Visualization Plasma Diagnosis Indicator Using Discoloration Reaction of Au and Pt Ions

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1. Introduction

In order to develop a new plasma diagnosis method by which the plasma condition can be diagnosed by a simple method such as the discoloration of the paper-like indicator caused by the reaction of the plasma, just like a pH test paper, we previously proposed the plasma chemical indicator (PCI) [1-3]. PCI is a piece of PET (polyethylene terephthalate) sheet strip on which a color indication mark is printed using ink that discolors through plasma chemical action. For example, the PCI is distinguishable to O_2 ($^1\Delta_g$) and $\cdot OH$, respectively. When the PCI was exposed to H_2O_2 or H_2O plasma, the color gradually shifted from the purple of original PCI toward dull light green and light bluish green respectively during 15 minutes of processing time with the action of $\cdot OH$. However, when the PCI was exposed to O_2 plasma, it also gradually shifted toward a pinkish color during 15 minutes of processing time with the action of O_2 ($^1\Delta_g$). The most interesting feature of the PCI is the ease of applicability to the two or three dimensional plasma diagnosis of the surface or the space which is in contact with the plasma. Since the PCI is a paper-like indicator, it is easy to install and arrange an arbitrary number of PCI on the place that is in contact with the plasma. Although the discoloration of PCI is premised on the plasma chemical reaction triggered by active species such as O_2 ($^1\Delta_g$) or $\cdot OH$ formed by 13.56 MHz rf plasma, it is necessary to confirm the influence of electrons and ions on the PCI discoloration.

As for electrons, it is known that electrons

cause damage to soft materials when the materials are put to SEM or EPMA observation, since electron energy is converted to heat as a result of interaction with the materials. Concerning ions, it also cause damage due to collision because of its relatively large mass compared to the electron. Although the action of such an electron and ion could be somewhat depressed in such a radio frequency of 13.56-MHz, it is important to know how much they affect on the discoloration of PCI individually.

In this research, discoloration properties of noble metal ions of Au and Pt by the interaction with electron and Ar ion (Ar^+) were utilized as the probes to visualize the degree of their influences individually.

2. Experiments

2.1. Preparation of Visualization Indicator

For the preparation of visualization plasma diagnosis indicator with Au ion (VI-Au) or Pt ion (VI-Pt) for the detection of the influence degree of electrons and Ar^+ in the Ar plasma were prepared by fixing these ions on the glass fiber filter with white color. The method is as follows: Glass fiber filter GC-50 (Advantec) with a diameter of 21 mm was used as a substrate. $HAuCl_4 \cdot 4H_2O$ and $H_2PtCl_6 \cdot 6H_2O$ were adjusted to 4.86×10^{-3} M and 9.72×10^{-3} M, respectively by ion exchanged water (all from Kanto Chemicals). And 0.1 mL of respective solution was soaked into a sheet of the filter, then vacuum dried before use. The color of VI-Au was light yellow and VI-Pt was white by visual observation.

2.2. Plasma Apparatus

Ion Coater IB-3 (Eiko) was used as the plasma apparatus. Two parallel disk-electrodes, cathode and anode electrodes were set upper and lower, respectively. As a plasma power supply, we used DC and radio frequency of 50 kHz (LF: low frequency) and 13.56 MHz (HF: high frequency). When a DC power supply is used, the action by ion sputtering will become dominant at the cathode, while the action by electron irradiation will become dominant at the anode. Therefore, it seems that the action of ion and an electron can be distinguished.

2.3. Measurements

2.3.1 Color Measurement

Discolorations of VI-Au and VI-Pt, after exposure to plasma were compared using the CIELAB color indicating system obtained from reflectance measurements results measured by the color analyzer NE-2000 (Nihon Denshoku). In CIELAB system, the L axis represents the lightness (L varies from 100 (for white) to 0 (for black), and a and b are the chromaticity coordinates ($+a$ is for red, $-a$ for green, $+b$ for yellow, $-b$ for blue).

2.3.2. Optical Emission Spectroscopy

Optical emission spectra are detected through an optical fiber by an optical spectrometer (Ocean Optics USB2000+) in the entire range from 200 nm to 900 nm. And the output of each plasma power supply was adjusted so that the spectral intensity for the specific peak observed might become equal.

3. Results and Discussion

3.1. Color Shift of VI-Au

It is well known that HAuCl_4 is easy to reduce and form Au nanoparticles with various attractive properties, such as catalytic ability, surface plasmon resonance properties, bactericides, and biological markers, electron-beam lithography [4] by reducing agent, thermal reduction reaction or photo-reduction.

Figures 1 and 2 indicate the color change of VI-Au and VI-Pt after thermal reaction using an ordinary electric furnace at various temperatures for 1 minute.

As shown in Figure 1, VI-Au showed various color due to surface plasmon resonance depending on their particle size. It was confirmed that the color of the VI-Au changed from original color of light yellow ($\diamond$) to positive direction of a -axis correspond to pink by thermal reaction. The lowest temperature to make difference in the color between original VI-Au and heated one is confirmed at 75°C or less.

Figure 1 The relationship between the temperature in the heat reaction and color of VI-Au.

Figure 2 The relationship between the temperature in the heat reaction and L-value of VI-Pt.

On the other hand, in the case of VI-Pt shown in Figure 2, the relation of L-value (expressing lightness) for VI-Pt vs. temperature were plotted, since Pt ion is colorless and does not show a color by plasmon resonance, even if Pt ion was reduced and nanoparticles were formed. The lowest temperature to make difference in the L-value between original VI-Pt ($\diamond$) and heated one is confirmed to 250°C or more.

