UDC 533.2

INDUSTRIAL APPLICATIONS OF TiO2 FILMS DEPOSITED BY ELECTRON-BEAM-EXCITED PLASMA OF METER-SIZE

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1. INTRODUCTION

TiO_2 materials have become important for environmental purification /1/. This is because many basic TiO_2 criteria, including sterilizing effects, deodorizing, dissolving, and hydrophilic effects, will some day be applied for the improvement of most of human life. With regard to environmental purification in particular, much attention is now being paid to antibacteria for colon bacillus, the dissolutions of NOx and environmental hormones, as well as anti-fog coating mirrors.

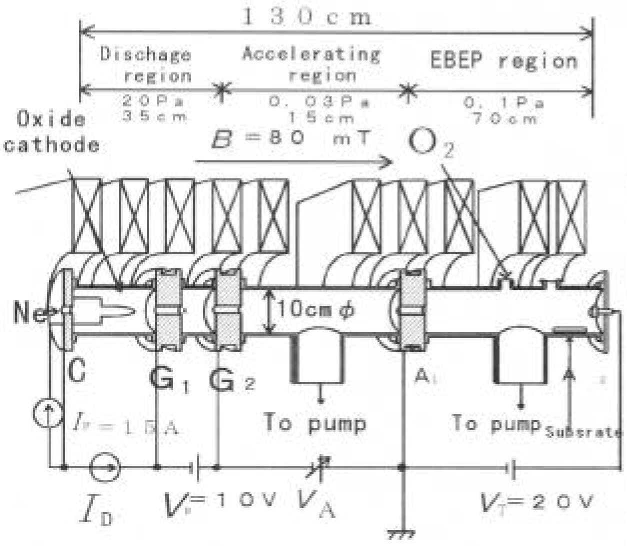

Fig.1 EBEP Apparatus

In this background, we reported here experimental control of the characteristics of TiO_2 film through plasma CVD using EBEP (Electron-beam-excited plasma) shown in Fig. 1. Using glass beads, glass plate and zeolate deposited by TiO_2 film with an optical catalyst, preliminary experiments were conducted on NOx and water-soluble ink dissolution, along with testing for hydrophilic effect. The advantage of EBEP-CVD is that the film quality can be directly controlled by beam accelerating voltage V_A, namely EEDF (electron energy distribution function) in an EBEP device /2/.

An method how to get a meter-size EBEP will be discussed here also.

2. EXPERIMENT

2-1. Deposition by EBEP

The details of EBEP apparatus are indexed by /2/ and /3/.The electron-beam was injected into the Ti metal target A_2. The Ti metal was melted by ohmic heating and evaporated. The polished glass substrates were placed near the Ti metal target A_2. The TiO_2 films of ~ 1 μm thickness were deposited on the glass plate, glass beads (diameter: 2 mm) and zeolates (diameter: 30 μm) for 30 minutes.The basic characteristics are shown in Table I.

Table I Summary of film characteristics

I_b [A] / V_A [V]	3	4	5
80	Anatase transparency	Anatase transparency	Anatase transparency
90	strong Anatase a little white	strong Anatase a little white	strong Anatase white
100	Anatase Rutile Ti_2O_3 light brown	Anatase Rutile Ti_2O_3 light brown	Ti_2O_3 violet

2-2. Applications and results

Fig. 2 shows the experimental system for NOx dissolution. The explain is shown by elsewhere/4/. The process to produce nitric acid on the catalyst glass beads coated by TiO_2 film from the chemical reaction of dissolution of NOx with HO_2, O and OH is as follows: (1) $NO + HO_2 \rightarrow NO_2 + OH$, (2) $NO + O \rightarrow NO_2$, (3) $NO_2 + OH \rightarrow HNO_3$, where the radicals of HO_2, O and OH are produced by the optical catalyst effect. The outline of result is as follows:

A typical output time course from a chemiluminescence NOx meter is shown in Fig.3 at the end. The NO gas concentration was kept constant at 9.89 ppm without catalyst beads as shown by the dotted line. The flow-rates of NO gas and wet air were 80 ml/min and 80 ml/min, respectively. At t=30 min, the amount of NO removal was 0.92 ppm as indicated by the vertical solid line on the left. When the accelerating voltage V_A was changed at I_D =5 A constant, the removal result was listed in Table II. The results of comparison between black-light and mercury lamp of optical catalyst were shown in Table III.

