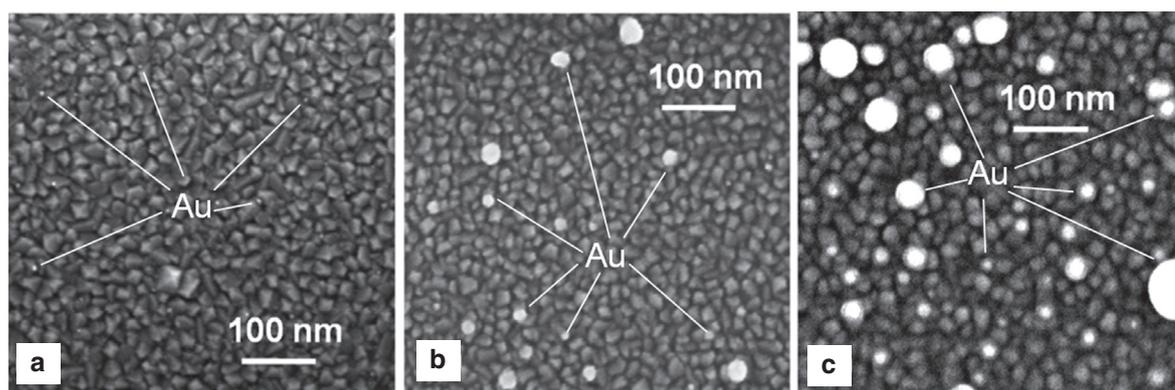


Fig. 13 SEM images of the In_2O_3 films modified by gold clusters deposited by SILD methods showing transpormation of big gold clusters: (a) – 1 deposition cycles; (b) – 4 deposition cycles; (c) – 8 deposition cycles. Bright spots are gold clusters.

Table 2 Average sizes of gold clusters formed by SILD methodology on the surface of the SnO_2 an In_2O_3 films.

Metal oxide	Grain size	Number of SILD cycles	Number of SILD cycles				
			0.5	1	2	4	8
SnO_2	10–30 nm	Average size of AuNPs, nm	$< 2\text{--}3$	3–6	4–7	5–10	10–30
In_2O_3	25–50 nm	Average size of AuNPs, nm	$< 2\text{--}3$	4–7	4–10	15–30	40–70

One can see from data presented above that gold clusters formed on the surface of the SnO_2 and In_2O_3 films by successive ionic layer deposition methodology have a size in the range of nanometers, corresponding to the maximum catalytic activity of these clusters [10], and this size can be controlled by the number of deposition cycles.

Model of the gold clusters growth

It is significant that the formation of clusters and no uniform continuous coatings is a common feature of all methods of noble metals deposition, especially conducted at temperatures exceeding 20–50 °C [63]. Typically, deposition of noble metals occurs through several major stages such as the formation of an atomically dispersed coating with its subsequent transformation into a 1D, 2D and 3D clusters. Basing on the conclusions made in [63, 68, 70, 71], we have assumed that the formation of gold clusters during SILD process takes place according the same mechanism. A simple model that describes the observed evolution of the gold nanoparticles morphology during SILD technology is shown in Fig. 14. This model explains the formation of the Au^0 nanoparticles at the surface of the SnO_2 films by distinguishing four stages. At the first stage, there is a formation on the tin dioxide surface of active sites, which appear in the process of treatment with a reducing agent due to the partial metal oxide reduction ($\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}$) [72]. At the next step of reaction, neutral or charged gold complexes interact with these surface centers, forming an atomically dispersed coating or array of the 1D Au^0 clusters. Further, these clusters-nucleuses become the centers of the growth of gold particles, which, after reaching a certain size due to migration on the surface and cluster-cluster aggregation,

