APPLIED PHYSICS LETTERS **91**, 121112 (2007)

Growth of plasmonic gold nanostructures by electron beam induced deposition

S. Graells
Institut de Ciències Fotoniques (ICFO), Parc Mediterrani de la Tecnologia, 08860 Castelldefels (Barcelona), Spain and Enginyeria La Salle, Universitat Ramon Llull, Quatre Camins 2, 08022 Barcelona, Spain

R. Alcubilla
Institut de Ciències Fotoniques (ICFO), Parc Mediterrani de la Tecnologia, Castelldefels 08860, Barcelona, Spain and Universitat Politecnica de Catalunya (UPC), c/o Jordi Girona 1-3, 08034 Barcelona, Spain

G. Badenes
Institut de Ciències Fotoniques (ICFO), Parc Mediterrani de la Tecnologia, Castelldefels 08860, Barcelona, Spain

R. Quidant[a]
Institut de Ciències Fotoniques (ICFO), Parc Mediterrani de la Tecnologia, Castelldefels 08860, Barcelona, Spain and Institució Catalana de Recerca i Estudis Avançats (ICREA), Passeig Sant Joan 10, 08010 Barcelona, Spain

(Received 18 July 2007; accepted 29 August 2007; published online 19 September 2007)

The authors report on the growth of organometallic dots for optical applications using electron beam induced gold deposition on a transparent substrate. The effects of the substrate material and the deposition parameters, such as beam current and water vapor pressure, on both the deposition rate and gold purity are investigated. *Ex situ* annealing of the sample is used as a purity improvement method. Scattering optical measurements on the purified dots reveal that they support localized surface plasmon resonances. This technique opens new perspectives in the fabrication of substantial height-base aspect ratio plasmonic nanostructures and may become particularly relevant for nonflat substrates. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2786600]

Engineering the plasmon properties of metal nanostructures requires an accurate control on their shapes and distribution. This is conventionally achieved by using electron beam lithography on electrosensitive polymers combined with thin metal film deposition and lift-off.[1] Direct local deposition of metals induced by a focused electron beam [electron beam induced deposition (EBID)] is an alternative method that has recently received a growing interest in microelectronics[2] and may become highly relevant to plasmon optics when involving noble metals. In particular, because it does not require using any resist, EBID is expected to enable higher height/base aspect ratios and render much easier nanopatterning on nonflat surfaces such as the extremity of an elongated scanning probe.[3,4]

EBID is the result of the local decomposition, by a focused electron beam, of precursor molecules adsorbed on a surface. The main parameters involved in the deposition process are the precursor composition, the electron beam current, the gaseous environment in the deposition chamber, and the substrate material. Generally, the precursors used for gold deposition are organic and based on *b*-diketonate: dimethylgold-acetylacetonate [Me_2Au (acac)], dimethylgold-(trifluoro)acetonate [Me_2Au (tfa)], and dimethylgold-(hexafluoro)acetonate [Me_2Au (hfa)]. Recently, gold trifluorophosphine–chloride (PF_3AuCl) has also been used as an alternative inorganic precursor.[5] EBID with organometallic precursors usually results in nanocomposite materials where metal is scattered within an amorphous organic matrix. Carbon and oxygen are undesired impurities limiting both electronic and optical properties. Several methods have been proposed in order to increase the purity of the deposited material: increasing the beam current,[6] heating the sample during[7] or after the deposition[8,9] and including reactive gases into the deposition system.[10,11] Another promising method consists in depositing in the presence of water vapor in an environmental scanning electron microscope (ESEM).[12]

In this letter, we investigate the deposition by EBID of organometallic gold nanostructures on glass substrates. Our results show the crucial importance of the surface conducting layer on the deposition quality. We also demonstrate that a suitable purification through postannealing of the deposited nanostructures can be used to confer them resonant plasmon properties.

In our study, the depositions were performed in a FEI Quanta 200 ESEM equipped with a gas injection system using dimethylgold-acetylacetonate as a precursor. The microscope is interfaced to a Raith Elphy Plus nanolithography system. With the aim of evaluating the evolution of the gold purity with the deposition parameters, a preliminary energy dispersive x-ray spectroscopy (EDX) compositional analysis was carried out on a silicon substrate. The sample consists of a 4×2 matrix of 1.75 μm^2 pads [see SEM image of Fig. 1(a)]. Each of the two lines corresponds to different beam currents, 250 and 175 pA (column voltage of 30 kV). For each beam current, three different pressure conditions were considered: high vacuum (1.1×10^{-6} torr) and ESEM modes at 0.8 and 0.08 Torr by introducing water vapor into the chamber. Carbon depositions (precursor valve closed) were also included to the sample as a reference. The deposition times for each pad were 20 min for gold and 90 min for carbon, respectively. The relative gold content on each pad was measured by EDX before and after a postannealing process.

