Amorphous multilayer meta-material based on cluster of nanoparticles and polymer thin films

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Abstract

We present a material concept based on nanoparticles clusters sandwiched between polymer layers and arranged in a thin film stack to combine. In this way we achieved to combine plasmonic resonances and multilayer interference and realized thin film bulk materials with unconventional optical properties. The technology is based on spin coating and polymerization and leads to high quality films with specific optical features. Samples with a variety of parameters were prepared and characterized by angle resolved spectroscopy. We present details how cluster concentration and multilayer interference influence the optical properties if such metamaterials.

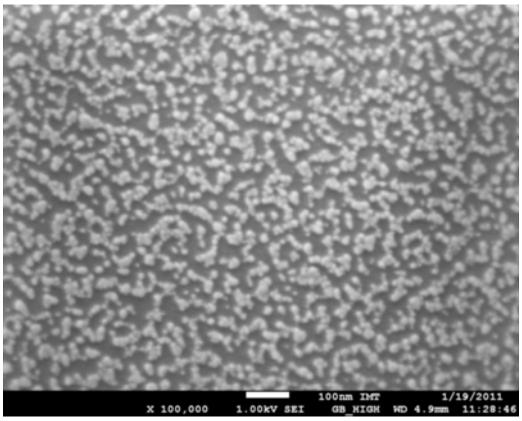
1. Introduction

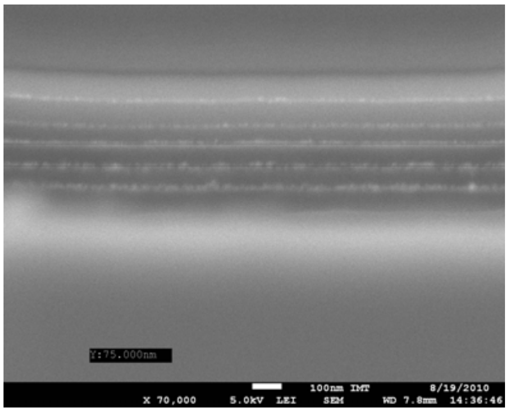
Material design based on metal nanoparticle polymer composite is often based regular arrangements of the plasmonic entities, hence the metal nanoparticles. In practice this is can only be achieved with high resolution structuring techniques such as e-beam writing. If physical chemistry and self organization is considered as fabrication means, often amorphous materials result with a statistical distribution of nanoparticle clusters. Such nanoparticle clusters show distinct optical properties and might be used to built up more complex matter that might include resonances on different lengths scale [1]. It has to be considered that a high efficiency material would need high volume fraction of plasmonic entities and that only a few techniques exist to realize assemblies under such conditions. In our work we try to use aggregation of particles and cluster formation, usually considered as not very useful, to realize materials with non-conventional optical properties. We use silver nanoparticle inks with high load to make layers of nanoparticle cluster and arrange these layers in thin film stacks. We can adjust the mean number of particles in clusters and the distance between such nanoparticle cluster layers. This gives us access to the plasmonic resonance coupling with clusters and the interference between cluster layers.

2. Amorphous cluster nanoparticle material

We report in this study on the fabrication of multilayer device based on alternating two materials with varying refractive indices along the direction normal to the solid substrate upon which the layers are deposited. To achieve the multilayered structure spin coating technique was used. The device consists of inclusion of metallic nanoparticles in multilayered system, fabricated by alternating thin layer of nanoparticles with layer of polymer, a typical situation for which interference appears and forms multilayer reflector. The range of the reflected wavelength is known as stopband and depends critically on layer thickness and effective refractive indices of the layers. An interesting situation appears when stopband of the thin film stack and the peak wavelength λ_0 of the plasmon resonance absorption band lay in the same spectral region [2, 3].

To realize such a situation we fabricated devices with amorphous nanoparticle cluster layers of different morphologies and a typical cluster layer is shown in Fig.1. We used nanoparticle inks with loads of c_w>60% (c_w – weight concentration in percent) and a mean nanoparticle diameters of 12 nm clearly visible in Fig.1 as single particles arranged in clusters.





a) b

Fig. 1 Electron microscope images (SEM) of nanoparticle cluster multilayer matter. a) A typical cluster layer arrangement is shown for 12 nm diameter nanoparticles on a single layer. b) A multilayer arrangement of such nanoparticle cluster layers with separation distance of 80nm is shown in cross section. (Images taken with in-lens detector SEI and standard detector LEI, cross-section preparation by freeze cracking in liquid nitrogen)

The silver nanoparticles with the mean size of 12nm, showed a strong plasmon resonance in solution at 395nm. The concentrations used to produce cluster layers were varied from 0.1/ml to 50 mg/ml (mg of solid content in ml of organic solvent). The position and shape of the resonance is strongly dependent on the initial concentration of colloidal solution. Using spin-coating technique, several arrangements of the NPs on the solid substrate are obtained by varying the concentration of the colloidal solution. We succeeded to vary the density from well separated single particles a dense film without destroying the resonance properties of nanoparticles. The cluster formation is a dynamic process and has to be done under well controlled environmental conditions. Typically it leads to shift of the plasmon absorption band and a development of a second peak indication coupling due to the close packing in the cluster. Figure 2 shows a typical behaviour for a cluster layer like this one given in Fig 1.a).