Separate experiments for dissolution of the water-soluble ink and for hydrophilic effect were carried out. The organic dissolution effect was evaluated by which the red color of water-soluble ink changes color, and through the optical catalyst changes from pink to transparent. The dissolvable effect by zeolates coating with TiO_2 film was tested and compared with that by beads. The results are summarized in Table IV.

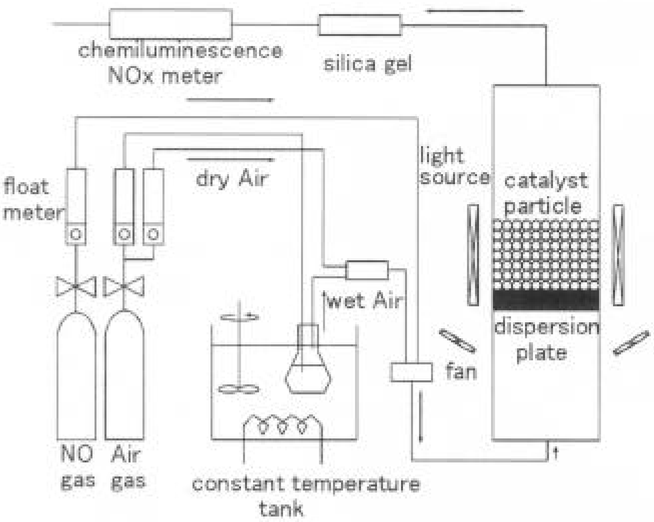

Fig.2. Experimental setup of removal of NO gas

3. DISCUSSIONS

From the X-ray diffraction patterns /4/, the thin film is composed by micro-crystals, does not made from amorphous. As the normal glass substrate is placed at 4 cm from the plasma beam and is not deformed by the heat, the crystal film will be formed at the temperature lower than 300 degrees. The film color listed in Table I will be important for the applications, for example, the transparent color is suitable for a mirror. The film formation temperature and the film color vs. the substrate position will become a key for the applications.

We discuss the removal of NOx. In Fig. 3, the amount of NO and NO_2 removal decrease with time, because HNO_3 deposited on the bead-surfaces with the hydrophilic effect should be removed to continue the chemical reaction. At t=150 min, the chemical reaction to NO and NO_2 becomes constant, which indicates the above reactions of NO $\rightarrow$ NO_2 and $NO_2 \rightarrow HNO_3$. The amount of NO removal is 0.59 ppm (9.89-9.3) at t=150 min as shown by a right vertical solid line. The amount of NO, 0.3 ppm (9.6-9.3) indicated by (a) becomes NO_2, while the remaining amount of NO, 0.29 ppm (0.59-0.3) indicated by (b) will be used to produce HNO_3 on the bead-surfaces. When the wet air increases, the amount of NO removal shows a maximum at a vapor concentration of 0.01 (H_2O-kg / dry air-kg)/5/. It was 0.008 in our case.

Table II Amount of removal of NO gas at t=30min versus V_A (black-light 135W, beads 20 g)

V_A (V)	Amount (ppm)
80	0.58
90	0.92
100	0.83

Table III Amount of removal of NO gas during 120 min versus light source (beads 20 g, V_A=90V, I_D =5 A, 160 ml/min, (a) 135W, (b) 100W)

Light source	Amount ($\times 10^{-5}$mol/m^2)
(a) black-light	6.89
(b) mercury lamp	9.15

Table IV Dissolution of red color of water ink 30 cc (I_D =4 A, (a) V_A=90 V;fluorescent lamp 15W, (b) and (c) V_A=80 V; black-light 75W)

Time (hours)	(a) Glass plate (4 cm^2)	(b) Beads (5 g)	(c) Zeolates (5 g)
3	Red	Red	Red
10	Pink	Red	Pink
24	Transparent	Pink	Transparent

Next, we discuss the EBEP parameters in Table II. From the X-ray diffraction patterns /4/, the composition of TiO_2 film was strong anatase when $V_A$was 90 V at I_D =5 A. For the NO removal experiment, the removal amount also becomes a maximum of 0.92 ppm at V_A =90 V and I_D =5 A.

