A Novel Electrode for Ozone Generation

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A new type of electrode for ozone generation was fabricated by radio-frequency (RF) sputtering. High current efficiency (8%) of ozone generation is achieved at a very low current density (ca. 10 mA/cm^2) with the electrode.

Ozone is a strong oxidizing agent with a high oxidation–reduction potential (1.51 V vs NHE), and it is used for the oxidation[1] of organic and inorganic substances, sterilization,[2–5] deodorization, decolorization,[6] and so on.[7–10] Since ozone readily decomposes into oxygen at normal temperature, its use in water treatment is advantageous. In practice, water with dissolved ozone (i.e., ozone water) has promising applications in the sterilization of tap water and sewage[11] and in silicon (Si) wafer cleaning in semiconductor device manufacturing.[12]

There are two methods to produce ozone water. The first involves producing ozone gas by UV[13,14] or electric discharge[15] followed by dissolving it into a solution. In the second method, electrolysis is used to directly produce ozone in a solution.[16] The latter method is preferred since it is a simple process.

Regarding the electrolysis method (using a cell separated by a cation-exchange membrane), Foller et al. reported that the current efficiency of ozone generation was more than 7% at a current density of 600 mA/cm^2 when β-lead dioxide (β-PbO_2) and 5 M H_2SO_4 were used as the anode and electrolyte solution, respectively.[17] However, the dissolution of poisonous lead (Pb) into the solution posed a problem, and only an acidic electrolyte solution was used. This has prevented the application of the PbO_2 system to water sterilization. Although platinum (Pt), another material that can be used to generate ozone, has the highest oxidation overpotential among the noble metals[18] and is stable in the solution, it does not necessarily have a high ozone production efficiency (less than 2% at a current density of 400 mA/cm^2).[17] By using a TaO_x and Pt composite insulator-coated Ti electrode fabricated by thermal decomposition (t-Pt/Ta), the authors discovered that the maximum current efficiency of ozone generation was 6% at a very low current density[19]—below 20 mA/cm^2. The possible mechanism of ozone generation during electrolysis is as follows. During the fabrication of the electrode, many cracks are formed on the Pt/Ta layer, which is an insulator, and the cracks that propagate to the Pt buffer layer formed between the Ti substrate and Pt/Ta layer serve as paths for the electrolyte. As a result, the current possibly concentrates in the Pt buffer layer and the electrode potential increases to the potential for ozone generation. However, ozone generation is not observed even when the current density is 150 mA/cm^2, a DSA-type Pt electrode is used as the anode, and the voltage between the electrodes is very high compared with that of the Pt/Ta electrode. Therefore, we should consider factors other than the current concentration in the Pt buffer layer. In this study, we examined whether the catalytic activity of tantalum oxide is one of the factors that plays a key role in ozone generation. In order to evaluate the characteristics of tantalum oxide, we formed a catalyst layer on a flat Si(001) surface by a radio-frequency (RF) sputtering method. In general, a film fabricated by thermal decomposition exhibits undesirable features, such as a concave–convex surface after chemical etching and a variation in the film thickness. These hamper the evaluation of the characteristics of tantalum oxide as a catalyst for ozone generation.

The electrodes for examination were prepared according to the procedure described below. A Si(001) substrate was pretreated with 5% hydrofluoric acid, and the silicon oxide film was removed. After rinsing with pure water, the substrate was introduced into the chamber of the RF sputtering equipment (ULVAC KIKO, Inc., RFS-200). In the sputtering process, a Pt film was first deposited on the Si substrate for 20 min at room temperature under an Ar gas pressure of 0.9 Pa and RF power of 100 W. The substrate-to-target distance was 60 mm. Second, a metallic Ta film was deposited on the Pt film, hitherto deposited on the Si substrate, for 5 min at room temperature under the same conditions. According to X-ray fluorescence analysis, the quantities of Pt and Ta were ca. 210 and ca. 17 µg/cm^2, respectively. Finally, the substrate with the deposited films was annealed at 600 °C for 30 min in air. This temperature is the same as that used for sintering the t-Pt/Ta electrode.[19]

According to Auger electron spectroscopic (AES) study, the Ta layer is completely oxidized and the Pt layer consists of platinum silicide, in which Si originates from the substrate. Moreover, Si is distributed evenly on the Pt layer and does not reach the Ta layer. Similarly, Pt does not penetrate the Ta layer. A scanning electron microscope (SEM) image of the electrode surface and a mapping image of Ta by AES are shown in Figure 1. Although the surface appears to be rather rough (Figure 1a), cracks observed on the surface of the t-Pt/Ta electrode are not seen in this case. Ta is uniformly distributed (Figure 1b). Figure 2 shows transmission electron microscope (TEM) images of the cross section of the electrode. As shown in Figure 2a, voids are observed on the platinum silicide layer near its interface with the

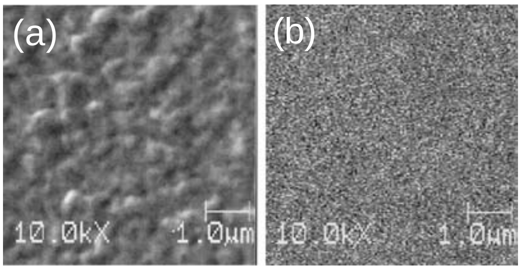

Figure 1. An SEM image of the electrode surface (a) and a mapping image of Ta (b) by AES.

