CHEMISTRY LETTERS, pp. 657-660, 1986.

PHOTOCATALYTIC DEPOSITION OF LIGHT-LOCALIZED POLYPYRROLE FILM PATTERN ON n-TYPE SILICON WAFERS

Hiroshi YONEYAMA* and Masahiro KITAYAMA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-oka 2-1, Suita, Osaka 565

Scanning a He-Ne laser beam on n-type Si wafers in acetonitrile containing pyrrole and $AgClO_4$ causes light-localized deposition of electroconductive polypyrrole films under such experimental conditions that the front surface of the wafer over which the laser beam is scanned is well-etched and the back of the wafer is damaged.

Light-localized imaging processes on semiconductors immersed in solution are interesting from the viewpoint of their applicabilities to display devices,1-3) fabrication of microelectronics,3-6) and printing systems.7) In these studies, several different principles have been used to form light-localized patterns; photoelectrochemical deposition of metallic oxides on n-type semiconductor electrodes such as TiO_2 and ZnO under anodic bias,1,2) that of metals on p-type semiconductor electrodes such as p-type GaAs and Si under cathodic bias,4) and light-localized images due to the production of colored solution species at n-type GaAs electrodes.3) In addition to these electrolytic processes, formation of light-localized film patterns by electroless processes has been reported; Karlicek *et al.*8) reported light-localized metal deposition *via* thermally induced reactions between semiconductor substrate (p-type, n-type, and undoped InP) and a H_2PtCl_6 solution, and Rose *et al.*5) succeeded in light-localized metal deposition on p-type Si wafers with assistance of internal bias which was induced by different contacts between the front surface and the back surface of the wafer; the back surface had ohmic contacts with plated zinc, while the front surface was metal-free and thereby a rectifying junction was formed in contact with metal deposition baths employed.

In this communication, we would like to report photocatalytic formation of light-localized patterns of electroconductive polypyrrole films on n-type Si wafers. It was reported previously9) that illumination of n-type Si wafers in acetonitrile containing pyrrole and $AgClO_4$ causes simultaneous deposition of polypyrrole on anodic surfaces of the wafer and Ag on its cathodic surfaces. The amount of polymerized pyrrole should in principle be equivalent to that of deposited Ag. Furthermore, it was revealed that defect-free illuminated surfaces serve as the anodic surfaces, while defect sites serve as the cathodic sites, especially in the dark. In the present study, we have applied this simultaneous deposition reaction to light-localized pattern formation of electroconductive polypyrrole film on n-type Si wafers, which may find application fields in semiconductor microelectronics.

The semiconductor wafers used were manufactured by Osaka Titanium Co. Ltd., and the resistivity ranged between 5 and 15 Ω cm. Its surafces were polished to a mirror finish by the manufacturer and this kind of surface is called here as a "smooth surface". One end face of the wafer was lapped with #500 emery papers to produce a lot of defects in its surface, and the resulting surface is called as a "damaged surface". After etched in 48% HF for 15 min, followed by rinsing with de-ionized water, the wafer was immersed in acetonitrile containing 0.1 M (1 M = 1 mol dm^{-3}) $AgClO_4$ and 0.1 M pyrrole. Before illumination of the smooth surface with a 25 mW He-Ne laser, the solution was de-aerated for longer than 30 min. The laser beam scanning system consisted of the laser mentioned above, two General Scanning G360 optical scanners driven by two driver amplifiers (NDC AX-200R), and a f:20 focusing lenz. The diameter of the laser beam spot on Si surface was ca. 0.4 mm. The amount of deposited polypyrrole was estimated from that of deposited Ag which was determined colorimetrically by using dithizone as a comlexing agent after dissolving the Ag in a HNO_3 solution.

When a fixed position of the smooth surface of the Si wafer was illuminated without deflecting the laser beam, polypyrrole deposition took place initially in the center of the illuminated area, and then propagated to the outer area to give a little deformed circular deposit. The growth of the mean diameter is shown in Fig. 1. The Ag deposition as a counterpart reaction of the polypyrrole deposition occurred not in localized places but over the entire surface of the back face of the wafer. The rate of the Ag deposition was non-linear with illumination time, as shown in Fig. 2. Thus, it is said that the polymer deposition also occurred nonlinearly with illumination time.

