Colloid Formation from Vacuum Deposited Au Thin Layer on a UV-light Pre-exposed Polysilane Film

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Vacuum deposited gold thin layer on a UV-light pre-exposed polysilane film underwent colloidal gold formation by heating. This process was found to accompany the degradation of polysilane by catalytic oxidation due to the formed colloidal gold. Such a phenomenon occurred in only the combination of polysilane and gold.

Composite materials consisting of novel metal colloids and polymer matrix are of growing interest in a wide range of application owing to their unique properties.[1-4] In general, colloidal novel metals have been widely used as a catalyst due to its high activity and selectivity for chemical reactions. Furthermore, these colloids are also excepted to show the unique electrical and optical properties as exemplified by third ordered nonlinear optics[5-7] and quantum size effect on their physical properties.[5]

Recently, we have found accidentally a peculiar, but very interesting phenomenon that the vacuum deposited thin-layered gold on a UV-light pre-exposed polysilane film suffered colloid formation embedded in the polysilane film with drastic color change from golden yellow to magenta when heated at 90 ℃. In this letter, therefore, we would like to present the preliminary observation on the present new phenomenon of Au colloid formation in Au/PMPS layered films by heat treatment.

Poly(methylphenylsilane) (PMPS) was used in this study as a typical polysilane because of its good film-forming ability and UV absorption suitable for UV-exposure from a Hg lamp. The polymer was synthesized by the Wultz-coupling from phenylmethyldichrolosilane according to the literature.[8] The PMPS film of typically 1 μm thickness on a glass plate prepared by spin coating from toluene solution was first exposed by UV-light (10 mW/cm^2 at 310-400 nm) from a Hg lamp (TOSCURE 401, Toshiba) usually for 1 min in air before Au deposition. As well-known, polysilanes undergo photodecomposition by UV-light irradiation in air, which is usually accompanied by the formation of Si-O-Si and Si-OH bonds followed by Si-Si bond scission of backbone chain. The present UV dose is enough to photodecompose only the surface layer of polysilane film. Then, the film was provided with a gold layer of about 10 nm by vacuum deposition. At this stage, the whole gold surface exhibited gold color with sufficient reflectance. When the sample was, however, heated at about 90 ℃ on a hot plate, color change to magenta occurred very rapidly within a few seconds only in UV pre-exposed area of the film, and simultaneously the reflectance from the surface decreased, whereas the UV unexposed area remained unaltered.

The typical example of such color change and the resulting spectrum change are shown in Figures 1 and 2, respectively. There can be read two distinct features of this phenomenon: First, such color change occurred only on the PMPS film exposed to UV-light before Au deposition and second, the absorption at around 520 nm appeared in a magenta-colored film well-corresponds to the typical color of Au colloid due to surface plasmon resonance as reported.[9, 10]

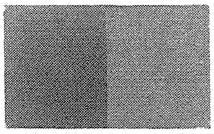

Figure 1. A typical example; the half area of left side corresponds to the UV-exposed area, where the color changed to magenta by heat treatment.

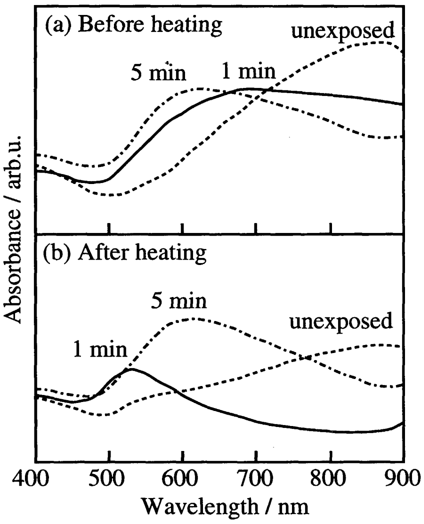

Figure 2. Absorption spectra of Au on PMPS films, which were treated by UV pre-exposure for various durations as indicated, a)before and b)after heating. PMPS itself has no absorption in the region above 400 nm.

To identify this UV pre-exposure effect, the spectral changes in the visible absorption of gold on the sample films UV-unexposed, and pre-exposed for 1 min and 5 min, are compared in Figure 2, respectively. For the sample pre-exposed for 1 min, a broad absorption above 500 nm tailing to the long wavelength region changed to the absorption peaked at around 520 nm by heating at 90 ℃. The sample without UV pre-exposure (dashed line), however, showed no change in the profile of spectrum except for a slight decrease in overall absorbance, even when the sample was heated above 150 ℃ (i.e., above the glass transition temperature T_g[11]). Moreover, Au deposition on the PMPS film exposed to UV-light longer than 5 min gave purple color peaked around at 600 nm, even before heating, but no spectral change occurred by subsequent heat treatment. These results indicate that Au evaporation on the PMPS film UV-

