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ELLIPSOMETRIC CONTROL OF PLASMONIC EVOLUTION AFTER HIGH-TEMPERATURE ANNEALING OF THIN GOLD FILM

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Abstract

Annealing of thin metallic films is well-known to influence parameters of resulting nanoparticles. Metal of the film coalescences into nanoparticles, which size and shape strongly depend on the temperature and time of the annealing as well as materials of the film and substrate, which in turn define the diffusion length, so the number and size of seeds on which nanoparticles grow. High temperature can results in recrystallization of nanoparticles creating faceted monocrystals.

In such a way annealing manages plasmonic properties of the resulting layer of nanoparticles via their size [1] and concentration on the surface [2].

Ellipsometry has demonstrated its ability to record plasmonic properties of system of interests [3] providing both amplitude and phase information. So, the aim of this work is to control by ellipsometry plasmonic properties of layers of nanoparticles created by high-temperature annealing of thin gold films.

1 Experimental

Gold films were thermally evaporated in vacuum of $5x10^{-6}$ torr on glass with gradient thickness due to the corresponding deposition of substrates in vacuum chamber according to the vapour source. Resulting thicknesses were in the range 7-3nm.

Annealing was made by the next protocol: samples were put for 5 minutes into the chamber heated to 190^{0}C and pumped out to 50 torr. After that the chamber was heated with the speed 80^0/min for 7 minutes till 750^{0}C. One portion of samples was kept at that temperature for 1 minutes and the chamber was opened to the air after that. The second similar samples were exposed to the air immediately after reaching of 750^{0}C temperature.

Ellipsometry used for the control of annealed samples measures two so-called ellipsometric angles Ψ and Δ bearing amplitude and phase information [4]. As by definition $tg\Psi=|r_p|/|r_s|$ where r_i are Fresnel reflection coefficients, behaviour of the angle Ψ reflects the excitation of localized plasmons by extremums due to the energy transfer to modes of the system of interest.

2 Results and Discussion

Results for the sample with the thickest film kept for one minute at 750^{0}C are shown in Figure 1. Mass thickness of the film in the shown areas is about 7, 6.7 and 6.2 nm correspondingly. Spectra of Ψ measured at angles of incidences 60^0, 70^0 and 75^0 are shown under the pictures. The arrow indicate evolution of spectra at the change of the initial thickness from 7 to 6.2 nm.

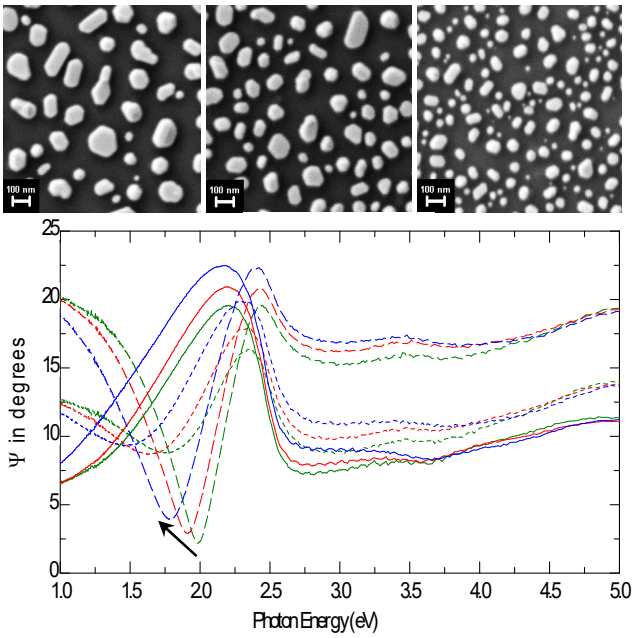

Figure 1 *Pictures of areas with the thickest film and corresponding spectra of Ψ angle.*

It is seen that keeping of annealed film at high temperature results in faceting of nanoparticles, e.i. recrystallisation happens. For thickest film resulted nanoparticles have the size of about 100nm, as for the thinnest area of this sample it is practically twice smaller with noticeably bigger concentration what decreases the separation of particles and correspondingly enhances their interactions. As the result it overcompensates the blue shift of the resonance for smaller particles and the final shift of localised plasmon is red.

