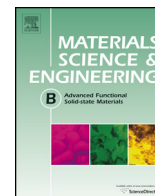




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Formation and characterization of silver nanoparticles embedded in optical transparent materials for plasmonic sensor surfaces

G. Schmidl^{a,*}, J. Dellith^a, H. Schneidewind^a, D. Zopf^a, O. Stranik^a, A. Gawlik^a, S. Anders^a, V. Tympel^b, Chr. Katzer^b, F. Schmidl^b, W. Fritzsche^a

^a Leibniz Institute of Photonic Technology (IPHT), Albert-Einstein-Str. 9, 07745, Jena, Germany

^b Institute of Solid State Physics, Friedrich Schiller University of Jena, Helmholtzweg 5, 07743, Jena, Germany

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ABSTRACT

Plasmonic nanostructures promise sensing capabilities with the potential for ultrasensitive and robust assays in life sciences and biomedicine. Silver island films represent an interesting and straightforward alternative for the implementation of substrate-attached plasmonic nanostructures. The temperature-induced particle-forming behavior of thin silver seed films deposited on glass substrates and on polycrystalline silicon films is represented. The measured extinction spectra reflect the different size distributions and shapes. The covering of the particles with different optical transparent film materials like ZnO, Al₂O₃, SiN_x, and SiO_x leads to a further shift in the resonance maximum due to their refractive index. The SiO_x system shows an additional long term change in the extinction spectrum in contrast to ZnO, Al₂O₃, and SiN_x. Thin silver films covered with Al₂O₃ were used in order to proof the system as a sensor element for analyte detection (glucose solution).

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1. Introduction

The study of nanoparticles (NP) produced by different methods, their fundamental properties, and consequently their numerous applications are of particular interest. Nanoparticles offer a different optical response compared to the same bulk materials and can be produced via chemical reduction processes [1,2], temperature-induced clustering [3–5], during a PVD deposition process [6], via lithographical processes [7], or with the help of Volmer-Weber growth [8–10]. The excitation of localized surface plasmon resonance (LSPR) in particles with different shapes and sizes exhibits a strong optical resonant scattering and an enhanced optical near field, which can be utilized for biosensing applications [11–13]. Because of the nanoscale dimension of individual sensors and the simple optical readout, LSPR based bioanalytic structures represent interesting options for cost-efficient parallel molecular detection, as envisioned for fields such as personalized medicine.

When multiplexing is of concern, particles are usually immobilized on solid substrates, often in an array. Thus, typical problems with solution-based manipulation, such as aggregation, can be avoided. Moreover, processing steps (like washing) are enabled,

and the position of a certain surface modification (of a defined capture molecule) can be encoded in the lateral position.

Gold and silver are typical metals for nanoparticle LSPR sensing. Gold nanoparticles have a decade-long tradition as labels in electron and later light microscopy, also in conjunction with biomolecules. Silver nanoparticles show even more promising optical properties, but their general application is hampered by their lack of stability under ambient conditions. In order to access this potential, passivation approaches have been discussed, in order to protect the particles from the environment (e.g., by embedding them in a shielding matrix). The degradation due to the insufficient temporal stability can influence the extinction spectra with respect to the maximum position as well as the modulation depth of the resonance. The aging of silver nanoparticles in particular by oxidation without – but also after – embedding in a thin film is of particular interest and has already been investigated for SiO₂ matrix films in [14–16].

Matrix materials such as SiO₂, Si₃N₄, ZnO, Al₂O₃, TiO₂, SrTiO₃, Y₁Ba₂Cu₃O_{7-δ}, or optically usable polymers [6,17–26] are utilized to take advantage of their specific electrical and/or optical thin film properties. In the case of embedding, on the one hand, the surrounding material can change the particle properties under the influence of an electromagnetic field. On the other hand, the particles can change the matrix material film properties. The aforementioned dielectric or insulating layers can be applied as conductive oxide by doping or as a pure passivation layer. They

* Corresponding author. Tel.: +49 0 3641 206314; fax: +49 0 3641 206139.
E-mail address: gabriele.schmidl@ipht-jena.de (G. Schmidl).

influence the plasmon resonance of the embedded particles by their different refractive indices, or the particles change the conductivity by manipulating the growth mechanism of the layer.

Thus, such embedded particle systems are of interest not only for plasmonic sensing, but also for electro-chromic devices [27,28] and other applications. Scattering or plasmonic effects based on particles can benefit, for instance, light trapping and are under investigation in thin film solar cells to increase absorbance and thus efficiency [18,29–32]. Furthermore, different plasmonic nanostructures can enhance the electromagnetic field, which may be applied in spectroscopic analysis, photochemical reactions, or bioimaging [33,34]. The change in current conduction mechanisms induced by gold nanoparticles was investigated in [35].

The paper presented here, demonstrates the implementation of silver nanoparticle layers with well-tailored functional plasmonic properties such as clear pronounced and small resonances. We show particle formation by annealing, the impact of different silver particle sizes and distributions, and the impact of matrix layer materials on the resulting optical behavior in order to change or optimize film or particle properties and to understand how deposition parameters influence the properties. In order to show the potential of these layers for future LSPR sensing applications, a change in LSPR could be detected upon changing the refractive index above the protection coating.

