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Structured strengthening by two-wave optical ablation in silica with gold nanoparticles

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ABSTRACT

Here we explored the morphological modification conducted by pulsed laser ablation in a high-purity ion-implanted silica substrate with embedded gold nanoparticles. The ablation process was performed by a two-wave mixing method at 532 nm with 26 ps pulse duration. The mechanical properties of the nanocomposites were characterized by nanoindentation and atomic force microscopy techniques. Analytical and experimental observations pointed out that an interference laser pattern can produce structured arrays at the sample surface. Besides, it is showed that the presence of periodic SiO_2/Au fringes strongly enhances the mechanical nanocomposites performance. Additionally, a statistical analysis was carried out to establish possible relations between mechanical characteristics and morphological features. Experimental measurements allowed us to consider that multi-wave metal/brittle interface interactions can be good candidates for developing selective effects based on metallic nanoparticles.

1. Introduction

Due to their fascinating properties related to plasmonic and high visible transparency, nanocomposites (NCs) combining dielectrics with metals have captured the enthusiasm of engineering research [1,2]. It is well known that interaction between dielectric and metal is generally weak [3], but the adhesion of metal to dielectric substrate can be substantially improved through the incorporation of metallic nanoparticles (NPs) [4,5]. In this regard, in order to accomplish enhanced characteristics, in recent years transparent reinforced composites based on nanostructures have drawn significant interest [3–7]. Different NPs in a nanocomposite show a high-performance in distinct physical phenomena because of their high area/volume ratio against the unmodified substrate. The size, density and morphologies of the NPs allow tailoring suitable conditions for mechanical applications [8]. However, brittle material still exhibits some undesirable features enclosing voids, cracks, and crazing, whereas in the ductile material, such features decrease [3]. Then, efforts have been done to improve the relation between the ductile/metallic characteristics of NCs [6,9,10].

Recently, the mechanical response of dielectrics surfaces has been enhanced prior to metal deposition [11,12]. For example, significant adhesion variations in the surface of polyethylene composite have been caused after a grafting treatment of gold NPs (AuNPs) coatings [11]; nevertheless, studies under comparable conditions differ from the reported conclusions [12]. It has been argued that gold coated pristine and plasma exposed samples result in a hardness increment, while the elastic modulus decreases.

Through structural analysis, it has been found that materials with finely tuned mechanical properties strongly depend on nanoparticle dimensions [13].

A crucial difficulty of NCs is that NPs tend to agglomerate, due to a higher surface energy [9]. As a consequence, some treatments have been designed looking for highly reproducible NPs distributions and sensitive substrates with morphological modifications depending on the application. Nonetheless, the efforts carried out for the morphological ordering, the experimental results still exhibit poor reproducibility. Similarly, a process to prepare gold or silver structures with micro or nanoscaled features have been carried out, specially designed for Surface Enhanced Raman Spectroscopy (SERS) studies [14]. Unfortunately, most of the structures obtained by novel techniques still lack of control for the structured NPs distribution [15].

However, advanced laser ablation techniques are becoming important alternatives for the development of new products for

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industry [16–20]. Results of mechanical evaluation indicate that the lap shear strength for laser ablated samples was significantly higher compared to specimens without previous treatment [17]. On the other hand, the ablation effect by multi-wave interaction can modify surfaces to present a well repetitive periodic array that depends on the wavelength employed [18,19]. As a result, laser ablation has been used to perform laser-machined lines, as indicated by a noticeable number of applications in microelectronics and micromechanics researches for applications as optical recording, circuit patterning, data driven and mask-less patterning [21–23].

A comparison of defined correlations between the laser polarization and the thermal gradient in femtosecond interactions has been proposed [24]; however, no association with the quantitative distribution of NPs through ablation process has been elaborated, but of course that it may play an important role.

Currently, several studies are focusing efforts on assisted laser nanostructuring by ablation processes. For instance, it has been demonstrated that production of nanostructured materials by continuous ultraviolet laser exposure allows the formation of periodic NPs arrangements [25]. Measurements of optical absorption spectrum reveal several narrow absorption bands due to Surface Plasmon Resonance (SPR) effects [26]. Therefore, regular distributions of metallic NPs provide the possibility to induce additional resonance bands related to the SPR, and also it may influence the mechanical response [26].

