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Title	Photoanodic Properties of Plasma Sprayed TiO_2 Coatings(Surface Processing)
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Citation	Transactions of JWRI. 1990, 19(2), p. 271-275
Version Type	VoR
URL	https://doi.org/10.18910/12265
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Photoanodic Properties of Plasma Sprayed TiO_2 Coatings†

Akira OHMORI*, Kyeung-Chae PARK, Yoshiaki ARATA***, Katsunori INOUE**** and Mobuya IWAMOTO******

Abstract

Plasma spraying has been used to prepare n-type polycrystalline TiO_2 coatings on titanium substrate as photoanodes. The photoanodic properities of plasma sprayed TiO_2 coatings depend on the extent of oxygen loss and impurity of TiO_2 particles during plasma spraying. These properties depending on plasma conditions, additives and heat treatment are elucidated in oxygen saturated solution of 0.1 N NaOH.

It is shown that the plasma spray atmosphere and plasma auxiliary gas, hydrogen, influence greatly the photoanodic properties of TiO_2 coatings. Moreover, the photoanodic current increases by heat treatment (400°C-90 min) in air and by addition of Y_2O_3 to TiO_2 coatings.

Bandgap (BG) and subbandgap (SBG) photocurrent transients of TiO_2 coatings electrode were explored as a function of the external applied bias and light wavelength. These photocurrent transients disappear at high anodic potentials and increase at high cathodic potentials.

Kinetic response of an anodic photocurrent which shows spike immediately and again increases with time after the light is turned on for plasma sprayed TiO_2 coatings, has been discussed with impurity center.

KEY WORDS: (Plasma Spraying) (Additive) (Heat Treatment) (Photoanodic Property) (Impurity Center)

1. Introduction

The water decomposition by an electrochemical cell with *n*-TiO_2 electrode was first demonstrated by Fujishima and Honda[1]. The process occurs when the TiO_2 electrode is illuminated by light of energy larger than the band gap (Eg=3.0 eV).

In such a case, because of the difference in the work function between TiO_2 and the electrolyte, the Schottky barrier is formed at the semiconductor-electrolyte interface. Electron-hole pair created by the incident photons are separated by the electric field of the barrier; the electrons move away from the surface into the bulk of TiO_2, whereas the holes accumulate at the TiO_2-electrolyte interface. At the interface, the holes discharge with hydroxyl ions evolving oxygen gas; the electrons move through the external circuit and discharge with protons at the counterelectrode evolving hydrogen gas[2].

Polycrystalline *n*-TiO_2 has been widly studied as a semiconducting electrode in photoelectrochemical cells. Several techniques for the preparation of the photoanodes are found in the literature, namely, thermal oxidation[3], anodic oxidation[4], chemical vaper deposition[5], sputtering[6], sintering[7] and sprayed coatings[8].

Plasma spraying is a well known technique in various industrial fields to obtain the reliable coatings of ceramics and would be practically well suited for large scale production. When TiO_2 (rutile) powders are plasma-sprayed, the TiO_2 coatings become a *n*-semiconductor whose properties depend on the extent of oxygen loss of TiO_2 particles during plasma spraying. The photoanodic properties of TiO_2 coatings depend greatly on plasma conditions and additives.

In this study, the photoanodic properties of plasma sprayed TiO_2 coatings were studied. And, effects of plasma spray atmosphere, exsistance of H_2 in plasma gas, additives and heat treatment on photoanodic properties of TiO_2 electrodes were discussed. The plasma spraying was used to prepare *n*-polycrystalline TiO_2 coatings on titanium-substrate. The photoanodic properties of the plasma sprayed TiO_2 electrodes were measured in oxygen-saturated solutions of 0.1 N NaOH.

2. Materials and Experimental Procedure

Materials used in this investigations were commercially available TiO_2 powders (M-102: METCO Ltd and PC-T: Nihon Abrasion Ltd) and titanium plate (25 mm×15 mm×3 mm) as substrate. The

† Received on November 5, 1990

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Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

crystal structure of these powders is rutile. Plasma sprayed TiO_2 coatings were prepared as photoanodes. **Table 1** shows chemical compositions of these powders.

