Localized surface plasmon resonances (LSPR) exhibited by plasmonic nanoparticles (PNPs) depend on PNP size, shape, distribution, and on the refractive index of the surrounding matrix. In this regard, efforts are undertaken to elucidate and control these parameters depending on growth conditions and post-growth treatment.

The structural properties of AlN thin films containing Ag PNPs were studied using TEM/HRTEM methods, and the results were correlated to the optical response. Magnetron sputtering (MS) was employed to deposit initially AlN:Ag multilayers with either amorphous (a-AlN) or nanocrystalline wurtzite-structured matrix (w-AlN) [1]. In one set of samples (series A), laser annealing (LA) using up to 700 mJ/pulse at 193 nm was employed in order to photomodulate the PNPs. In a second sample series (series B), flash thermal annealing (TA) was applied sequentially after MS deposition of each Ag layer, followed by LA in order to tailor the final microstructure.

In sample series A, LA dissolved the multilayer structure up to approximately half of its initial thickness, as shown in Figs. 1(a) and 1(b). This influence was more intense in the a-AlN case. Sample series B comprised just four 3 nm thick Ag interlayers embedded between AlN layers of 12 nm nominal thickness. TA led to complete structural reorganization resulting in dissolution of the layers and to a rather homogenous PNP distribution in the a-AlN case [Fig. 2(a)]. In the w-AlN case, an inhomogenous PNP distribution was obtained, as larger PNPs were confined into two zones, one close to the substrate and one close to the surface. After LA, the homogenous PNP dispersion was destroyed in the a-AlN case, and larger PNPs were created [Fig. 2(b)]. For the w-AlN matrix, the PNP-zone close to the substrate was not dissolved, but still an improved PNP arrangement was obtained.

PNP enlargement by LA was described as an Ostwald ripening phenomenon. Larger PNPs were found close to the film surface, due to the enhanced Ag surface diffusivity. TA promoted Ag segregation, leading to even larger PNPs. The w-AlN crystallinity appeared almost unaffected, due to the strong ionic character of the atomic bond. Crystallinity was found to limit PNP enlargement as shown in Fig. 3, due to the resistance of the lattice to deformation. Overall it was demonstrated that controlled annealing processes can be employed to modulate the LSPR signal depending on the initial structure of the samples, as well as on the matrix crystallinity.

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Fig. 1: Cross sectional bright field (BF) TEM overall images of multilayer a-AlN:Ag nanocomposites. (a) The nanocomposite prior to LA, comprising twenty Ag layers of 3 nm thickness with a 7 nm periodicity. (b) The nanocomposite after LA showing dissolution of the top half layers and ripening of PNPs.

Fig. 2: Cross sectional BF TEM overall images of a-AlN:Ag nanocomposites (a) after combined MS-growth plus sequential TA, and (b) after post-growth LA of the sample.

Fig. 3: HRTEM image showing Ag PNPs embedded in nanocrystalline w-AlN following LA treatment. Ag(111) and AlN(010) d-spacings are indicated.