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Light-Induced Oxidative Deposition of Polypyrrole on the Back Surface in the Dark of n-Type Silicon Wafer Photocatalysts

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A variety of surface conditions of n-type Si wafers were prepared by etching for different time damaged surfaces that were prepared by lapping with emery papers, and the effect of flaws in the wafer surfaces on photocatalytic deposition behaviors of polypyrrole and silver from acetonitrile containing pyrrole and $AgClO_4$ was investigated. It was found that if the front surface of the wafer to be illuminated contained a fairly high amount of defects and the back surface in the dark was defect-free, oxidative polymerization of pyrrole occurred on the back surface in the dark with the simultaneous deposition of silver on the front surface as long as the diffusion length of positive holes is greater than the thickness of Si wafers.

Flaws in semiconductor surfaces play an important role in semiconductor photocatalysis.[1-3] For example, high photocatalytic activities of n-type single crystal wafers appear when their illuminated surfaces are well-etched and their back surfaces in the dark are heavily damaged. The flaws have both favorable and unfavorable effects in semiconductor photocatalysis. The favorable effect is that the flaws produce in the forbidden zone of semiconductors intermediate energy states which serve as channels for transferring photogenerated electrons from the conduction band to electron scavengers in solution under upward bending of the bands,[1,4] while the unfavorable effect is that the flaws work as the recombination centers.[5-7]

Then it will be of interest to investigate how greatly the apparent photocatalytic activities of semiconductors are affected by changing the abundance of flaws either in illuminated front surfaces or in the back surfaces in the dark, or in both. The present study has been initiated to investigate this subject using n-type Si wafers. The reaction system chosen here was simultaneous deposition of polypyrrole and silver from acetonitrile containing pyrrole and silver perchlorate.[2,8] By using this reaction system, the effective cathodic sites and photoanodic sites of semiconductor surfaces can be recognized by observing the places where the silver and polypyrrole deposition take place, respectively. It will be shown that under special configurations of the front and back surfaces of the n-type Si wafers the positive hole-consuming polypyrrole deposition evidently takes place on the back surface of n-type Si wafers in the dark as a result of effective supply of the positive holes by diffusion only.

Experimental

n-type Si single crystal wafers were purchased from Osaka Titanium Co. Except where specially noted, the experiments were carried out using wafers of 0.6 mm thickness and of 2.4 Ωcm resistivity. The surface of the wafers was polished to mirror finish by the manufacturer. This surface is denoted here as mirror-finished surface. The mirror-finished surface was lapped with No. 500 emery papers when it was intended to prepare defect-containing surfaces. The surface prepared by this damaging is denoted here as damaged surface. The flaws produced in this way must have had the depth comparable to the particle size of the abrasives which was judged to be 34 μm on average.[9] The damaged surface was etched in a mixture of 1 part of 46% HF and 20 parts of 61% nitric acid for different time to remove the defects to different degrees. The etching rate was reported to be 13 μm min^{-1} [10] for this etchant.

For the photocatalytic deposition experiments, edges and undesired parts of the Si wafers were coated with polyfluoroethylene oligomer (Difloil, #200, Daikin Industries), and after mounting in a flexible plastic frame, the Si wafers were hung in a deposition bath which consisted of 0.1 M pyrrole and 0.1 M $AgClO_4$ (1 M=1 mol dm^{-3}) dissolved in acetonitrile. For electrochemical experiments, the back face of the Si wafers was pasted by a Ga–In alloy to make ohmic contact where an electrical lead wire was attached with Dupont conducting silver paint. The Si wafer was then mounted in a Teflon electrode holder. The surface exposed to electrolyte solutions was 7 mm diameter.

Just prior to both photocatalytic experiments and photoelectrochemical experiments, the Si was immersed in 46% HF for more than 30 min to remove surface oxide films, followed by washing in a stream of deionized water. The electrolyte solutions and the deposition bath were bubbled by argon for more than 20 min to purge dissolved oxygen. The electrolytic cell had one compartment with a quartz window for illumination of the electrode. Cyclic voltammograms were obtained with the use of a potentiostat (Nikko Keisoku, DPGP-1), a potential sweeper (Nikko Keisoku, NPS-2) and an X-Y recorder (Yokogawa, Type 3077). The electrolyte solutions were prepared from reagent grade chemicals.

