

Electrolyte-electrode interfacial study for Si electrodeposition in ionic liquid.

J. Komadina^a, Y. Ishibashi^b, Y. Tsuyuki^b
Y. Zhang^b, Y. Fukunaka^{cde}, P. Pianetta^f, T. Homma^{bc}

^a School of Engineering, UC Merced, Merced, CA

^b Dept of Appl. Chem., Waseda University, Tokyo, Japan

^c JST-CREST

^d Japan Aerospace Exploration Agency (JAXA)

^e Nanotechnology Research Center (NTRC),

Waseda University, Tokyo, Japan

^f Stanford Synchrotron Radiation Lightsource (SSRL)

We have previously reported electrodeposition of Si from the ionic liquid trimethyl-n-hexylammonium bis(trifluoromethylsulfonyl)imide (TMHATFSI or $[N_{6111}][Tf_2N]$)¹, as well as the formation of Si nanodots² and nanopillars³ on a gold substrate by nanoimprintation of UV-curable resin (TR-21, Toyo Gosei Co) with a quartz mold⁴. Currently, crystalline and high-purity deposits of silicon prepared below 100°C have only been reported in the literature for liquid metal cathodes⁵.

Electrochemical quartz microbalance (EQCM) impedance analysis allows for *in situ* estimation of mass-charge ratio (m/z) and instantaneous measurement of solution viscosity in an electrochemical process. We have observed impure silicon electrodeposition with an apparent Si m/z suggestive of a 4-electron reduction of silicon^{6,7}. However, these results are questionable due to large increases in the QCM damping coefficient. More recently, we have seen improved EQCM accuracy using a mixture of organic solvent and ionic liquid as electrolyte.

The molecular layering of ionic liquids and adsorption on the deposition frontier surface appears to have a significant influence on the chemistry of electrodeposition in such electrolytes⁸. We are presently engaged in examining the changes in the electrolyte-electrode interface structure with cathode potential by x-ray reflection measurements at the Stanford Synchrotron Radiation Lightsource. Preliminary results, Fig 1, indicate a structural change during negative biasing of n-type Si in contact with a mixture of acetonitrile and TMHATFSI, consistent with reports for pure ionic liquid electrolytes published by other groups.

This presentation will discuss the progress of our studies of the Si electrodeposition mechanism and impurities in light of our results at SSRL and the corresponding *in-situ* and *ex-situ* Si deposition measurements at Waseda University.

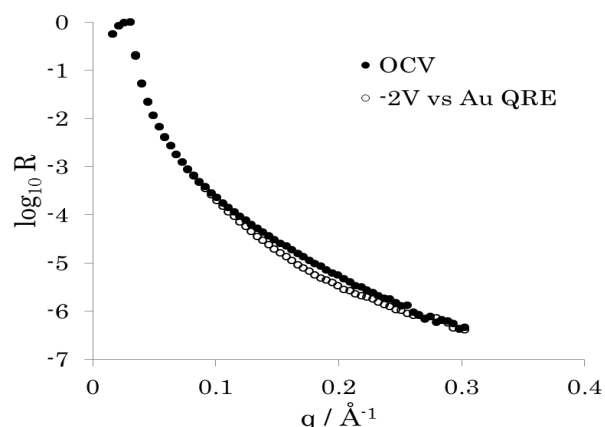


Fig 1 – 13.5keV X-ray reflectivity of unbiased (●) and biased (○) n-Si electrode in mixture of TMHATFSI and acetonitrile.

¹ Y. Nishimura, Y. Fukunaka, T. Nishida, T. Nohira, R. Hagiwara. *Electrochim. Solid State Lett.* **11** (9) D75-79 (2008)

² Y. Nakano Master's Thesis, Waseda University, 2010.

³ T. Homma, J. Komadina, Y. Nakano, T. Ouchi, T. Akiyoshi, Y. Ishibashi, Y. Nishimura, T. Nishida, Y. Fukunaka. *ECS Transactions*. 220th ECS Meeting, Boston, MA, USA. Abstract #247. (in review)

⁴ T. Ouchi, Y. Arikawa, Y. Konishi, and T. Homma. *Electrochim. Acta*, **55**, 8081-8086 (2010).

⁵ J. Gu, E. Fahrenkrug, and S. Maldonado. *J. Amer. Chem. Soc.* (2013). Online, in press.

⁶ J. Komadina, T. Akiyoshi, Y. Ishibashi, Y. Fukunaka, T. Homma. *Electrochim. Acta* (in press, available online)

⁷ J. Komadina, T. Akiyoshi, Y. Ishibashi, X. Wang, Y. Fukunaka, P. Pianetta, T. Homma. 222nd Meeting of the Electrochemical Society, Oct 10, 2012. Abstract #3352.

⁸ Molten Salts and Ionic Liquids 18. 222nd Meeting of the Electrochemical Society, Oct 2012.