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Photo-induced evolution of copper sheets from cluster molecules and its application to photolithographic copper patterning

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Abstract. UV photoexcitation of (t-butylethynyl copper)$_{24}$ cluster films induces segregation of the crystals into metallic and organic phases and leads to evolve the metallic sheets sandwiched by organic polymers. The growth of the metallic crystals in the plane of the photo-electromagnetic field is attributed due to plasmon-plasmon interaction among nanoparticles embedded in dielectric polymer matrices. The surface enhanced photochemical reaction of residual cluster molecules on the photon incident direction is expected to take an important role for joining the metal particles to produce a metallic sheet. We can apply this phenomenon for photolithographic copper pattern generation on a flexible base plate.

PACS. 68.37.-d Microscopy of surfaces, interfaces, and thin films – 68.37.Lp Transmission electron microscopy (TEM) (including STEM, HRTEM, etc.) – 68.55.-a Thin film structure and morphology – 78.20.-e Optical properties of bulk materials and thin films – 78.67.-n Optical properties of low-dimensional, mesoscopic, and nanoscale materials and structures – 81.16.Rf Nanoscale pattern formation

1 Introduction

Generation of hot electrons in nanoparticles can be performed with efficient energy pumping from light harvesting π electron networks of organic matrices to metallic clusters and nanoparticles. Nitzan and Brus [1] presented a theoretical model for enhanced photochemistry of molecules interacting with electromagnetic fields and isolated microscopic metal particles. They predicted the importance of energy transfer from excited molecules to higher order ($l > 1$) multipole resonances in the metal particles. Later, Chen and Osgood succeeded to observe the growth of elliptical Cd particles and their well alignment with the electric field of the 257 nm light [2]. Metallic copper is the best material for electronic conduction because of its low resistivity and enthalpy of fusion. We have developed a method of the photolithographic metallic copper pattern generation with organometallic cluster molecule films. There has been a big gap for growing copper nanoparticles to a single copper sheet. The application of the UV radiation field on an organometallic-cluster molecular film is expected to induce photochemical reduction of metallic cations to produce metallic nanoparticles. The metal particles can produce hot electrons in plasmon states not only by the direct optical excitation but also through efficient energy transfer from the light harvesting π electron networks of the organic environment. The hot electrons oscillating with the electromagnetic field couple with excited phonon states and activate the motional rearrangement of metal atoms. An organometallic cluster molecule, (t-butylethynyl copper)$_{24}$; [Cu–C≡C–^{t}Bu]$_{24}$ (^{t}Bu:–C(CH$_3$)$_3$) contains the light harvesting unit of ethynyl chromophore and the lowest excited state is the π-d charge transfer triplet state. Figure 1 shows the crystal structure of [Cu–C≡C–^{t}Bu]$_{24}$ [3,4]. As seen in the figure, c-axis is 2.228 nm in contrast to a = 1.419 nm and b = 1.526 nm. The 24 copper atoms form a S-shaped

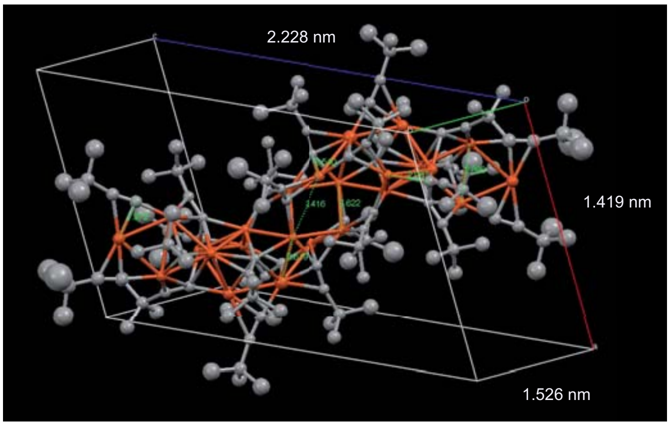

Fig. 1. (Color online) Crystal structure of (t-butylethynyl copper)$_{24}$ cluster molecule from reference [4]. Red line: a-axis, green line: b-axis, and blue line: c-axis. Hydrogen atoms are omitted in the figure. Orange balls are copper cations and grey ones carbon atoms.

