Laser induced spinodal dewetting of Ag thin films for photovoltaic applications

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Plasmonics is a promising approach to enhance light trapping properties of thin-film solar cells. Excitation of surface plasmons is characterised by a strong scattering and an enhancement of the electric field in the vicinity of the metal nanoparticle. These properties can be used to reduce the optical losses due to incident light reflection and to increase the optical absorption within the cell. Absorption can be enhancenced in the required wavelength region by tuning the surface plasmon resonance controlling the nanoparticle's size, shape, and local dielectric environment. Ag nanoparticles obtained by laser induced dewetting of metastable Ag thin films on SiO_2 have been characterized. Size and characteristic patterning length dependency of nanoparticles on film thickness have been determined and spinodal dewetting has been identified as the process responsible for nanoparticle formation. The tunability of the plasmon resonance has been demonstrated through the manipulation of particle size and dielectric environment.

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1. Introduction

With the growing interest for photovoltaics (PV) technologies, many approaches for PV cell design are developed. The most important success criterion is the cost per watt of PV-generated electricity, which motivates a reduction in material utilization facilitated by enhanced optical absorption. In that context metallic nanoparticles are interesting due to plasmonic resonances that can give rise to pronounced optical absorption, field localization, and scattering effects [1]. As shown on Fig. 1, two different examples of reducing the physical thickness of the photovoltaic absorber layers while keeping its efficiency thanks to the use of metallic nanoparticles, can be considered. First, nanoparticles can be used as subwavelength scattering elements which can increase the effective interaction volume of the propagating waves from the sun. Second, an increase of the absorption cross-section in the semiconductor layer can be achieved thanks to the localized field enhancement.

In this study we have obtained Ag nanoparticles due to dewetting upon cw laser annealing. Laser annealing has the advantage to be a reliable and cost-effective technique to process surface nanoscale metallic structures. Conventional techniques for nanoparticle formation utilize high-temperature processing, but these processes are not compatible with glass substrates or thin-film stacked structures usually employed in mass production. The alternative laser annealing technique reduces the thermal budget and allows local processing.

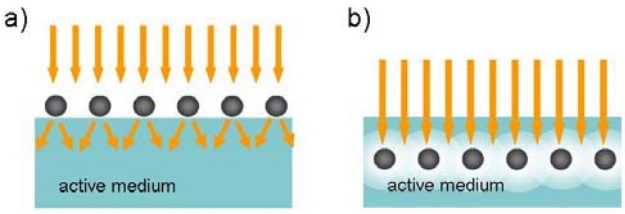

Fig. 1 (a) Schematic of a photovoltaic cell with metallic nanoparticles placed on the surface of the cell. Light is scattered into the semiconductor thin film by the nanoparticles leading to an increase of the optical path length in the cell. b) Schematic of a photovoltaic cell with nanoparticles embedded in the active layer. The excitation of localized surface plasmons in the nanoparticles creates a near-field enhancement which can result in the increase of the absorption.

2. Dewtting of Ag thin films and nanoparticle formation

It is known that metallic films evaporated on glass as a flat film are in a metastable state and dewet upon annealing in the solid as well as in the liquid state. Dewetting of a metastable liquid film can develop via two different mechanisms [2]: nucleation or spinodal deweeting. For the case of nucleation, in general, the growth of holes leads to the accumulation of the material along the perimeter of the holes and to the formation of elevated edges which end up in nanoparticle formation. In spinodal dewetting the instability ruptures the film spontaneously and the characteristic surface modulation length scale is proportional to the square of the film thickness (h) while the particle size scales with $h^{5/3}$ [2,3].

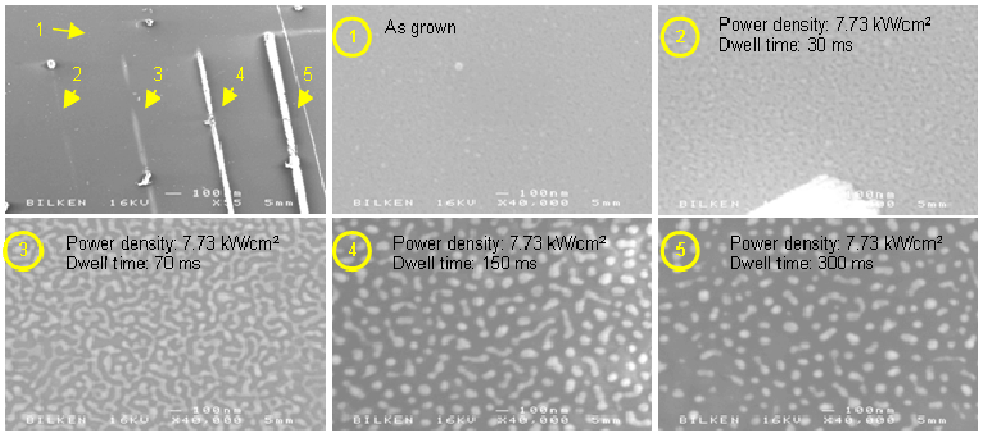

Fig. 2. SEM images of different laser annealing of 11.5 nm Ag layer on SiO_2 with increasing dwell times.