2. Materials and methods

For the experiments we used BOROFLOAT® glass substrates with a thickness of 2.8 mm. All substrates were cleaned beforehand via a standard ultrasonic cleaning procedure using acetone and isopropanol. Some of them were covered with polycrystalline (pc) Si produced by deposition of 200 nm amorphous silicon using e-beam evaporation [36,37] with subsequent laser crystallization (cw laser, 808 nm, line focus 12'0.1 mm², $I = 12 \text{ kW/cm}^2$, LIMO GmbH). The beam profile was a top-hat for the long dimension ($L = 13 \text{ mm}$) and a Gaussian for the short dimension (full width at half maximum $d_{\text{FWHM}} = 80 \text{ }\mu\text{m}$).

The silver layers were deposited by thermal evaporation. The deposition was performed in an oil free high vacuum system at a pressure of 2×10^{-7} mbar with a deposition rate of 0.05 nm/s. Samples with 3 nm, 9 nm, and 15 nm silver seed films were manufactured in order to investigate the influence of the seed layer thickness and, consequently, the size, shape, and distribution of the particles as well as the substrate material on the resulting resonance peak position. Close to the deposition process, an annealing process was performed in a furnace in ambient air. Each sample was annealed for 90 minutes at 180 °C in correspondence to [30], but it is well known that temperature, time and seed layer thickness affect the resultant particle sizes and distribution [38,39].

As matrix materials optically relevant layers such as SiO_x, SiN_x, ZnO, and Al₂O₃ were used and investigated. All these compounds were undoped, which means they are electrically nonconductive at low frequencies. These layers were produced via plasma-enhanced chemical vapor deposition (PECVD - SiO_x and SiN_x) and thermal atomic layer deposition (ALD - Al₂O₃ and ZnO) processes at 200 °C, as well as via reactive rf-sputtering (SiO_x). Thus, in the case of SiO_x we can compare the influence of deposition methods. The layer thickness was fixed at 80 nm for the basic experiments. The PECVD process of SiN_x and SiO_x was performed in a Sentech SI 500D system. For the SiN_x, a plasma of silane diluted in He, ammonium, and argon was used. The chamber pressure was 12 Pa and the power of the inductively coupled plasma (ICP) source was 700 W. For SiO_x, oxygen was used instead of ammonium. The chamber pressure was 2 Pa and the ICP power was 500 W. Al₂O₃ layers (1 nm and 80 nm thick, respectively) were deposited with a rate of 0.1 nm/cycle at

$p = 1$ mbar from the precursor gas trimethylaluminium (TMA) and water. The purging gas was N₂ in order to remove the unreacted precursors. The same ALD equipment (Benelq TFS 200) was used for manufacturing ZnO layers (80 nm), but here with a rate of 0.25 nm/cycle. Diethylzinc (DEZ) was applied as the precursor. The thin sputtered SiO_x films were prepared by rf-magnetron sputtering with a power of 50 W. In the vacuum chamber a background pressure below 1×10^{-4} Pa was realized. During sputtering an Ar flow of 20 sccm and an O₂ flow of 10 sccm lead to an operation pressure of 15 mTorr. In addition, the target-substrate-distance of about 80 mm results in a deposition rate of about 2 nm/min.

All deposition and annealing steps were evaluated via scanning electron microscopy (SEM, JEOL JSM-6300F) using the back-scattered electron (BSE) mode (providing a contrast due to the atomic number). Light elements such as Si appear dark; in contrast, heavy elements such as silver appear bright.

For spectral measurements, a UV/Vis/IR spectrometer combined with an integrating sphere (JASCO-V 670) was used. The particle size distributions were determined from SEM images using the image data processing program OPTIMAS 6.51 by Media Cybernetics.

To perform extinction measurements or LSPR shift investigations upon adding of an analyte solution, the matrix layer thickness was reduced and varied from 1 nm to 30 nm in order to ensure a sufficient penetration depth. The optical characterization of the solution-induced shift due to the refractive index change (in our case, aqueous glucose solutions of various concentrations were used as a model substance) is based on optical transmission micro-spectroscopy [40,41] using an immersion objective for liquid detection as described [42]. This method is performed to study individual or a low number of nanoparticles, comparable to the single particle studies conducted in biosensing (e.g., of DNA) [42]. In contrast to the single particle studied in [42], due to the higher surface density only small ensembles of particles could be resolved and, therefore, spectroscopically studied.

3. Results and discussion

3.1. Characterization of temperature-induced Ag particle formation on different substrates

In a first step, we investigated the morphology and optical behavior of the seed silver films in dependence on film thickness. In Fig. 1a (top), SEM images and photographs of these layers on BOROFLOAT® glass are presented. The growth starts with islands (Vollmer-Weber growth mode) for 3 nm of Ag until the islands touch each other and begin to form a 3-D network via coalescence for 9 nm and 15 nm of film thickness [10,43]. By way of explanation, the given thickness value corresponds to the thickness, which a dense film with the same amount of material would have (the amount of deposited material is the value controlled during deposition by means of a quartz microbalance). However, deposited films with a thickness of less than 15 nm do not form a continuous layer. During the annealing process, temperature-induced self-assembling (due to dewetting) is observed for all investigated samples, as seen in Fig. 1a (bottom). More or less isolated islands were generated. In general, solid metal films are unstable in the as-deposited state and dewet or agglomerate to islands when heated below the melting point. This process is driven by surface energy minimization and depends on temperature, annealing time and film thickness. The dependence of thin film dewetting behavior is well discussed in literature [38,39,44,45]. There are described three phases of the dewetting process starting from a continuous film: first, nucleation and hole formation; second, the holes growth and interconnection of islands; and third the formation of separate

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