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exposed too long seems not to cause further Au colloid growth by heating. Thus, the present thermally induced Au colloid formation on PMPS film is crucially related to the degree of photodecomposition of the PMPS film surface, since 1 min irradiation with the present UV intensity photodecomposed only about one third of the whole PMPS from the surface with gradation, owing to the well-known self-breaching effect.[12] In other words, for the present Au colloid formation on the PMPS film there must exist the decomposed surface of PMPS by the UV pre-exposure at least. This partially decomposed surface are probably considered to take an important role as a trigger responsible for the subsequent thermal reaction as well as molecular motion of the polymer surface. On the other hand, in the PMPS film decomposed completely due to the long UV pre-exposure, Au clusters from an evaporation source seem to slip into the softened PMPS film during vacuum deposition. Au clusters were stabi-lized by some interaction with photodecom-posed PMPS and thereby no change occurs on subsequent heat treatment. Actually, an Au colloid suspension in toluene prepared from the film with magenta color is stable for over 8 months without aggregation.

As shown in Figure 3, more interestingly, the observation of AFM (Atomic Force Microscopy) revealed that the vacuum deposited gold particles on the pre-exposed PMPS film disappeared completely from the surface and slipped into the PMPS film by heating. The TEM (Transmission Electron Microscopy) observation recognized primary Au particles of about 10 nm in diameter, well-corresponding to the value expected from the absorption peak of 520 nm and theoretical prediction.[9, 10]

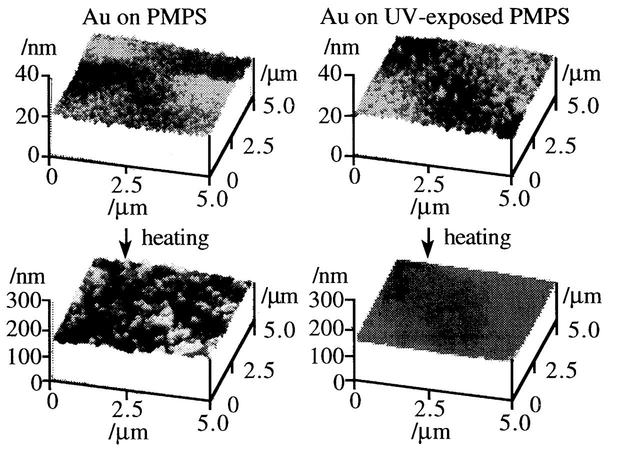

Figure 3 AFM images of Au on PMPS and pre-exposed for 1 min PMPS film surfaces before and after heat treatment.

Noguchi et al.[13] reported similar Au colloid formation in a Au/nylon 11 laminated film, for which they concluded that the relaxation of a thermodynamically highly strained nylon 11 layer prepared by vacuum deposition or by rapid-quenching led to the Au colloid formation upon heat treatment. In our case, however, even if UV pre-exposed PMPS film was once heated up to 150 ℃ (above T_g) and cooled down slowly to ambient temperature before Au deposition, this film still showed Au colloid formation. Thus, present Au colloid formation is not cased by the relaxation of thermodynamically unstable polymer surface introduced by UV-exposure, similarly to the case of nylon11.

Most important result to become a key for solving the mechanism is shown in Figure 4. If we inspect the spectrum change of PMPS during Au colloid formation, the typical absorption (peaked at 340 nm) attributed to Si-Si sequence of the polymer backbone almost disappeared in the magenta-colored film, this means that during Au colloid formation the PMPS was almost completely decomposed. In fact, the drastic increase of Si-O-Si vibrational band was confirmed in FT-IR spectra of the film upon heating. It was also confirmed that the present phenomenon did not occur in inert gas atmosphere or under vacuum condition. For other metals examined, Ag and Cu, no spectral change of PMPS was observed although the color change due to similar colloid formation took place in the case of Ag.

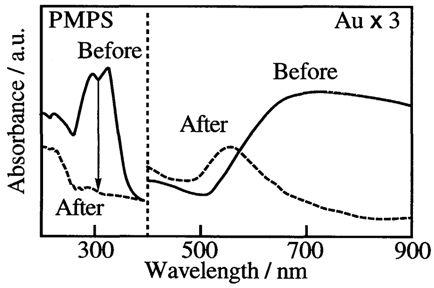

Figure 4. Change of the absorption spectrum of an Au on pre-exposed for 1 min PMPS layered film upon heat treatment.

These results apparently indicate that some catalytic polymer degradation due to oxidation initiated by Au colloids preformed by vacuum deposition within a UV-pre-exposed surface layer occurs on heating up to the temperature at which molecular motion begins to start. In the present stage, we are at least taking such a driving factor for the present peculiar phenomenon in the Au/PMPS film into consideration. The detailed mechanism is now under investigation.

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11 UV-exposure on PMPS film for 1 min led to decrease in its T_g from about 110 ℃ to 70 ℃. Almost decomposed PMPS film, furthermore, exhibited low Tg far below at the room temperature.
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