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Plasmonic behaviour of sputtered Au nanoisland arrays

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ABSTRACT

The specificity of the formation of Au sputtered nanoisland arrays (NIA) on a glass substrate or on a ZnO thin film doped by Ga is demonstrated. Statistical analysis of morphology images (SEM, AFM) exhibited the Log-normal distribution of the size (area) of nanoislands—their modus A_M varied from 8 to 328 nm^2 depending on the sputtering power density, which determined the nominal thicknesses in the range of 2–8 nm. Preferential polycrystalline texture (111) of Au NIA increased with the power density and after annealing. Transverse localised surface plasmonic resonance (LSPR; evaluated by transmission UV–vis spectroscopy) showed the red shift of the extinction peaks ($\Delta\lambda \leq 100$ nm) with an increase of the nominal thickness, and the blue shift ($\Delta\lambda \leq -65$ nm) after annealing of Au NIA. The plasmonic behaviour of Au NIA was described by modification of a size-scaling universal model using the nominal thin film thickness as a technological scaling parameter. Sputtering of a Ti intermediate adhesive ultrathin film between the glass substrate and gold improves the adhesion of Au nanoislands as well as supporting the *formation of more defined* Au *NIA structures of smaller dimensions.*

1. Introduction

Noble metal nanostructures have been widely investigated in label-free biological sensor applications [1,2] due to localised surface plasmon resonance (LSPR), which is a coherent oscillation of the free electron gas in metal nanoparticles excited by electromagnetic radiation, particularly in the optical range. Trends in the development of plasmonic technologies include efforts to produce Au/Ag nanoparticles of controllable shape, size and porosity with the aim of improving LSPR tunability and of simplifying the technological procedure [3]. Innovative physical technologies have been developed recently, as an alternative to traditional chemical reduction methods for obtaining metal (Au, Ag) nanoparticles: laser ablation/pulsed deposition, electron-beam/nanosphere lithography [4]; thermally induced dealloying and dewetting on pre-patterned substrates by nanoimprint lithography [5], electron-beam [6] and evaporation [7] depositions of Au island films, and sputtering of nanostructured/porous Au films and nanoisland arrays [8–10]. The application of LSPR sensors requires a solid transparent support, e.g., a glass substrate or transparent conductive oxide (TCO) films. ZnO doped by Ga (GZO) belongs to TCO films that have attracted attention due to their nontoxic nature, cost-effectiveness and easy fabrication [11].

Our aim was to simplify the technological procedures of the formation of Au plasmonic nanostructures (island-like shape) directly by sputtering without masking and lithography. The structural, morphological and optical properties of sputtered Au nanoisland arrays (on Corning glass or GZO/Corning glass substrates) were studied and compared to the universal size-scaling plasmon coupling model [12,13]. Moreover, the description of the plasmonic behaviour of sputtered Au NIA is presented by using thin film technological parameters, such as the RF power density and the nominal thickness.

2. Experimental techniques

We used the deposition concept of sequential (cyclic) sputtering [14]: Fig. 1. In this dynamic mode of deposition, the substrate holder rotated under the target. The RF diode sputtering system Perkin/Elmer 2400/8L was used for deposition of GZO films and Au NIA on Corning glass substrates. The nominal thicknesses of Au island films (2–8 nm)—sputtered from an Au target with diameter 203.2 mm at RF power 75–300 W—were determined by a Dektak profilometer. Post-deposition annealing was carried out in the sputtering chamber immediately after deposition (300 °C/2 h) and in an external furnace (air: 500 °C/5 h). The morphology of the nanostructures was analysed by scanning electron

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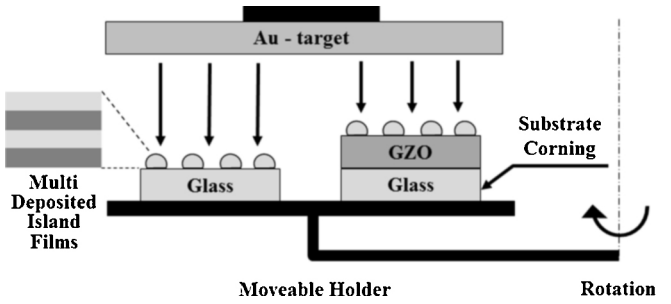

Fig. 1. Schematic layout of sequential sputtering.

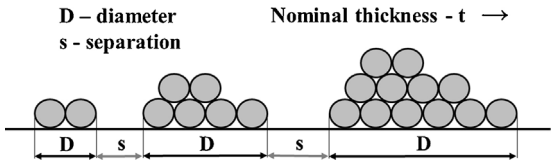

Fig. 2. Schematic model of the early growth stage of sputtered Au island films.

