XPS, Impedance and Photo-Electrochemical Characterisation of Passive Films on Ni and Ni-18Cr Alloy in Sulphuric Acid Solution

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Properties of passive films on Ni and Ni-18Cr formed in acid solution are characterised in order to discuss semiconductor properties of passive films. Materials were polarised in deaerated 0.1 kmol m^{-3} H_2SO_4 at various potentials for up to 24 hours. Photo current generated by irradiation of monochromated light, and capacitance by means of electrochemical impedance were measured for a series of potentials in less noble direction from the film formation potential. The passive films were also characterised using XPS and AES.

As we have already reported[1], passive film consists of two layers. Therefore, photo current generated on the passive film also consists of two components with different band gap energies and flat band potentials respectively. In this study, it is observed that Ni-18Cr exhibits two energy band gaps of 2.5 and 3.7 eV, that might be derived from outer hydroxide and inner oxide layer, respectively. Figure 1 shows photo current spectrum for passive films on Ni-18Cr alloy formed at various film formation potentials, E_f, assuming that photo current is generated by indirect transition. Negative photo current is observed for most of potential range in the passive region, and increases with decreasing potential with intercept to x-axis, which indicates flat band potential, being approximately 650 $mV_{Ag/AgCl}$. This means energy band in passive film decrease in the outward direction from substrate/film to film/solution interface and that passive film seems to be *p*-type semiconductor. Figure 2 shows the Mott-Schottky plot of capacitance measured for passive film formed on Ni-18Cr. Capacitance of the passive films showed no typical straight line observed for semiconductor layer, but exhibited complicated behaviour. We have reported previously[2] that, passive film formed on Cr and Fe-Cr alloys in acid solution exhibits conflicting results obtained by capacitance measurements and photoelectrochemical response. The photo electrochemical response exhibits negative photo current (absolute value of) which increases with decreasing applied potential in the most of passive potential region. That is behaviour usually observed for *p*-type semiconductor. On the other hand, Mott-Schottky plot of capacitance obtained for space charge layer of passive film reveals typical *n*-type semiconductor behaviour. On the other hand, passivity formed in neutral solution reveals *n*-type semiconductor behaviour for both two measurements. The results obtained in this study are also inconsistent. It is difficult to present a consistent model describing the duplex semiconductor with different type and band gap. A layer structure with hetero junction would be discussed.

References

[1] S. Fujimoto, O. Chihara, and T. Shibata, Materials Science Forum, 289/292 (1998), 989-996.

[2] S. Fujimoto, O. Chihara, K. Somiya, and T. Shibata, Proceedings of the Passivity in Localized Corrosion (Int. Symp. in Honor of N. Sato), Honolulu, The Electrochem. Soc., PV 99-27, p.360-366 (2000).

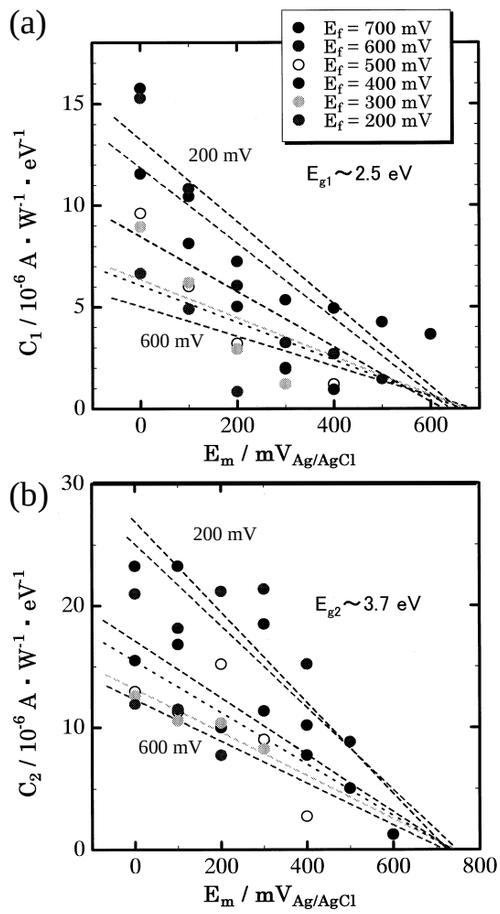

Figure 1 Photo electrochemical spectrum for passive films on Ni-18Cr alloy. (a) Component showing band gap energy of (a) 2.5 eV, and (b) 3.7 eV.

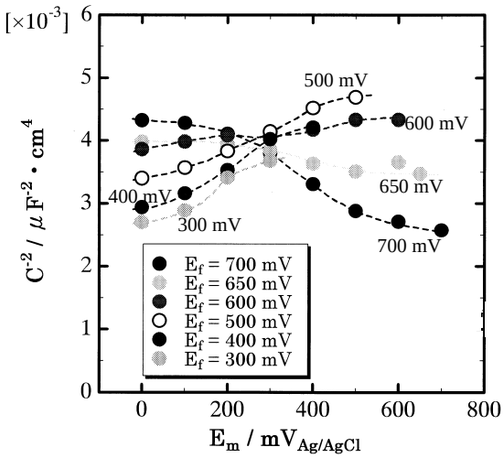

Figure 2 Mott-Schottky plot of capacitance measured for passive film formed on Ni-18Cr for various potentials