Such a behaviour can be proven by simple consideration of the material balance. Total volume of the initial film coincides with the sum volume of resulted nanoparticles. So it can be shown that for the same amount of material the average interparticle distance $a \sim R^{3/2}$ where R is the average size of particles. At the same time there is scaling in nanoplasmonics. Particles polarizability is proportional to R^3 as the near-field of a plasmon is proportional to R^{-3}. It means that if everything is measured in the size of particles, no interaction changes at the system scaling. As in our case at decreasing of the size in two times the interparticle distance decreased in almost three times we have final red shift of the resonance.

Similar results are for the sample without keeping at high temperature, however the size of nanoparticles is about twice smaller and there is no faceting as there was no time for atomic diffusion at high temperature.

The opposite situation is for the sample with the thinnest film. Results for two areas with the mass thickness of about 4.3 and 4 nm are shown in Figure 2.

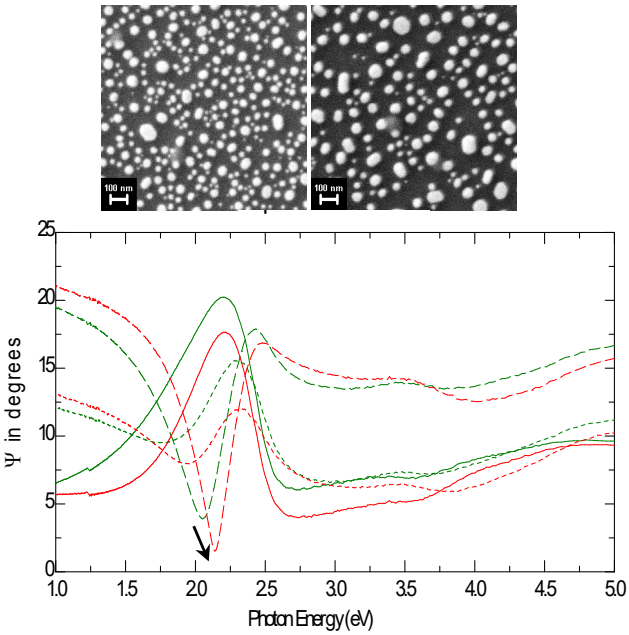

Figure 2 *Pictures of areas with the thinnest film and corresponding spectra of Ψ angle.*

In this case noticeable increasing of the interparticle distances decreases their interactions and we have relative blue shift.

It is worth to note that samples with the mass thickness in the range 5.7-5.3nm give after annealing localized plasmons independent on the initial thickness. The position of those resonances depend on the used annealing protocol. Annealing without keeping the sample at 750^0C produces particles of 30-50nm in size with the localized resonance about 2.4eV. Keeping the sample at 750^0C increases the size of nanoparticles to 100-150nm with much bigger spreading. So the resonance is much wider with the energy about 2.1eV as it should be for bigger particles.

3 Conclusions

Ellipsometry demonstrates that plasmonic properties of annealed films strongly depend on the initial mass thickness of the film. It is interesting to note that general dependence of the resonance with the change of the initial thickness does not depend on the annealing protocol.

4 References

[1] C.F. Bohren, and D.R. Huffman, *Absorption and scattering of light by small particles* (Wiley, New-York, 1983).

[2] Persson B.N.J., Lateral interactions in small particle system, J. de Physique Colloque 44(C10):C10-409-419 (1983).

[3] Bortchagovsky E.G., Mishakova T.O. and Hingerl K., Ellipsometry of layers of nanoparticles with the account of depolarization, Thin Solid Films 571:625-630 (2014).

[4] R.M.A. Azzam and N.M. Bashara, *Ellipsometry and polarized light* (North-Holland, Amsterdam, 1977).