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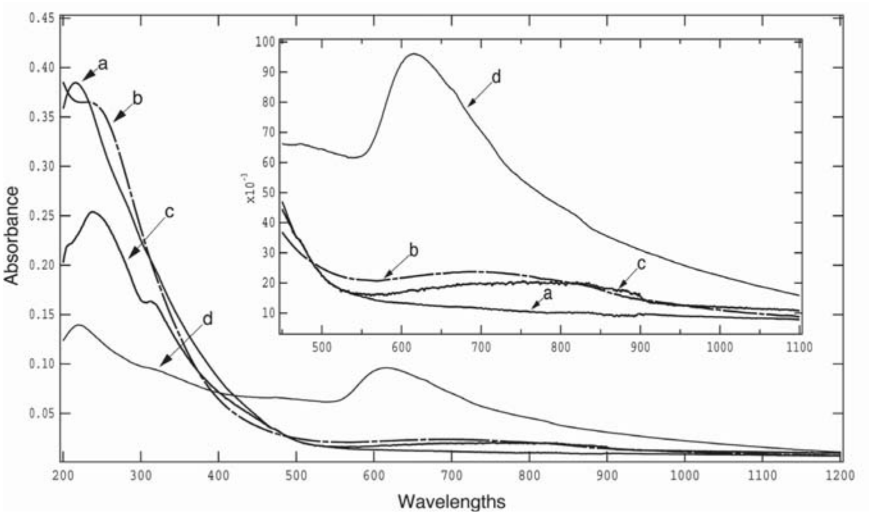

Fig. 2. Electronic absorption spectra of solid films of (t-butylethynyl copper)$_{24}$. (a) Original film, (b) UV lamp (high pressure mercury) irradiated for 2 h, (c) 12 000 shots of KrF laser pulse irradiated at an energy density of 1 mJ/cm^2, (d) heated at 250 °C for 2 h.

skeleton attached with a outer cover of hydrophobic 24 ^{t}Bu groups. It is expected that the S-shaped molecular plane is situated in parallel to the base plate surface of quarts or organic polymers. Photoexcitation of [Cu–C≡C–^{t}Bu]$_{24}$ films induces segregation of the crystals into metallic and organic phases.

2 Experimental

n-Hexane solution of [Cu–C≡C–^{t}Bu]$_{24}$ cluster molecules is used at a concentration of (1–5) × 10^{-4} M for the preparation of thin films with the aid of a spin-coater. Surface and cross-sectional observation of the copper acetylide film on a silicon (111) surface is done with a scanning electron microscope (SEM), and the optical absorption measurement is performed for the films on quartz plates. A typical thickness of the film on the silicon is 15 nm for a coater rotational speed of 1500 rpm. Slower rotation provides thicker films. For high resolution transmission electron microscope (HRTEM) measurement with a JEOL JEM-3200, the solution is coated on a collodion membrane with a 200 mesh disk. The cross sections of the photo-irradiated films are observed by sectional slicing of the films on a polyimide layer attached on an epoxy base plate with a microtome as thin as 70 nm.

3 Results and discussion

n-Hexane solution of [Cu–C≡C–^{t}Bu]$_{24}$ at 5 × 10^{-4} M is used for making a film on a base plate (quartz, silicon, or polyimide). After measuring the optical absorption spectrum, we heat the film at 250 °C for 2 hours, or irradiate UV light from a high pressure mercury lamp or a KrF 248 nm excimer laser. Figure 2 shows the absorption spectra of non-treated [Cu–C≡C–^{t}Bu]$_{24}$ film on a quartz plate (a), the film irradiated with Hg lamp for 2 h (b), the film irradiated with 12 000 shots of KrF laser pulses at a power density of 1 mJ/cm^2 (c), and the heated film (d). The non-treated film is almost transparent at the visible region as seen in spectrum (a). The electronic absorption of 1×10^{-5} M of [Cu–C≡C–^{t}Bu]$_{24}$ in n-hexane starts from 530 nm to higher energies and the phosphorescence spectrum starts from 520 nm to lower energies with a peak at 610 nm. This means that the monomer cluster molecule does not show any recognizable absorption around 600 nm. Spectrum (b) is composed of the plasmon band with a maximum at 610 nm and a tail toward the low energy side. It also shows a strong absorption band at 247 nm. The plasmon band at 610 nm is assigned to originate from the spherical Cu particles [5–7]. The strong UV absorption comes from the polymer matrix with π electrons. On the other hand, spectrum (c) shows a very broad absorption from 900 nm to 540 nm with a peak at 700 nm. Spectrum (d) is also very broad but the intensity is much stronger at lower energy region as compared with the broad band in spectrum (c). The broadness or flatness of the band suggests the formation of particles with high polydispersity such as cube-shaped or plane-shaped large size particles [6]. Jana et al. reported that the cube-shaped particles with sizes of 150–250 nm show a broad absorption band from 400 nm to 800 nm with a maximum at 550 nm [6]. The difference in the spectral shapes is well understood by comparing the TEM images of the respective films.