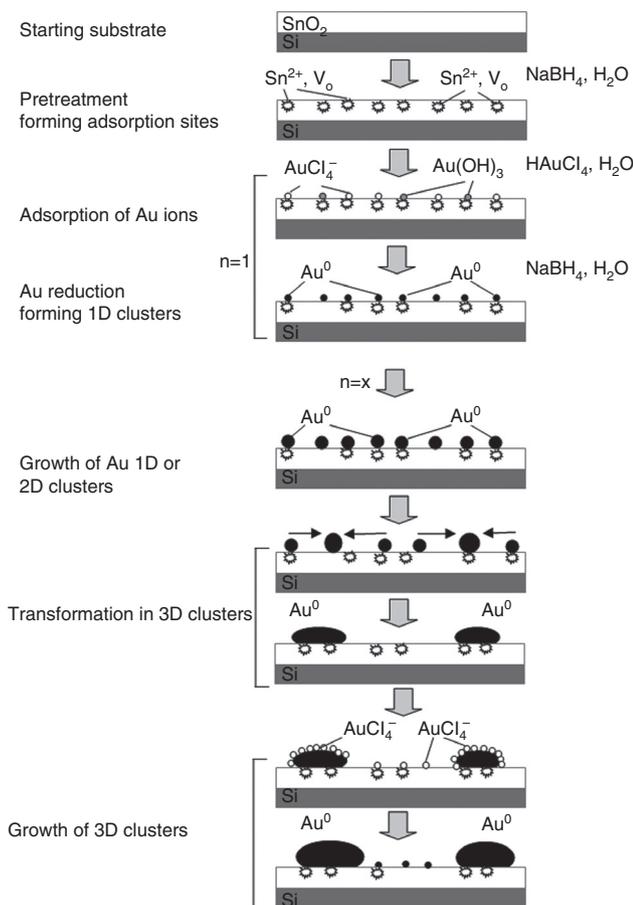


Fig. 14 Model of the formation of Au^0 nanoparticles on the surface of the SnO_2 films during the SILD process.

are being transformed into the 3D clusters. According to estimations made for gold clusters formed at room temperature at the surface of single crystal by thermal evaporation, the critical cluster size for this aggregation mechanism lies in the range from approximately 1.3 nm to 2.1 nm; such clusters contain from 5 to 7 gold atoms. Description of possible mechanisms of the clusters aggregation has been reported [73, 74]. Further, the growth of the gold coating on the film surface takes place mainly through the increase of these 3D clusters.

It is important that the regularity of the gold clusters growth established by us, is also typical for the process of the colloidal particles formation [75–78]. For example, it was found that during reduction of chloroauric acid, the growth of the gold colloidal particles occurs relatively slow, until it achieves some critical dimension (about 2 nm). After that these particles become condensation nuclei for further reduction of gold ions and the growth of gold nanoparticles is being greatly accelerated.

To explain the effect of accelerated growth of gold clusters, one can suggest several hypotheses. For example, it is known that the reaction of sodium borohydride hydrolysis takes place in aqueous solution [49].



It is seen that in accordance with this reaction, hydrogen is one of the products of the reaction of borohydride decomposition. Hydrogen can then be absorbed or adsorbed by gold clusters through a dissociative pathway [79, 80], and further participate in the reduction reaction of gold during subsequent treatments in HAuCl_4 . In other words, a decomposition of the reagent (NaBH_4), happening on the surface of gold clusters, should stimulate the adsorption and reduction of gold ions. This means that this process should promote predominant gold deposition on already formed gold clusters compared with the surface of metal oxide free from clusters. Electron exchange between gold cluster and metal oxide, which can be accompanied by both spontaneous and electrochemically driven deposition processes [galvanic displacement reaction such as (8)], may also contribute to a predominant gold deposition on gold clusters [81].



However, it seems that the most realistic explanation is based on a model of a two-step process of nucleation and subsequent growth of colloidal metal nanoparticles. Experiment showed that the redox potential in the $M_{\text{ion}}/M_{\text{atom}}$ and $M_{\text{ion}}/M_{\text{particle}}$ systems becomes more negative compared with a bulk metal [82–86]. For example, the redox potential in the $\text{Au(III)}/\text{Au}_{\text{bulk aq}}$ system is +1.5 V relative to the normal hydrogen electrode (NHE). But for the $\text{Au(III)}/\text{Au}_{\text{atom aq}}$ system, electrode potential is –1.5 V relative NHE, and for the $\text{Au(III)}/\text{Au}_{\text{particle aq}}$ system the redox potential has some intermediate value [87]. This means that the formation of atomic metal from ion is much more difficult because of the large negative potential in the $M_{\text{ion aq}}/M_{\text{atom aq}}$ system. In other words, the rate of the growth for clusters with bigger size is higher. That is why, in our opinion, the increase in the number of deposition cycles leads to an increase in the dispersion in the cluster sizes, and gold clusters with abnormally large size start dominating at SEM images.

Meanwhile, it should be noted that the above described process does not exclude the formation of new active centers [88, 89], and therefore, the appearance of new gold clusters on the free surface of the metal oxide (see last scheme in Fig. 14). This means that under certain conditions, the clusters may have a bimodal size distribution. But we have to recognize that if there is a heat treatment, such a condition is unlikely because of the high mobility of gold clusters at elevated temperatures.

