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SUBMICRON-WIDE PATTERN OF SILVER WIRE STABILIZED ON FUNCTIONALIZED SUBSTRATES

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A stable submicron-wide electric conductive pattern consists of silver nanoparticles/polymer composite is established via photolithographic procedure, in which the introduction of furan-functionalized surface for the chemical anchoring of the pattern was a significant contrivance. Due to the strong anchoring between narrow-patterned film and the treated substrate, submicron-wide patterns stands up well against the development and annealing process. Approximately 180 nm-wide nanopattern has been achieved by the irradiation of 488 nm light. The width is well below the dimension of the incident light wavelength. Time dependence of the electric resistance of the composite thin film during annealing process has been measured at 200°C, and an optimum annealing time was found. The achieved volume resistivity after the optimum annealing was evaluated as $\sim 8 \times 10^{-4}$ *Ohm·cm that was determined by four-probe measurements.*

Keywords: chemical anchoring; electric conductive pattern; furan-functionalized surface; metal nanoparticles; photolithography

INTRODUCTION

Following the development of nano-science and nano-technology research field, a variety of techniques for the fabrication of nanoelements such as nanoparticles, nanotubes and nanowire have been widely reported [1–5].

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Although it is a matter of course that the invention of nano-scale elements and the development of their fabrication method are important, the patterning or orientation control of nano-scale elements are also key technology for nano-science and nano-technology. The lack of effective assemble procedures of nano-scale elements may bring about a serious barrier in order to realize a nano-devices in the framework of bottom-up processing scheme. For example, a fabrication technology of conductive nano-wire is one of the most useful item for realizing nanometer-sized device circuits. The establishment of such technology makes us possible to connect nano-elements each other and to form two-dimensional electrical linkage.

In the circumstances, we have started to investigate that two-dimensional pattern fabrication of electric conductive nano-wire from the viewpoint of top-down technology. For our first example, a composite system of metal nano-particles and photo-reactive polymer was adopted as an object. The schematic illustration of the concept is depicted in Figure 1.

It is because that this kind of composite system is reasonable from several technological viewpoints. The first one is that photo-reactive polymer allows a facile optical patterning, and it also acts as a nano-particle support and an anchoring matrix on the substrate. Then any

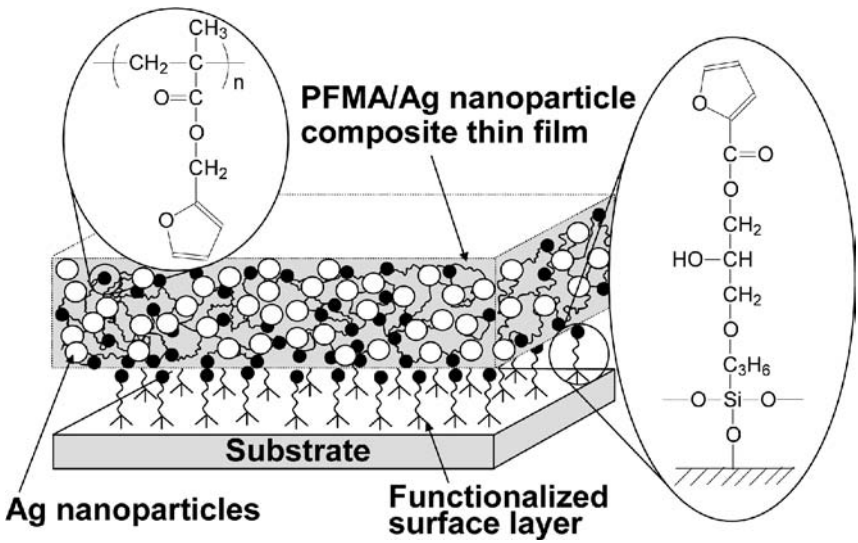


FIGURE 1 Schematic illustration of metal nanoparticle/polymer composite sample prepared on a glass substrate with furan-functionalized surface. (open and solid circles indicate silver nano-particles and furan end-group, respectively.)