Then, VI-Au and VI-Pt were investigated to determine whether electrons and ions could be distinguished through these discolorations.

Figures 3 and 4 show the relationship between applied voltage and color shift expressed by a and b in CIELAB when VI-Au is exposed to DC Ar plasma for 1 minute using Ion Coater. Figure 3 displays the results when the VI-Au is placed on an anode, whereas Figure 4 shows the results when the VI-Au is placed on a cathode.

As shown in Figures 3 and 4, when the VI-Au with original color of light yellow ($\diamond$) made contact with DC Ar plasma for 1 minutes at anode

Figure 3 The relationship between the voltage in DC plasma and the color of VI-Au at anode. Unfilled plot with numbers showing the elapsed time after contact with the plasma.

Figure 4 The relationship between the voltage in DC plasma and the color of VI-Au at cathode. Unfilled plot with numbers showing the elapsed time after contact with the plasma.

or cathode, it shifted toward plus direction of a-axis and negative direction of b-axis, corresponding to the color of light pink to light bluish pink, right after exposure to the plasma at both electrodes (expressed by filled plot). And yet this shift toward the positive direction of a-axis was kept for a few hours in atmospheric conditions after exposure to the plasma (expressed by unfilled plot with numbers showing the elapsed time after contact with the plasma). This indicates that formed Au nanoparticles are not stable, and continue growing to their stable particle size after exposure to the plasma. Concerning the shift to negative direction of b-axis, the shift amount right after contact with the plasma was increased in proportion to the applied DC voltage. And it turned out that the

discoloration behavior by the electron and ion of DC plasma differs from it due to heat reaction according to the increase of applied voltage shown in Figure 1. Judging from these results, the VI-Au is perceived as an indicator sensible to plasma with low capability to distinguish an electron and ion.

Figure 5 shows the result of the experiment carried out using a similar manner as Figures 3 and 4, but HF of 13.56 MHz was used instead of DC, and VI-Au was placed on the ground electrode. HF input power was adjusted so that the emission intensity of the plasma might become equal to DC plasma.

Figure 5 The relationship between the input power in HF plasma and the color of VI-Au at ground electrode. Unfilled plot with numbers showing the elapsed time after contact with the plasma.

It turned out that discoloration behavior by HF plasma in Figure 5 is well conformable in discoloration behavior by the heat reaction of Figure 1 rather than that by DC plasma shown in Figs. 3 and 4. That is, in the case of HF plasma, electron action is reduced so that the influence on the discoloration on VI-Au hardly appears. When discoloration by the HF plasma of Fig. 5 is compared with that by the heat reaction of Fig. 1, it was found that the irradiation for 1 minute of 25W to 75W HF plasma is almost equivalent to discoloration by a heat reaction with a temperature of 50 to 200°C. Although the results for the 50 kHz of LF plasma were omitted here, it was found that the color of the VI-Au after contact with the LF plasma is located in between the one after contact with the HF plasma and the one after contact with the DC plasma on the chromaticity coordinates. This indicates that a little more actions by the electron and ion than HF plasma are included in discoloration by LF plasma.

3.2. Color Shift of VI-Pt

Figure 6 show the result of an experiment carried out in a similar manner as Figures 3 and 4, but VI-Pt was used instead of VI-Au. In Figure 6, both results were plotted: one when the VI-Pt is placed on an anode, and another when the VI-Pt is placed on a cathode.

As shown in Figure 6, when the VI-Pt with original color of white came into contact with the DC Ar plasma for 1 minute at anode (●), the color of the VI-Pt became grayish so that L-value is decreased with the increase of voltage. This tendency indicates that the more electron energy is increased the more the Pt ions reduce and L-value decreases.

Figure 6 The relationship between the voltage in DC plasma and the L-value of VI-Pt at anode and cathode.

*: When the HF (▲) Ar plasmas were applied with the same emission strength with DC Ar plasma.

On the contrary, when the VI-Pt came into contact with the DC Ar plasma for 1 minute at cathode (■), L value was settled in a slight reduction. This tendency indicates that the reduction of Pt ion hardly takes place by Ar^+ bombardment at DC voltage of 0.75 kV or less.

From the above results, it was found that VI-Pt is thought to be available as an indicator that can distinguish the action of the electron and ion in DC plasma.

Although the results for the LF and the HF Ar plasmas were omitted here, it was found that the L-values were kept at the original level when the input power was increased.

Finally, the actual test using PCI was carried out by contacting it with DC, LF and HF Ar plasmas, and the color shifts expressed by a and b in CIELAB were plotted in Figure 7.

It was found that the color of PCI was drastically shifted when the DC plasma was applied, shifting toward green at the anode (●) and shifting toward gray at the cathode (■). On the other hand, little shift was recognized with LF (+)

Figure 7 Change of the color when the PCI is exposed to respective DC, LF, and HF plasma. In the case of DC plasma, PCI is installed on the anode and the cathode, and, in the case of LF and HF plasma, it is installed on the ground electrode.

and HF (▲). From these results, it can be said that the effects of electrons and ions on the discoloration of PCI is relatively small when it is applied in the radio frequency plasma. And the slight shift from this original can be considered as the background in a plasma atmosphere.

4. Conclusion

We have investigated the effects of electrons and ions on the discoloration of PCI using VI-Au and VI-Pt indicators as the probe to detect these actions visually. The actions of the electron and ion in DC plasma were distinguished by VI-Pt. The discoloration action to VI-Au by the action of the electron in rf plasma was similar to the discoloration action by a heat reaction. In addition, the effects of electrons and ions on the discoloration of PCI are slight when it is applied in the radio frequency plasma of 13.56 MHz.

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