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Nano-structure and optical properties (plasmonic) of graded helical square tower-like (terraced) Mn sculptured thin films

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ABSTRACT

Graded helical square tower-like terraced sculptured Mn thin films (GHSTTS) are produced in three stages with different number of arms using oblique angle deposition together with rotation of substrate holder about its surface normal, plus a shadowing block fixed at the centre of the substrate holder. The structural characterization of the produced samples was obtained using field emission scanning electron microscope (FESEM) and atomic force microscope (AFM). Results showed a structural gradient with distance from the edge of the shadowing block, which in turn is responsible for the decrease in the volume of void fraction and increase of grain size. Plasmon absorption peaks observed in the optical analysis of these nano-structures showed that their wavelength region and intensity depend on the polarization and the incident angle of light, as well as the distance from the edge of the shadowing block. According to our model and discrete dipole approximation (DDA) calculations, when the number of parallel nano-rods of different lengths and radii are increased the peak in the spectrum shifts to shorter wavelengths (blue shift). Also when the diameters of the nano-rods increases (a situation that occurs with increasing film thickness) the results is again a blue shift in the spectrum. The presence of defects in these sculptured structures caused by the shadowing effect is predicted by the theoretical DDA investigation of their optical spectra. Good agreement is obtained between our theoretical results and the experimental observations in this work.

1. Introduction

The geometrical shape and size of nano-structures have direct influence on their different properties. This has interested many researchers to investigate the properties of these structures in different areas of science such as optics, electronics and biophysics. Nanostructures of noble metals (i.e., Au, Ag and Cu) have attracted researchers' attention because of their localized surface Plasmon resonance (LSPR) property. When the electrons in nano-structured noble metals are excited by incident light, optical resonances occur because of the collective oscillation of conduction electrons. This collective excitation is known as localized surface plasmon [1]. At those incident light wavelengths where the surface Plasmon resonance occurs the surface electric field increases, which is the basis of surface enhanced Raman spectroscopy [2,3]. LSPR depends on the composition [4–6], surrounding environment [6] and geometry of the metallic nano-structure [7–9].

This phenomenon because of its numerous applications has been subject of many investigations, [e.g.,10–17] most of which are concentrated on noble metals (gold and silver). The reason for choosing noble metals is that they show many oscillations and a varying refractive index [18], which in turn are responsible for sharp changes in the optical spectra of these materials as thin films, leading to pronounced Plasmon peaks in their extinction spectra. However, the geometrical structure of nano-particles from which the thin film is formed also has a strong influence on the plasmonic properties although they may be made of the same material [7,17,19]. Therefore, we may be able to fabricate nano-structures with as many as possible sharp corners or protruding tips acting as hot spots for increasing the electric field at these points.

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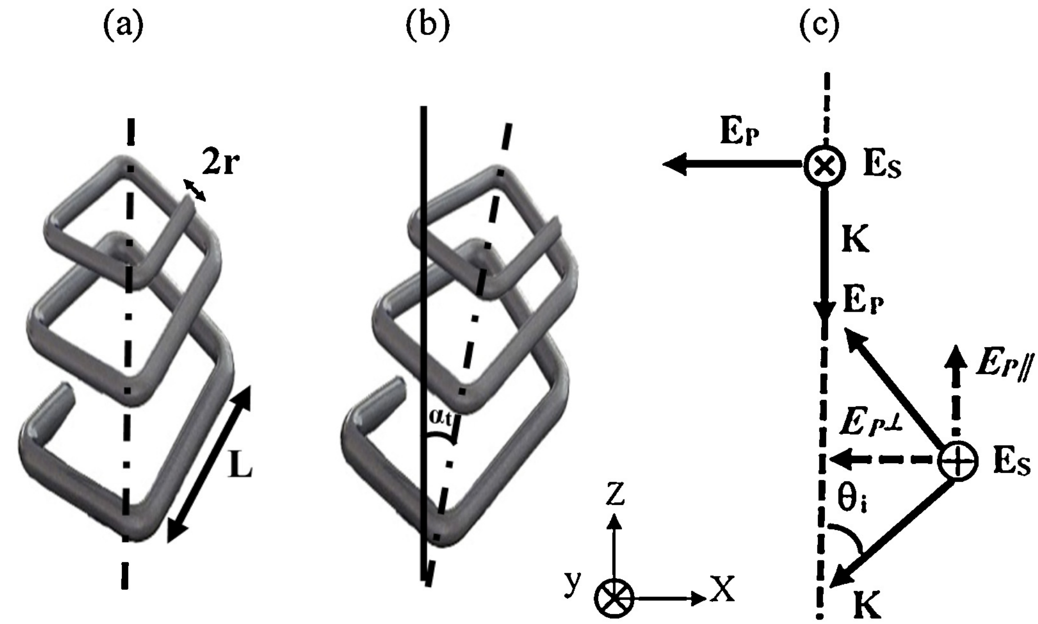