two-dimensional conductive patterns are possible to obtain via a lithographic procedure very easily in our proposed system. Usually, it often occurs that the width of the desirable pattern getting narrower the durability of the pattern against processing steps (such as development) gets decreased. In order to eliminate this undesirable risk, we have introduced an anchoring layer (photo-reactive group) that binds the patterned film to the substrate via covalent bond. This was achieved by using a glass substrate with a furan-functionalized surface. The second is that the migration and agglutination of the metal nano-particles in a polymer matrix become to be carried out well with the particle size smaller. Namely, diffusion constant changes in inverse proportion to the particle size. It is also known that melting temperature of metal nano-particles is remarkably reduced compare to that of the bulk. For example, the value of approximately 300°C is reported for 2 nm-diameter gold nano-particles [6]. These facts mean that metal nano-particles are essentially useful for the electric conductive pattern formation. In a variety of metals, gold and silver are very good materials. Since the size of these metal nano-particles can be controlled precisely via chemical reduction method [7] and are also excellent electric conductors, silver metal has been taken up in the experiments of this study. Finally, the composite system of metal nano-particles and photo-reactive polymer are considered to have merits from a viewpoint of industrial production such as great potentialities for low-cost and vacuum-free processing, low-temperature (or, non-thermal but optical) curing procedure, and offering a flexible wiring.

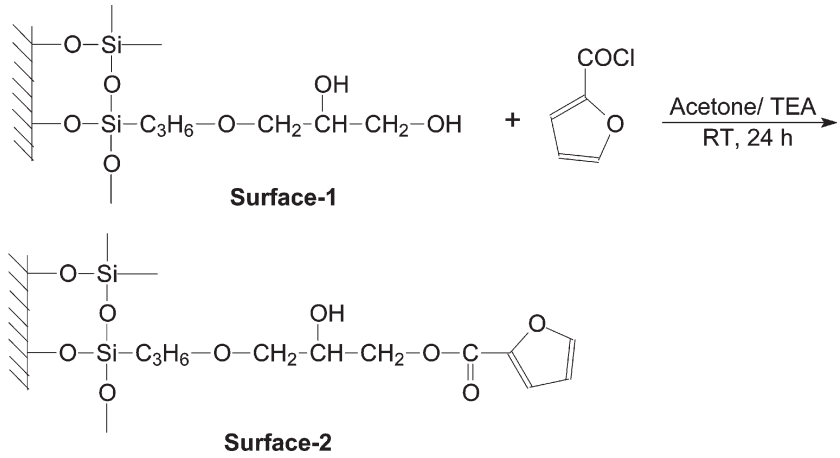
EXPERIMENTAL

Materials

Fullerene (better than 99% pure) and 2-furoic chloride were produced from Tokyo Chemical Industrial Co., Ltd., and γ-glycidoxypropyltrimethoxy silane (GPS) was obtained from Aldrich Chemical Co. Silver nano-particles were provided from Harima Chemicals, Inc. All reagents were used without purification unless otherwise noted. Distilled water was prepared in a purification system (WG221S, Yamato Scientific Co., Ltd.). Conventional glass slides (S-1111, Matsunami Glass Ind., Ltd.) were used as substrates. PFMA was prepared according to a procedure previously reported by Arai and co-workers [8].

Chemical Modifications of Glass Surface

The surface treatment of glass substrates was basically referred that of reported in ref. [9]. The individual steps are summarized briefly in the



SCHEME 1 Chemical modification of glass surface.

following (Scheme 1). The substrates were subjected to an ultrasonic cleaning in a washing agent (Extran MA 01, Merck Ltd.) in order to eliminate organic contamination from the surface. After the cleaning, the substrates were rinsed with distilled water and dried up. Then, the substrate was placed in a reaction vessel to which was added 1% (v/v) GPS and 0.2% (v/v) triethylamine in anhydrous toluene. The vessel was stirred and kept at 70°C for 4 h before washing with toluene and acetone. It was then dried in a vacuum overnight at 50°C. The obtained surface bearing terminal epoxy group was hydrolyzed by immersing the substrate in a 100 mM NaCl solution adjusted to pH 4 and 10 mM HCl, and heated to 70°C for 30 min, followed by rinsing with distilled water and drying in a vacuum. Finally, the surface (i.e., Surface-1 in the Scheme 1) baring terminal hydroxyl groups was then immersed in a solution of 2-furoic chloride (26 mg, 0.2 mmol) in acetone of 20 ml with pyridine (23 mg, 0.3 mmol), which was stirred at room temperature for 24 h. It was then rinsed with distilled water and acetone and dried in vacuum. The substrates (i.e., Surface-2 in the Scheme 1) with furan-functionalized surface were stored in N_2 atmosphere.

