Pulsed laser deposition of Au nanoparticles on ZnO nanostructures

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Abstract. Au nanoparticles and ultrathin gold films were obtained on the surface of thin (100 nm) ZnO films on Si (001) by pulsed laser deposition (PLD) at high argon pressure by sputtering a pure gold target with a CL3100 pulsed excimer laser (λ = 248 nm) at room temperature. The dependence of the size and distribution of nanoparticles on the argon pressure (PAr), the power density of laser radiation (j), and the number of laser pulses (N) was investigated. Also, to obtain nanostructures, axial and non-axial deposition was used, where the substrate was located perpendicular and parallel to the plasma torch, respectively. Stable modes of obtaining gold nanoparticles with high uniformity and average size from 4 to 10 nm were demonstrated. The modes of stable and reproducible deposition of ultrathin Au films (23-42 nm) and percolation structures (18-20 nm) were also demonstrated. Thus, PLD is a reliable and flexible tool for obtaining nanoparticles and ultrathin Au films the average size and thickness of which can be predictably controlled by varying the deposition parameters. This technique is well suited for coating with gold nanoparticles the surface of nanostructured materials based on chemically active substances that are particularly sensitive to surface cleanliness, which cannot be coated by standard methods.

1. Introduction

Au nanoparticles are of great interest due to their unique physical and chemical properties. These properties and a number of dimensional physical parameters (mean free path of the charge carriers, De Broglie wavelength, etc.) depend on the size of nanoparticles and are determined by the proportion of surface atoms [1,2]. Bulk gold is inert, but exhibits pronounced chemical and catalytic activity at sizes less than 100 nm [3]. This fact makes Au nanoparticles attractive for catalysis [4-7]. Due to their optical and electrical properties, Au nanoparticles are used in the diagnosis and therapy of various diseases [8, 9, 10], enhanced Raman scattering [11], to increase the efficiency of solar cells [12], nanosensorics [13, 14], etc.

Modern methods of synthesis should ensure the obtaining of nanoparticles not only of controlled size, but also structure. At the moment, there are several methods for the stable production of Au nanoparticles, for example, the method of thermal annealing of ultrathin gold films [15], methods based on sputtering of pure gold in liquids [16], in vacuum. Turkevich method [17], variations of chemical methods based on the decomposition of metal salts [18] under the influence of ionizing radiation [19], microwave radiation [20], as well as usage of various reducing agents such as NaBH4 [21], hydrazine [22], citrate [23]. Also the biological methods based on the so-called "green approach" are known: nanoparticles are synthesized using non-toxic reducing agents [24, 25]. The methods mentioned provide consistent and stable results, but have some drawbacks. For example, to reduce the agglomeration of...
nanoparticles, stabilizers are introduced into the suspension \cite{26}; as a result, in addition to nanoparticles, a number of reaction by-products and complex compounds are formed \cite{27}. Another drawback is rather limited lifetime of obtained suspensions. When applying nanoparticles from solutions and suspensions to the surface of chemically active nanomaterials one may encounter undesirable chemical reactions and contamination of the chemically active surface. For example, it is extremely important to the semiconductor surface to remain clean while using nanoparticles in the gas sensors based on semiconductor nanorods \cite{28,29}. For this reason, it is necessary to use purely physical methods for obtaining nanoparticles for some applications. In this work, Au nanoparticles were obtained by pulsed laser sputtering of a gold target in vacuum. Dependence of size and distribution of nanoparticles on the deposition parameters was shown.

2. Experimental Section
Gold was sputtered by PLD using a CL7100 KrF laser ($\lambda = 248$ nm). The pulse duration was 15–20 ns and the energy of one pulse was 300 mJ. Laser radiation was focused through a transparent sapphire window onto the surface of a rotating target located inside a VCL103 vacuum chamber. A gold disc was used as a target. The vacuum chamber was evacuated to a pressure of 2.5 Pa before argon injection. Thin (100 nm) ZnO films, previously deposited on Si (001) by PLD, were used as substrates. Thin ZnO films (100 nm) on silicon were obtained by PLD with the following parameters of a pure zinc oxide target: substrate temperature 500 °C, $j = 2$ J/cm$^2$, $N = 1000$, oxygen pressure 2 Pa.