Illumination of the Si wafers was carried out using either a 500 W xenon lamp (Ushio, ULX-500-O) or a 25 mW He-Ne laser (NEC, GLG-5700). In the former case light from the lamp was passed through a Toshida glass filter L-39 to cut off wavelengths shorter than 390 nm. The illumination intensity was usually 0.45 W cm^{-2}.

The rate of simultaneous deposition of polypyrrole and silver was evaluated by determining the amount of the deposited silver as a function of the illumination time. For this purpose the deposited silver was dissolved with nitric acid, neutralized with sodium hydroxide, and determined colorimetrically at 620 nm using dithizone as a complexing agent.

Results

Photoelectrochemical Properties of n-Type Si Having a Variety of Damages. The mirror-finished surface had smooth surface as judged from pictures taken by a scanning electron microscope (SEM) with magnification of 20000, while the damaged surface had irregular ditches with sharp edges as shown in Fig. 1(a). With increasing the etching time the sharp edges of the flaws became smooth as Figs. 1(b) to (d) show. Considering the depth of flaws of the dam-

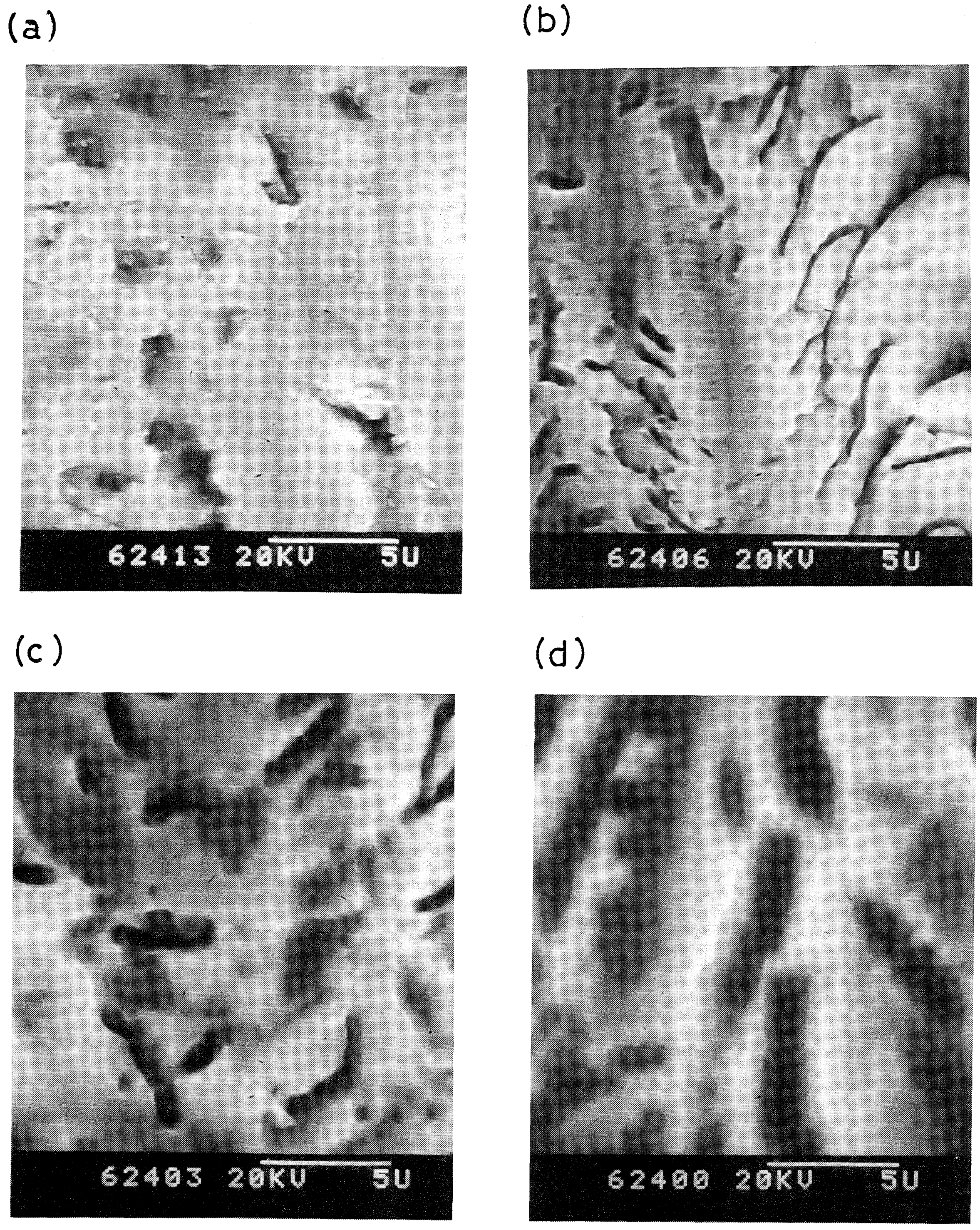

Fig. 1. Pictures of n-type Si surfaces containing a variety of damages. (a) Abraded with No. 500 emery papers (damaged surface), (b) etched of the damaged surface for 30 s, (c) etched for 60 s, and (d) etched for 5 min.

aged surface (34 μm) and the etching rate (13 μm min^{-1}), the flaws should be eliminated by the 3 min etching if the etching proceeds at the flaws only. However, the etching occurred not only in the flaws but also in the mirror-finished surfaces, it took much greater time to eliminate completely the flaws from the surface. According to the SEM pictures shown in Fig. 1, the 5 min etching of the damaged surface gave fairly smooth surface, and its electrochemical properties were found to be very close to those of the mirror-finished surface, as will be shown below.

Cyclic voltammograms of four kinds of n-type Si electrodes having different surface conditions, taken at an initial potential scan in propylene carbonate containing 10 mM ferrocene, are shown in Fig. 2. Illumination by the xenon lamp did not affect the shape of cyclic voltammograms at the damaged electrode, which behaved as if it were a metal electrode. In contrast, illumination caused photosensitized oxidation of ferrocene at the mirror-finished electrode, as shown in Fig. 2(d), though this electrode in the dark showed no appreciable reactivity for oxidation of ferrocene, as expected for n-type semiconductor electrodes.

The electrodes having different degrees of surface damages showed intermediate voltammetric behaviors between the mirror-finished and the damaged electrodes, depending on the degree of the surface damages. The onset potential of anodic photocurrents shifted negatively with increasing the etching of the damaged surface as shown in Fig. 3, and simultaneously anodic currents in the dark decreased; the onset potentials were not, however, affected by the etching. On the other hand, if the electrode contained a relatively high amount of defects in the electrode surface, the cathodic current was eventually the same as that at Pt electrodes, while if a large parts of surface flaws were eliminated, the onset potential was shifted towards negative potentials finally to reach the onset potential at the mirror-finished electrodes.