Figure 3 shows the difference in the TEM images of the films prepared on collodion membranes with three conditions: (a) heated at 250 °C for 2 h, (b) irradiated with a high pressure mercury lamp for 2 h at 16 mW/cm^2 for 253.7 nm, and (c) irradiated with 12 000 shots of KrF laser pulses at a weak energy of 1 mJ/cm^2. The heated film exhibits spherical or polyhedral particles with somewhat discrete sizes of 3.5 nm, 7 nm (main), and 11 nm. These are embedded in a polymer matrix produced by the polymerization of [–C≡C–^{t}Bu]$_n$. This feature is in consistent with the appearance of the strong plasmon band at 610 nm characteristic of spherical copper particles [3–5]. The photo-irradiated films show images completely different from the heated one. The lamp irradiated film shows metallic domains of 5–20 nm which are in contact with other domains but each one exhibits random orientation of the lattice axes. This random orientation is changed in

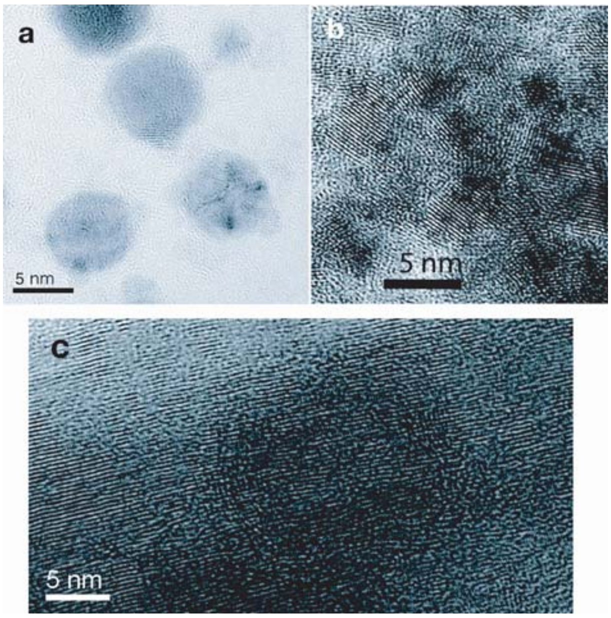

Fig. 3. High resolution TEM images of the spin-coated (t-butylethynyl copper)$_{24}$; (a) heated at 250 °C for 2 h, (b) irradiated with a high pressure mercury lamp for 2 h, (c) irradiated with 12 000 shots of KrF laser pulses at an energy density of 1 mJ/cm^2.

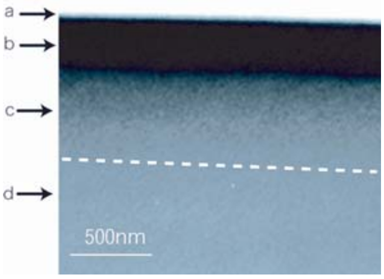

Fig. 4. A TEM image of the cross-section of a thick film of (t-butylethynyl copper)$_{24}$ irradiated with 12 000 shots of KrF pulses at 3 mJ/cm^2. The cross-sectional plane of the photolyzed film was sliced into a piece of a film as thin as 70 nm. (a) Top polymer layer as thin as 20 nm, (b) metallic copper layer as thick as 300 nm, (c) polymerized $[-C{\equiv}C{-}^tBu]_n$ layer, and (d) base polyimide plate.