During deposition of nanoparticles some parameters of PLD remained unchanged, for example, $j$ (2 or 3.7 J/cm$^2$), target-substrate distance (3.5 cm), preliminary vacuum (2.5 Pa), temperature (room temperature), target rotation speed (~ 90 rps). Variable parameters were $P_A$ and the $N$.

Au nanoparticles were obtained by axial (Figure 1) and non-axial (Figure 2) deposition.

Figure 1. Schematic representation of axial PLD

Figure 2. Schematic representation of non-axial PLD
The images of nanoparticles and ultrathin gold films were obtained using a Zeiss Supra 25 scanning electron microscope; the analysis of the obtained images and correlation with the deposition parameters were performed using the ImageJ and OriginLab software.

3. Results and discussion
A group of samples was obtained on the surface of thin zinc oxide films by PLD. Each sample was obtained with different synthesis parameters such as: \( N \), \( j \), and \( P_{\text{Ar}} \). The images of the deposited nanoparticles obtained using an electron microscope (Figure 3, 4) were processed using the ImageJ software.

**Figure 3.** Au nanoparticles obtained at \( P_{\text{Ar}} = 70 \) Pa

**Figure 4.** Au nanoparticles obtained at \( P_{\text{Ar}} = 100 \) Pa

During the processing, the total number of nanoparticles in each image and the area of each particle were obtained. To simplify the search of particle sizes, all of them were represented as spherical ones. Particles cropped by the edges of the image were excluded from the calculations. To measure thickness of the obtained ultrathin gold films (Figure 5) we used the tools of the standard Zeiss Supra 25 scanning electron microscope software.
In order not to clutter up the text with a large number of figures, we will below present the information obtained in the analysis of the most interesting samples and discuss only the parameters of stable and reproducible preparation of Au nanoparticles.

**Figure 6.** Size distribution of Au nanoparticles for axial PLD with the following deposition parameters: a) $P_{Ar}=100$ Pa, $j=2$ J/cm$^2$, $N = 500$; b) $P_{Ar}=70$ Pa, $j=2$ J/cm$^2$, $N = 500$; c) $P_{Ar}=70$ Pa, $j=3.7$ J/cm$^2$, $N = 250$; d) $P_{Ar}=70$ Pa, $j=3.7$ J/cm$^2$, $N = 150$
Using an axial PLD, isolated Au nanoparticles with good uniformity and high density were obtained at argon pressures of 70 and 100 Pa at $j = 2$ J/cm$^2$ and 500 pulses (Figure 6a, b), as well as at $j = 3.7$ J/cm$^2$ and an argon pressure of 70 Pa at 250 (Figure 6c) and 150 (Figure 6d) pulses. As $P_{Ar}$ increased from 70 to 100 Pa, the nanoparticles grew larger due to their fusion with each other. When $N$ exceeded 350 pulses, percolation structures with a thickness of 18 nm and more were formed due to more intense fusion of particles. When $N$ exceeded 500 pulses, ultrathin Au films with a thickness of 23 nm and more were formed. When $N$ was less than 150, the uniformity of the distribution and particle size deteriorated. The same phenomena happened at $P_{Ar}$ above 150 Pa and below 70 Pa. The most stable and reproducible mode of Au nanoparticle deposition for axial geometry was the mode with the following parameters: $P_{Ar} = 70$ Pa, $j = 3.7$ J/cm$^2$, $N = 250$. In this mode, Au nanoparticles with an average size of 9.06 nm were reproducibly obtained, and the number of fused particles and large agglomerates was minimal. In fact, there were no gold particles larger than 12 nm on the surface of the samples. In more detail axial deposition results are shown in Table 1.

### Table 1. Parameters of axial PLD with good reproducibility

| Ar pressure, Pa | $j$, J/cm$^2$ | Number of pulses | Size of particles/ thickness of film |
|----------------|--------------|-----------------|------------------------------------|
| 70             | 2            | 500             | 6.28 nm                            |
| 70             | 3.7          | 150             | 6.86 nm                            |
| 70             | 3.7          | 250             | 9.06 nm                            |
| 70             | 3.7          | 500             | Percolation 18 nm                  |
| 70             | 3.7          | 750             | Percolation 19 nm                  |
| 70             | 3.7          | 1000            | film 23.87 nm                      |
| 100            | 3.7          | 150             | 7.89 nm                            |
| 100            | 3.7          | 250             | 8.48 nm                            |
| 100            | 3.7          | 500             | Percolation 18 nm                  |
| 100            | 2            | 500             | 4.87 nm                            |

The average particle size was found by fitting histograms in the OriginLab software using a log-normal distribution. Non-axis deposition results are shown in Table 2 in more details.