Light-localized polypyrrole patterns can be deposited not only by the photocatalytic processes mentioned above but also by electrolytic processes in which the

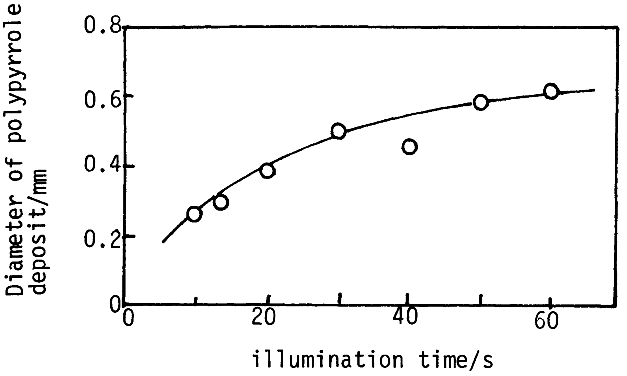

Fig. 1. Peripheral growth of polypyrrole deposits observed when a fixed position of the smooth surface was illuminated without deflecting light beam from a 25 mW He-Ne laser. Solution: 0.1 M $AgClO_4$ + 0.1 M pyrrole/acetonitrile.

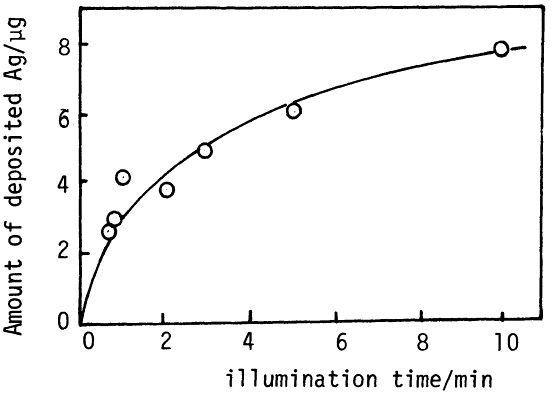

Fig. 2. The amount of deposited Ag on the damaged surface in the dark as a function of illumination time of the front surface. Experimental conditions were the same as those shown in Fig. 1.

smooth surface of n-type Si electrodes is anodically polarized under localized illumination in electrolyte solutions containing pyrrole. It was found from electrolytic preparation of polypyrrole films in acetonitrile containing 0.1 M pyrrole and 0.1 M $LiClO_4$ that the peripheral growth of deposited polypyrrole patterns occurred also in this case, and it became more significant with choosing more anodic deposition potential, as shown in Fig. 3. It is well-established[10,11] that anodically prepared polypyrrole films are electronically conductive. We think that this nature of the deposited polymer film is responsible for the peripheral growth of the deposited polymer patterns with illumination time. Photogenerated positive holes enter into the deposited polymer film from the Si substrate and then reach the deposited polymer/electrolyte solution interface where polymer deposition takes place. The peripheral growth which worsens the resolution of the light-localized polymer deposition continues until the deposited film becomes thick enough to block photon incidence into the Si substrate. The potential dependence of the growth rate can be explained in terms of potential dependence of recombination probabilties of photogenerated charge carriers.

Photocatalytic deposition of light-localized polypyrrole patterns was further investigated with scanning the laser beam. The distance chosen for the laser beam scanning was 5 mm, and the rate of scanning was varied from 0.01 to 0.2 mm s^{-1} when single scanning was made. Much faster scanning rates were chosen when the laser beam scanning was repeated over the same line shape in the smooth surface. It was found that in cases of single scanning the scanning rates less than 0.2 mm s^{-1} were required for the formation of light-localized patterns to be recognized by the naked eyes. It is concluded by combining this threshold scanning rate with the diameter of the laser beam that in our experimental conditions irradiation of every surface sites for longer than 2 s was required to produce polypyrrole patterns. Repetition of the beam scanning did not result in any marked influence on the produced polypyrrole patterns as long as a total illumination time was the same. A pattern produced by cycling the beam scanning for 10 min at the rate of 10 mm s^{-1} is shown in Fig. 4.