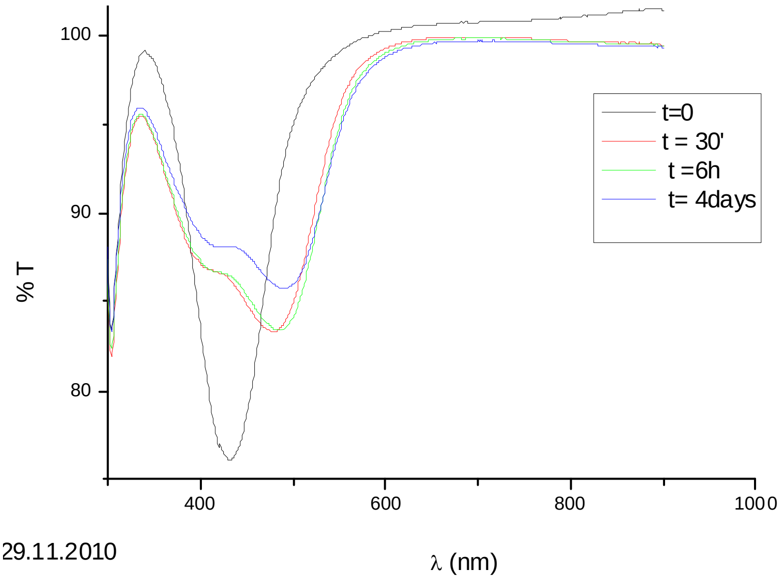


Fig 2. Transmission spectra of single layer nanoparticle cluster assembly for different times after preparation. The evaporation of the solvent leads to a cluster formation and the short distance between particles in the cluster leads to resonant coupling and multiple peaks.

Note that clusters show no particular order and have a certain size and position distribution. When such films are arranged in a multilayer structures reflection peaks are developed. Figure 3 gives reflection curves of such cluster multilayers for different separation distances. A reflection peak is visible that moves to higher wavelengths for larger polymer separation films as it is typical for a multilayer interference.

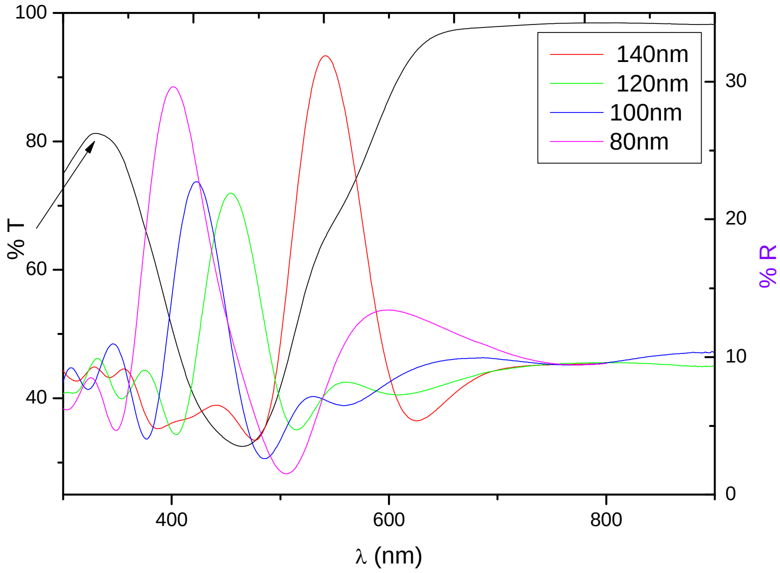


Fig. 3 Reflection of nanoparticle cluster multilayer materials for different separation distances. The stack contains always 11 layers and starts and finishes with a polymer layer. For a separation distance of 80 nm the transmission is plotted at the left.

3. Conclusion and perspectives

Amorphous nanoparticle cluster multilayer assemblies are a promising material concept to realize unusual optical material properties. It gives the possibility of tuning plasmonic resonance coupling by engineering of the cluster size and distribution. The multilayer built up adds a second degree of design freedom. This comes to the expense of a multilayer deposition process. In our case we use spin-coating at the same parameters which leads to a convenient and fast techniques to system fabrication. A detailed analysis of optical properties will be given and an evaluation of the potential for refractive index engineering and metamaterials application will be presented. A first application that can be envisaged are plasmonic absorbers [3,4].

References

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