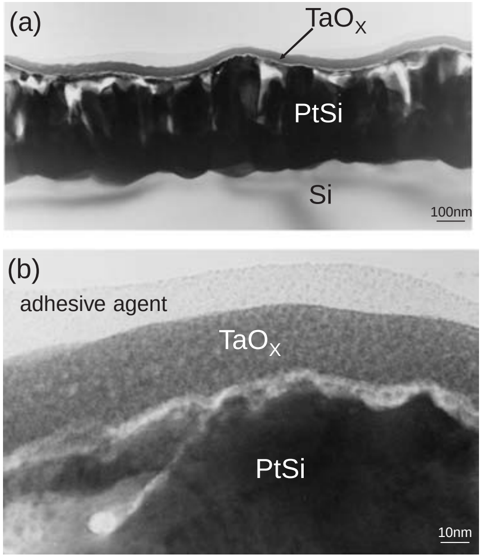

Figure 2. TEM images of the cross section of the electrode.

tantalum oxide layer. However, no voids or cracks are observed on the tantalum oxide layer, although undulations are visible along the platinum silicide layer. In addition, in the enlarged TEM image shown in Figure 2b, the electrolyte appears to be unable to pass through the layer despite the presence of spaces (white regions in the tantalum oxide layer), which are of the order of subnanometers. Therefore, the electrode reaction is considered to proceed on the surface of the tantalum oxide layer.

Figure 3 shows the variation in the amount of ozone generated and current efficiency dependence on the current density, with the assumption that the reaction consumes six electrons. A cell separated by a cation-exchange membrane (Nafion®) was used to evaluate the ozone generation. A Pt plate was used as the cathode. The distance between the anode and cathode was 1 cm. One hundred fifty milliliters of laboratory-prepared-model tap water[19] was used as the electrolyte in both the anode and cathode compartments. The solution temperature was maintained at 15 °C and the electrolysis time was 1 min. The amount of ozone generated was measured by colorimetry (HACH DR/4000U). As shown in Figure 3, a high current efficiency (8%) is achieved even at a very low current density (ca. 10 mA/cm^2). Thus, electrolysis is possible even if the surface of the electrode is completely covered with nonmetallic tantalum oxide. The voltage between the electrodes during electrolysis at ca. 20 mA/cm^2 was approximately 90 V, which is comparable with that during electrolysis using the platinum (silicide) electrode as the anode (ca. 75 V). This may be because electrons are transferred via Fowler–Nordheim tunneling or through the impurity level in the tantalum oxide layer since this layer is comparatively thin (ca. 20 nm). The high current efficiency is possibly due to the following reason. While using a metallic electrode, the electrode reaction at the anode occurs when the empty level near the Fermi level receives electrons from the electrolyte. On the other hand, while using an insulating electrode, the electrode reaction at the anode occurs when the empty level near the bottom of the conduction band, which is higher than the Fermi level by half of the band gap, receives electrons from the electrolyte. The work functions (difference between the vacuum and Fermi levels) of platinum and tantalum are 5.65 eV[20] and 4.25 eV,[21] respectively. In addition, the bottom level of the conduction band of tantalum oxide is higher than the Fermi level of tantalum.[22] Therefore, the current efficiency of ozone generation increases because the electronic transfers occur at a higher energy level as compared with the case of the platinum electrode.

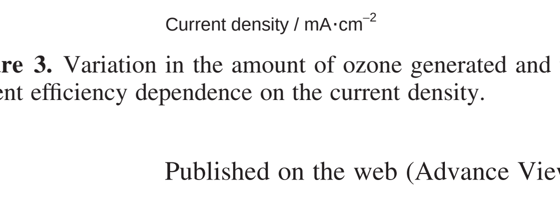

Figure 3. Variation in the amount of ozone generated and the current efficiency dependence on the current density.

As described above, tantalum oxide is effective as a catalyst for ozone generation. It is remarkable that very high current efficiency, ca. 8%, is achieved at a very low current density (ca. 10 mA/cm^2). For higher current efficiency, the control of film flatness and oxidation conditions are currently being studied.

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