Preparation of Photosensitive Film

The silver nano-particles of about 5 nmϕ were mixed with furan-based photo-reactive polymer (Polyfurfuryl methacrylate: PFMA) and Fullerene (C_{60}) at the weight ratio of 70.0:29.8:0.2. Number averaged molecular weight of the PFMA polymer measure was 2.2×10^4. Fullerene was used

as a photosensitizer and an initiator for the furan photo-oxidation in this system. The mixed materials were dissolved into toluene at the concentration of 12 wt%. Dark-brown homogeneous dispersion was obtained whose absorption maximum and absorption edge are about 460 nm and 670 nm, respectively. Thin films of the composite systems ($\sim$135 nm-thick) were obtained by spin coating onto virgin and surface modified glass substrates treated with a silane-coupling reagent bearing a furan functional group.

Imaging and Annealing

Then the optical patterning was performed with a photomask under the irradiation of a continuous wave Ar^+ ion laser beam (circular polarized 488-nm) at an intensity of $\sim$50 mW/cm^2 in the air for 10 min. The whole process of the optical patterning were performed in the ambient condition in contrast to the lithographic process with usual photoresist materials that requires vacuum or any gas-purge and temperature controlled condition. After the light irradiation, the film was annealed on a hot plate at 100°C for 1 min in order to complete a photo-triggered crosslinking reaction. Next, the film was developed in toluene/methanol (2/1,v/v) solution for 4 min, then performed ultrasonic cleaning in toluene/methanol (1/3, v/v) solution for 1 min, and finally rinsed with methanol. The sample was then annealed again on a hot plate under a stream of nitrogen at 100°C for 1 min and at 200°C for 40 min in order to induce an agglutination of the silver nano-particles for a formation of electric conductive pathway in the film. During the annealing process, the color of the film changed from dark-brown to metallic originated from a development of plasmon resonance reflection.

Characterization

Molecular weight of obtained polymer, PFMA, was estimated by gel permeation chromatography with two Tosho columns (G4000HXL and G3000HXL) using THF as the eluent at 40°C after calibration with standard polystyrene. UV-visible spectrometer (UV-3100s, Shimadzu Co.) was used to confirm the surface modification by furan functional group. AFM images of the surfaces on the samples were taken with a Nanoscope III of Digital Instruments in a tapping mode operated under ambient conditions. The cantilever used was a commercially available etched silicon probe (TESP, Digital Instruments, Inc.) with a length of 125 μm and resonant frequencies of 294–356 kHz. Electric resistivity measurements were carried out by means of a four-probe technique, using a high-performance low resistivity meter (MPC-T600, Dia Instruments Co., Ltd.).

RESULTS AND DISCUSSION

The UV spectrum of a substrate after the chemical modification process was investigated by using a UV-vis spectroscopy to confirm the surface density of furan-functionalized silane on the surface. Figure 2a and b show the spectrum for the substrate and the calibration curve obtained by using 2-furoic chloride as a model compound, respectively. From the results, the surface density of the furan-functionalized silane was calculated as $\sim 26\,\text{Å}^2$/silane. The dimensions are almost the same with that of the calculated surface density for the occupation area of the furan moiety ($\sim 25\,\text{Å}^2$), which means that the functional moieties are introduced almost in a close packing on the surface.

As a preliminary experiment, the necessity of the anchoring layer on the glass substrate for optical patterning of the PFMA polymer has been