Despite further attempts to study the structural properties of NPs by mechanical tests performed at micro-nanoscale [7], the influence of NPs incorporated into transparent materials is still partially understood. The inclusion of metallic NPs in transparent materials provides the possibility to obtain outstanding optical properties capable to control ultrafast optical functions; besides, the resulting NCs could be also contemplated for developing nanomechanical actions. With this motivation, in this work we have focused our efforts on the mechanical interaction between embedded metallic NPs and silica (SiO_2) substrate. A two-wave mixing method was employed to prepare a superficial NPs distribution. The mechanism that contributes to the mechanical enhancement in the composite was described by a submicron lines patterning at the sample surface. Notably, the information of the SiO_2 substrate behavior under hydrostatic deformation is vital for the reliability of transparent composite-based mechanical devices.

According to the mechanical test designed to analyze the improvement of surface engineered materials [20,27], the morphological and mechanical effects were explored by Atomic Force Microscopy (AFM) and nanoindentation techniques in the present work. We believe that the current research can be helpful to achieve a better knowledge of the process responsible for NPs distribution modification in NCs developed by laser irradiation methods. These analyses yield more insight into the mechanism for the creation of regular morphologies, as well as material modifications for physical properties enhancement.

2. Materials and methods

2.1. Materials, and optical study technique

The ion-implantated NCs were prepared using the 3MV Tandem accelerator Pelletron (NEC 9SDH-2). A high-purity silica glass was used as substrate, with OH content less than 1 part per million (ppm), and impurity content less than 20 ppm. The implantation was performed at room temperature, fluence of around 2.8×10^{16} ions/cm^2, with 2 MeV Au^{2+} ions. After the implantation, the sample was thermally annealed in an oxidizing atmosphere (air) at a temperature of 1100 °C for 1 h [28]. The concentration depth profile distribution of Au and the ion fluences were obtained by Rutherford Backscattering Spectrometry (RBS) measurements using a 2.54 MeV $^4He^+$ beam.

2.2. Laser ablation process

A single pulse provided by a Nd–YAG laser system EKSPLA Model PL2143A with wavelength $\lambda = 532$ nm was employed for irradiation of the sample in a two-wave mixing configuration. The Full Width at Half Maximum (FWHM) pulse duration was 26 ps. The optical beams had linear and parallel polarizations. The geometrical angle of the incident rays was about 9.5°. The maximum pulse energy in the experiments was 0.1 mJ. The irradiance rate of the interacting beams was 1:1. The irradiance that corresponded to the beams at the beginning of the interaction was about 12.2 GW/cm^2 each. The radius of the beam waist at the focus in the sample was measured to be 0.1 mm. The spatial pulse overlapping was estimated to be approximately 1.2 mm. Then, the center of the sample was located in the focus of the interaction in regards that the silica sample thickness was 1 mm.

2.3. Surface morphology characterization

2.3.1. AFM studies

Initially, the sample surfaces were inspected by optical microscopy (OM). The characterization of the morphology was evaluated before and after laser ablation experiments through AFM observations. A standard Non-Contact mode AC in an Asylum MFP 3D SA microscope was employed. A silicon probe (cantilever) with a rectangular geometry of 160 μm was selected for the data acquisition.

2.3.2. SEM and energy dispersive spectroscopy (EDS)

The Si and Au elements at the ablated sample surface were characterized by using SEM and EDS, with a Philips XL30 ESEM system. These observations were employed to determine the presence and distribution of the dielectric and metallic materials at the periodic array morphology that was generated by the ablation process.

2.4. Nanoindentation test

2.4.1. Nanoindentation test calibration

The mechanical properties were determined in a Nanomechanical Test Instrument Hysitron using a Berkovich tip. The nanoindentation system was calibrated using a fuse silica standard sample with surface roughness of $R_a = 1.2$ nm from a 5 μm^2 micrograph. The Poisson's ratio value, as well as the elastic properties of the Berkovich indenter was taken from literature [29]. The nanoindentation tests were carried out in a load control mode keeping constant both, load and unload rates, varying the maximal loads, leading each experiment with a total time of 20 s.

2.4.2. Load–displacement curves

Following the Oliver and Pharr method [30], the load–displacement curves (P–h) were analyzed in order to calculate hardness H and reduced elastic modulus E_r of the sample.

These properties were determined from three measured parameters; maximum load P_{max}, displacement h_{max} and the contact stiffness S. The contact depth was calculated by the mathematical expression:

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S} \tag{1}$$

where ε is a constant which depends on the indenter geometry, with a value of about 0.75 associated to a Berkovich indenter, and