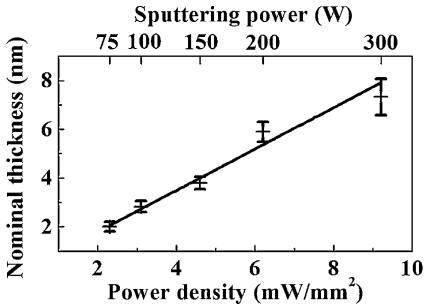

Fig. 3. Nominal thickness of Au nanoisland films vs. RF sputtering power (RF power density).

microscopy (SEM) JEOL 7500F and by atomic force microscopy (AFM) PARK XE 10. Their crystalline structure was investigated by X-ray diffraction (XRD) using the X-ray diffractometer X'Pert Pro with a Bragg-Brentano goniometer and Copper Kα radiation source (λ = 0.154 nm). UV–vis transmission spectra was measured using Ocean Optics 4000 UV–vis Spectrometer in the spectral range 300–900 nm.

3. Results and discussion

We have to point out the specificity of the formation of nanostructures by exploiting early stages of thin-film growth. Sputtered non-continuous island Au films were grown according to the Volmer-Weber model [15]: for the formation of nuclei, clusters and islands and their coalescence, see Fig. 2. The nominal thickness measured by the mechanical Talystep method gives the value that characterises only the "envelope" of the NIA, which implicitly contains data of the amount of deposited material, its distribu-

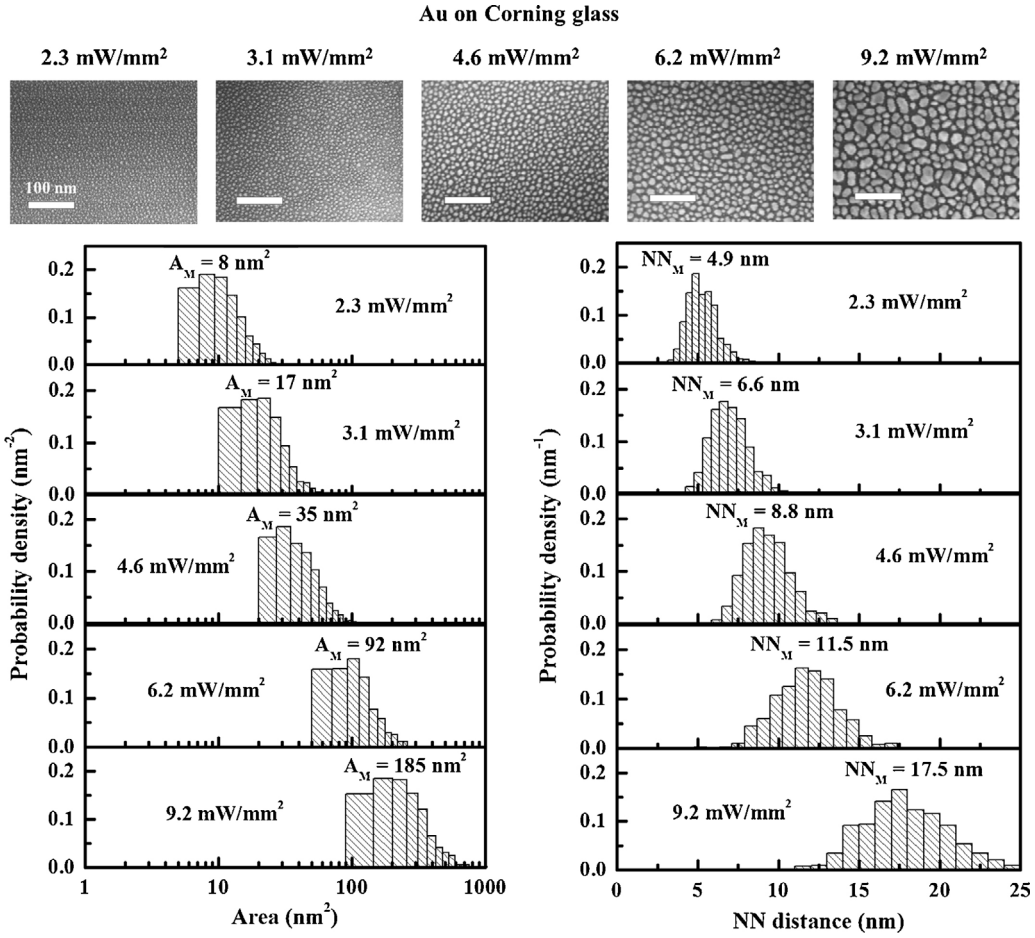

Fig. 4. SEM images of Au nanoisland arrays sputtered on Corning glass substrate at different power densities/nominal thicknesses: 2.3 W/mm²/2.4 nm, 3.1 mW/mm²/2.8 nm, 4.6 mW/mm²/3.8 nm, 6.2 mW/mm²/5.9 nm, 9.2 mW/mm²/7.3 nm; statistical distribution of nanoisland areas and near neighbour distance (A_M and NN_M are the corresponding moduses).

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