Plasma spraying was performed with a plasma spray system—METCO 7 M. Spraying environment was ambient air, and plasma working gas were Ar (100 *l*/min) and Ar (100 *l*/min)+H_2 (10 *l*/min). Plasma power was 38 kW and spraying distances were 100 mm. and as additives added to M102-TiO_2 powders, various metal and oxide powders (purity; 99.99wt%) were used.

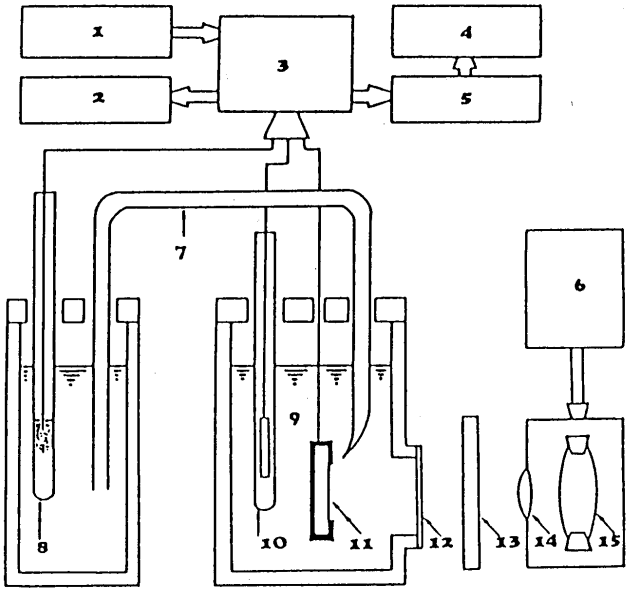
After plasma spraying, the coatings were heat-treated in the electrical furnace under ambient air and they were cooled slowly in furnace from heat treated temperture to room temperature.

In order to perform the measurement of photoanodic properties, ohmic contacts were established by directly attaching a copper wire to the conducting substrate-Ti plate. All the nonphotoactive parts of the photoelectrode were afterwards covered with silicone rubber to avoid photoresponse, leaving an active area of 1 cm^2.

The measurements of photoanodic properties were performed using a three electorde cell equipped with a quartz window and 0.1 N NaOH solution saturated with oxygen as shown in **Figure 1**. The counterelectrode was a Pt foil and a standard calomel electrode was used as reference. The working electrode was illuminated by white light from a high pressure 300W Xe lamp. Monochromatic light was obtained by interference filter. The light intensity was measured with a Eppley Thermopile, E6. A potentiostat and function generator were used for regulating the potential of working electrode. All the measurements were performed at room temperature.

Table 1 Chemical compositions of plasma spray TiO_2 powders (wt%).

	TiO_2	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	Na_2O
PC-T	99.2	0.20	0.12	0.42	0.03	0.06	0.02
H-102	98.6	1.03	0.08	0.07	0.13	0.05	0.04



1 Function generator
2 X-Y recorder
3 Potentiostat
4 Personal computer
5 Multimeter
6 Power supply
7 Salt bridge
8 Saturated calomel electrode
9 0.1 N NaOH-aq.
10 Counter Pt electrode
11 TiO_2 electrode
12 Quartz window
13 Optical filter
14 Quartz lens
15 Xe lamp

Fig. 1 Photoelectrolysis apparatus with side view of cell.

3. Results and Discussion

3.1 Effects of plasma spray condition on photoanodic properties of plasma sprayed TiO_2 coatings

Figure 2 presents the current-potential curves obtained for TiO_2 coatings using METCO-TiO_2 powder under illumination and in dark. These were typical curves for plasma sprayed TiO_2 coatings electrodes. The plasma spray atmosphere were air, and Ar 100 *l*/min and Ar 100 *l*/min+hydrogen 10 *l*/min as plasma gas. The potential scanning rate in this study was always 400 mV/min.