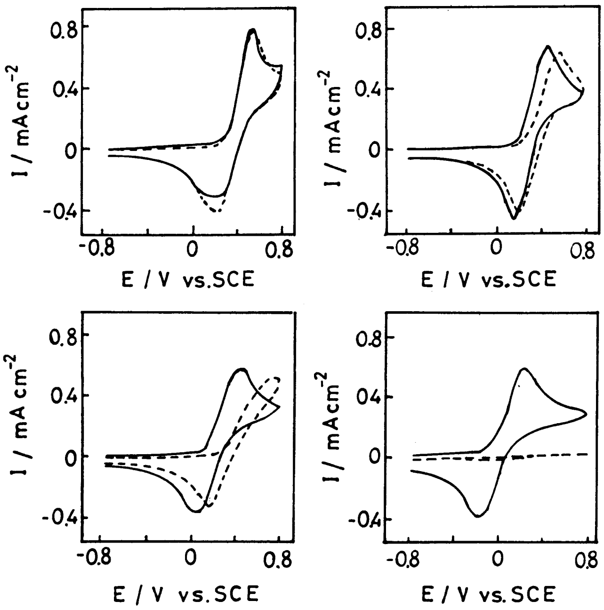

Fig. 2. Cyclic voltammograms of n-type Si electrodes in propylene carbonate containing 10 mM ferrocene and 0.1 M tetrabutylammonium perchlorate. The illumination intensity by the xenon lamp was 10 mW cm^{-2}. dE/dt=50 mV s^{-1}. Solid line: taken under illumination. Dashed line: taken in the dark. The electrodes were prepared by etching the damaged surface for (a) zero s, (b) 30 s, (c) 1 min, and (d) 5 min.

It is concluded from the results shown in Figs. 2 and 3 that the electrode surface prepared by etching the damaged surface for 15 s to 1 min possessed both semiconductor and metal electrode properties, because illumination caused negative shifts of anodic current onsets, but the onset potential of both anodic and cathodic currents in the dark were the same as those at the Pt electrodes.

The Effect of Surface Defects on the Photocatalytic Deposition Reactions. Figure 4 shows the amount of deposited silver with the illumination time, obtained when the front surface of the wafer was prepared by etching the damaged surface for different times and the back surface was the damaged one. The rate of the deposition reaction increased with the elimination of surface damages of the front surface, suggesting that the recombination of the photogenrated charge carriers in the illuminated surface controlled the rate of the deposition reaction. The silver deposition preferentially took place in the back damaged surfaces in the dark, and the polypyrrole deposited on the illuminated surfaces irrespective of whether this surface was mirror-finished or defective.

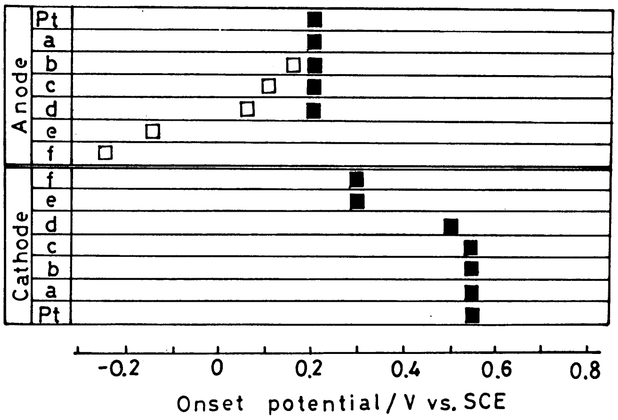

Fig. 3. The onset potential of anodic currents and cathodic currents, evaluated from cyclic voltammograms taken in a solution containing 10 mM ferrocene as shown in Fig. 1. (□) the onset potential of anodic currents under illumination of the electrode. (■) the onset potential in the dark. The etching time of the damaged Si electrode was (a) zero, (b) 15 s, (c) 30 s, (d) 1 min, (e) 5 min, (f) mirror-finished surface.

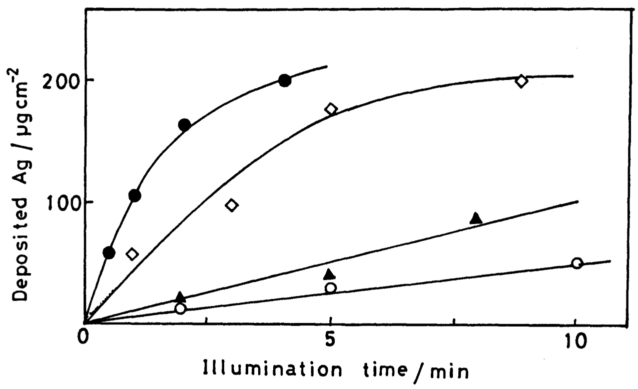

Fig. 4. Time course of silver deposition obtained when the front surface of n-type Si wafers contained flaws of different degrees, and the back surface was damaged. Solution: acetonitrile containing 0.1 M pyrrole and 0.1 M silver perchlorate. Illumination: 0.45 W cm^{-2} xenon light. The etching time of the damaged surface to prepare the front surface was (○) 1 min, (▲) 3 min, and (◇) 5 min. (●) well-etched front surface.

