In-situ micro Raman study of iron behavior in borate buffer solution

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If some agreement is now obtained in the literature [1, 2] concerning the formation of a spinel–type passive film on iron electrode in borate buffer solution, the behavior of this passive film during subsequent oxido-reduction cycles has not been clarified. Raman spectroscopy is a perfectly suitable technique for *in-situ* studies. However, obtaining SERS (surface enhanced Raman spectroscopy) requires to "activate " the surface by depositing gold [3] or silver [4,5] nanoparticles before of after iron passivation with all the questions raised by this technique.

This work demonstrates that a strong enhancement of the Raman signal may be obtained by using ultrathin epitaxial iron films (ca 20 ML) electrodeposited on Au(111). This new approach enables the *in situ* study of the formation and dissolution of the passive layer. It is shown that the close proximity of the gold layer *underneath the iron layer* is a key issue.

EXPERIMENTAL

(111) gold films were evaporated on freshly cleaved mica. Prior to use the sample was flame annealed. Iron deposition was performed at –1.5 V in a pH 4 sulfate iron solution (1 mM). Immediately after preparation the Fe/Au sample was transferred into the Raman cell containing a pH 8.4 borate solution. A platinum wire was used as counter electrode and the mercury sulfate electrode (MSE) was connected to the cell with a double junction to avoid contaminations by SO_4^{2-} anions. A Labram Raman spectrometer (Horiba) was used with slits fixed at 100µm, confocal hole at 200µm. The magnification of the objective was x20 outside the solution and x80 in solution. The intensity of the 10 mW HeNe laser was adjusted using neutral density filters to avoid thermal effects.

RESULTS

Under appropriate conditions, Fe/Au(111) ultrathin films are (110) textured bcc iron [6]. Figure 1 compares the cyclic voltammetry of polycrystalline iron and of a Fe/Au(111) ultrathin film in borate buffer solution of pH 8.4. Prior to scanning the potential towards positive values, the surface was pre-polarized for 5 min at –1.5V to remove the native oxide. The main difference between curves is the appearance, on the negative going scan, of the reduction peak at –1.2 at the Fe/Au(111) electrode.

Figure 2a-c shows the bias dependence of the Raman spectrum of a Fe/Au(111) electrode. Spectrum (a) corresponds to native oxide and is consistent with magnetite Fe_3O_4. Spectrum (b) was obtained on the passive layer grown by stepping the potential from –1.5 V to at +0.2V. The peak may be decomposed into two contributions at 678 and 730cm^{-1} attributed to oxidized spinel with Fe^{3+} in octahedral and tetrahedral sites. This result is in agreement with *in-situ* X-Rays studies [2]. Spectrum (c) was recorded after reduction of the passive layer at –0.9 V. A pure, intense spectrum of Fe_3O_4 is obtained, presenting 3 of the 5 bands expected for a spinel structure. For comparison, spectrum (d), recorded with a bulk iron electrode, *was independent of the applied bias and showed only a small peak at 880cm^{-1} corresponding to borates in solution.*

It should be noted that the above SERS effect disappears for iron layer thicker than 30 ML. Further results, especially as a function of the iron thickness will be presented at the conference to discuss the possible origin of observations.

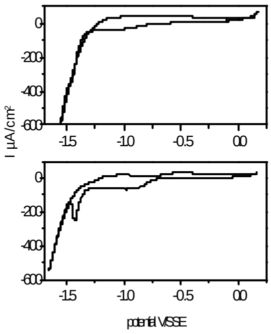

Fig. 1 :

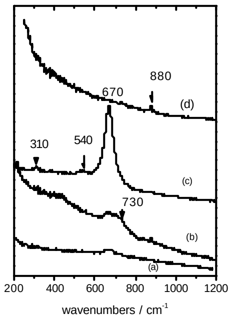

Fig. 2 :

Fig. 1: Cyclic voltamogramms (5 mV/s) of Fe electrodes in pH 8.4 borate solution (a) Bulk polycrystalline iron (b) Fe/Au(111) ultrathin film.

Fig. 2: (a-c) Raman spectra on a Fe/Au(111) electrode: native oxide (a), passive film at +0.2V (b) and passive film at –1V (c). Spectrum (d) was recorded on bulk iron. It was independent of bias.

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