Transactions of the Materials Research Society of Japan 25 [1] 119-121 (2000)

Photo-electrochemistry on Electrochemically Self-assembled Superlattice

Seiichiro Nakabayashi* and Kazunori Nagai

Department of Chemistry, Faculty of Science, Saitama University,
255 Shimo-Ohkubo, Urawa 338-8570
Fax: +81-48-858-9424, e-mail: Sei@chem.saitama-u.ac.jp

A Cu/Cu_2O multiple quantum well (MQW) was self-assembled on a polycrystalline copper or a platinum (111) surface. In the room temperature, this MQW showed a negative differential resistance (NDR). The thickness of the quantum confined layer (Cu_2O layer) was estimated to be 1.2nm by the bias voltage at the current maximum. By using this MQW as a photo-electrode, the photocurrent and the Mott-Schottky relation were observed in an aprotic electrolyte.

Key wards: negative differential resistance, MQW, self-organization, non-linear electrochemistry, photo-electrochemistry

A super-lattice is the one of the most functional and artificial materials. High quality multiple quantum well (MQW) such as GaAs/GaAlAs and InAs/AlSb have been synthesized by the molecular beam epitaxy method.[1] These materials are commonly used for the quantum electronics devices; for example, a resonant tunnel diode or a self electro-optic device.[1,2] In the field of the photo-electrochemistry, the possible superiority of a MQW than a common bulk semiconductor electrode has been reported in considering that the hot electron cooling rate is much slower in the MQW compared to the one in the bulk.[3-5] However, we believe that the expected quality of the MQW for the photo-electrochemical applications must be different from the one for the electronics applications. For the solar applications, the required area of the MQW must be much larger than the one for the device applications and the electronic quality is more tolerant. This suggests that the fabrication in the ultra-high vacuum (UHV) chamber is not always the best process for producing the solar grade MQW.

Recently, an electrochemical self-assembling method was discovered to form a layered nano-structure of Cu/Cu_2O.[6,7] In this article, we have synthesized this Cu/Cu_2O MQW and examined it's quantum confined function and finally used it as a photoelectrochemical cathode in an electrolyte solution.

The Cu/Cu_2O MQW was synthesized in a beaker containing 0.6M $CuSO_4$ and 3M $CH_3CH(OH)COOH$ aqueous solution. The pH of the solution was adjusted to be 9.0 by adding NaOH. The three electrodes were set in this electrolyte solution; the working electrode was a copper disk (surface area, A=0.71 cm^2) or a Pt(111) disk made by the Clavilier method[8] (A=0.028cm^2). The reference and the counter electrodes used were a saturated calomel electrode (SCE) and a copper wire, respectively. The electrolysis was conducted under a constant current; -50 μ A/cm^2. The spontaneous self-sustained oscillation was observed just after the beginning of the experiment using this electrolysis, which was shown in Figure 1. This self-sustained oscillation was robust and continued for more than 5 hours when the volume of the electrolyte solution was 700ml. However, in the relatively small beaker such as 100ml, this oscillation was terminated in a short time. The mechanism for this volume effect has not been cleared, yet. In both cases, the surface was quickly covered by a deposited material, because a cathodic process was occurring on the electrode. The electrochemical quartz crystal microbalance (EQCM) observation had revealed that Cu_2O layer was formed at the anodic potential pulse.[6,7] In the rest of the time, copper deposition was occurred on the surface.

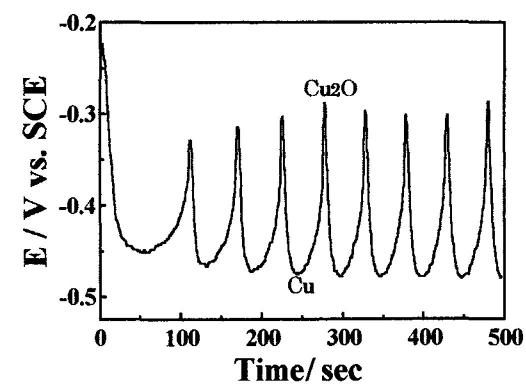

Fig.1 Self-sustained non-linear electrochemical potential oscillation for producing a self-assembled layered nano-structure.