Regardless of using hydrogen as plasma gas, the current of TiO_2 coatings were greater under illumination than in dark, because of formation of electron-hole pair by light. And, regardless of illumination,

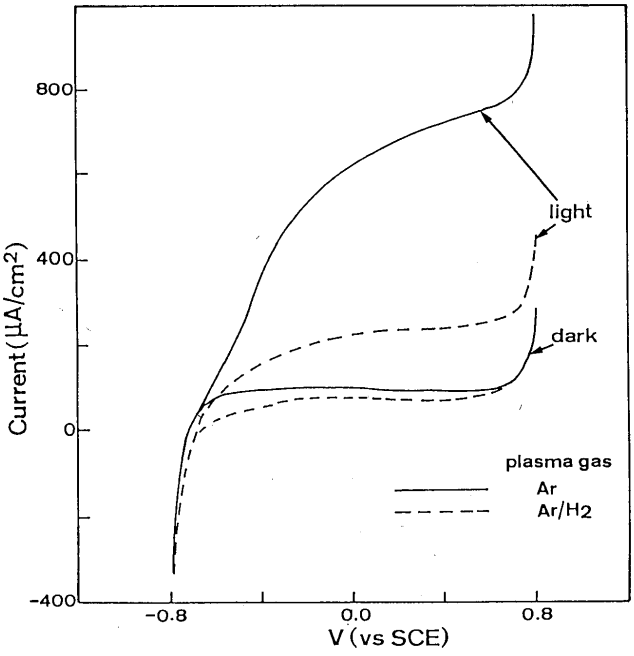


Fig. 2 Current-potential curves for plasma sprayed TiO_2 coatings produced by plasma gas Ar and Ar/H_2 in air.

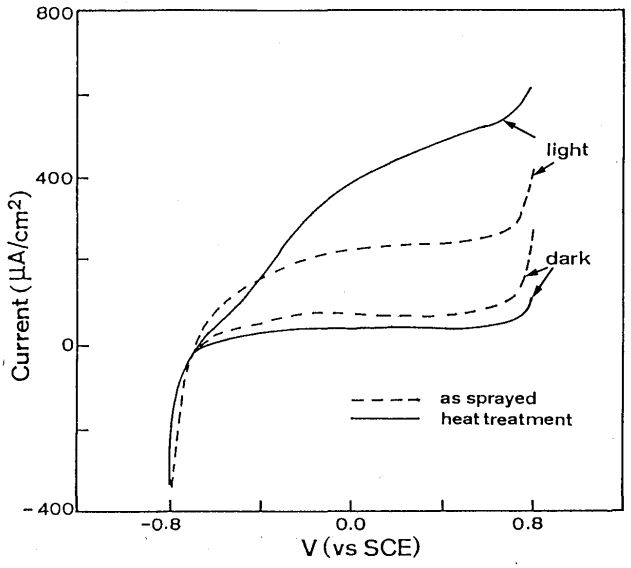


Fig. 3 Current-potential curves for plasma sprayed TiO_2 coatings produced by plasma gas Ar/H_2 in air and heat-treated at 400°C during 90 minutes.

the current and |Eo| (the absolute value of potential at zero current) of TiO_2 coatings produced with Ar 100 *l*/min were greater than with Ar 100 *l*/min+hydrogen 10 *l*/min as plasma gas.

The current of TiO_2 coatings produced with Ar 100 *l*/min as plasma gas increased greatly with increase of applied potential, and regardless of illumination, Eo (the potential value at zero current) of TiO_2 coatings were same value.

Figure 3 presents the current-potential curves for TiO_2 coatings plasma sprayed using METCO-TiO_2 powder and heat treated at 400°C during 90 minutes, under illumination (Xe lamp light) and in dark. The plasma spray atmosphere were air and Ar 100 *l*/min+hydrogen 10 *l*/min as plasma gas. The current of this TiO_2 coating increased by heat treatment. But, the current of TiO_2 coating heat-treated at 700°C became zero.

3.2 Effects of additives on photoanodic properties of plasma sprayed TiO_2 coatings

Figure 4 shows the current-potential curves for TiO_2 coatings using two kinds of powders TiO_2 powders (METCO) and 1wt% Y_2O_3-TiO_2 (METCO) powders. The plasma atmosphere were air and Ar 100 *l*/min+hydrogen 10 *l*/min as plasma gas and these coatings were heated in air at 400°C during 90 minutes after plasma spraying. The Xe lamp light was illuminated on the electrodes. The photocurrent for 1wt% Y_2O_3-TiO_2 coatings was greater than that of TiO_2 coatings and |Eo| of 1wt% Y_2O_3-TiO_2 coatings was larger than that of TiO_2 coatings.

