Laser-induced fluorescent micro-structures in silver nanoparticle based films

Sanjeev Kumar Kandpal, Aimee Co, Kody Allcroft, David J. Neivandt, Douglas W. Bousfield, Michael D. Mason *

Department of Chemical and Biological Engineering, University of Maine, Orono, ME 04469, United States

ABSTRACT

An optical method for the formation of micron sized line features within silver nanoparticle based films using focused laser irradiation is developed. The observed light-induced effect is a strong function of light flux producing line features with widths of less than 5 μm, which can be controlled by careful selection of the focused incident beam waist. A potentially useful local feature is generated just outside the region of laser exposure; the film displays significant fluorescence emission across the visible spectrum. The source of the fluorescence is attributed to the presence of hydrated citrate salts that have been decomposed due to local heating and recrystallized as confirmed by electron microscopy and confocal fluorescence spectroscopy.

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1. Introduction

Applications of functional microstructures have increased in number over the past decade, while at the same time expanding broadly into new commercial and industrial sectors [1–6]. In previous decades, developments were dominated by the need of the electronics industry to produce smaller and more tightly packed conductive lines and other dielectric structures necessary for device miniaturization and cost reduction [1,5]. More recently, fluid handling devices, channels, and sensors and pumps are being developed to achieve precise control of fluid flow at the microscale, while reducing chemical consumption. In sensor applications, engineered micro-structures are now generated that can be used to detect ultra-small quantities of chemicals using techniques such as Surface Enhanced Raman Scattering (SERS) [7]. Developments in micro-optics and photonics make use of micro-lenses, waveguides and low cost gratings to produce hand-held analytical devices [3,4].

Over the past several decades engineers have labored to develop increasingly complex fabrication methods capable of achieving the manufacturing precision necessary for the applications mentioned above. For the micro-electronics industry, where the highest precision is mandated, advanced clean room techniques, such as electron beam lithography and photolithography, are most common. For many small scale or somewhat less sophisticated

applications, these techniques are not cost effective. Printing methods, such as ink-jet, flexography, offset and gravure are now able to produce both conducting and non-conducting features with dimensions of interest [8]. While significant cost benefits have been achieved with these methods, feature sizes are typically limited to greater than 50 μm [9,10]. Additionally, the use of high temperatures is required to produce conductive features; inducing unwanted thermal stress which prohibits the use of many desirable substrates, increases production time, and elevates cost. Provided that these limitations can be overcome, there remain a large number of potential commodity applications of microstructures such as: anti-counterfeiting, barcoding, or product branding and marketing, as well as lower cost prototyping which could significantly impact the fields of chemistry [11], biology [12], catalysis [13], to name a few.

One of the high volume potential applications of microstructures is in the area of *laser marking*. Broadly speaking, *laser marking* is used to code a large range of products with a small amount of variable data such as expiration dates or lot numbers. The marking usually consists of a mixture of lines of text and machine readable codes. To be of significant interest to industry, new marking methodologies must be cost effective, safe, fast, and suited for surfaces which may be of irregular shape and varying chemical composition.

Recently, nanoparticle based coatings have been investigated for use in place of traditional polymer photoresist formulations [14]. As opposed to traditional photolithography, where the entire substrate is simultaneously illuminated during photo-exposure,

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* Corresponding author. Tel.: +1 207 581 2344.
  E-mail address: mmason@umche.maine.edu (M.D. Mason).

these new approaches make use of focused energy sources such as laser radiation to draw structures. Laser induced pyrolysis is a new technique in which the focused laser is used to decompose the organic surfactant around the nanoparticles in the coating to sinter the nanoparticles (such as Au, Ag) together, making a conductive feature along the path of laser exposure [15].

While promising, these new techniques use formulations consisting of high metal content and toxic organic surfactants to disperse nanoparticles and stabilize the formulation. Additionally, these approaches are typically tasked with producing conductive structures [14,15]. In the work reported here, we have used a low metal (Ag) content nanoparticle film, and an aqueous based dispersant to generate structures in the range of 1–5 μm width during exposure to a well-controlled and focused light source. In addition the current method results in a unique attribute of the features not previously observed in other related techniques. Here the laser generated structures selectively demonstrate fluorescence at their edges. In addition to being of significantly lower cost than other laser based methods, this approach holds potential for electronic and optical structures, such as: printed capacitors [16], environmentally sensitive fluorescence structures (temperature, humidity, pH) [17], or fiduciary marks for fluorescence imaging [18].

2. Experimental

2.1. Synthesis of Ag nanoparticles and film preparation

Silver nanospheres were prepared using well established single-pot redox chemical techniques [19–21]. According to these reports particle nucleation is initiated when aqueous metal ions (Ag^+) are made insoluble (Ag^0) through chemical reduction. Layer-by-layer growth continues until the source of metal is exhausted. Following growth, excess reducing agent becomes physisorbed to the nanoparticle, leaving a negatively charged surface, electrostatically stabilizing the colloid against aggregation [20]. For the work presented here, reagents included silver nitrate $AgNO_3$ (soluble metal salt) and trisodium citrate dihydrate $Na_3C_6H_5O_7 \cdot 2H_2O$ (reducing agent and stabilizer), both of which were used as purchased (Sigma Aldrich).