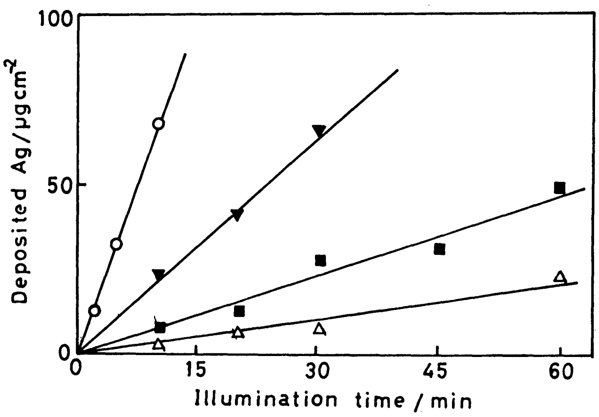

Fig. 5. As in Fig. 3, but for cases when both front and back surfaces of n-type Si wafer were in the same surface conditions. The etching time of the damaged surface for the preparation of each surface was (△) 30, s, (■) 1 min, and (▼) 5 min. (○) the well-etched surface.

Figure 5 shows the time course of silver deposition obtained when both the front and back surfaces were the same with respect to the defects. In such cases, the rate of the deposition reaction was increased by eliminating the surface damage. As shown in the figure, the highest rate was achieved when both the front and back surfaces were mirror-finished. However, the rate obtained was by far lower than that achieved when the front surface was mirror-finished and the back surface was damaged, as will be recognized by comparing Fig. 5 with Fig. 4. The deposition of both silver and polypyrrole took place in the illuminated front surface for the cases of 30 to 60 s etching of the damaged surfaces, but with further increase in the etching time, the silver deposition occurred on the back surface.

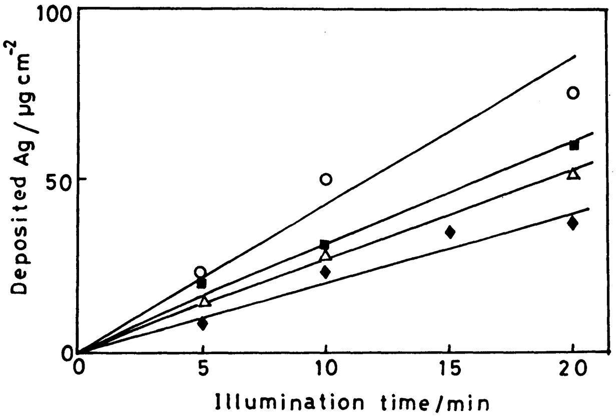

Fig. 6. As in Fig. 4, but for such surface conditions that the back surface was well-etched and the front surface was prepared by changing the etching time of the damaged surface for (■) 1 min, (△) 3 min, (◆) 5 min, and (○) 10 min.

Figure 6 shows the amount of deposited silver with illumination time for the case when the front surface was that prepared by etching the damaged surface for different time and the back surface was mirror-finished. The rate of silver deposition in that case was not so greatly influenced by the etching time of the damaged surface as that shown in Figs. 4 and 5. The interesting result obtained here is that the polypyrrole deposition took place on the mirror-finished back surface if the front surface was prepared by 30 to 60 s etching of the damaged surface, though the deposition on the front surface also took place with a less extent, as will be noticed from Fig. 7. In those cases, the silver deposition took place on the illuminated defective surface. With an increase in the etching time of the front surfaces, however, the polypyrrole deposition became to occur on the illuminated front surface. Simultaneously, the silver deposition became to take place on the back surface. It was found that the etching for 5 min was enough to change the major deposition place in such a manner as described above.

