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COALESCENCE THRESHOLD TEMPERATURE IN Ag NANOISLAND GROWTH BY PULSED LASER DEPOSITION

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Abstract. In this study, Ag nanoislands were deposited on glass and Si(100) at substrate temperature from 25 to 450 °C by Pulsed Laser Depositions (PLD). The growth of Ag nanoislands was evidenced from optical absorption surface plasmon resonance (SPR) bands. SPR peaks was not evidently observed in the spectrum of sample deposited at 25 ºC, but sample deposited at 150 ºC presented a broad SPR peak around λ=870 nm. SPR peak showed a blue shift to 540-550 nm and became narrower as the substrate temperature increases. Atomic Force Microscope (AFM) showed that by increasing deposition temperature to 350 and 450 ºC, Ag islands grow in height and diameter and the number of island decrease among the surface. Two-probe measurement of electrical resistance of films was also recorded during deposition processes to recognize the coalescence of Ag nanoislands. The results show that the deposition at temperatures below 250 ºC leads to a sharp decrease in film resistance while at higher temperatures the islands were separated without resistance decline. To determine coalescence threshold temperature, resistance variation was measured for a cooling substrate, from 300 down to 200 ºC, substrate. The result revealed that the coalescence of Ag begins near 230 ºC.

1. Introduction

Recently, numerous studies have been focused on the deposition of metal films on different substrates, because the layers interface plays an important role in their wide applications such as catalysts, microelectronic and photovoltaic devices. The growth of atomically flat thin metal films is of great importance both scientifically and technologically. However, the formation of three-dimensional islands on a substrate in the early stages of layer growth (Volmer-Weber growth mode) is very common in thin-film deposition processes. On the other hand, recent discoveries in nanoscience and nanotechnology present opportunity for applications of metal thin-films with a nanostructured morphology such as porous layer, nanoparticles and quantum dots of noble metal deposited on insulator or semiconductor substrates. For example, there is growing interest in utilizing the optical properties of silver nanoparticles as the functional component in various products and sensors. Silver nanostructures being used in numerous technologies and incorporated into a wide array of consumer products that take advantage of their desirable optical, conductive, and antibacterial properties[1-5]. Silver nanoparticles are extraordinarily efficient at absorbing and scattering light and, unlike many dyes and pigments, have a color that depends upon the size and the shape of the particle [6].

Different method have been used so far for deposition of Ag thin films on different substrates including sputtering [7, 8] , evaporation [9], chemical vapor deposition (CVD) [10] and pulsed laser deposition (PLD) [11-13]. PLD presents some advantages over other

and become narrower as the substrate temperature increases to 250, 350 and 450 ºC. The low extinction at high wavelength region arises from increasing in transmittance of the films because it will be shown by AFM images that the higher substrate temperature gives a structural open layer in which light will be able to transmit through the particle separating space. Generally, there is a correlation of the peak position, red shift and widening of the SPR with the increase of the mean diameter of nanoparticles and widening of size distribution [11, 20, 21].

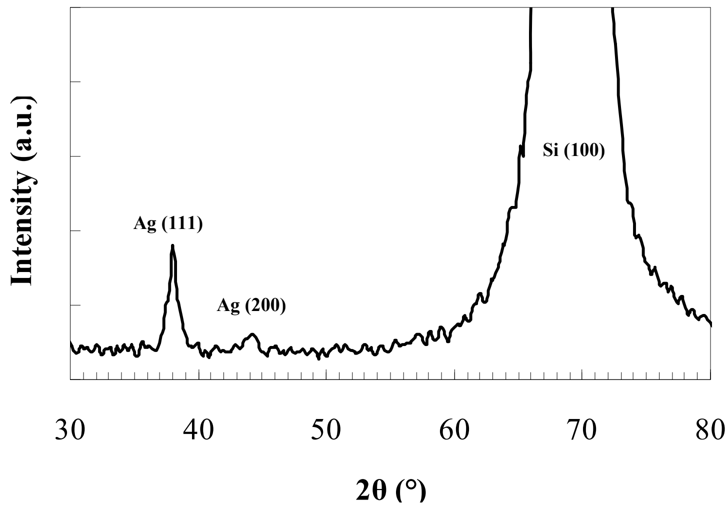

Fig. 1. XRD pattern of Ag/Si(100) deposited by PLD at 450 ºC.