An experiment for hydrophilic effect on glass plate was also carried out. The view of the hydrophilic effect is shown in Fig. 4.

The optical catalyst effects are compared between black-light and mercury lamp in Table III. The NO removal amount of 9.15×10^{-5} mol/m^2 by the mercury lamp is larger than that by black-light. It is due to the fact that the optical spectrum of mercury lamp was broad more than that of black-light .

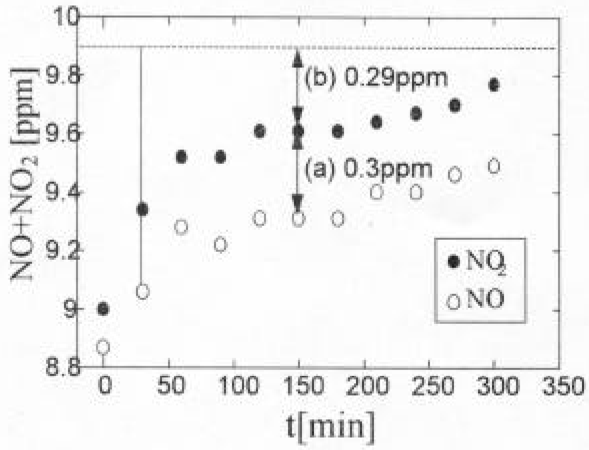

Fig.3.Output from chemi－luminescence NOx meter (V_A =90 V, I_D =5 A, beads 20g, black-light 135W, (a) NO→ NO_2, (b) NO_2→ HNO_3)

Next, we discuss the dissolution of the organic matter of water-soluble ink. In the first column in Table IV, a glass plate deposited by TiO_2 film was placed in 30 cc of the red water-soluble ink, where the color became transparent color over 24 hours. In the second and third columns, 5 g of beads and zeolates was also put in the water-soluble ink, where the color change with zeolates was faster than that with beads. This is due to the fact that the surface reaction area of zeolates was larger than that of beads.

The experiment on the hydrophilic effect was successful (Fig. 4), where the glass coated by TiO_2 film did not collect moisture. Coating mirrors without heater will be widely used in a bath and as a rear view mirror for traffic control.

Finally, we discuss here on EBEP of large area of meter-size for industrial apparatus. In order to request of users, Kawasaki Heavy Indust. Ltd. of Japan has

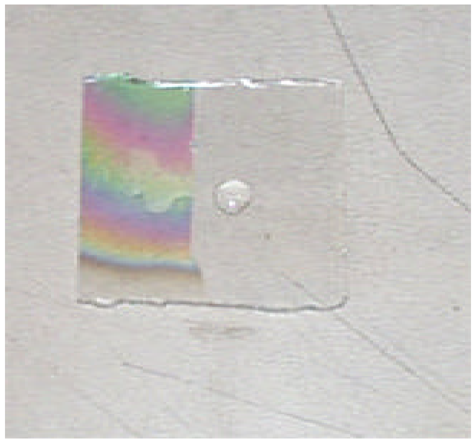

Fig.4. View of hydrophilic effect on glass; the left and right half sides are with and without TiO_2 film(V_A =80V,I_D=4A, fluorescent lamp 15W)

developed RS(ring shape)-EBEP, which will be useful to control and fabricate TiO2 film. And as for Ti source, a large area DC magunetron suputtering gun will be developed.

It is concluded that the dissolvable amount of NO gas was about 10^{-4} mol/m^2 during 120 minutes with an NO flow-in rate of about 100 ml/min and bead amount of 20 g whose surfaces were coated by TiO_2 film using controlled-electron-beam-excited plasma. The dissolution of organic matter was achieved.

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