Since addition of 1% Y_2O_3 to TiO_2 coatings and heat treatment (400°C, 90 min.) decrease amounts of oxygen

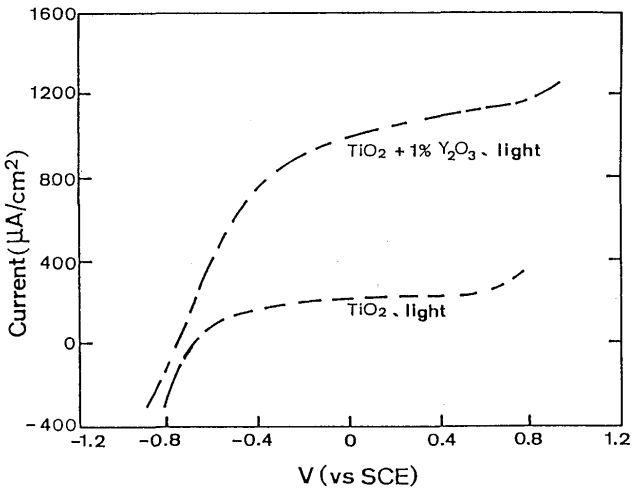


Fig. 4 Current-potential curves for plasma sprayed TiO_2 and 1% Y_2O_3-TiO_2 coatings produced by plasma gas Ar/H_2 in air and heat-treated at 400°C during 90 minutes.

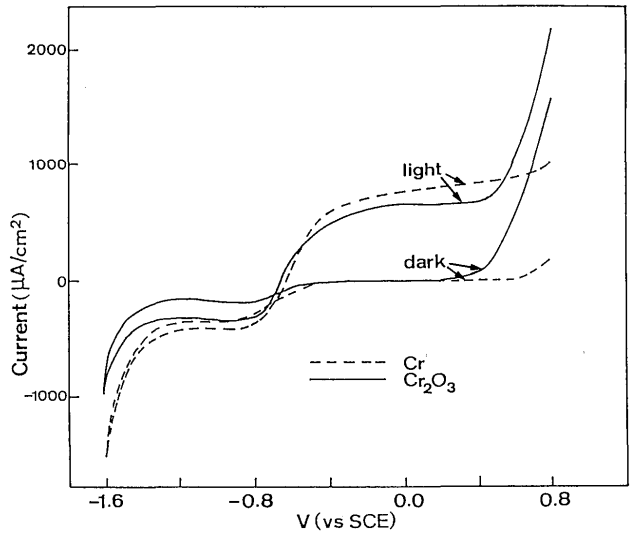


Fig. 5 Current-potential curves for plasma sprayed 1% Cr_2O_3 and 0.5% Cr-TiO_2 coatings produced by plasma gas Ar in air.

loss in TiO_2 coatings, the photocurrent of the coating becomes higher.

Figure 5 presents the current-potential curves for TiO_2 coatings using two kinds of powders added 1wt% Cr_2O_3 or 0.5wt% Cr to TiO_2 powders (METCO) under illumination and in dark. The plasma atmosphere was air and Ar 100 *l*/min as plasma gas. The anomalous photoresponse of the current-potential curves at cathodic potential were obtained by these additive to TiO_2 coatings comparing with the TiO_2 coating. Moreover, the shape of the curves depends on the wavelength of the incident light as well as on additive to TiO_2 coatings.

Electrons from the conduction band or from high energy surface states (lying less than 0.5 eV below the conduction band edge) contribute to oxygen reduction in the dark[9,10]. Oxygen reduction and the anomalous

photoresponse both occur at a potential close to V_{FB}. This behavior seems likely to us that the anomalous photoresponse could come from an enhancement of the oxygen reduction rate due to the reduction of additives.

3.3 Anodic current-potential and time behavior

While BG photoresponse in n-TiO_2 is known to be due to O^{-2}-Ti^{+4} electronic transitions, photogenerated holes reaching the interface with the electrolyte at the O_{2P} band, SBG photoresponse mechanisms are not well known. The bulk band gap are involved in the sub-bandgap excitation process, can be associated with cationic impurities and/or lattice defects[11].

