

Novel Patterning of Gold Using Spin-Coatable Gold Electron-Beam Resist

Ki-Chul Kim, Im-Bok Lee, Dae-Joon Kang, and Sunglyul Maeng

ABSTRACT—Conventional lithography methods of gold patterning are based on deposition and lift-off or deposition and etching. In this letter, we demonstrate a novel method of gold patterning using spin-coatable gold electron-beam resist which is functionalized gold nanocrystals with amine ligands. Amine-stabilized gold electron beam resist exhibits good sensitivity, 3.0 mC/cm^2 , compared to that of thiol-stabilized gold electron beam resists. The proposed method reduces the number of processing steps and provides greater freedom in the patterning of complex nanostructures.

Keywords—Patterning method, gold electron-beam resist, functionalized gold nanocrystals.

I. Introduction

The development of advanced biosensors for the diagnosis and monitoring of diseases is an extremely important matter. Fundamentally, a biosensor is derived from the coupling of a ligand-receptor binding reaction to a signal transducer [1]. There have been many studies on biosensors with various signal transduction methods, including optical [2], electrochemical [3], piezoelectric [4], magnetic [5], and mass spectrometric [6] phenomena. The nanoscale optical biosensor is based on the unique optical properties of certain materials such as silver and gold nanostructures. Van Duyne and others reported a nanoscale optical biosensor based on localized surface plasmon resonance (LSPR). Triangular silver nanostructures were fabricated with nanosphere lithography (NSL) [7]. The peak extinction wavelength of the LSPR spectrum is dependent on the shape, size, and interparticle

spacing of the nanoparticles as well as its dielectric properties and those of the local environment. Therefore, the control of shape, size, and interparticle spacing of the noble metal nanostructures is critical in the LSPR spectrum. The use of NSL allows easy formation of noble metal nanostructures, but it does not allow control of shape, size, and interparticle spacing. Conventional lithography methods have many processing steps, including spin coating of a resist, patterning, development, deposition of a noble metal, lift-off of the excess noble metal or deposition of a noble metal, spin coating of a resist, patterning, development, etching of the excess noble metal, and removal of the resist. The lift-off and etching processes are very difficult steps in nanoscale patterning. Contamination from etched materials is an obstacle in the patterning of nanostructures. Our novel gold patterning method using spin-coatable gold electron-beam resist is a very simple and contamination free method. It has a few processing steps including spin coating of the gold electron-beam resist, writing the patterns using an electron beam, and removing the unexposed gold resist from the substrate with a suitable solvent. In this letter, we present our spin-coatable gold electron-beam resist of passivated gold nanocrystals with amine ligands. We demonstrate a novel gold patterning method using this resist.

II. Experimental Details

We synthesized amine-stabilized gold nanocrystals in toluene using a method pioneered by Brust and others in the early 1990s [8]. An aqueous solution of hydrogen tetrachloroaurate (III) trihydrate (20 mL, 5 mM) was mixed with a solution of tetraoctylammonium bromide in toluene (10 mL, 25 mM). The two-phase mixture was vigorously stirred until all of the tetrachloroaurate was transferred into the

Manuscript received Aug. 16, 2007; revised Sept. 28, 2007.

Ki-Chul Kim (phone: + 82 31 290 5946, email: kckim30@skku.edu), Im-Bok Lee (email: imbokl@skku.edu), and Dae-Joon Kang (email: dj kang@skku.edu) are with the BK21 Physics Research Division, Sungkyunkwan University, Suwon, Rep. of Korea.

Sunglyul Maeng (email: slm221@etri.re.kr) is with the Cambridge-ETRI Joint R&D Center, ETRI, Daejeon, Rep. of Korea.

organic layer. A solution of 1-hexadecylamine in toluene (5 mL, 0.13 M) was added to the organic phase. An aqueous solution of sodium borohydride (5 mL, 0.1 M) was slowly added with vigorous stirring. After further stirring for 24 h, the organic phase was separated. Then, it was evaporated to 20 mL and rinsed with a mixed solution of 100 mL of acetone and 100 mL of methyl alcohol to remove the excess amines.

The structural properties of the amine-stabilized gold nanocrystals were characterized by various analyses, including high resolution X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and high resolution transmission electron microscopy (HRTEM).