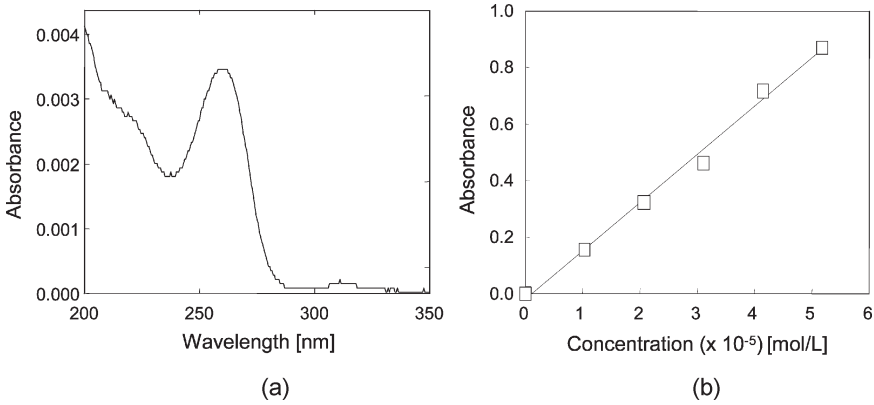
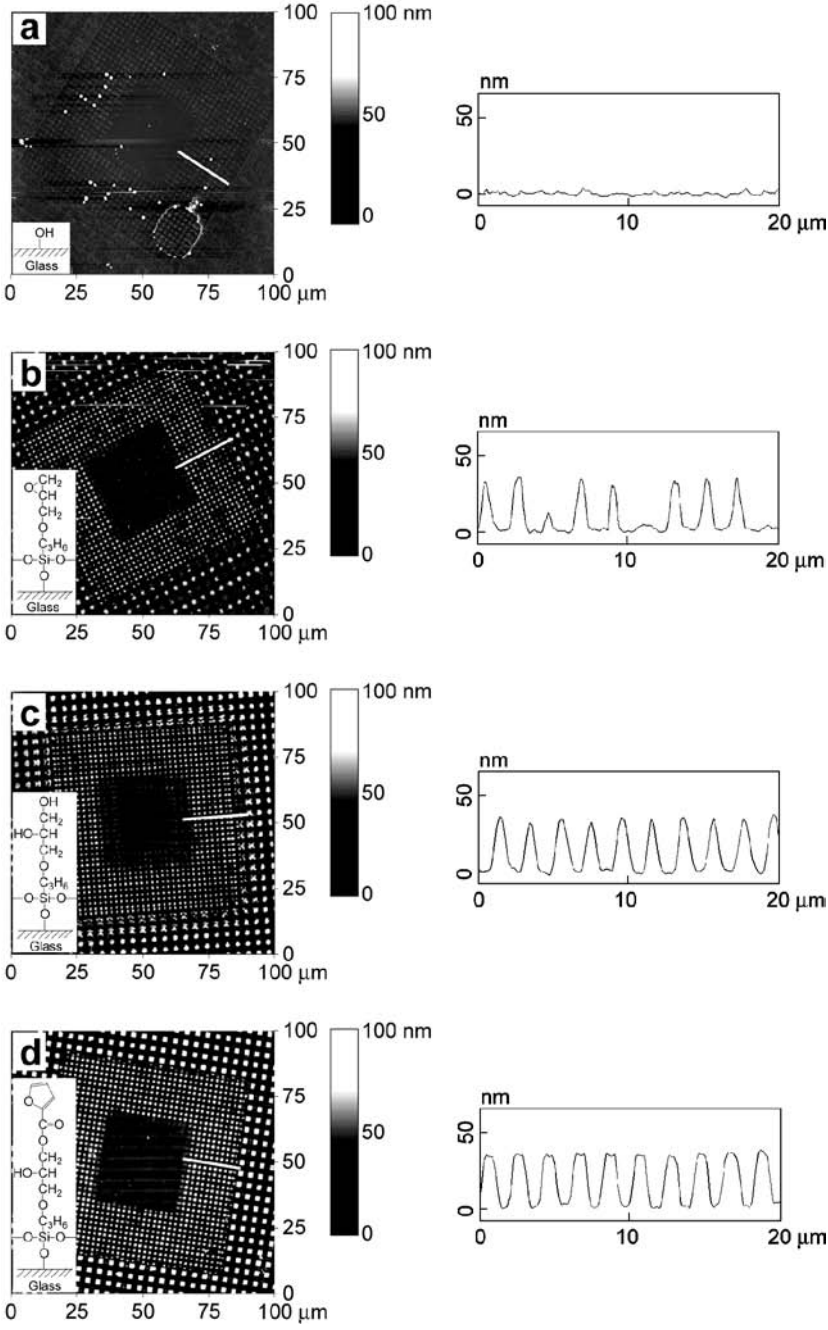


FIGURE 2 Characterization of the furan-modified substrate: (a), absorption spectrum of a quartz plate modified with a furan functionalized silane-coupling agent on its surface; (b), calibration curve between absorbance and concentration of solution of model compound 2-furoic chloride in chloroform. The chemical modification of the quartz plate was performed as the same modification procedures for the glass slide mentioned in experimental section.

