Conductive Circuit Formation on Organosilicon Films by Patterning with UV

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This paper concerns a novel method for the preparation of silver metal from $AgBF_4$ by reduction with polysilanes, and an application of the method to the direct formation of conducting pattern on the surface of organosilicon polymers in combination with UV light lithography without any other promoters, reductants and photoresists.

Polysilane has received much attention due to its unusual electrical and chemical properties, and its solvent-soluble and film-forming properties.[1] High hole mobility is an electrical characteristic of polysilanes. This stimulates research on their application as conducting materials when combined with electron-acceptor dopants such as I_2.[2] A chemical characteristic of Si-Si chemical bonds is that they are readily photooxidized to Si-O-Si and Si-OH bonds upon exposure to ultraviolet light. These chemical/electrical properties of polysilanes have already been applied to photoresist,[3] patterned electrophotography,[4] and selective dyeing.[5] Electroless deposition is a method of depositing metal on the surface of materials through chemical reaction. Formation of fine metal patterns using electroless deposition combined with photoreaction has been widely used.[6 - 7] However, conventional photoreactive techniques require a promoter (such as palladium metal), a reductant (such as phosphorus or boron compound), and a photoresist.

In this paper, we report a novel technique for the formation of silver patterns on a silicon polymer surface using only the inherent reducing power and photoreactivity of polysilane. No other promoters, reductants and photoresists are required.

Poly(methylphenylsilane) (PMPS) and poly(dihexylsilane) (PDHS) were prepared from the corresponding dichlorosilanes according to the Wurtz polymerization.[8]

Poly(phenylhydrogensilane)(PPHS) was prepared by the Harrod method.[9] This reaction is convenient for the preparation of polysilanes with Si-H bonds, however, the product has a very low glass transition temperature (Tg). The Tg of polysilanes is more important than the molecular weight for ease of film formation. We found that the Tg of polysilanes can be controlled by the reaction temperature during polymerization. Polymerization at higher temperature produces a polymer with lower molecular weight, but higher Tg. By carrying out the reaction at 100 ℃ for 24 h, and at 150 ℃ for 6 h, the polymers of Tg 40 ℃ were obtained. In polymers having Tg higher than 25 ℃, the ^{1}H NMR peaks of Si-H at 4.8 - 6.0 ppm decreased, and a new ^{29}Si NMR peak observed at -120 ppm was assigned to branched polymer structures.

Polysilane films about 0.2 μm thick were formed on glass plate or silicon wafer by spin-coating(3000 rpm, 10 s, 5-10 % (w/w)% toluene solution), followed by drying under reduced pressure(5 Torr, 50 ℃, 1 h). Silver salt treatment of the polymer film was performed by coating with 5 wt% ethanol solution of $AgBF_4$, followed by air drying at room temperature and subsequent heating at 50℃. Color of the polysilane films changed drastically by contact with $AgBF_4$. Changes of UV-vis spectra of the polymer films are shown in Figure 1.

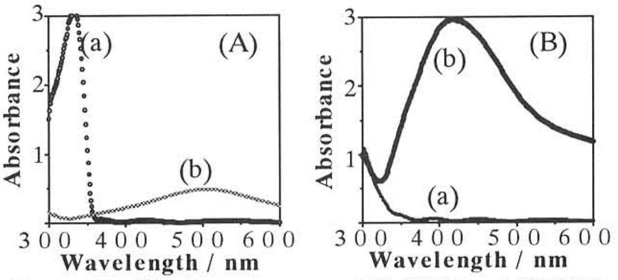

Figure 1. UV-vis spectroscopy of PMPS(A) and PPHS(B) treated with AgBF4 solution. (a) Polysilane blank, (b) AgBF4-treated polysilane.

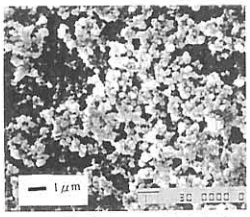

Figure 2. SEM image of silver colloids by using PMPS and AgBF4.

Characteristic bands at 333 nm attributable to Si-Si bond of PMPS disappeared after treating the films with silver salt. Additionally, in the FT-IR of PPHS film treated with silver salt, absorptions attributable to SiOSi-H and Si-O-Si newly appeared at 2180 cm^{-1} and 1100 cm^{-1} along with the disappearance of Si-Si-H absorption at 2098 cm^{-1}. This behavior strongly indicates that the polysilanes are oxidized by contact with $AgBF_4$ accompanying the formation of colloidal silver[10] as shown in Figure 2.