By using the electrode on which about 200 layers had been self-assembled, the current transporting perpendicular to the synthesized layers was measured as a function of the bias voltage , which was applied between the attached copper wire by using the silver paste on the surface and the other end of the copper electrode. The obtained current-voltage curve was shown in Figure 2, which shows a couple of negative differential resistance (NDR) started at $\pm$0.42V. Based on the conventional resonant tunneling model, the length of the quantum confined layer (Cu_2O layer) is estimated as[1,6]

$$L = h/(8m^*eE_{peak})^{1/2}$$

where h , e and E_{peak} represent Planck's constant, the elementary charge and the voltage at the current maximum, respectively. The effective mass of the confined carrier (a hole in this case) was represented by m*, which was 0.61 times that of the free electron mass. Thus, the length of the confined layer (Cu_2O layer) was estimated to be 1.2nm, which was on the same order of the one estimated by the Faraday law from the oscillation in Figure1.

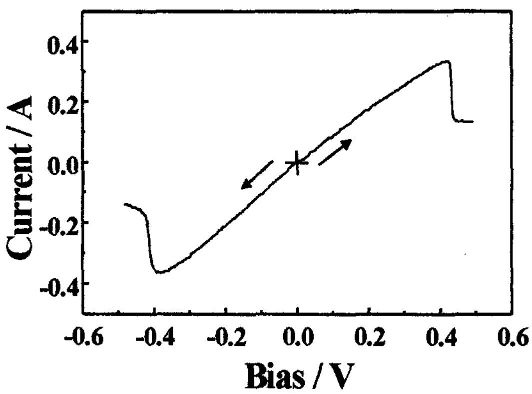

Fig.2 Current and bias potential relationship, transporting perpendicular to the synthesized layers.

In order to confine the layered structure, the optical interference by the layered structure was observed. Under 2.0-3.0mA/cm^2 and pH=9.8-10 in the solution, the color of the electrode surface could be controlled blue to red depending on the period of the potential pulse intervals. Furthermore, the apparent color was changed by the angle of the observation. Under these enlarged spacing conditions, however, the synthesized film never showed the quantum confined response.

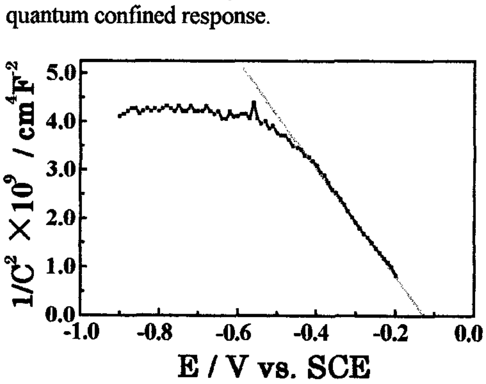

Fig.3 Mott-Schottky relationship on the synthesized MQW electrode.

The film on which NDR obtained was deposited on a Pt(111) and the photo-electrochemical response was measured in an acetonitrile containing 0.1M tetrabutylammonium perchlorate. The space charge capacitance was measured by using an impedance analyzer, (HP4292A/LF) and the Mott-Shottky relation[5] was plotted in Figure 3. The linear relationship was obtained from -0.2 V to -0.4V. In more anodic potential region than -0.2V, anodic dark current was observed. By the extrapolation of the plot, the flatband potential (E_f) was -0.12 V. The acceptor density (N_a) was 10^{21} /cm^3 under an approximation of a spatially constant dielectric constant (ε) of 7.60, which is the value of the pure Cu_2O.[9] The potential where the plot deviated from the linear relationship was -0.45V. From this potential, the length of the space charge layer increased over the total thickness of the self-assembled MQW. These results are qualitatively identical with the one reported with GaAs/GaAlAs MQW.[5] The thickness of the space charge layer can be estimated as

$$L = \{2\varepsilon\varepsilon_0/eN_a(E-E_f)\}^{1/2}.$$

But, the estimated total thickness of the MQW layer from the Mott-Shottky plot (5nm) was much smaller than the one estimated by the Faraday law (200nm). This is probably due to the present ambiguity of the dielectric constant of the MQW.