Figure 7 shows an example showing the occurrence of the polypyrrole deposition on the mirror-finished back surfaces as well as on the illuminated defective surface that was prepared by etching the damaged surface for 1 min. The illumination was made in that case by a He–Ne laser beam of ca. 0.5 mm diameter. According to this figure, there is a remarkable difference in the deposited patterns between the front surface and the back surface. In the front surface, the size of the deposition was near to that of the laser beam, but in the back surface the deposited polypyrrole occupied a much greater area. It seems important to remark here that if the front surface was unchanged but the back surface was changed from the mirror-finished surface to the damaged one, the polypyrrole deposition took place exclusively on the front surface. Figure 8 shows the time course of the Ag deposition onto two kinds of n-type Si wafers whose front surfaces were the same and prepared by 1 min etching of the damaged surface, but whose back surfaces were different; one was mirror-finished and the other damaged. The deposition reaction at the Si wafer whose back surface was damaged stopped occurring at earlier illumination time than that at the wafer whose back surface was mirror-finished. The reason for this is that the photodeposition reaction does not proceed anymore when the deposited polypyrrole on the front surface becomes thick enough to absorb completely the incident photons, and such events are achieved more easily when the back surface of the wafer was damaged, because in that case the polypyrrole deposition took place exclusively on the front surface.

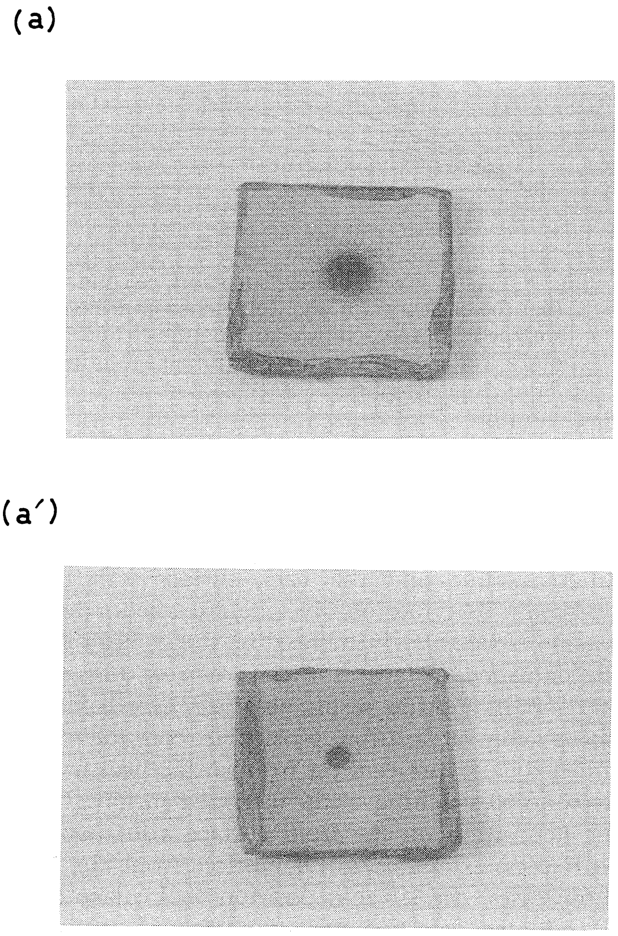

Fig. 7. Pictures showing the polypyrrole deposition on the well-etched back surface in the dark of n-type Si wafers of 0.6 mm thickness and of the resistivity of 2.4 Ωcm. The front surface was prepared by etching the damaged surfaces for 1 min, while the back surface was well-etched. Illumination was made by ca. 0.5 mm diameter He-Ne laser beam. (a) The back surface in the dark after illumination for 20 min, and (a′) the front surface at the same time.