---

[a] Electronic mail: romain.quidant@icfo.es

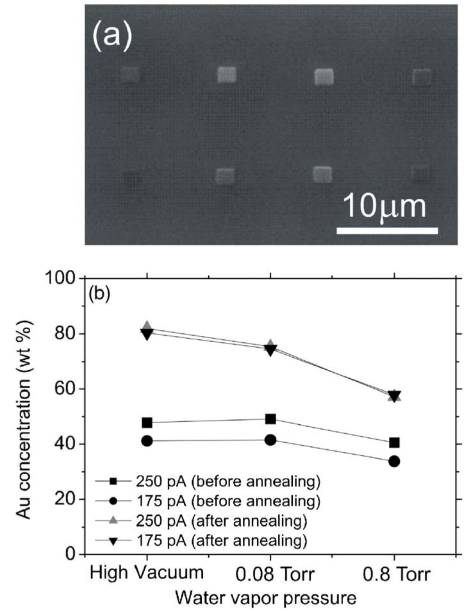

FIG. 1. (Color online) (a) SEM image of a sample used for compositional analysis. (b) Evolution of gold purity with different beam currents and water vapor pressures.

We used an EDX Inca series 200 (Oxford Instruments) with an ultralight window that permits carbon detection. The beam voltage was set to 7 kV to minimize the substrate influence and the collection time was 100 s. The concentration analysis was performed by using the standardless analysis of DTSA software provided by NIST.[13] In this analysis, a thin layer model with thickness of 500 nm was used and a background correction was also applied.

The results are summarized in Fig. 1(b) where the evolution of the gold concentration in weight versus pressure and current is plotted. In agreement with Ref. 6, an increase of beam current from 175 to 250 pA results in higher gold purity. Also, the gold concentration is found to slightly decrease in ESEM mode. By postannealing the samples in air at 400 °C for 30 min the deposition purity[9] can be substantially improved due to the elimination of the lesser stable elements (C and O) from the original deposit. An increase of approximatively a factor of 2 was achieved under high vacuum leading to a gold purity of 82%. SEM imaging on the annealed pads reveals some inhomogeneity (not shown) that we attribute to the clustering of gold originally dispersed within the organic matrix. Comparison of these results with the literature is not straightforward due to differences in the deposition conditions and the precursors used. Botman *et al.*[9] reported a gold concentration of about 95% using the same precursor and *ex situ* annealing of the sample. This concentration is about 15% higher compared to our results but the depositions were carried out with a beam current of 620 pA, three times higher than in our experiment. Our results are closer to those of Koops *et al.*[7] that reported gold concentration improvements from 40% to 83% by heating the sample during the deposition process, when using Me_2Au (tfa) from the same family of *b*-diketonate precursors.

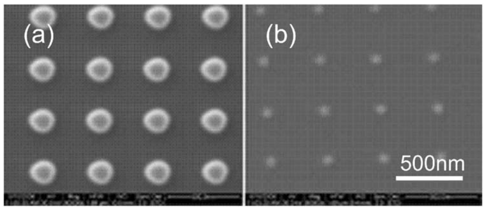

FIG. 2. SEM imaging of a matrix deposited on Si substrate under high vacuum before (a) and after (b) annealing.

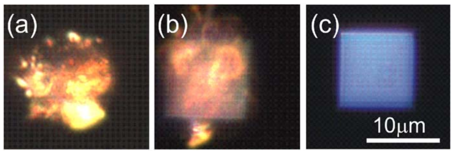

FIG. 3. (Color online) Dark field imaging of a matrix deposited (a) on an ITO substrate. (b) on an ITO substrate coated with 4 nm Ti, and (c) on a glass substrate coated with 4 nm Ti.

