Fabrication of spherical GeSbTe nanoparticles by laser printing technique

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Abstract. By using the laser printing technique, for the first time we fabricate spherical nanoparticles of germanium-antimony-telluride alloy possessing a high refractive index and amorphous-to-crystalline phase transition. The nanoparticles are examined by means of optical dark field micro-spectroscopy, which shows scatterers with different colours (with different optical resonances). The direct measurements of their diameters by using the transmission electron microscopy reveal that the nanoparticles’ colours are related to different sizes of the nanoparticles. While most of nanoparticles are homogeneous, our study shows that some fabricated particles have a core-shell structure.

1. Introduction

Metamaterials are artificial media having extraordinary properties that do not exist in nature. With this concept, metamaterials can control over the parameters of propagating waves in almost arbitrary way. The basic metamaterial functionality is due to resonant behaviour of its structural elements called by meta-atoms [1]. Two-dimensional counterpart of metamaterials, referred to as metasurface, which is formed by arranging meta-atoms in a plane was shown to modify polarization, phase and amplitude of light in this planar geometry [2,3]. Going from microwaves down to optical spectral range, the conventional metal-based metamaterials obtain a number of restrictions including inevitable Ohmic losses and the absent of magnetic response in visible and near infrared. All-dielectric metamaterials with a high refractive index and low losses, for example silicon at near infrared, have attracted a lot of attention in recent years [4]. Manipulation of light due to Mie resonances for spherical nanoparticles, both magnetic and electric modes, make it possible to scale the structure sizes in a wide range for operating from microwaves to optical frequencies [5]. It can open a door for using high dielectric index nanoparticles in the field of colour engineering [6,7], as well as for nonlinear harmonic generation [8,9] and nanothermometry [10].

Higher levels of metasurface functionality require the tuning or switching of their dielectric properties, especially for applications. By exploiting nonlinearities one cannot archive strong modulation of the response. Recently the phase transition between crystalline and amorphous silicon was demonstrated for switching the Mie resonance in silicon nanospheres, however, silicon have relatively weak dielectric contrast between amorphous and crystalline phases and it requires a high...
temperature for the transition [11]. Among others phase changing optical materials, Ge-Sb-Te (GST) alloy attracts a lot of attention in photonics because its giant dielectric contrast between amorphous and crystalline phases [12]. As this compound has a similar structure between amorphous and crystalline phases, the structural transition can be reversibly triggered very fast with extreme change in high refractive index range from \( n=4 \) to 5.5 with low losses in near infrared [13]. According to these properties, GST was used for tuneable nanoantennas and metasurfaces fabricated by lithographic techniques [14]. However the lithography is unsuitable to produce nanoantennas of spherical shape that can be described analytically by the rigorous Mie theory. Recently a laser printing technique [15,16] was shown to synthesize spherical nanoparticles of silicon with magnetic and electric Mie resonances in optical range. In this work we report the fabrication of spherical GST nanoparticles by using the laser printing technique.

2. Results and discussion
The GST nanoparticles are fabricated by the laser-induced forward transfer method [16]: a receiver glass substrate is placed on a donor glass substrate with a deposited thin film of GST (Fig. 1a). The distance between substrates is about 50 \( \mu \mathrm{m} \). The radiation of an ytterbium-doped femtosecond solid-state laser (TeMa-150, Avesta Poject, 1050 nm, repetition rate 80 MHz, pulse duration 150 fs) in a single pulse mode provided by a pulse picker system (Avesta Poject) is focused by an infinity corrected objective (10×NA=0.28 Mitutoyo Plan Apo) on a thin film-glass interface into a spot with a diameter of 4.6 \( \mu \mathrm{m} \). By exploiting laser printing we fabricate about 1000 GST nanoparticles which are studied by means of dark filed microscopy. In the dark-field images, isolated nanoparticles manifest themselves as coloured spots mostly yellow, but there are also blue, purple, red and green nanoparticles (Fig. 1b). Similar different colours in silicon nanoparticles are attributed to a wide distribution of their diameters governing the excitation of Mie resonances at certain wavelengths [15,16].

Figure 1. (a) Schematic Illustration of fabricated GST nanoparticles by laser printing. (b) Dark-field image of GST nanoparticles.

To analyze the presence of different colours in the dark-filed images (Fig. 1b) we simulate scattering cross section of GST nanoparticles by exploiting CST Microwave Studio (commercially available software). The simulation yield the nanoparticle diameters have to lay at least in the interval
between 60 and 200 nm. The wide diameter distribution we associate with the relatively high energy per pulse in our fabrication set-up. Indeed, the applied laser fluence is higher than 100 mJ/cm², which is related the regime of phase explosion induced by ultrafast overheating of the irradiated material [17, 18].

To measure diameters of GST nanoparticles directly, we use transmission electron microscopy (TEM). The similar scheme is implemented for fabrication of nanoparticles on a special TEM grid which is applied instead of the receiver glass substrate shown in Fig. 1a. Our results show that nanoparticles have nearly spherical shapes and the diameters are in the range of \( D = 40-300 \) nm with the peak in its distribution at 150 nm. 15\% of particles have diameter in the range 140-160 nm which is corresponding to the yellow colours being in a good agreement with the dark field images (Fig. 1b). According to the previous works, this size distribution allows for existing Mie resonances in the visible and infrared ranges [4, 5, 15]. Furthermore, it is possible for us to study the scattering properties of nanoparticles by using Mie theory.

Figure 2a shows a relatively homogenous phase in amorphous state. However, the TEM images for larger particles are different and they demonstrate a core-shell structure (Fig. 2b). Since the laser energy applies with a gradient profile, one can assume that the ablated particle is not always amorphous completely. The core-shell nanoparticles are defined by two diameters. Figure 2b depicts a core-shell particle having diameters: 105 nm for the core and the external diameter 293 nm for the whole particle, whereas homogeneous GST sphere in Fig. 2a has a diameter of 104 nm. One can speculate that the large particles are cooled down longer than the small particles [9]. This is the main reason why we observe the growth of crystalline grain forming the core of the larger nanoparticles. We also anticipate that after the heating by additional continuous wave irradiation the structure of core-shell particle becomes homogeneous in the crystalline phase owning to temperature-induced amorphous-to-crystalline transition.

![TEM images of homogenous GST nanoparticle of small (a) and large (b) structure of sizes.](image)

**Figure 2.** TEM images of homogenous GST nanoparticle of small (a) and large (b) structure of sizes.

3. Conclusion
In this study we have demonstrated novel method of fabrication of GST spherical nanoparticles by the femtosecond laser printing technique. The existence of different colours in dark field image was due to nanoparticle size distribution in our experiment. The investigation of GST nanoparticles by TEM has further confirmed the non-monodisperse size. The TEM images have revealed core-shell structure of the larger particles. However the smaller nanoparticles have exhibited homogeneous internal structure. We believe the developed laser printing technique opens a way for design of tuneable all-dielectric
nanostructures and metasurfaces composed from the high refractive index GST nanoparticles. Combining the fascinating properties of GST the laser printing allows GST nanoparticles to compete with the conventional metallic nanoparticles in colour engineering, which has become an important field of research and applications in the last years.

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