The deposition of polypyrrole on the back surface in the dark of Si wafers was further investigated by using Si wafers of different resistivity and thickness. The experiments were carried out with almost the same surface configuration as that employed in the experiments whose results are given in Fig. 7; the front surface of the wafer was prepared by etching the damaged surface for 30 s and the back surface was mirror-finished. All the results including those shown in Fig. 7 are given in Table 1. It is recognized

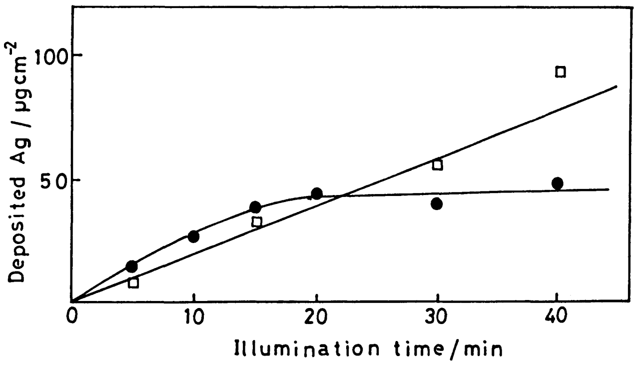

Fig. 8. Time course of the Ag deposition onto n-type Si wafers having different surface conditions in the back surfaces. The front surface was prepared by etching the damaged surface for 1 min for both cases, but the back surface was (□) well-etched and (●) damaged. Illumination: 0.45 W cm^{-2} xenon lamp.

Table 1. The Occurrence of Positive Hole-Consuming Polypyrrole Deposition on n-Type Si Wafers of Varous Resistivities and Thickness

Resistivity	Thickness	Deposition of polypyrrole		Diffusion length of positive hole
ohm cm	mm	Illuminated front surface	Back surface in the dark	mm
0.77	0.4	Occurred	Occurred	0.45
2.8	1.1	Occurred	Not occurred	0.63
2.8	0.9	Occurred	Not occurred	0.63
2.8	0.3	Occurred	Occurred	0.63
2.4	0.6	Occurred	Occurred	0.61

The front surface was prepared by etching the damaged surface for 30 s, while the back surface was well-etched. Illumination was made by a 25 mW He-Ne laser of ca. 0.5 mm beam diameter.

from the results shown in the table that the polypyrrole deposition on the mirror-finished back surface did not always take place.

Discussion

The most interesting result obtained in this study is that the oxidative deposition of polypyrrole occurred on the mirror-finished back surface if the front surface was prepared by etching the damaged surface for 30 to 60 s. Discussion on this result will be made first for the case of using the He-Ne laser as a light source.

The light penetration depth estimated from the inverse of the absorption coefficient at 632 nm is ca. 3.2 μm,[11] while the flaws in the surface prepared by ething the damaged surface for 30 to 60 s would leave the flaws of ca. 28 to 21 μm depth on average based on the assumption that the damaged surface originally contained flaws of 34 μm depth and the etching rate was 13 μm min^{-1}.[10] Accordingly, illumination of such surface will result in photogeneration of charge carriers in a surface region containing defects. Such speculation seems valid, judging from the SEM pictures of the electrode surfaces shown in Figs. 1(b) and (c), where fairly deep ditches are seen in the surfaces prepared by 30 to 60 s etching of the damaged surface. Photocurrent-potential bahaviors given in Figs. 2 and 3 also suggest that in cases of etching the damaged surface for 30 to 60 s the photogeneration of charge carriers occurred in the surface containing defects, because the onset potential of anodic photocurrens at the electrodes preprared by 30 to 60 s etching of the damaged surface was more positive than that at the mirror-finished surface.

The thickness of the space charge layer of n-type Si wafer having 2.4 ohm cm resistivity in the deposition bath is estimated to be 0.45 μm by using an well-established equation[12] under the assumption that the band bending is 0.4 V[2,3] and 2.4 Ω cm n-type Si contains 2.4×10^{15} cm^{-3} donors which is estimated from a donor concentration (N_d) vs. resistivity relation published as Fig. 5 of Ref. 13. The estimated space charge thickness is valid for well-etched surfaces and the values become small with an increase in the defect concentration.[5,7] The reviewer questioned why N_d was not determined by the Mott-Shottky plots of differential capacitances of the semiconductor electrodes. The Mott-Shottky plots may be a convenient way to determine N_d, but in many cases frequency dispersions appear in the plots, giving inaccurate determination of it. It has been shown for TiO_2 electrodes[14,15] that special surface treatments are necessary to eliminate the frequency dispersion in the plots.