the laser irradiated film. Although the atoms are not so well aligned as three-dimensional crystalline metals, it is recognized that the lattices are on a way to be fixed along a favorable direction over the whole area. This suggests that the metal atoms are located in a nearly two-dimensional sheet or, in other words, the structural constraint along the direction perpendicular to the film plane is rather weak. The observation of the lattice patterns with a spacing of 0.26 nm is in consistent with the copper-copper distance seen in (111) plane of copper fcc crystals. Thus we can recognize that the laser excitation can evolve a very wide sheet of copper atoms from the cluster molecules. From the SEM observation of the films deposited on silicon plates, the thickness of the films was estimated to be 15–50 nm.

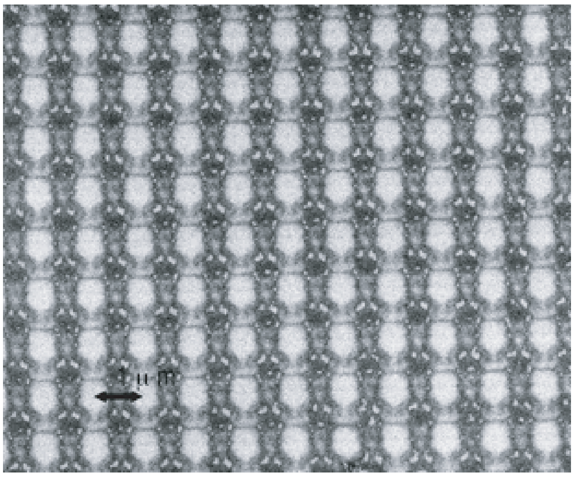

Fig. 5. A SEM image of the copper dot array pattern on silicon (111) surface obtained after washing non-photolyzed (t-butylethynyl copper)$_{24}$ with n-hexane. The black parts are the base silicon area and white parts are the top cover of the organic polymer on metallic copper disks. The arrow bar is 1 μm long.

In order to observe the metallic layer clearly, we repeated the coating to make a cluster molecule film on a polyimide base plate to be as thick as 900 nm. Figure 4 shows the cross-sectional TEM image of the film irradiated with 12 000 shots of KrF pulses at 3 mJ/cm^2. The black metallic layer is 300 nm thick. On the top of the metallic layer, one can see the white layer as thin as 20 nm that is attributed to one part of the polymer layer, $[-C{\equiv}C{-}^tBu]_n$. The main part of the polymer layer is located below the metallic layer and it is as thick as 550 nm. It is interesting that the metallic copper layer is located toward the light incident plane of the film and the most of the polymer part is located below the metallic layer. This means that the original metal atoms in the cluster molecules situated on the bottom of the film travel more than 500 nm to the upper upon the photoexcitation. Since the charge-neutralization reaction with metallic cations and ethynyl anions occurs on the light incident side, the metal atom aggregation will be induced toward the light incident direction as well as toward the photon electric field in the film plane, the primary generated metal particles are expected to grow toward the light-incident direction by accumulating the newly neutralized copper atoms on this side. Thus the growth rate of the metallic particles located on the incident side can be faster than those located on the other side deeper and the larger plasmon dipole moment of bigger particles is expected to attract smaller particles located deeper in the photon field.

An application of this phenomenon is the photolithographical metallic pattern generation. For the check of the possibility, we used the chromium masks fixed on a quartz plate. This mask is the square dot arrays (1 μm × 1 μm) aligned at every 1 μm. Figure 5 displays a SEM image of the copper dot array made by this photolithograph of the film on the silicon (111) surface. The non-reacted cluster molecules were washed out with n-hexane.

The black parts are the see-through exposure of the silicon base plate and the white parts are metallic disks covered with the thin organic polymer layer. The thick polymer layer also exists between the copper disks and the silicon base plate insulating the disks from the base plates. Due to the imperfect contact of the chromium photomask with the cluster film, the dot pattern is accompanied with satellite mustaches produced by light interference effects. The photolithograph patterns suggest that the sub-micron patterning can be made by good contact of the masks with the film. This method is applicable for making any copper pattern with several hundred nm widths. After removing the thin polymer layer on the top by UV laser-sputtering, one can deposit or cover semiconductor domains on the selected copper disks or lines.

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