SEMICONDUCTING PROPERTIES OF PASSIVE FILM FORMED ON TITANIUM IN AQUEOUS SOLUTIONS.

Dong-Yung Kim* and Hyuk-Sang Kwon*

*Dept. of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejon 305-701, Korea

The passive films formed on Ti at low potentials(0-5V_{SCE}) in an aqueous solution were often reported to have an amorphous structure[1] or crystalline structure composed of anatase and rutile[2] . In this work, the structure of passive films formed on Ti at low potentials (-0.5 ~ 0.5 V_{SCE}) in pH 8.5 buffer solution and also in an artificial seawater were examined by examining the semiconducting properties of the passive films by photo-electrochemical and Mott-Schottky analyses for the films.

The photocurrent (i_{ph}) spectra for the passive films formed on Ti showed straight lines in $(i_{ph}h\nu)^{0.5}$ vs photon energy ($h\nu$) plot and $(i_{ph}h\nu)^2$ vs $h\nu$ plot, which meant that the passive films have direct and indirect electron transition sources. The band gap value (E_g), obtained from $(i_{ph}h\nu)^{0.5}$ vs $h\nu$, for passive film formed on Ti in pH 8.5 buffer solution was found to be greater than that for a thermal oxide film formed on Ti in air at 400 ℃. The slop (β) of a linear part in the (log i_{ph}) vs $h\nu$ plot, shown in Fig. 1, was associated with the disorder energy($1/\beta$) of the film[3]. The disorder energy of passive film, determined from the absorption tail of photocurrent spectrum, was much greater than that for the thermal oxide film formed on Ti in air at 400 ℃. The greater E_g and the higher disorder energy for the passive film compared with those for the thermal oxide film suggest that the passive film on Ti exhibited more disordered structure, such as amorphous structure, than the thermal oxide film. However, the straight lines in the $(i_{ph}h\nu)^2$ vs $h\nu$ plots, shown in Fig. 2, suggests that both the passive film and the thermal oxide film exhibits a characteristics appeared only for crystalline semiconductors[4]. So we conclude that the passive film on Ti is composed of a disordered structure, and has some amount of crystalline Ti oxide in a mixture of amorphous and crystalline structure or duplex layer structure. To investigate effects of Cl ion on semiconducting properties of passive film on Ti, the semiconducting properties of passive film on Ti in pH 8.5 buffer solution is compared with those in artificial sea water. Cl^- made little effects on photocurrent spectra and band gap energy. Donor density for passive film formed in artificial sea water was greater than that in pH 8.5 buffer solution by 4×10^{19} cm^{-3}.

References

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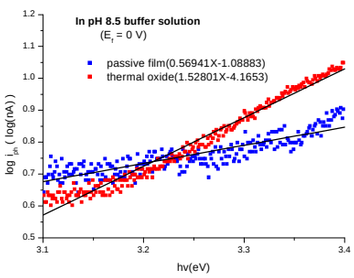

Fig. 1. log(i_{ph}) vs $h\nu$ plots for the passive film and thermal oxide film (400 ℃, 1 hour) formed on Ti in deaerated pH 8.5 buffer solution.

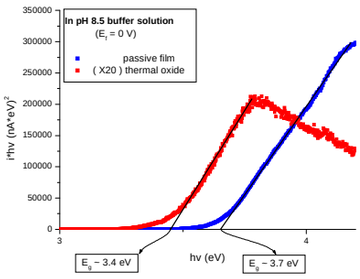

Fig. 2. $(i_{ph}h\nu)^2$ vs $h\nu$ plots for the passive film and thermal oxide(400 ℃, 1 hour) formed on Ti in deaerated pH 8.5 buffer solution