It is known from the above estimation that the thickness of the Si wafers used in the present study was much greater than the sum of the light penetration depth and the space charge layer. Accordingly, positive holes must be supplied to the back surface by diffusion to cause the polypyrrole deposition there. To confirm this view, the diffusion length of positive holes (L_h) is estimated by inserting into Eqs. 1 and 2 the published data on the life time (τ_h)[16] and the mobility (μ_h)[17] both of which are available as a function of N_d.

$$L_h = (\tau_h D_h)^{1/2} \tag{1}$$

$$D_h = \mu_h kT/q \tag{2}$$

where D_h is the diffusion constant of positive holes. To estimate τ_h and μ_h, knowledge on N_d was required, and this was done from the resistivity values of the wafers using the published N_d vs. resistivity relation.[13] The estimated τ_h and μ_h of 2.4 Ω cm n-type Si, for example, were 3.4×10^{-4} s and 430 cm^2 V^{-1} s^{-1}, respectively. By using τ_h and μ_h estimated as a function of resistivities the diffusion length of positive holes is obtained also as a function of the resistivities, as shown in Fig. 9. In Table 1, the diffusion length of positive holes estimated in this manner is given. It is noticed from this table that the polypyrrole deposition took place on the mirror-finished back surface when the diffusion length of positive holes was greater than the thickness of the Si wafers used.

According to the above analysis, the thickness of Si samples used in the experiments whose results are given in Figs. 4 to 6 was shorter than the diffusion length of positive holes. Nevertheless, the polypyrrole deposition did not occur on the back surface if it was either damaged or contained a relatively high amount of defects. The main reason for this is that the presence of flaws in the back surface in the dark results in the annihilation of positive holes there. On the other hand, the presence of flaws is favorable for the silver deposition, as already described above. Furthermore, it must be remarked here that the polypyrrole deposition did not occur on the mirror-

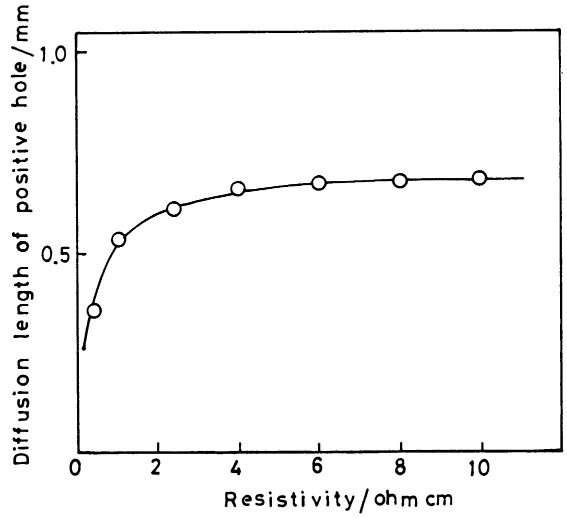

Fig. 9. The diffusion length of positive holes as a function of resistivity of n-type Si single crystals at 25 °C.

finished back surface if the front surface was also mirror-finished. Main reason for this is as follows. Since the bands are bent upward in the deposition bath, the energy structure of the illuminated mirror-finished surface is suited for the polypyrrole deposition there, but the photogenerated electrons are forced to move towards the bulk, where they recombine with positive holes that are supplied by diffusion. According to the results, the silver deposition took place on the back surface if both front and back surface were mirror-finished. Adsorbed silver ions may generate surface states which contribute to the silver deposition.[18] However, it is noticed that the rate was relatively low in that case, compared to that obtained when the front surface was mirror-finished and the back surface was damaged.

It is quite reasonable to consider that charge carriers supplied by diffusion contribute to heterogeneous reactions, but the present study have made clear that the contribution becomes appreciable under a special configuration of semiconductor surfaces; the back surface is mirror-polished and the front surface contains both anodic and cathodic sites. It is believed that the same should hold in photocatalysis of semiconductor powders.

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