### Table 2. Parameters of non-axial PLD with good reproducibility

| Ar pressure, Pa | $j$, J/cm$^2$ | Number of pulses | Size of particles/ thickness of film |
|----------------|--------------|-----------------|------------------------------------|
| 70             | 3.7          | 1000            | film 37.35 nm                      |
| 70             | 3.7          | 100             | 4.8 nm                             |
| 150            | 3.7          | 1000            | film 42 nm                         |
| 150            | 3.7          | 100             | 6.35 nm                            |

In order not to clutter up the text, the tables demonstrate only the results that were obtained with good reproducibility. For the axial PLD geometry, it was not possible to obtain reproducible and stable results at a $j = 2$ J/cm$^2$ for $N$ greater or less than 500 in the entire pressure range from 70 to 150 Pa. The deposition mode with increased focusing of laser radiation ($j = 3.7$ J/cm$^2$) turned out to be more stable and made it possible to reproducibly obtain Au nanoparticles at $N = 150$ and 250 pulses and $P_{Ar}$ in the range from 70 Pa to 100 Pa. In this case, the dependence of the average size of nanoparticles on the number of laser pulses (Fig. 7) indicates that the growth rate of particles decreases with increasing pressure.
Figure 7. Dependence of the average size of Au nanoparticles on the number of laser pulses for different $P_{Ar}$.

Figure 8 shows the histograms of the size distribution of Au nanoparticles obtained by off-axis PLD. For this sputtering geometry, axial PLD parameters were used with the most stable and reproducible results. However, with $N > 100$ pulses and $N < 100$ pulses, stable results were not obtained.

Figure 8. Size distribution of Au nanoparticles for non-axial PLD with the following deposition parameters: a) $P_{Ar} = 70$ Pa, $j = 3.7$ J/cm$^2$, $N = 100$; b) $P_{Ar} = 150$ Pa, $j = 3.7$ J/cm$^2$, $N = 100$

Also, at $P_{Ar}$ greater than 150 Pa and less than 70 Pa, the spread of nanoparticle sizes was too large. The most uniform in size and distribution Au nanoparticles were obtained with the following deposition parameters: $P_{Ar} = 70$ Pa, $j = 3.7$ J/cm$^2$, $N = 100$. The average nanoparticle size was ~ 4.8 nm, the maximum size did not exceed 10 nm. About 80% of the particles were between 2 and 8 nm. As the argon pressure rises to 150 Pa, larger nanoparticles up to 14 nm appear, the number of particles from 2 nm to 8 nm decreases to 55%, and the average particle size increases to 6.35 nm.

Thus, PLD is a reliable tool for obtaining Au nanoparticles and ultrathin Au films. The flexibility of this method makes it possible to obtain nanoparticles of various sizes (from 4 nm to 10 nm) and distributions without heating in a high argon pressure by varying $j$, $N$, the deposition geometry, and $P_{Ar}$.
With PLD it is possible to coat structures with chemically active surfaces with nanoparticles when contamination and surface degradation of the active surface that occur with other application methods is critical. It is planned to assess and predict the behavior of the strength properties of such modified surfaces using the mathematical apparatus proposed by the authors in the previous works [30-33].

4. Conclusion
PLD makes it possible to obtain Au nanoparticles uniformly distributed over the substrate surface and exhibit a small scatter of sizes. The modes of stable and reproducible production of Au nanoparticles with an average size of 4 to 10 nm, ultrathin Au films with a thickness of 23 nm and percolation structures (agglomerated particles) with a thickness of 18 nm were revealed. Larger Au particles can be obtained by thermal decomposition of percolation structures and ultrathin Au films in vacuum or in argon atmosphere. The results obtained prove that by means of PLD at high argon pressure, particles of different sizes and with different distributions over the substrate surface can be obtained. Also, specific modes of obtaining structures were demonstrated and the dependences of the average size of Au nanoparticles on the PLD parameters were indicated. Thus, PLD is a reliable tool for reproducible deposition of Au nanoparticles of the required size and can be used in cases where the deposition of particles by other methods can adversely affect the properties of the objects to be coated.

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