In order to prevent unwanted surface deposition a 500 ml round bottom reaction flask was rigorously cleaned with concentrated nitric acid, followed by caustic detergent and thorough rinsing with ultrapure 18 MΩ water. In this flask 600 mg of trisodium citrate was dissolved in 160 ml of 18 MΩ water and brought to a constant temperature of 95 °C using an oil immersion bath. In a separate vessel, 40 mg of silver nitrate was dissolved in 40 ml of 18 MΩ ultrapure water. A molar excess of approximately 30:1 was used to ensure rapid nucleation of particles and impart electrostatic stability before and after evaporative concentration. The silver solution was rapidly added to the round bottom flask and brought back to the same temperature (95 °C) while stirring vigorously. The temperature was maintained until the reaction was complete (~1 h), achieving a translucent yellow–orange color. The resulting solution was allowed to slowly cool to room temperature. The distribution of nanoparticle sizes within the solution was determined using Dynamic Light Scattering (DLS) (Malvern, Zetasizer Nano-ZS), and confirmed by Transmission Electron Microscopy (TEM) (Philips CM-10) and UV–Vis Absorption Spectroscopy (Ocean Optics USB4000) as shown in Fig. 1.

Though strongly absorbing, the as synthesized nanoparticles solutions proved to be too dilute to form continuous nanoparticle films. To increase the number density of particles, the solution was concentrated ~8-fold (0.013–0.102 wt%) using rotary evaporation (Rotovap) (BUCHI R-205). Subsequently, films were
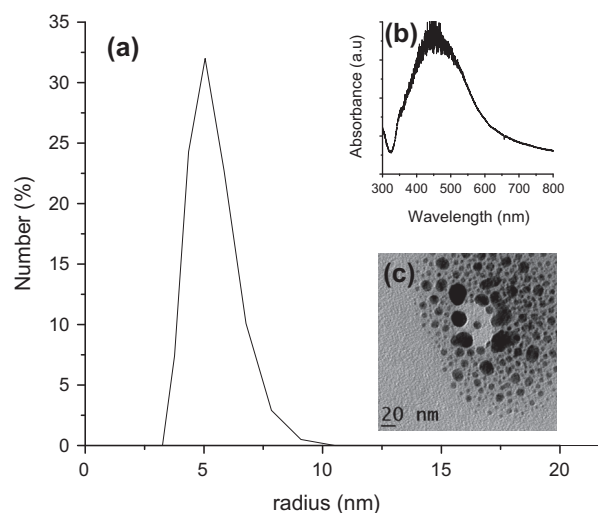

Fig. 1. (a) Size (number) distribution of freshly made Ag nanoparticles, (b) UV–Vis absorbance spectra of freshly made Ag nanoparticle solution and (c) TEM image of the freshly made Ag nanoparticles.

prepared by drop casting 100 μl of this solution onto standard glass coverslips. The cover slips (Fisherfinest #1) were cleaned by soaking in 20% Contrad 70 for 6 h followed by thorough rinsing with 18 MΩ ultrapure water. The drop cast films were allowed to air dry slowly in a fume hood over a period of ~8 h. To minimize unwanted effects of air flow or dust, an inverted petri dish was used to cover the drying samples.

2.2. Formation and characterization of line features

To produce visible features, the drop cast films were subjected to 532 nm irradiation from a continuous wave diode pumped solid state laser in a custom build hybrid scanning confocal microscope and spectrophotometer, shown schematically in Fig. 3. While the peak absorption efficiency would be closer to 450 nm, as indicated by the peak in Fig. 1b, this corresponds to less common and more expensive laser source. In fact, 532 nm absorption by Ag is above 80% of the peak absorption and readily produces the desire effect. In this instrument the incident laser (45 mW, typically), was focused to a near diffraction limited spot using one of two objective lenses (0.4 or 0.65 NA). An *x–y* scanning stage (i^2, New England Affiliated Technologies, Inc.) was used to translate the sample under the focused beam in a predetermined pattern controlled via a custom LabVIEW software package and hardware interface. For all films presented here a constant scan rate of 0.07 mm/s was used. This instrument is equipped with a broadband light source (Kohler illumination), widefield image collection optics and CCD camera (Princeton Instruments, SPEC-10) allowing for simultaneous observation of the film (120 μm × 160 μm) during exposure.

In a separate measurement, using the same custom built instrument, localized fluorescence emission spectra were obtained at different morphological features within the LIS structure. In this case, 473 nm CW laser excitation (20 μW) was directed towards the sample with a broad band beamsplitter, and focused to a diffraction limited spot using the 0.65 NA objective mentioned above. As indicated in Fig. 3, the resulting fluorescence emission was collected in the reflection geometry using the same objective, passed through the beamsplitter, and directed into an optical fiber (CeramOptec, spot-to-slit fiber bundle). Emission spectra were obtained by passing light from the fiber into a ¼ meter grating monochromoter (Acton) and onto a LN_2 cooled CCD camera system (Princeton Instruments). Additional structural and photolumines-