FIGURE 3 AFM images of patterned C_{60} doped PFMA film (30 nm-thick film) that does not contain silver nanoparticles. The films were spin coated on (a) a virgin glass slide as well as a surface treated glass slide with (b) an epoxy-, (c) a hydroxy- and (d) a furan-functionalized silane-coupling reagents. The cross-sections in the right-side figure are relative to the position where indicated by the white line in the left-side AFM images, respectively. The insets of the left-side AFM images indicate the condition of the glass surfaces.



examined. The quality of photolithographic pattern for the samples with and without glass surface modified by silane coupling reagents was compared through surface observation using an atomic force microscope (AFM). Figure 3 (a) clearly indicates that the pattern was almost washed away after the development process when the polymer was just spin-coated on a virgin glass substrate. On the other hand, even though the experimental procedure was exactly the same, the pattern remained satisfactorily when it was fabricated on the surface of glass substrate with furan-functionalized silane coupling reagent (Fig. 3 (d)).

This result suggests that the anchoring layer between the photo-reactive polymer thin film and the glass substrate is indispensable for the optical micro- (or nano-) patterning. We also examined the same patterning experiment with the sample prepared on the glass substrates treated by silane coupling reagent bearing other functional groups such as epoxy and hydroxyl group, which are not able to crosslink with the PFMA polymer upon the light irradiation. As shown in the Figure 3 (b) and (c), their patterns remained at some extent but were not clear as Figure 3 (d). This is understood, that the introduction of silane coupling reagents bearing epoxy or hydroxyl groups are effective in increasing the degree of adhesion of the polymer thin film, but are not strong enough since the anchoring force is just originated from a physical interaction but not a chemical bonding.

We also confirmed that the introduced anchoring layer works on the C_{60} doped PFMA composite thin film containing silver nanoparticles as well, corresponding to the result in Figure 3. In this experiment, a mixing ratio of the silver nanoparticles were adjusted approximately 70 wt% in order to ensure the formation of electric conductive pathway in the film, though such a high concentration of metal nano-particles may bring about