For applications to plasmon optics we are interested in submicrometer-sized gold three-dimensional nanostructures with sizes of the order of 100 nm featuring a localized surface plasmon resonance in the visible range of frequencies. On the basis of our previous results, 30 × 30 gold dot matrices (period = 350 nm) were fabricated on a silicon substrate in both high vacuum and ESEM mode at 0.08 Torr. In both cases, the beam current and the column voltage were fixed at 250 pA at 30 kV. The postannealing was performed in air at 400 °C for 30 min, as described previously. After annealing, a dramatic size reduction of the dots was observed. Dots deposited under high vacuum experienced a diameter reduction from 189 [Fig. 2(a)] to 68 nm [Fig. 2(b)]. A similar trend was observed for dots deposited in ESEM mode (from 178 to 68 nm). Atomic force microscope also enabled us to evaluate the change in the dots height which went from 110 nm down to 48 nm under high vacuum and from 125 to 64 nm in ESEM mode. Since the probe beam size of the EDX system we use does not allow structural inspection on individual dots, we opted for an indirect evaluation of their gold purity using scattering measurements in reflection-mode dark-field optical microscopy combined with a microspectrometer. Dark-field imaging of the deposited matrices before and after annealing shows a color change from white blue to yellow red. While these observations tend to indicate the creation of a selective scattering band associated with the dot's localized surface plasmon (LSP) resonance, we were not able to clearly measure the spectroscopic change with our setup. The weak signal from the dots may be partially attributed to the "quenching" of their LSP resonance by the strong absorption of the substrate in the corresponding range of frequencies.

Encouraged by these results on silicon, we extended our study to transparent substrates which offer further flexibility for optical applications. A new gold dot matrix sample was prepared on a glass substrate coated with a thin layer of

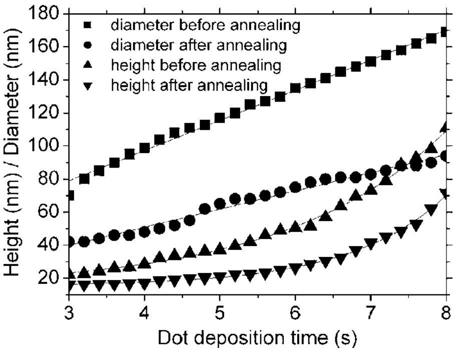

FIG. 4. Evolution with the deposition time of the dot diameter and height on Ti coated glass substrate before and after annealing.

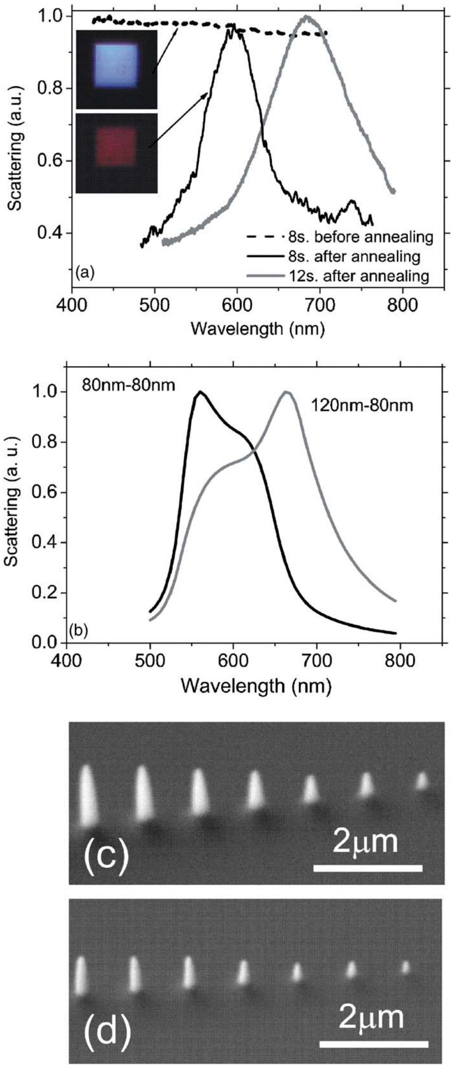

FIG. 5. (Color online) (a) Scattering dark-field spectroscopy on 30×30 matrices deposited with two different deposition times (8 and 12 s) on Ti coated glass substrate (beam current of 250 pA, high vacuum) before and after annealing at 400 °C. (b) Calculated scattering power spectrum for cylindrical gold dots with base of 80 nm and height of 80 nm (black) and base of 120 nm and height of 80 nm (gray). High aspect ratio gold needles grown with deposition times ranging from 30 s to 3 min: (c) before and (d) after annealing (45° tilt images).

indium tin oxide (ITO), widely used in e-beam lithography.

While SEM imaging on the prepared samples showed well defined dots, low contrast patterns can be observed between them. Dark-field imaging reveals that these patterns, which dominate the scattering image, are actually located below the surface plane [see Fig. 3(a)]. This effect is attributed to a chemical reaction between the acetylacetonate precursor and the oxidized layer of the substrate.