The amine-stabilized gold nanocrystals were diluted with cyclohexane for spin coating on a Si substrate. The thickness of the passivated gold nanocrystals was controlled by the spinning speed. The writing of the gold patterns was performed with a JOEL JSM-6460, operating at an accelerating voltage of 30 keV, a beam current of 50 pA, and a spot size of 48 nm. To obtain the optimal dosage of the electron beam, the exposure dose varied from 0.1 mC/cm² to 12.0 mC/cm². The pattern size was 1.2 μm×3.2 μm. The unexposed amine-stabilized gold nanocrystals were removed with a xylene for 90 s. The morphology and thickness of the gold patterns were analyzed by atomic force microscopy (AFM) in non-contact mode.

III. Results and Discussion

Figure 1 shows an HRTEM image of the amine-stabilized gold nanocrystals. The size of the passivated gold nanocrystals is around 5 to 10 nm. The shape of the gold nanocrystals is almost spherical. The solution of the diluted gold nanocrystals was dropped on a Si substrate and air dried. An XRD analysis was performed with a scanning rate of 2 degrees per minute. The wavelength of the X-ray was 1.54178 Å in the XRD

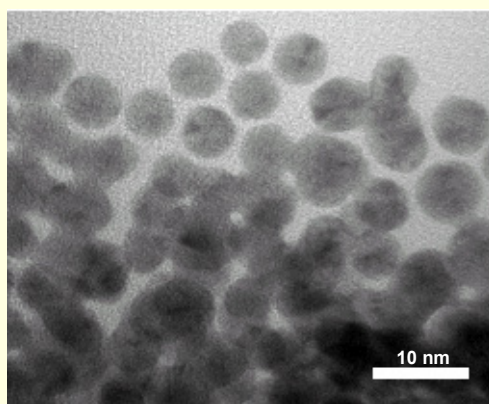


Fig. 1. HRTEM image of the amine-stabilized gold nanocrystals.

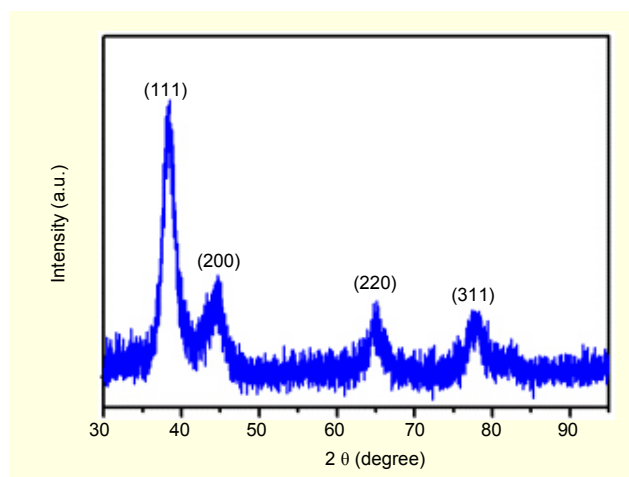


Fig. 2. XRD pattern of the amine-stabilized gold nanocrystals.

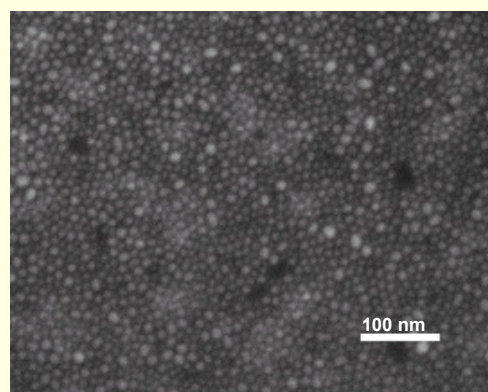


Fig. 3. FE-SEM image of the spin-coated gold nanocrystals on a Si substrate. Spinning speed is 4,000 rpm.

analysis. The XRD pattern of the amine-stabilized gold nanocrystals is shown in Fig. 2. The XRD peaks of the passivated gold nanocrystals matched well with the standard XRD reference peaks (JCPDS: #04-0784).

Figure 3 shows an FE-SEM image of the spin-coated gold nanocrystals. The optimal spinning speed is 4,000 rpm for uniform, pinhole-free coating. Pinholes are generated at speeds higher than 4,000 rpm (not shown).