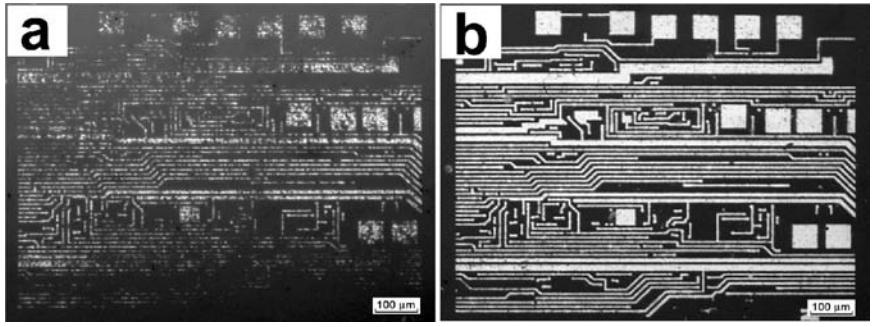


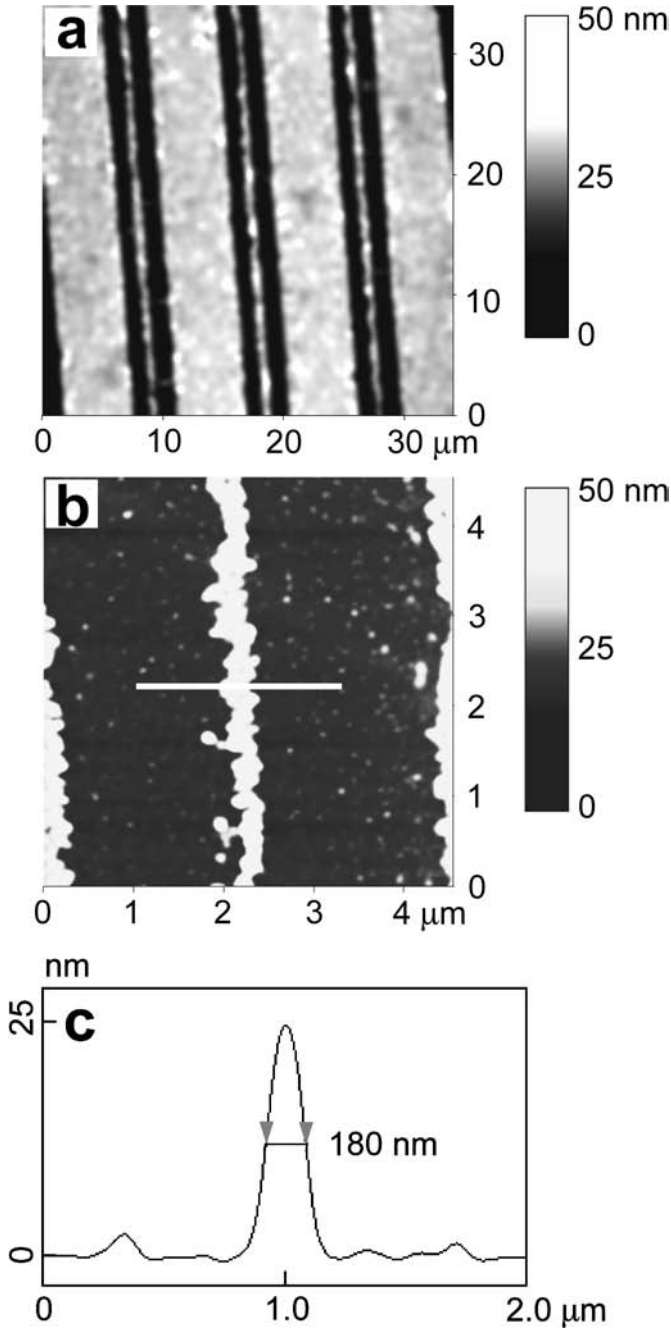
FIGURE 4 Photographs of C_{60} doped silver nano-particles/PFMA composite thin film (25 nm-thick film) patterned on (a) virgin and (b) furan-functionalized glass substrates.

a risk to decrease patterning durability at some extent. Figure 4(a) and (b) show the photographs of the composite thin film formed on the virgin and furan-functionalized glass substrates, respectively. It is understood that a clear-cut high quality pattern could be obtained on the surface modified glass in contrast to that of the virgin one, even though the samples were treated with the same experimental procedure.

This result gives an obvious evidence for the role of the furan-functionalized layer mentioned above. Also, it is confirmed that the pattern could be clearly fabricated without any serious degradation of the patterning durability even in the metal rich composite film as far as it is fabricated on the furan-functionalized glass substrates. In other words, the chemical and physical durability of the obtained pattern was fairly high, in spite of the content of the PFMA polymer (supporting matrix) was only $\sim$30 wt% in this composite system. Namely, it is considered that the affinity between the silver nano-particles and the PFMA polymer is quite good and, as a result, the silver nano-particles are wrapped and fixed by the polymer chains in the film. Since the furan units are able to crosslink each other via photo-oxidation induced polycondensation, the PFMA forms three-dimensional network structure. It is expected that the obtained patterns are anchored strongly via covalent bonding to the glass substrate bearing furan units on the surface. Consequently, the silver nano-particles are able to remain in the polymer matrix even after developing treatment in spite of the submicron-wide pattern and the low content of polymer. In addition, the high concentration of the metal nanoparticles in the composite material is absolutely important for the formation of conductive micro- or nano-wire. However, there is a trade-off relationship between the quality of the pattern using the composite system and electric conductivity, which is totally depended on the content of the polymer matrix and metal nanoparticles, respectively. Therefore, from this point of view, we can conclude that the introduction of the photo-reactive anchoring layer between the composite film and the glass substrate is one of the crucial ways to achieve our purpose.

Figure 5 shows the typical example of submicron-wide pattern of the C_{60} doped silver nano-particles/PFMA composite thin film fabricated on the furan-functionalized glass substrate. The image was obtained by the AFM. From the cross section analysis, the full width at half maximum of the wire was approximately 180 nm. The resolution of the pattern may be improved further, if another excitation method such as the irradiation of optical near field, electron beam and X-ray are employed.