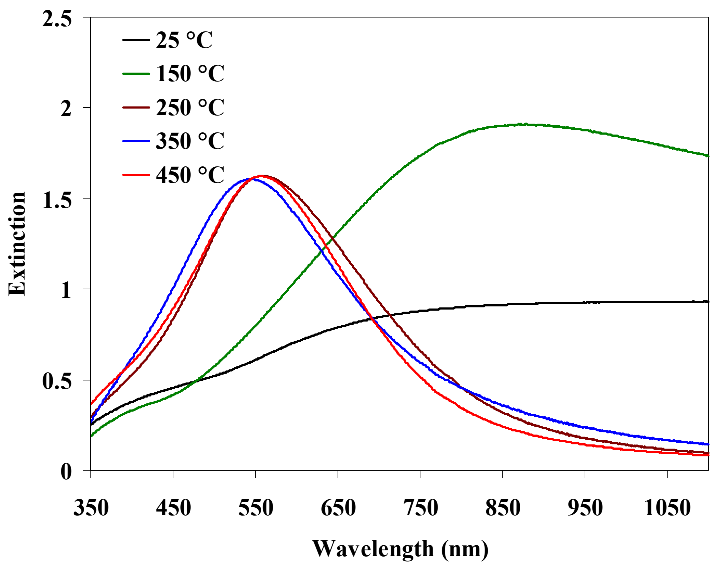

Fig. 2. Optical extinction of Ag/glass deposited at different substrate temperatures, from 25 to 450 ºC. XRD pattern of Ag/Si(100) deposited by PLD at 450 ºC.

In order to have a three-dimensional (3D) view of the Ag nanoparticles and to measure their height the films were analyzed by AFM. 3D AFM images and corresponding z-height distribution histogram of Ag/Si(100) deposited at different substrate temperatures are shown in Fig. 3. As figure shows, sample deposited at 150 ºC indicates a continuous surface including some Ag particulate deposited from plume specimens. Sample deposited at 250 ºC mainly involves many small islands of Ag almost uniformly distributed. By increasing

In the following, electrical resistances of growing film are studied for films growth both on substrate with constant temperatures and on a substrate that is cooling during deposition process. The first one is used for measurement percolation thickness (or the number of laser shots required for percolation) and the other one for recognizing a percolation threshold temperature limit below which obtaining a contiguous percolated film will be possible. Figure 4 shows the Ag/glass electrical resistance R versus the numbers of incident pulses measured in situ during growth at different temperatures of 25, 150, 250, 350, and 450 ºC. Furthermore, a different sample was initially deposited at 450 ºC then it was allowed to cool down to 25 ºC, then deposition continued over the prior one by which an Ag 25 ºC /Ag 450 ºC /glass structure was achieved.

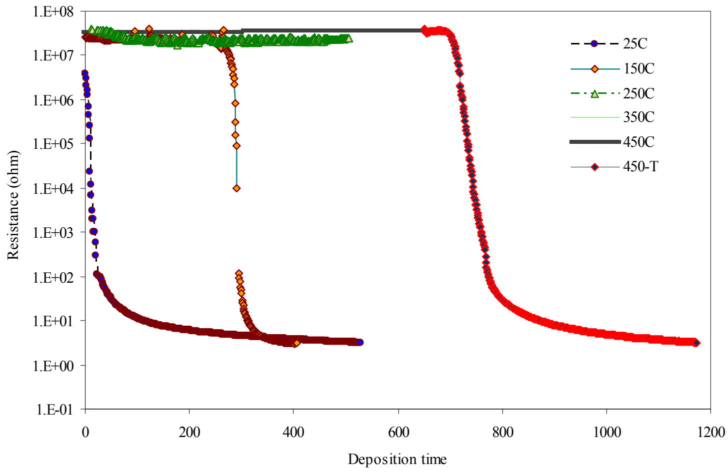

Fig. 4. Time variation of Ag/glass resistance at different substrate temperatures.