With the aim of minimizing this reaction, the deposition was repeated by coating ITO with a 4 nm titanium layer. A weaker effect was thus observed in the optical inspection although it was still significant enough to prevent reliable spectroscopy on each matrix [see Fig. 3(b)]. Finally it was decided to opt for a bare glass substrate coated by a 4 nm titanium layer. This layer is conductive enough to avoid charge effects and reasonably maintains the substrate transparency while minimizing the "quenching" of the dots resonance. While no significant reaction occurred in this case [see Fig. 3(c)], a slight reduction of the deposition rate was observed. In the following, attention was focused on the high-vacuum mode to maintain reasonable deposition times.

In order to evaluate the growth rate on Ti-coated glass, a dot matrix with increasing deposition time, ranging from 3 to 8 s, was fabricated. The beam current and column voltage were kept at 250 pA and 30 kV. As seen in Fig. 4, within the deposition time range considered, the evolution of the dot height follows a monotonous increase. While the deposition rate for 8 s was found to be significantly weaker compared to the case of a silicon substrate, we observed a smaller size reduction after annealing (40% difference in height and 20% in diameter). This tends to indicate that the proportion of gold on Ti-coated glass is higher.

Scattering spectroscopy under unpolarized light of matrices grown with 8 s deposition time was performed both before and after annealing [Fig. 5(a)]. Prior to annealing, the scattering signal showed an almost flat level across the whole visible range. The 30 min annealing at 400 °C led to a dramatic change of the matrix color. Its scattering spectrum features a clear maximum centered at around 600 nm (full width at half maximum of about 80 nm) that we attribute to the dot LSP resonance. In order to check this hypothesis, another matrix with longer deposition time (12 s) was prepared (the base diameter and the height of the dots became 120 and 80 nm, respectively). In good agreement with numerical simulations based on the Green dyadic method, considering pure gold, the scattering resonance is thus found to be red shifted by about 80 nm and significantly broadened [Fig. 5(b)]. A further increase of the deposition time enables growing gold needles with aspect ratios up to 5:1 for 3 min [Figs. 5(c) and 5(d)]. Remarkably, they are not bent by the annealing and their aspect ratios are nearly preserved.

In this letter, the use of EBID as a fabrication technique to grow plasmonic gold nanostructures over a transparent substrate is demonstrated. We have shown that purity and reactivity issues of organic precursors can be partially solved by using a Ti-coated glass substrate combined with *ex situ* annealing. This method enables us to grow resonant plasmonic nanostructures with significant base-height aspect ratio, impossible to achieve with lift-off techniques.

[1] P. Rai-Choudhury, *Handbook of Microlithography, Micromachining and Microfabrication* (SPIE, Bellingham, WA, 1997), p. 139.

[2] S. J. Randolph, J. D. Fowlkes, and P. D. Rack, Crit. Rev. Solid State Mater. Sci. **31**, 55 (2006).

[3] O. Sqalli, I. Utke, P. Hoffman, and F. Marquis-Weible, J. Appl. Phys. **92**, 1078 (2002).

[4] T. H. Taminiau, R. J. Moerland, F. B. Segerink, L. Kuipers, and N. F. van Hulst, Nano Lett. **7**, 28 (2007).

[5] I. Utke, P. Hoffmann, B. Dwir, K. Leifer, E. Kapon, and P. Doppelt, J. Vac. Sci. Technol. B **18**, 3168 (2000).

[6] H. W. P. Koops, J. Kretz, M. Rudolph, M. Weber, G. Dahm, and K. L. Lee, Jpn. J. Appl. Phys., Part 1 **33**, 7099 (1994).

[7] H. W. P. Koops, C. Schossler, A. Kaya, and M. Weber, J. Vac. Sci. Technol. B **14**, 4105 (1996).

[8] S. Graells, R. Quidant, R. Alcubilla, and G. Badenes, Proceedings of the First International Workshop on Electron Beam Induced Deposition, 2005 (unpublished), Vol. 1, pp. 52 and 53.

[9] A. Botman, J. J. L. Mulders, R. Weemaes, and S. Mentink, Nanotechnology **17**, 3779 (2006).

[10] A. Folch, J. Tejada, C. H. Peters, and M. S. Wrighton, Appl. Phys. Lett. **66**, 2080 (1995).

[11] A. Folch, J. Servat, J. Esteve, J. Tejada, and M. Seco, J. Vac. Sci. Technol. B **14**, 2609 (1996).

[12] K. Mølhave, D. N. Madsen, A. M. Rasmussen, A. Carlsson, C. C. Appel, M. Brorson, C. J. H. Jacobsen, and P. Bøggild, Nano Lett. **3**, 1499 (2003).

[13] Joseph Goldstein, *Scanning Electron Microscopy and X-ray Microanalysis* (Springer, New York, 2003), p. 427.