First we characterized the dewetting phenomenon of the silver thin film. Ag films with thicknesses ranging from 10 to 30 nm were thermally evaporated on SiO_2 substrates. The depositions were performed at 10^{-6} Torr and the sample was placed at 25 cm above the source. All the samples were evaporated at the same deposition rate of 1 Å/sec. For the obtaining of nanoparticles, different thickness samples mounted on a translation stage were irradiated by a focused Ar^+ laser beam. Figure 2 shows SEM microscopy images of different lines inscribed by translating the samples under the focused beam with different translation speeds. At the early stage of dewetting (small dwell times) we can notice discontinues wormlike formations which break up to form small particles as the dwell time increases. Figure 3 shows an AFM image and a SEM image of nanoparticles obtained upon laser irradiation of a 10 nm thick Ag layer. The average size of the particles is 70 nm and the height of the particles can be determined from the AFM image giving an average height of 50 nm. We can thus deduce that the shape of the particles is rather oblate.

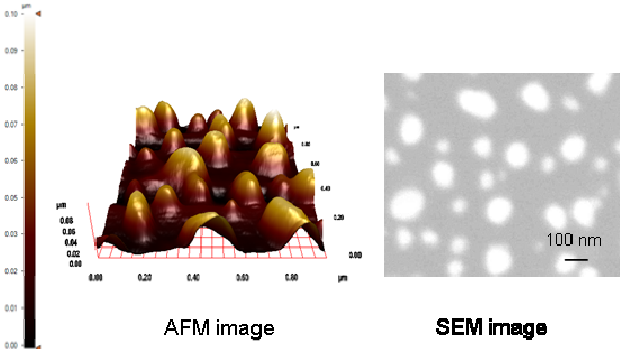

Fig. 3. AFM and SEM images of laser annealed 20 nm thick Ag layer on SiO_2.

The dependency of the characteristic patterning length scale Λ (ie: average distance between particles) and the particle size on the initial film thickness have been verified. On Figure 4 we can see that Λ varies, with a good approximation, as $\Lambda \alpha h^2$ and the particle diameter *d* as $d \alpha h^{5/3}$. This can be taken as evidence for spinodal dewetting as the process responsible for the nanoparticles formation.

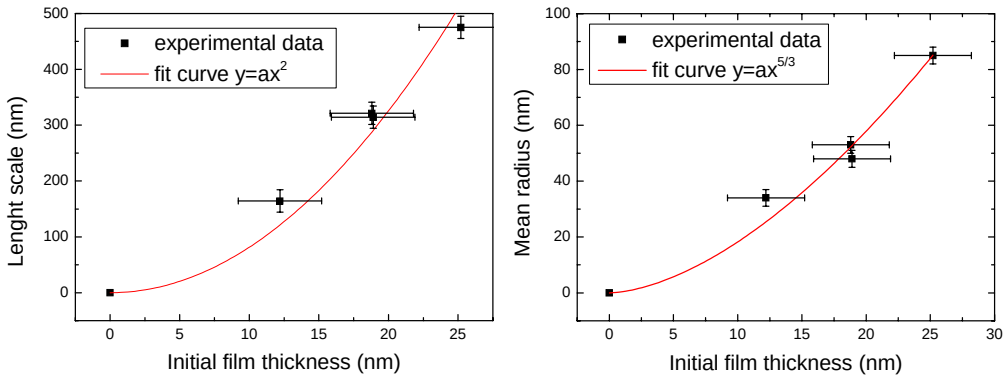

Fig. 4. Characteristic patterning length scale and particles' mean radius obtained after annealing of different thickness Ag layers as a function of initial layer thickness.

3. Resonance properties of ag nanoparticles

After the structural characterization of the nanoparticles obtained by laser annealing, we have investigated the absorption properties of the films. Figure 5 shows the absorbance spectra of different films with Ag nanoparticles of different sizes. When compared with the as-grown Ag layers which have a broad absorbance spectrum, an absorbance peak, related to the surface plasmon resonance (SPR), is seen in the spectra of the nanoparticle films. The SPR frequency can be expressed as [4]:

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1+2\varepsilon_m}},$$

where ω_p is the plasma frequency and ε_m is the permittivity of the medium which can be taken as the average [5] of the substrate and the surrounding medium and can be written as $\varepsilon_m = (\varepsilon_{sub} + \varepsilon_{ext})/2$.

