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Optical characterization of $YBa_2Cu_3O_{7-\delta}$ thin film modified gold nanoparticles

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ABSTRACT

We report on the influence of $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films on the self-organized formation of gold nanoparticles. A thickness variation of the YBCO film allows one to actively control the size of the particles and their density distribution. In this context, the particle forming process is discussed. The YBCO matrix can be removed in order to reduce the particle density on the substrate. The remaining modified particles can be used in plasmonic applications. Combining scanning electron microscopy and dark-field microscopy permits one to identify a correlation of the measured scattering spectra with the physical properties of each studied particle. A clear assignment of spectrum and particle is supported by a new Ti-marker technology and image processing. Growth parameters allow the scientist to tune the spectral peak position of the plasmon resonance and the spectral bandwidth.

1. Introduction

Plasmonic sensors based on metal nanoparticles are a powerful, label-free and newly emerging sensing approach. For bioassays, surface-immobilized particles are preferred, because typical solution based problems, such as aggregation, are prevented. Moreover, the required washing or solution exchange steps are possible without the need for centrifuging or by similar alternative methods. The attachment process of chemically prepared nanoparticles (NP) to the substrates is a complex step in producing NP on surfaces. In order to overcome the complicated and time consuming multiple fabrication steps, a preparation of particles directly at the surface would reduce preparation time and costs. For example, nanoparticles can be prepared directly at the substrate surface by a dewetting process of thin metal films [1–4]. Furthermore, in recent years different multilayer systems have been manufactured with various physical vapor deposition (PVD) methods to produce Au or Ag nanoparticles on surfaces. Embedding nanoparticles in dielectric matrix materials like ZnO, SiO_2, ZrO_2 or TiO_2 have also been investigated in order to utilize the effect of surface plasmon resonances or the plasmonic effect of noble metal particles in general [5–10]. A reason to investigate NPs in combination with an YBCO matrix is the observed influence of the NPs on the persistent superconductivity of YBCO devices [11]. That suggests a correlation or interaction between plasmonics and superconductivity. Since anisotropic nanoparticles promise more efficiency, recently a method for fabrication of anisotropic Au nanoparticles in a crystalline $SrTiO_3$ (STO) matrix has been presented [12]. Compared to nanolithographic methods, bottom-up self-assembly approaches promise a cost-efficient realization of the required metal nanostructures. In previous publications [13–15] relationships between the formation of gold nanoparticles and the $YBa_2Cu_3O_{7-\delta}$ (YBCO) deposition could already be shown. However, in the first optical experiments it was difficult to distinguish between particles and other scattering objects (precipitates) using dark-field microscopy. In this paper, we present a systematic investigation of the plasmonic effects at which the development of a new marker technique provides a clear correlation between scattering spectra and investigated particles on the single particle level. This enables us to use the spectroscopic properties of individual particles with known physical properties (size, shape, etc.), in order to tune the process parameters for the realization of optimal sensor performance.

2. Materials and methods

2.1. Sample preparation

Using magnetron sputtering, a thin Au-layer of 1–10 nm thickness was deposited on STO-substrates which allowed a crystalline

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growth of the YBCO matrix. After heating the samples to 1050 K in an oxygen atmosphere of 50 Pa, a dewetting of the initial Au layers could be observed, leading to a self-organization of crystalline Au nanoparticles [16]. Apart from the Au film thickness, the dewetting process depends on the Au/substrate interfacial energies, partial pressure, temperature and time [17–19]. Subsequently, pulsed laser deposition (PLD) was used to overgrow those particles by an YBCO matrix of variable thickness (here: 50–250 nm). YBCO is well known as a superconducting material, if it is deposited at a specific growth mode. The deposition conditions can influence the growth mode (stoichiometry) which in turn determines the forming particle shape (pyramidal up to spherically) [15]. Standard parameters have been used to induce a *c*-axis orientation of the thin film matrix. The laser was set to a repetition rate of 5 Hz and an energy density of 2.2 J/cm^2 (laser spot size 2–3 mm^2) at the target to guarantee optimum growth conditions and a high crystalline quality (background atmosphere of 50 Pa pure oxygen). A substrate–target distance of 40 mm was found to be ideal for the YBCO film growth of the right stoichiometry. After deposition, the samples were slowly cooled to room temperature at a rate of 50 K/min in an oxygen atmosphere of 800 mbar to induce the orthorhombic YBCO phase. Details for that process can be found elsewhere [15].

YBCO is optically opaque and is soluble in liquids. Hence, it must be removed before analyzing the biomolecules. Exactly this solubility may be used in order to reduce the number of NP which adheres on the surface after having firstly removed the YBCO matrix with the embedded NP. Treating the samples with 1 wt%. citric acid aqueous solution causes dissolution of the YBCO. After about 15 min only a few Au nanoparticles will remain on the substrate since many are washed away. Thus, it is possible to adjust the surface concentration of particles.