The characteristic of the electric resistance during the annealing process was acquired as a function of the time elapsed (Fig. 6). The resistance decreased dramatically during the first stage of annealing (till $\sim$15 min), then it gradually reached the minimum value after about 40 min. The



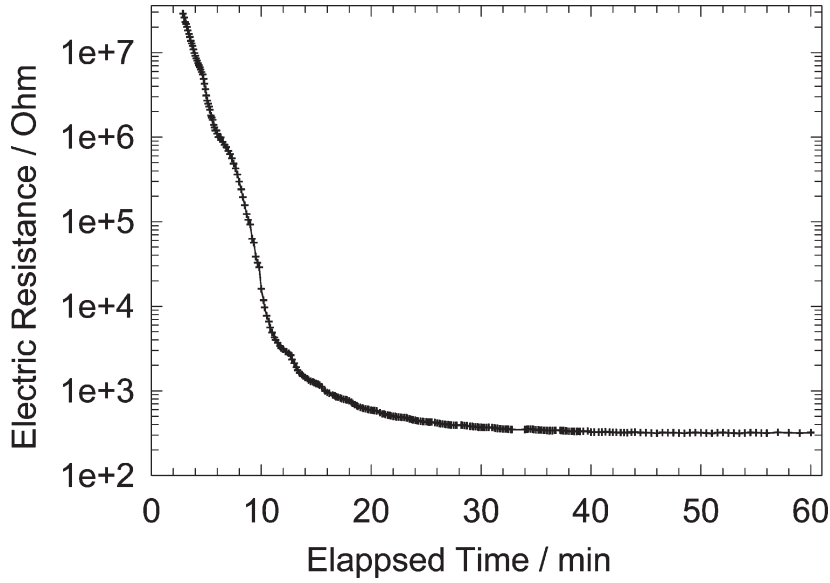


FIGURE 6 Time dependence of the electric conductivity of the C_{60} doped silver nano-particles/PFMA composite system (135 nm-thick film).

resistivity of this composite system was measured, independent of the *in situ* measurement after an annealing treatment for 40 min on the hot place at 200°C filled with nitrogen gas. The achieved volume resistivity was $\sim 8 \times 10^{-4}$ Ohm·cm evaluated by four-probe measurement. The mechanism for the appearance of electric conductivity in this composite system is considered as following: the silver nano-particles dispersed homogeneously in the PFMA polymer are activated by heating and are allowed to migrate and agglutinate with each other. Thus the electric pathway is formed spontaneously during annealing process. This is correlated with a color change of the composite film to exhibit a metallic luster during the annealing process. In fact, the agglutination mechanism has been studied by Oku *et al.* [10,11] for gold nanoparticles 200°C, in which the nano-particles were covered by organic surfactant. They concluded that the metal nano-particles tend to coalescence during annealing due to the surface diffusion of gold

FIGURE 5 AFM topographic (a, b) and cross section (c) images of submicron-wide pattern of the C_{60} doped silver nano-particles/PFMA composite thin film (25 nm-thick film). The cross-section in (c) is relative to the position where indicated by the white line in (b).

and organic surfactant and surface tension of the nanoparticles. Furthermore, Zhao *et al.* [12] recently reported the melting properties of sized-selected isolated silver nanoparticles. Namely, even though the melting point (T_m) of an isolated silver nanoparticles with diameter of ~ 5 nm is calculated as $\sim 800^{\circ}$C, the surface overlayer melt at a critical temperature T_c which is well below the melting point T_m. That is because of the more weakly bound and less constrained in their thermal motion [13,14] than those in solid core.

SUMMARY

In summary, we explained a fabrication method of submicron-wide electric conductive patterns using silver nanoparticle/polymer composite formed on furan-functionalized substrate. It was confirmed that the furan-functionalized anchoring layer is indispensable for the optical micro- (or nano-) patterning of the composite film, which brings about the significant durability and fixation on the substrate caused by the chemical interaction between the film and the anchoring layer. Furthermore, the pattern of the composite was successfully formed on the anchoring layer, even though the composite contains silver nanoparticle at very high mixing ratio ($\sim$70wt%). After annealing process, the film possessing low resistivity has been successfully achieved. It was also confirmed that the full width at half maximum of the photofabricated pattern could be reduced to 180 nm at the least in our experiment. The width can be reduced further, when the fine-tuned lithographic technique such as near-field optical lithography is employed. Our photofabrication technique of an electric conductive sub-micron pattern is one of the promising processing methods for nanoscale electric devices.

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