Conductivity of the film was measured at room temperature by two-probe technique using a film sample formed on the glass plate equipped with gold electrodes. Electrical conductivity of $AgBF_4$-treated polysilanes and polysiloxanes carrying same side chains are compared in Table 1. The conductivity is affected by main chains and side groups of polymers. Reducing power of the Si-Si and Si-H bonds plays an important role in the elevation of conductivity. Polysilane with Si-H (PPHS) showed a conductivity of more than 1 K Scm^{-1}. Even the polysiloxane with Si-H (PPHSO) gave the conductivity of more than 100 Scm^{-1}. On the other hand, conductivity of polysiloxane having methylphenyl side groups (PMPSO) was not improved by treatment with $AgBF_4$. These results suggest that conductivity is increased through the reduction of silver salt to silver metal.

Polysilane can be selectively photooxidized by exposure

Table 1. Physical properties and electrical conductivities of polysilanes and polysiloxanes treated with $AgBF_4$

Polymer	MW	Tg / ℃	Conductivity[a]
PPHS	2,600	40	1130
PMPS	46,000	80	380
PDHS	910,000	42	2×10^{-3}
PPHSO[b]	5,000	- [d]	220
PMPSO[c]	80,000	- [d]	4×10^{-6}

[a] Conductivity / S cm^{-1} : 5wt% $AgBF_4$ EtOH solution was applied to the polysilane film, heated at 50°C and cooled to room temp.
[b] PPHSO: Poly(phenylhydrogensiloxane)
[c] PMPSO: Poly(methylphenylsiloxane)
[d] The polymers were crosslinked in order to determine film thickness by UV(254 nm, 5 J cm^{-2}) irradiation.

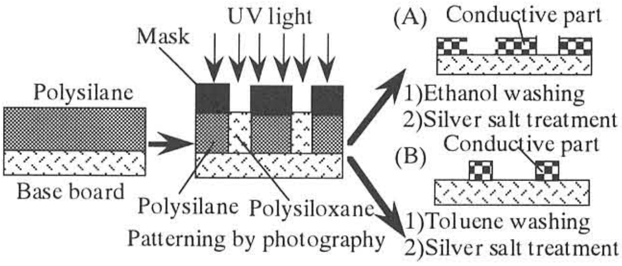

Figure 3. Photochemical fabrication of conductive patterns by using polysilane films and silver salt. (A) Positive pattern by PMPS, (B) Negative pattern by PPHS.

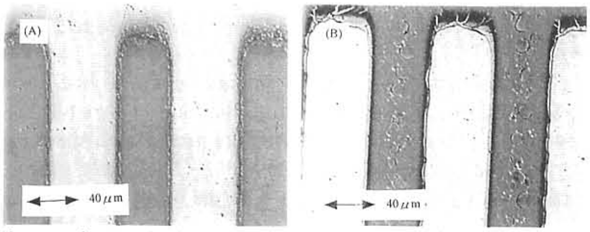

Figure 4. Typical conductive patterns by using polysilane films and silver salt. The dark line pattern indicates silver conductive pattern in the photograph. (A) Positive pattern by PMPS, (B) Negative pattern by PPHS.

to UV in air. Each film was exposed to UV light of 1 J cm^{-2} with an 8 W low-pressure mercury lamp (254 nm, 2.5×10^{-3} Nm cm^{-2}) through the pattern mask. During UV irradiation, the Si-Si bond was photooxidized to siloxane, and the reducing power of polysilanes(except PPHS) disappeared.

Since the UV exposed parts of PMPS film can be readily removed by alcohol(due to scission of the polymer backbone and generation of Si-OH bonds), the photochemical fabrication of a conductive pattern is possible by combination of the silver deposition. In practice, after the UV exposed parts of PMPS were washed in ethanol for 5 s and spin-dried by 3000 rpm for 10 s, a positive pattern was obtained by immersing in 5 wt% $AgBF_4$ ethanol solution for 30 s, followed by washing in ethanol for 10 s to remove the excess silver salt, and by oven-drying at 100 ℃ for 1 h.

The same process, however, was not applicable to the branched PPHS film, because the film was crosslinked by UV and became insoluble to solvents. Since the UV-exposed parts of PPHS film also show high conductivity by treatment with silver salt, the UV-exposed PPHS gives a negative pattern by removing unexposed parts with toluene before treatment of the film with silver salt solution.

In practice, after the UV-irradiated film of PPHS was washed in toluene for 5 s and spin-dried by 3000 rpm for 10 s, the conductive path comprised of polysiloxane was formed by immersing in 5 wt% $AgBF_4$ ethanol solution for 30 s, washing in ethanol for 10 s to remove the excess silver salt, and by oven-drying at 100 ℃ for 1 h.

As shown in Figure 3 and 4, two types of conductive patterns were possible. Optical microscopy revealed that a line pattern of 40 μm width was easily attained.

In conclusion, we have demonstrated a new method for the preparation of conductive silver patterns on the organosilicon polymers. This is accomplished by a combination of UV lithography and silver salt treatment. Unlike conventional methods, no other additives or processes are required. The positive pattern from PMPS film and the negative pattern from PPHS film were obtained by treating with $AgBF_4$ after UV irradiation, followed by washing in ethanol or toluene.

References and Notes

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