Photocurrent, (Pc)-time relation at a fixed potential induced by intermittent illumination was examined. A typical photoresponce of n-TiO_2 was schematized in **Figure 6**. The stationary photocurrent (Pc-st) reached after enough time of illumination, and the initial photocurrent spike (Pc-in) is obtained at the moment the light illuminate by constant illumination fiux (Io). When the light is turmed off, the cathodic current spike (Pan-in) of back reaction is superimposed on the anoic photocurrent. This back reaction can be considered as decrease in surface potential due to illumination, photopotential and surface electron-hole recombination process[12,13,14].

Figure 7 shows the ratio of Pc-st/Pc-in obtained from photocurrent-time transient behavior of TiO_2 coatings added 1wt% Y_2O_3 as a fuction of the applied potential for BG light (380 nm), SBG light (476 nm) and Xe lamp light.

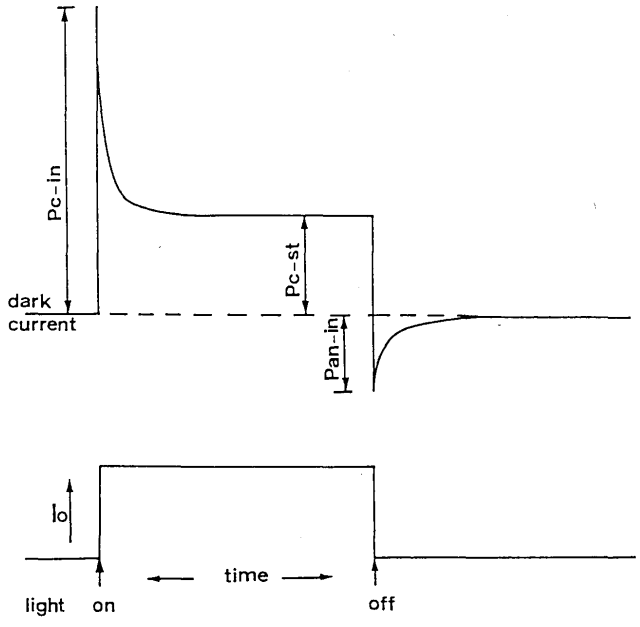


Fig. 6 Typical transient photoresponse of plasma sprayed TiO_2 coatings.

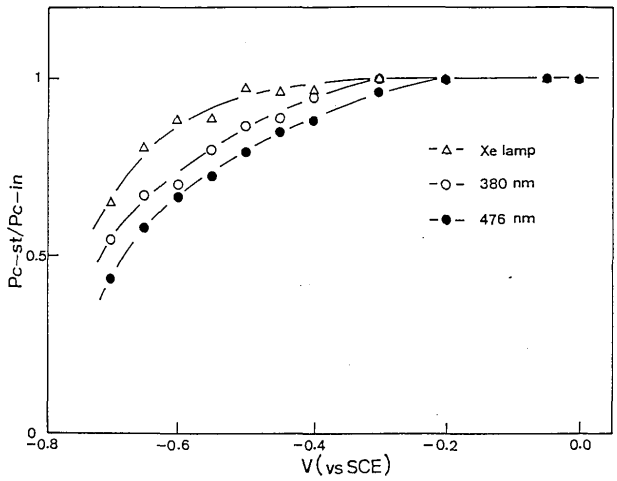


Fig. 7 Potential dependence of the transient ratio, (Pc-st/Pc-in) for photoresponse obtained with the polychromatic light of 300 W Xe lamp, 380 nm and 476 nm in 1% Y_2O_3-TiO_2 coatings produced by plasma gas Ar/H_2 in air and heat-treated at 400°C during 90 minutes.

From Fig. 7, at higher anodic potentials than −0.2 V, the transient practically disappears, and Pc-st/Pc-in becomes 1, which means that for every photon absorbed efficiently in the SC depletion layer a photogenerated hole is able to reach easily the interface between TiO_2 coatings and the electrolyte, and oxidize a water molecule[11].

At cathodic potentials, the ratio decrease and is large in order of Xe lamp light, BG light (380 nm), SBG light (476 nm). Where, the light intensity is large in order of Xe lamp light, BG light (380 nm), SBG light (476 nm), and $|Eo|$ is small in order of SBG light (476 nm), BG light (380 nm), Xe lamp light in 1% Y_2O_3-TiO_2 coatings (thickness: 40∼50 μm).