The AFM images of gold patterns created using the proposed method are shown in Fig. 4. The gold pattern array consists of five rows and six columns. The exposure dose was assigned to each pattern according to the dosage values shown in Fig. 5. The lower images of Fig. 4 represent the scanning height of the third row gold patterns. The patterns of the fifth row cannot be observed due to the insufficient electron beam dose. The exposure dose for the whole gold pattern, the pattern of the fourth row and fifth column, is 1.5 mC/cm². This means that the minimal suitable exposure of the electron beam to strip the hexadecylamine ligands which cap the layer of gold

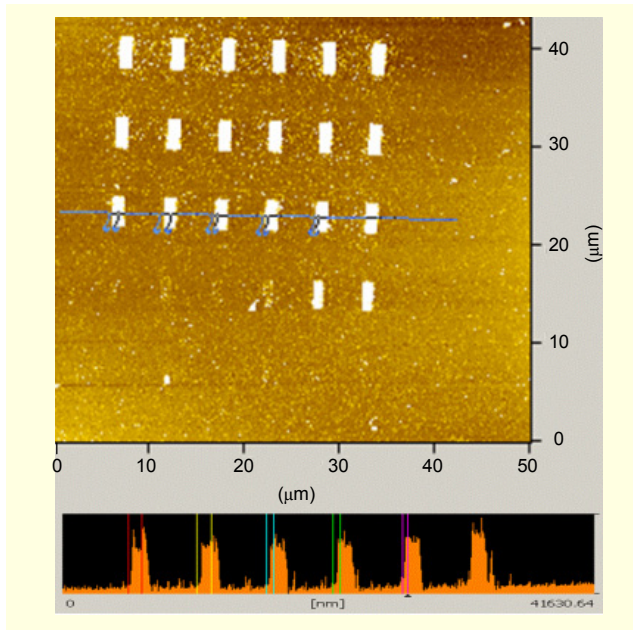


Fig. 4. AFM images of the gold patterns using the proposed patterning method.

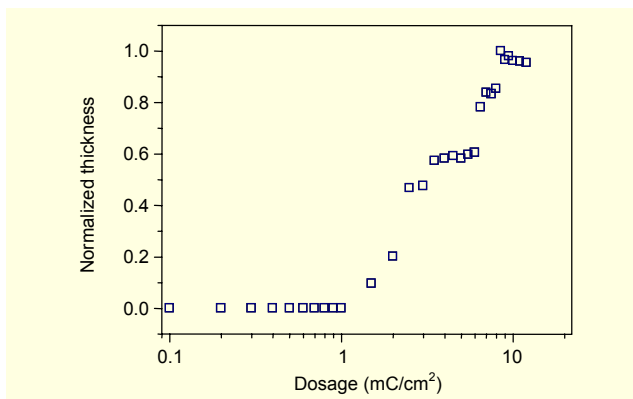


Fig. 5. Exposure response curve of the spin-coatable gold electron beam resist.

nanocrystals is 1.5 mC/cm^2 . This value is much lower than the 7 mC/cm^2 of thiol-stabilized gold resists [9]. The hexadecylamine ligands are stripped from the surface of the gold nanocrystals by electron-beam exposure. Presumably, this occurs through cleavage of C-H and C-C bonds [9]. Once the ligands are stripped, the gold nanocrystals stick to the Si substrate.

Figure 5 shows the exposure response curve of the spin-coatable gold electron-beam resist. The sensitivity is measured at half the height of the normalized thickness. The sensitivity of the amine-stabilized gold resist is 3.0 mC/cm^2 . The maximal thickness of the gold pattern is 56.7 nm at a dose of 8.5 mC/cm^2 . The thickness of the gold patterns is saturated to around 55 nm at doses above 9.0 mC/cm^2 .

IV. Conclusion

We synthesized a spin-coatable negative-tone gold electron-beam resist which was stabilized with hexadecylamine. A novel gold patterning method was demonstrated with gold resist. The amine-stabilized gold resist exhibited better sensitivity than thiol-stabilized gold resists [9]. The results of this study would be very helpful for realizing well-controlled nanoscale optical biosensors using the LSPR effect.

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