Using photolithography, ion beam etching and subsequent Ti sputtering it is possible to prepare marker structures in the shape of a line of a few hundred nm thickness that are labeling regions of interest. It is important that the very same position on a sample could be relocated. The marker material needs to be chosen well, because it has to be resistant to the chemicals utilized in the different processing steps, e.g. citric acid and other chemicals. Moreover, it should be conductive to avoid negative charging effects in scanning electron microscopy (SEM). Consequently Titanium was identified as a suitable material for that purpose.

2.2. *Sample characterization*

In Fig. 1(a) the scheme of sample preparation is presented. The Ti-marker structure indicates the region of interest. In order to examine the nanoparticles on the YBCO-surface, besides SEM, dark-field micro-spectroscopy (DFMS) was used to address the optical properties in the visible spectral region. Instead of measuring an integral signal coming from a large area with many particles, including defects and disturbing objects, we analyzed only a small circular area of about 1 μm diameter with the spectrometer. This region marked by the green spot (dashed circle) is shown in Fig. 1(b). Note that individual nanoparticles cannot be resolved in this dark-field microscope picture, since they are too small to scatter sufficiently and too close to each other. All of the visible, bright dots originate from other objects (i.e. droplets caused by PLD [15], excessive phases or precipitates of the growing YBCO) and is caused by the strong scattering of impinging light due to the large object size. Parts of the Ti marker can also be seen in the left and lower part, which can easily be identified through the strong scattering signal caused by the height difference of Ti and YBCO. SEM pictures of the very same area resolve the Au nanoparticles clearly, as depicted in Fig. 1(c). Now, a semitransparent overlay of both pictures reveals the nanoparticles that were investigated in the DFMS (Fig. 1(d)). This processing is very important for a clear analysis of corresponding single particle properties.

3. Results and discussion

3.1. *YBCO modification of the Au nanoparticles*

Our first focus was on how gold nanoparticles, which were formed after the dewetting process of the gold seed layer and was modified by YBCO matrices of different thicknesses. In order to determine the particle size distribution and density the SEM images of the YBCO surface are analyzed. From previous publications [14,15] it can be seen that the density of Au nanoparticles on the YBCO surface can be reduced by increasing the thickness of the YBCO matrix. This can be explained by the fact that more and more particles are overgrown as the matrix gets thicker. However, it is still unclear how the spatial distribution of the particles as well as the particle size distribution on the surface is influenced by the thickness of the YBCO matrix in detail.

Fig. 2 shows the experimentally determined Au particle distribution of three samples, each with a 5 nm initial Au seed layer covered with an YBCO layer of different thickness. It can be seen that the control group is the blue distribution when no YBCO matrix has been deposited, where the red and green distributions show the effect of applying an YBCO matrix of differing thickness. All distributions can be directly compared, since the data were extracted from equal areas.

The size distribution was calculated via the image data processing program OPTIMAS 6.51 by Media Cybernetics (Rockville, USA) and an in-house ALI-macro (Analytical Language for Images) program using the SEM images. The essential function of the ALI-macro is an object segmentation and classification using thresholds for parameters like the minimal perimeter, the circularity, the ratio of horizontal and vertical Feret diameters to avoid artifacts. The SEM-magnification always ensures a perimeter greater than 10 pixels for the nanoparticles. The diameters of objects in the shown histograms are calculated as diameters of circles with the equal area.

A higher number of gold particles are detected when there is no matrix applied, because they are fully visibly and not obscured by the matrix itself. This is clearly shown by the height of the blue distribution peak in Fig. 2. In this case, it is also observed that the mean particle diameter is smaller and the distribution of different sizes is narrower than in the case of an applied YBCO matrix. Whilst the number of detected gold particles falls significantly with the increase of the matrix thickness, the mean gold particle diameter remains the same at about 80 nm. The smaller number of particles on top of thicker films is in perfect agreement with formerly reported results and can be explained by an ongoing overgrowth process. However, the apparent change of the mean particle diameter, as well of the diameter distribution in presence of a matrix thin film, leads to the conclusion that the particles are not just overgrown and partially lifted to the top of the thin YBCO film but measurably modified by the matrix. Especially a comparison between the 50 nm and the 250 nm thick YBCO films shows some interesting correlations. It is remarkable that both Au nanoparticle size distributions have the very same mean diameter. Also the shape of the distribution function does not change if the YBCO film thickness increases; besides the relative drop in the number of particles no differences can be found. This apparent likeness indicates that particles of all sizes are treated equally, contrary to the possible assumption that small particles might be more easily overgrown during matrix growth and would vanish in thicker films. An increase of the deposition time by 10 min, when comparing a 50 nm YBCO layer (2 min and 30 s) and a 250 nm YBCO layer (12 min and