As suggested from Fig. 2, the quantum efficiency for the polymer deposition varies with illumination time. If the value is estimated from the tangent of the curve given in Fig. 2 for the first 2 s-illumination, it is around 1%. The efficiency dropped down, however, to 0.025% with illumination for longer than 4 min.

It is of interest to measure the electrical conductivity of the deposited polypyrrole film to confirm that it possesses a high conductivity similar

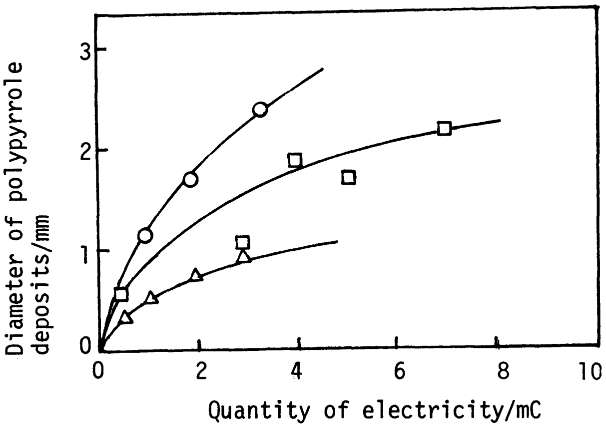

Fig. 3. Time-course of broadening of light-localized polypyrrole patterns on n-type Si electrodes formed by anodic polymerization of pyrrole. Solution: 0.1 M pyrrole + 0.1 M $AgClO_4$/acetonitrile. Anodic potential *vs.*SCE: (○) 0.4 V, (□) 0.3 V, (△) 0.2 V.

to that reported for electropolymerized polymers.[10,11] Conductivity measurements, however, were failed to be done, because it was difficult to remove the polymer pattern from the Si substrate. Considering that the polymer deposition occurs as an anodic process of the photocatalytic reaction employed here, produced polymer patterns must be of a high conductivity.

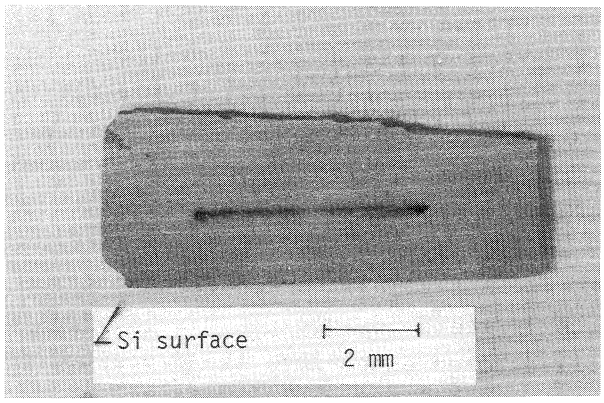

Fig. 4. Light-localized polypyrrole pattern produced by cycling laser beam scanning for 10 min at 10 mm s^{-1} over a 5 mm distance. The solution used was the same as that given in Fig. 1.

The present study has an important implication in showing a new technique for light-localized pattern formation of polymers on semiconductor surface, which is believed to be useful for fabrication of semiconductor microelectronics. The polymer pattern formation by photocatalytic deposition processes must be superior to that by electrolytic deposition processes in the point that the former does not need any electritical connection to semiconductor substrates in light-patterning processes. By searching a variety of photocatalytic reaction systems in which polymer deposition is involved, light-localized patterns of various kinds of polymers including electroconductive polymers and insulating ones will be possible to be fabricated.

This work was supported by Grant-in-Aid for Scientific Research No. 60550576 from the Ministry of Education, Science and Culture.

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(Received January 21, 1986)