## STUDY OF PASSIVE OXIDE FILMS ON METALS USING INFRARED SPECTROSCOPY

Vivek Srinivasamurthi<sup>1</sup>, Hugh S.Isaacs<sup>2</sup>, Lisa Miller<sup>3</sup>, Nebojsa Marinkovic<sup>4</sup>, Gordana Adzic<sup>2</sup> and Sanjeev Mukerjee<sup>1</sup>

<sup>1</sup> Department of Chemistry, Northeastern University, Boston, MA-02115

<sup>2</sup> Materials Science Department And <sup>3</sup> National Synchrotron Light Source Brookhaven National Laboratories, Upton, NY-11973

<sup>4</sup>Center for Synchrotron Biosciences, Albert Einstein College of Medicine, NY- 10461

The types of oxide films formed on valve metals (e.g., Al, Ta, Zr) have been the subject of study in many areas including corrosion, integrated circuits and capacitors. A number of techniques including XANES [1,2], Kelvin probe, ellipsometry and other surface scanning tools have been used to characterize these oxides. This work focuses on the use of synchrotron based infrared microspectroscopy to follow the growth kinetics and structure of anodic oxide films on Al, Ta, Zr etc., based on current density, solution composition etc. Ta anodic oxides films grown in acid solutions have been studied using multiple external reflection infrared spectroscopy [3].

The advantages of the synchrotron radiation as a unique infrared source in the mid and far spectral region have been clearly demonstrated [4, 5].

- (i) The infrared spectrometer equipped with a microscope has the ability to restrict the size and shape of the illuminated spot on the sample.
- (ii) The high brightness synchrotron infrared source allows smaller regions to be probed with acceptable signal to noise ratio [6,7].

In our work, anodic oxide films of Ta, Al, Zr are grown in near neutral solutions at different current densities until the desired voltage is reached. Infrared reflectance measurements on these oxide films show a strong Al-O bond vibration at 950cm<sup>-1</sup> while the vibration of the Ta-O bond exhibits a broad peak at 925cm<sup>-1</sup>. Shifts in the Ta-O vibration at higher potentials have been observed. The shifts could be due to a change in the structure of the oxide film. The characteristics of the oxide films on these valve metals including the type of oxides and the metal-to-oxygen bond vibrations will be discussed in relation to their growth kinetics, thickness and solution composition.

## Acknowledgment

This work was performed under the auspices of the U.S. Department of Energy, Division of Materials Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76CH00016

## References

- 1. L.J.Oblonsky, A.J.Davenport, M.P.Ryan, H.S.Isaacs and R.C.Newman, *J. Electrochem. Soc.*, **144**, 2398 (1997).
- 2. S.Virtanen, P.Schmuki, M.Buchler and H.S.Isaacs, *J.Electrochem. Soc.*, **146**(11), 4087

- (1999).
- 3. Takamura T. and Kihara-Morishita H., *J. Electrochem. Soc.*, **122**, 386 (1975).
- 4. Duncan W.D. and Williams G.P., *Appl. Optics*, **22**, 2914 (1998).
- Carr, G.L., Dumas, P., Hirschmugl, C.J. and Williams, G.P., Infrared synchrotron radiation programs at the National Synchrotron Light Source. Nuovo Cimento della Societa Italiana di Fisica, [Sezione] D: Condensed Matter, Atomic, Molecular and Chemical Physics, Biophysics; 20D (4), 375-395 Apr 1998. ISSN: 0392-6737.
- J.A. Reffner, P.A. Martoglio and G.P. Williams, *Rev. Sci. Instr.* 66, 1298 (1995);
- 7. G.L. Carr, J.A.Reffner and G.P. Williams, *Rev. Sci. Instr.* **66**, 1490 (1995).