From the proposed model (Fig. 9), indicated above transformation of Au^0 nanoparticles from 1-D clusters to 3D aggregates supposes that Au^0 clusters can migrate along the surface of metal oxides. Studies of Carrey et al. [68] and Santra et al. [70] have shown that gold clusters really have high mobility. In particular, Carrey et al. [68] have established that the diffusion of small gold clusters on the amorphous alumina surface can be faster than the diffusion of atoms. Also, Santra et al. [70] have found that gold clusters on the flat planes initially grow two-dimensionally to a critical diameter, after which 3D thickening of the cluster begins. This means that coalescence of gold clusters really can start indeed when the clusters reach a certain size, as it was assumed in our model. The same conclusion was made by Matolin and co-workers [10, 90], while studying the formation of the palladium clusters. It has been shown that during the initial period of Pd deposition

the formation of atomically dispersed coating or 1D clusters takes place, and only when a certain degree of surface coverage is achieved, the transformation of 1D or 2D clusters in 3D particles occurs. According to [71, 90], this transformation begins at an average clusters size which is in the range of 3–4 nm.

Under this model, the size of 1D clusters formed during the first deposition cycle, apparently, should be determined by the number of adsorption centers formed on the substrate surface during one deposition cycle. This means that with superfluous number of adsorption sites, already first deposition cycle can form the 3D clusters, the size of which may be far from optimal. We believe that we had exactly this situation while using long treatments in solutions of NaBH_4 and HAuCl_4 .

It is clear that the proposed model of gold clusters forming has been greatly simplified. It is known that the process of the surface clustering is structurally sensitive [61, 62, 91]. This means that the size of the deposited clusters would depend not only on the conditions of formation, but also from the surface geometry of modified metal oxides, i.e., from the presence of steps, terrace and facets, size of faceting planes, degree of surface reduction, and others [63, 92]. In particular, we believe that an increase of the area of crystallographic planes faceting the grain should be accompanied by an increase in the size of clusters, which can be accumulated on this surface. In other words, the cluster size would depend on the grain size. The larger the grain size is, i.e., the area upon which the gold clusters nucleate and grow, the greater is the size of the clusters which can be formed on such grains. This means that for the same degree of the surface coverage by gold, the number of clusters will be smaller, while the distance between the clusters will be bigger on the surface of metal oxide films with the bigger grain size.

It should be noted that the results we obtained are consistent with this statement. Gold clusters, deposited on the films with a small grain size, were visually observed only when a large number of deposition cycles was used. As a result, gold clusters readily observed in the SEM images appear primarily on the crystallites with maximum size (see Fig. 12). The same result, indicating that the size of the nanoparticles formed on the surface of metal oxides strongly depends on the grain size, was reported by Frolov et al. [93] for the palladium clusters formed on the surface of the tin dioxide grains. In particular, they have found that if palladium was deposited on coarse crystalline SnO_2 grains with the size of 15–100 nm, clear clustering of Pd into nanoparticles of 5–10 nm is being observed. However, such clustering was definitely absent in the SnO_2/Pd samples with the grain size smaller than 15 nm.

Conclusions

Studies have shown that successive ionic layer deposition technology can be applied for the controlled formation of gold nanoparticles on the surface of various substrates. For example, it was shown that during SILD process, the concentration of active sites on the metal oxide surface and the size of gold particles formed can be controlled by both the concentration of the solutions used, and the number of SILD cycles. Thus, successive ionic layer deposition methodology, employing separate and multiple stages of adsorption and reduction of adsorbed species, has considerable potential for customizing the properties of the deposited metal nanoparticles. In particular, it has been shown that during the gold nanoparticles deposition on the surface of the tin and indium oxide films by SILD methodology, conditions can be realized under which the size of gold nanoclusters may be controllably varied between 1–3 nm and 50 nm. It is important that gold clusters having size in indicated range can be received without using any surfactants. This means that successive ionic layer deposition technology can be used for purposes that require the presence of gold nanoclusters with desired size on the metal oxide surface, in particular in catalysis and gas sensor applications. In addition, our experiment showed that SILD methodology allows synthesizing gold nanoparticles without impurities, even at room temperature, and without additional thermal treatment.

Acknowledgments: This work was supported by the Russian Foundation for Basic Research (grant RFBR № 09-03-00892a), by St. Petersburg State University, Russia (grant SPbGU), by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (2013K000315), by the Korean Sci-

ence and Engineering Foundation (KOSEF) NCRC grant (No. R15-2008-006-01002-0) funded by the Korean government (MSIP), and by Basic Science Research Program through the NRF of Korea funded by the MSIP (2012R1A1A2041564). This work was partly supported by State Program of Republic of Moldova in the framework of scientific project 11.817.05.10F. The study of samples morphology partially performed in Electron Microbeam Analysis Laboratory (EMAL) of University of Michigan, USA and in Nanotechnology Centre of St-Petersburg State University, Russia. The authors are thankful to Prof. J. Scwhank, Dr. X.Y. Chen and Dr. Yu.V. Petrov for providing research assistance and technical advices.

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