Because the Helmholtz layer is sufficiently thin, for semiconductor electrodes in the photoelectrolysis of water, the tunneling constant becomes smaller than surface recombination time constant. When the semiconductor and electrolyte are separated by a thin insulating film on semiconductor, a large value of tunneling constant should be obtained for tunneling through the film as well as the Helmholtz layer. Clearly, the thicker the film, the larger the value of tunneling constant. On the other hand, the surface recombination time constant decrease with the increase in the surface concentration of holes which can be proportional to the light intensity of illumination. Thus, for some large value of tunneling constant, it would be possible that as the intensity of illumination increases, the transition occurs from the recombination-controlled process in which the photocurrent of holes across the interface is proportional to the light intensity, to the tunneling-controlled process in which it depends little on the light intensity[15].

Accodingly, we can reckoned that the recombination controll of transient behavior increased (i.e. the ratio, Pc-st/Pc-in, decreased) with the decrease of light intensity and |Eo| for illumination light in 1% Y_2O_3-TiO_2 coatings.

3.4 Photourrent-time behavior in open circuit

The current-time behaviors of TiO_2 coatings in open circuit for constant illumination flux were same features, as shown in Fig. 6. In this section, abnormal photoresponse behavior was discussed.

Figure 8 shows photocurrent-time relation of TiO_2 coating using TiO_2 powders (Nihon Abrasion Ltd) contained a large amounts of Fe, for various monochromatic lights. The plasma sprayed atmosphere was air and Ar 100 *l*/min as plasma gas)

For 325~398 nm wavelengths, the photocurrent increased slowly to a value after much rapid increase when a light is illuminated, and decrease with time. At 476 nm wavelength, however, the photocurrent had maintained a constant value after rapid increase and decrease with time. When light was switched off, the situation was just the reverse of that when illumination started.

This kinetic responce of photocurrent is a result of impurity trapping. During the initial part of the excitation, impurity holes are trapped, and later an appreciable free carrier density can be supported and photocurrent again increases. After illumination is turned off, slow decay attributed to the existance of traps within the space charge layer.

This abnormal photoresponse behavior was observed also in TiO_2 coatings plasma-sprayed using TiO_2 powders added Cr_2O_3 or Ni. The bulk states of TiO_2 coatings are associated with impurity (Fe, Cr and Ni ion)[16,17], they revealed a band of states centered at 2.0 eV below the conduction band edge that appears to be the band surface active states in oxygen evolution.

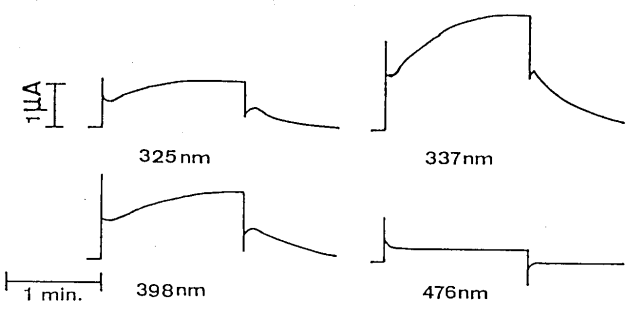


Fig. 8 Time dependence of the photocurrent and decays for various light wavelengh in plasma sprayed TiO_2 coatings produced by TiO_2 powders (Nihon Abrasin Ltd).

4. Conclusions

1) The photocurrent of plasma sprayed 1wt% Y_2O_3-TiO_2 coatings was greater than that of TiO_2 coatings and |Eo| (potential value at zero current) of 1wt% Y_2O_3-TiO_2 coatings was larger than that of TiO_2 coating.
2) The anomalous photoresponse of the current-potential curves at cathodic potential were obtained by additive (Cr_2O_3 or Cr) to TiO_2 coatings comparing with the TiO_2 coatings.
3) The kinetic responces of photocurrent were observed in TiO_2 coatings added Cr_2O_3 or Ni. The bulk states of TiO_2 coatings are associated with impurity ion. The phenomenon is a result of the impurity trapping. During the initial part of the excitation, impurity are trapped, and later an appreciable free carrier density can be supported and photocurrent again increases.

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