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Tanaka Tomohito, Takishita Hiroshi, Sagawa Takashi, Yoshikawa Susumu, Hayase Shuzi

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Electrochemiluminescence Devices Consisting of ZnO Nanorods Vertically Grown on Substrate

Tomohito Tanaka, Hiroshi Takishita, Takashi Sagawa, Susumu Yoshikawa, and Shuzi Hayase

Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu 808-0196

Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011

(Received April 1, 2009; CL-090323; E-mail: hayase@life.kyutech.ac.jp)

Unique behaviors of electrochemiluminescence from a device consisting of ZnO nanorod (Cell-1) are reported. Cell-1 emitted more intense electrochemiluminescence than cell consisting of two flat electrodes (Cell-2). The onset potential at which the emission started was 1.5 V for Cell-1, which was lower than 2.5 V for Cell-2. The unique behaviors were explained by asymmetric collision modes of emitting species (Ru\(^{II}\) and Ru\(^{III}\)) in the nanospace among ZnO nanorods and were characteristic to the ZnO nanorod array.

Electrochemiluminescence (ECL) originates from solutions consisting of emitting molecules. For example, ECL from Ru complexes, Ir complexes, rubrene, poly(phenylenevinylene), emitted more intense electrochemiluminescence than cell consisting of two flat electrodes (Cell-2). The onset potential at which the emission started was 1.5 V for Cell-1, which was lower than 2.5 V for Cell-2. The unique behaviors were explained by asymmetric collision modes of emitting species (Ru\(^{II}\) and Ru\(^{III}\)) in the nanospace among ZnO nanorods and were characteristic to the ZnO nanorod array.

Figure 1. ECL device structure consisting of ZnO nanorods (Cell-1).

Figure 2. Relationship between luminescence and applied potential (AC 60 Hz). Cell-1-t-X: X stands for the length of ZnO nanorods.

ECL response was observed with a Topcon Model BM-9 luminance meter. ECL intensity for Cell-1 was higher than that of Cell-2 as shown in Figure 2. The onset potential at which the emission starts was 1.5 V for Cell-1, which was lower than 2.5 V for Cell-2. In addition, the onset potential decreased as the ZnO nanorods became thicker. The results strongly demonstrate that the decrease in the onset potential is associated with the ZnO nanorod structure.

The current–potential curve showed that the current density of Cell-1 was higher than that of Cell-2 at each potential. In addition, the current density increased with an increase in the ZnO-nanorod thickness. For example, the current density was 29 mA cm\(^{-2}\) for Cell-2, 46 mA cm\(^{-2}\) for Cell-1-t-4.0 (length of ZnO nanorod: 4.0 µm), 50 mA cm\(^{-2}\) for Cell-1-t-8.1 (length of ZnO nanorod: 8.1 µm), and 52 mA cm\(^{-2}\) for Cell-1-t-11.5 (length of ZnO nanorod: 11.5 µm) at 3 V, where X of Cell-1-t-X stands for the length of the ZnO nanorod. The large surface area of the ZnO nanorods would be responsible for the higher
current density, because they are an n-type semiconductor and electrons can diffuse in the ZnO nanorods. The ECL efficiency of Cell-1 was higher than that of Cell-2, and the efficiency increased as the ZnO nanorods became thicker. For example, the efficiency was 0.1mW-1 for Cell-2, 0.03mW-1 for Cell-1-t-4.0, 0.07mW-1 for Cell-1-t-8.1, and 0.10mW-1 for Cell-1-t-11.5. The high efficiency of Cell-1-t-11.5 can be explained by the increase in the collision frequency between these emitting species (RuII and RuIII) not by mere increase in the amount of electrons injected from the vast surface of the ZnO nanorods.

Figure 3 shows the time-dependent response of ECL for Cell-1-t-4.0, Cell-1-t-8.1, and Cell-2, where polarity of the potential is described as that of an electrode with ZnO nanorods. The response curve of Cell-2 on polarity change from positive to negative (A region in Figure 3) was the same as that from negative to positive (B region in Figure 3) because the cell structure is symmetrical. However, the response curve for Cell-1-t-4.0 had a sharp peak on the polarity change from positive to negative (C region in Figure 3), and a broad peak on the polarity change from negative to positive (D region in Figure 3). In the case of Cell-1-t-8.1 which has a thicker ZnO nanorod layer than Cell-1-t-4.0, the difference in the response curve between E and F regions (Figure 3) was pronounced more than that between C and D regions; namely, the slope of the curve in F region was gentler than that in D region. The asymmetrical response curve can be explained by a model shown in Figure 4. ECL originates from RuII which is formed by the collision of RuI and RuIII, where the former is formed on a cathode and the latter is formed on an anode. In the case of Cell-1, RuIII was reduced to RuI on the surface of both a transparent conductive layer (F-doped SnO2, FTO) and ZnO nanorods when the negative potential was applied (Figure 4-1), during which the nanospace among ZnO nanorods is filled with RuI on the surface of the FTO only not on the surface of ZnO nanorods (Figure 4-2), because ZnO has n-type character. The RuIII gradually diffuses in the nanospaces among the ZnO nanorods and collides with RuI remaining in the nanospaces. Therefore, the emission lasts for a long time. The response curve of C region is explained as follows: When the positive potential is applied, RuIII diffuses from the bottom of the FTO surface not from the surface of the ZnO nanorods. The nanospace is filled with RuIII (Figure 4-3). When the polarity was changed from positive to negative, electrons are injected from both of the ZnO nanorod and FTO surfaces to form RuI (Figure 4-4). Therefore, RuIII is surrounded immediately by RuI, and the collision between RuI and RuIII occurs swiftly, resulting in giving a sharp emission curve (C in Figure 3). The difference in the response curves between E and F regions was much more pronounced because Cell-1-t-8.1 has thicker ZnO nanorods. The broad emission of D and F regions is responsible for the increase in the emission strength. Results of Cole–Cole plot supported the explanation that the diffusion of Ru ion species is suppressed in Cell-1. For example, a semicircle associated with Ru ion diffusion is about 80Ω for Cell-1 and 40Ω for Cell-2. The interaction between Ru ion and ZnO nanorod surface may be responsible for the slow diffusion. Results on CV measurements of Cell-1 showed that the reduction potential of RuIII shifted positively by 1.0V, compared with that of Cell-2. The difference between the onset potentials for reduction and oxidation of RuIII observed by the CV measurements was 2.5V for Cell-2, and 1.5V for Cell-1. These values are consistent with 2.5V of onset potentials at which emission starts for Cell-2 and 1.5V for Cell-1. In this stage, the reason why the reduction potential and the onset potential for emission of Cell-1 were extensively lower than that of Cell-2 is not fully understood.

References