Fig. 1. Simulation figures of helical square structure with the corresponding view directions. **L** and **r** are the length and the radius of each nano-rod, respectively. α_t is the growth angle of helical columns. The definition of the incident polarization directions as well as decomposition of the *p*-polarized field by changing the incident light direction is shown in (c).

By changing the polarization of the incident light we may adjust and control the plasmonic peaks. Therefore, by fabricating sculptured thin films with different geometrical shapes we may investigate the influence of shape on the plasmonic properties, irrespective of the material itself. Many researchers have previously worked and reported on the shape and geometry of single nano-particles or the effect of the surrounding medium on the behaviour of a single nano-particle [20–22]. However, to the best of our knowledge, we may only refer to two works which extended this kind of study to an assembly of sculptured nano-particles which form the structure of the thin film rather than a single nano-particle [19,23].

In recent years the oblique angle deposition technique (OAD) has provided the facility for production of different nano-structures with varying anisotropy [24]. OAD (vapour incident angle less than 85°) and glancing angle deposition (vapour incident angle greater than 85°) together with rotation of the substrate holder about its surface normal are used for fabrication of 3D nano-structures in different fields of study [25,26].

Brett and Krause [27] by using the OAD technique in conjunction with rotation of the substrate holder about its surface normal while fixing a shadowing object/block at the centre of the substrate holder, produced helical nano-structures called graded chiral nano-sculptured thin films. Savaloni et al. [28] used the same kind of setup to produce graded chiral zig-zag silver sculptured thin films. The slope of these graded structures decreases on increasing the distance from the shadowing block, hence their nano-structure and their different properties varies with distance from the shadowing block. The optical behaviour of these structures is studied theoretically by Babaei et al. [29].

In our earlier work [23] we used manganese, rather than a noble metal and produced different shaped nano-particles (i.e., helical rectangles and helical pentagon) and investigated their plasmonic properties by introducing a model for the sculptured structures made of nano-rods, and considered all of the possible states (positions) that one nano-rod may have with relation to its neighbouring nano-rods in the helical rectangles and helical pentagon (see Fig. 7 in Ref. [23]). In the extinction spectra of simple Mn nano-rods, pronounced plasmon peaks were not observed [30] because the refractive index of Mn, unlike noble metals, does not show much variation with wavelength [18]. As mentioned in Ref. [23] the use of Mn should not restrict our findings to this material as the geometry of the structure is the main feature that influences the results.

In the present work, the geometry of the Mn nano-particles within the structure of our thin films is changed to graded helical square tower-like terraced shape (GHSTTS), which is totally different from that discussed earlier and so the model for calculation of extinction spectra presented in our earlier work [23] is extended here to cover the situations created by this geometry.

The graded helical square tower-like terraced shaped sculptured thin films (GHSTTS) were produced by oblique angle deposition together with the rotation of the substrate sequentially by 90°, while a shadowing block was fixed at the centre of the substrate holder having substrates mounted on it at different distances from the edge of the shadowing block. In addition the length of the arms of the second and third pitches of the GHSTTS were reduced by a third and two thirds relative to the length of the arms of the first pitch, hence terraced structures as well as slanted shapes in which the tilt angle changes with distance from the edge of the shadowing block were formed. Hence, their structure provides numerous hot spots which in turn can be responsible for the plasmonic resonances.

We used the discrete dipole approximation (DDA) method to simulate and calculate the scattering cross-section of Mn nano-rods in the form of combinations of different number of nano-rods with different lengths and diameters as well as different tilt (growth) angles.

The structural characteristics of these nano-sculptured thin films are analysed, while their optical properties for different polarizations and different incidence light angles and azimuthal angle as a function of distance from the edge of the shadowing block are also studied. The structures of GHSTTS produced in this work are periodical in two normal and parallel directions with respect to the substrate surface, are anisotropic and as mentioned above are grown with graded growth angle with distance from the edge of the shadowing block. Hence, the surface plasmon resonance peaks can be adjusted by distancing from the edge of the shadowing block and using different incidence angles of polarized light.