In Fig. 5 we can observe that the resonance peak shifts toward higher wavelengths as the mean size of the nanoparticles increases. Indeed the cross-section for absorption of incident radiation by a spherical nanoparticle is proportional to the particle size and is given by (in the case where the particle size, *a*, is small compared to the incident wavelength) [4]:

$$C_{abs}(\lambda) = \pi a^2 4\left(\frac{2\pi n_m a}{\lambda}\right)\mathrm{Im}\left(\frac{\varepsilon-\varepsilon_m}{\varepsilon+2\varepsilon_m}\right),$$

where a is the particle is the particle radius, ε_m the permittivity and n_m the refractive index of the medium.

Fig. 5 also shows that the absorbance peak gets broader as the particles size increases and, as can be expected, as the size distribution of the particles increases.

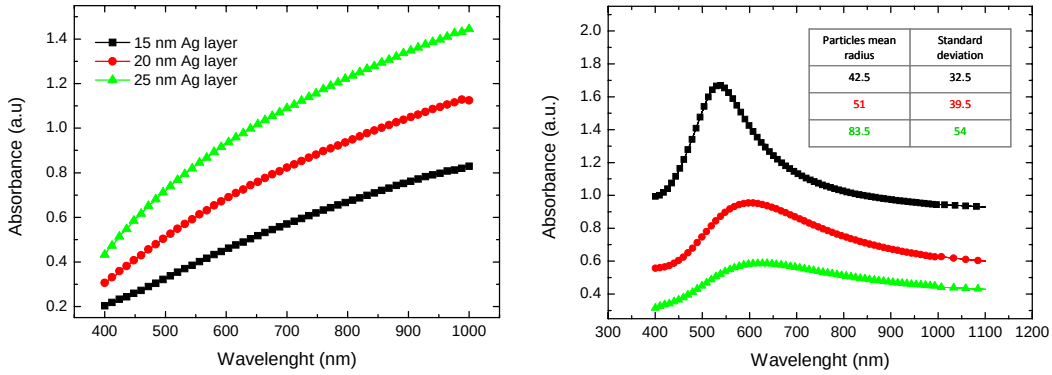

Fig. 5. Absorbance spectra of as-grown Ag layers on SiO_2 (a) and absorbance spectra of the corresponding samples after nanoparticles formation (b).

In addition to the particle size, the dielectric medium surrounding a nanoparticle can also affect its resonance characteristics. Indeed from Eq. 1 it can be seen that by varying ε_m the surface plasmon frequency can be tuned, and that the increase of the permittivity will lead to a red-shift of the resonance frequency. We have fabricated embedded nanoparticles in different dielectric environment by growing on top of the nanoparticles film a cap layer of different refractive index materials as SiO_2, Si_3N_4 or Si. A 40 nm cap layer has been grown on nanoparticles array with a mean diameter of 70 nm. As can be seen on Figure 6, with the increase of the refractive index of the nanoparticles' environment the plasmon frequency shifts toward higher wavelengths. The evolution of the resonance peak position with respect to the refractive index of the local environment can be seen in the inset. The SPR is significantly red-shifted. We also note that, in addition to the red-shift of the SPR, a second order mode appears as the refractive index increases. It is then possible to tune the SPR across the entire solar spectrum by increasing the surrounding medium's index of refraction.

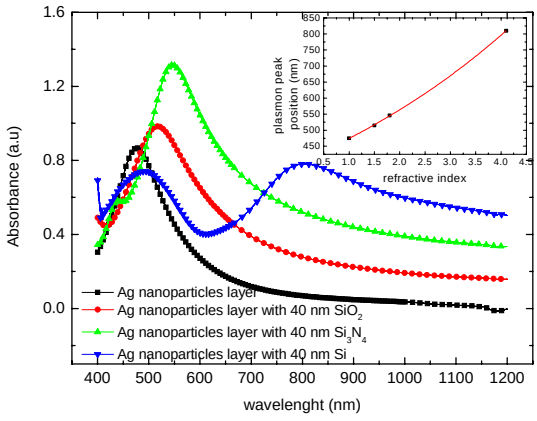

Fig. 6. Absorbance spectra of Ag nanoparticles layer without and with 40 nm cap layers of different index materials.

4. Conclusions

We have demonstrated the formation of nanoparticles using cw laser annealing. Spinodal dewetting has been identified as the process responsible for the nanoparticle formation. Particle size, distribution and surrounding dielectric environment effects on Plasmon resonance have been identified. We have shown that the plasmon resonance frequency can be tuned over an extended frequency range. Thus photovoltaic layers can absorb the full solar spectrum using light trapping through the resonant scattering and concentration of light by metal nanoparticles.

Acknowledgements

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