As figure shows, the lowest temperature film, 25 ºC, presents a sharp reduction in resistance as the laser illumination begins, then it gradually drops to several ohms by further laser illumination. The drop in resistance is the result of Ag nanoislands coalescence which gives formation of a conducting network. Based on other works, it is expected that when the metal film reaches percolation, a precipitous drop in the resistance will be observed [22]. A coalescence threshold is defined as the thickness where the first conducting link forms across the surface and the electrical resistance decreases rapidly as the film starts coalescing [23]. It should be noted that the nearly constant value before any drop in resistance is observed, originates from plume-substrate contact hence the points measured before coalescence cannot be interpreted as film resistance. The resistance of sample deposited at 150 ºC has a similar reduction curve but it appears after illuminating ~2500 pulses, and before, it remains almost constant. In contrast, deposition above 250 ºC does not represent any reduction in resistance even after 6000 pulses. Temperature dependence of island coalescence is more evidenced by the resistance variation of Ag 25 ºC /Ag 450 ºC /glass sample. In this case, after delivering ~7000 pulses at 450 ºC no coalescence is observed while after cooling the sample down to 25 ˚C, the sharp decrease in resistance is observable but with a little delayed after the beginning of pulse illumination. According to these results, deposition of Ag above a special temperature limit results in growing films containing disconnects islands. It can be attributed to the increased migration length of silver atoms and the decreased saturated island density at high temperature. To confirm such a temperature dependence effect and find a temperature limit below which coalescence can occur, the resistance variation of a typical sample was monitored during deposition on a substrate with a temperature-cooling rate from 300 down to 210 ºC (Fig. 5).

As can be seen, the electrical resistance of growing Ag film during period of cooling remains constant above 230 ºC even after 7700 pulses, as is predicable from the previous resistance curves, while below this temperature, it gradually decreases and 1270 pulses after that, when temperature reaches from 230 to 220 ºC, the sudden decrease in resistance can be observed. This sharp decline of resistance is due to the reduced substrate temperature and partially to increased Ag film thickness. When the deposition continues, the coalescence between the separated islands happens in a smaller thickness for low substrate temperatures. Regarding to gradual decreasing of resistance at 230 ºC it can be concluded that percolation of Ag islands is performed below this temperature.

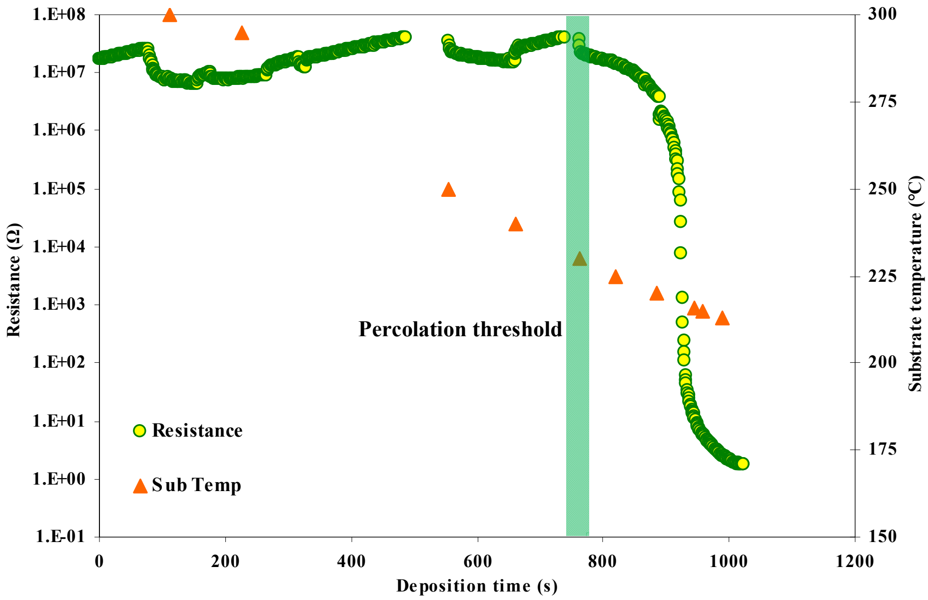

Fig. 5. Resistance variation during deposition Ag/glass during cooling period of substrate from 300 down to 210 ºC.

4. Conclusions

In this study, Ag films were grown on Si(100) and glass substrates by PLD at different temperatures.

It was revealed that produced films involve Ag nanoislands. The islands become highly separate at higher temperatures. We found a coalescence threshold temperature for Ag islands around 230 ºC.

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