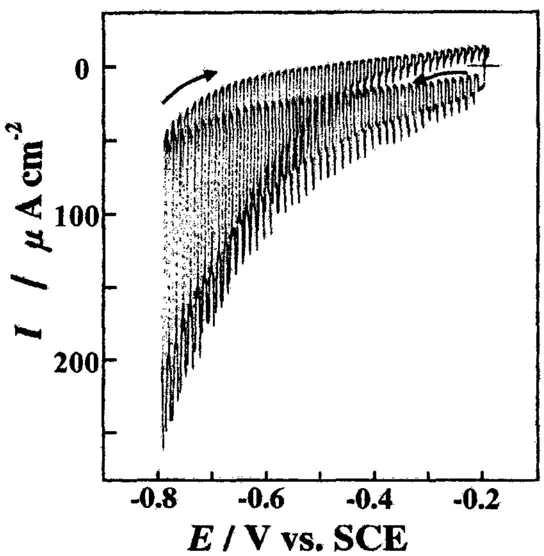

Fig.4 Photo-current and electrode potential curve under chopped irradiation of Argon laser (514.5nm) on the synthesized MQW electrode.

The photo-current response was measured by using a chopping irradiation of Argon laser (532nm). The cathodic photoresponse was certainly observed but the saturation of the photo-current was not observed. At this stage, no specific electron acceptor was added in the solution, then, the observed photocurrent was due to the reductive photo-degradation of the MQW layer. The study on the detailed photo-electrochemical response with several kinds of electron acceptor in the solution is on going in this laboratory.

This work has been partly supported by Grant-in-Aid for Scientific Research on Priority Area of Electrochemistry of Ordered Interfaces from the Ministry of Education, Science, Sports and Culture, Japan. One of the author (K.N) thanks Mr.M.Nawa for his assistance.

References and Notes

1 J.H.Davies, "The Physics of Low-Dimensional Semiconductors," Cambridge University Press, Cambridge (1999).
2 H.M.Gibbs, "Optical Bistability: Controlling Light with Light," Academic Press, New York (1985).
3 Y.Rosenwaks, M.C.Hanna, D.H.Levi, D.M.Szmyd, R.K. Ahrenkiel, and A.J.Nozik, Phys.Rev.B., **48**, 14675 (1993).
4 C.A.Parsons, M.W.Peterson, B.R.Thacker, J.A.Turner, and A.J.Nozik, J.Phys.Chem., **94**, 3381(1990).
5 C.A.Parsons, B.R.Thacker, D.M.Szmyd, M.W.Peterson, W.E.McMahon, and A.J.Nozik, J.Chem.Phys., **93**, 7706 (1990).
6 J.A.Switzer, B.M.Maune, E.R.Raub, and E.W.Bohannan, J.Phys.Chem.B., **103**, 395 (1999).
7 J.A.Switzer, C.-J.Hung, L.-Y.Huang, E.R.Switzer, D.R.Kammler, T.D.Golden, and E.W.Bohannan, J.Am.Chem.Soc., **120**, 3530 (1998).
8 J.Clavilier, J.Electroanal.Chem., **107**, 211 (1980).
9 T.E.Haward Jr, in: D.R.Lide(Ed.), "CRC Handbook of Chemistry and Physics," 77th ed., CRC press, New York(1996).

(Received December 17,1999 ; Accepted February 15,2000)