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Vacuum deposited gold thin layer on a ultraviolet (UV) light pre-exposed polysilane film undergoes colloidal gold formation by heating. This process was found to accompany the degradation of polysilane by catalytic oxidation due to the colloidal gold formed. Incorporating a titanyl phthalocyanine (TiOPc) pigment layer as a photon-thermal energy conversion layer in-between polysilane film and substrate, we have succeeded in demonstrating experimentally the possible application of such phenomenon to a new optical recording system.

Keyword: polysilane; ultraviolet light; pre-exposure; colloidal gold; titanyl phthalocyanine; optical recording

INTRODUCTION

Polysilanes have attracted much attention because of their unique photochemical and electrical properties^[1, 2] In particular, their excellent hole mobility of the order of 10^{-4} cm²V⁻¹s⁻¹ has been considered to be applicable to photoreceptors for electrophotography. On the other hand, polysilanes have also received considerable attention as radiation-sensitive materials in microlithography because they undergo photodecomposition on irradiation with UV-light as well as various types of ionizing radiation.

Recently, we have found a peculiar, but very interesting phenomenon that Au thin layer on UV-light pre-exposed polysilane undergoes Au colloid formation with drastic color change by heating.^[3, 4] Furthermore, it has been

found that during Au colloid formation the degradation of polysilane proceeds by catalytic oxidation due to the Au colloid formed. Since this phenomenon was accompanied by a considerable reduction in the reflectance of the light from originally lustrous Au surface, an application of this phenomenon occurred to us as a novel optical recording medium compatible with common system such as CD-R (recordable) and CD-ROM (read only memory).

Au Colloid Formation

Poly(methylphenylsilane) (PMPS) was used in this study as a typical polysilane. The PMPS film of typically about 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 usually for 1 min in air before Au deposition. By such UV-light irradiation in air, the UV-exposed area suffered photodecomposition of only the film surface. 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 $^{\circ}\text{C}$, color change to magenta occurred very rapidly within a few seconds only in UV pre-exposed area of the film, and simultaneously the reflectance of 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.

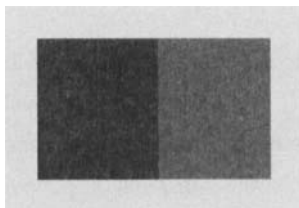


FIGURE 1 A typical example; the half area of left side corresponds to the UV-exposed area, where the color changed to magenta by heat treatment.

(See Color Plate II).

Upon the heat treatment, the broad absorption of Au film tailing above 500nm changed to a distinctive absorption peaked at around 520nm, which corresponds to the surface plasmon resonance of Au colloid as reported.^[5, 6] The TEM (transmission electron microscopic) 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. At the same time, the absorption attributed to Si backbone located at 330nm was found to disappear in the magenta-colored area. This means that during Au colloid formation 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. These results apparently indicate some catalytic polymer degradation due to oxidation initiated by Au colloids.

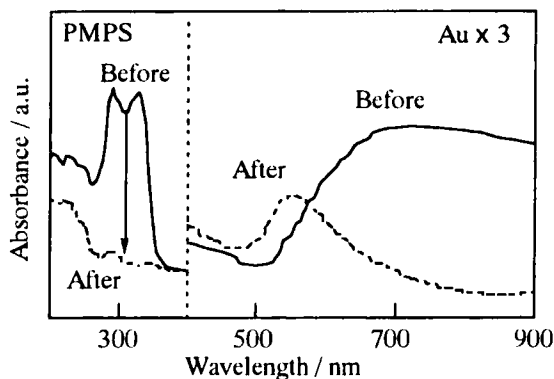


FIGURE 2 Change of the absorption spectrum of an Au on pre-exposed PMPS layered film upon heat treatment.

Application as Optical Recording Media

Since this phenomenon was accompanied by a considerable reduction in the reflectance of the light from originally lustrous Au surface, a novel application of this phenomenon occurred to us as an optical recording medium

by incorporating a TiOPc (titanyl phthalocyanine) pigment layer as a photon-thermal energy conversion layer because the present phenomenon is essentially based on thermal event.

The photograph shown in Figure 3 demonstrates the formation of clear pits with a reduced reflectance spot of a few micrometers in diameter on the layered film by irradiating a focused short laser pulse. We emphasize the advantage of the present optical memory media that are applicable for any laser system just by replacing dyes or pigments for energy conversion matching to the laser source.

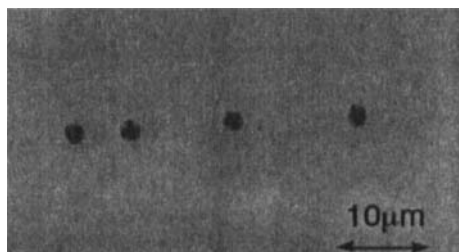


FIGURE 3 Microphotograph of pits registration due to Au colloid formation. A 830nm diode laser pulse (14mW, 10μsec) was focused.

In summary, we have found that an Au thin layer on a PMPS film pre-exposed to UV-light leads to the formation of Au colloid embedded in PMPS on heating. And, we have demonstrated that this phenomenon can be applicable to a novel write-once type optical-recording medium, utilizing a photon-to-thermal energy conversion layer.

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