In recent papers in this journal, \(^1\textsuperscript{---}^3\) in situ studies of stress evolution and mechanical behavior of silicon and germanium as lithium-ion battery electrode materials were presented. Stress evolution in the thin films during lithiation and delithiation was measured by monitoring the substrate curvature with a multibeam optical sensor (MOS) wafer curvature system consisting of a laser source and a CCD camera to capture the reflected beam-array from the sample surface. The electrochemical cell assemblies were very similar in all three papers (Fig. 1 in Refs. 1, 2, 3). These studies provide a particularly valuable source of information for further research since the experimental conditions are well defined and the experiments are well documented.

On the other hand, there are two differences between the experimental setup depicted in Refs. 1, 2 (Fig. 1) and that shown in Ref. 3 (Fig. 1):

i) In the first two cases \(^1\textsuperscript{2}\) the solution level is higher than the silica plate so the reflecting surface is submerged in solution, while in Ref. 3 the top face of the silica wafer is out of the liquid phase and is in contact with a gas phase.

ii) In the experimental arrangement shown in Ref. 3 (Fig. 1) the laser beam is reflected from the “back side” of the wafer, that is by the metal surface in contact with the Ge film.

At first sight, the above dissimilarities appear to have little impact on the results, however, a closer inspection of the equations used to calculate the curvature of the electrode reveals that some of the reported stress values in Refs. 1, 2 may not be completely correct.

This claim is supported by the following arguments. According to Ref. 2 “Stress evolution in the a-Si films during lithiation and delithiation was measured by monitoring the substrate curvature with the MOS setup . . . The system consists of a laser source that generates a single focused beam, two etalons arranged orthogonally to each other to generate a \(2 \times 2\) array of beams, and a CCD camera to capture the reflected beam-array from the sample surface. The relative change in the distance between the laser spots on the CCD screen gives the sample curvature, \(\kappa\), as

\[
\kappa = \frac{\cos \phi}{2L} \left\{ \frac{D_0 - D}{D_0} \right\}
\]

where \(D\) is the distance between the laser spots and \(D_0\) its initial value, \(\phi\) is the reflection angle of the beam, and \(L\) is the optical path length from sample to the CCD camera.”

Although the bending beam technique is already well established for monitoring of curvature changes in vacuum or in gaseous environment, its application in multiphase systems is not without problems.\(^4\textsuperscript{---}^7\)

In some papers reporting results on electrochemical bending beam experiments (i.e. experiments carried out in systems consisting a liquid phase), schemes of experimental arrangements can be found in which the direction of the reflected beam before and after passing the optical window or the air/solution boundary is indicated incorrectly, since the effect of refraction is ignored.\(^2\) It is well known, that in the case of non-normal incidence, if the deflection of a light beam is measured outside the phase where the mirroring surface is located, the deflection angle should be usually corrected according to Snell-Descartes law of refraction. According to this law, when light travels from one medium into another the incident and refracted rays lie in one plane with the normal to the surface; are on opposite sides of the normal; and make angles with the normal whose sines have a constant ratio to one another. This problem (concerning the electrochemical bending beam experiments) was first discussed by Láng and Seo in Ref. 4 for the special case of normal incidence. It is clear that if the incident beam is exactly perpendicular to the optical window (or to the air/solution interface), no refraction occurs, which makes the situation simpler, and the calculations easier.\(^2\) Consequences of refraction for the multiple beam optical sensor (MOS) technique have been outlined by Van Overmeere, Vanhumbeeck and Proost in Ref. 8. According to these authors by using the small-angle approximation the following equation can be used to calculate the sample curvature from the spacing between the beams:

\[
\kappa = \cos \phi \left\{ \frac{D_0 - D}{D_0} \right\} = c^*_M \left\{ \frac{D_0 - D}{D_0} \right\} \text{,}[2]
\]

where \(c^*_M\) may be called the refraction corrected mirror constant. This equation is formally very similar to the equation for curvature measurements in air (i.e. Eq. 1 in the present case), but includes a correction factor equal to \(1/n_s\) (\(n_s\) is the refractive index of the solution with respect to air), and this correction factor is the same as the one found by Láng and Seo for the single-beam technique. In practice this means that, for a given curvature change in the sample, the resulting measured change in the beam spacing will be amplified by a factor \(c^*_M\), which is equivalent to increasing the sample to CCD distance and hence, the sensitivity of the measurement”.

It should be noted here that it is not always necessary to measure the parameters \(\phi, L\) and \(n_s\), since the refraction corrected mirror constant can be determined also by an alternative (experimental) procedure. For the calibration a reference surface of known curvature can be used, such as a high precision concave or convex mirror of known curvature that would take the place of the sample in an identical experimental setup. According to the authors of Ref. 2 “The factor \(c\phi/2L\), known as mirror constant, is specific to a setup and is obtained by calibrating the system in Fig. 1 with a reference mirror of known curvature in the sample plane”. However, placing the mirror of known curvature “in the sample plane” is insufficient, since the reference surface of known curvature should be submerged into the electrolyte solution, and such a procedure is not without difficulties. Unfortunately, the steps of the calibration procedure were not reported in the paper.

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Anyway, without the refractive index of the solution (and without an appropriate calibration method), it is impossible to determine correctly the values of the curvature of the electrode, $\kappa$, and the changes in the (surface) stress. Since refractive indexes of electrolyte solutions are about 1.33–1.50, therefore the complete neglect of the bending of the laser beam due to refraction at the optical window may cause an error of about 25–30% in the determination of $\kappa$. (It should be noted that another source of error is associated with the lateral shift of the laser beams due to the optical window.) Taking into account the above facts it is quite surprising, that in the papers no reference was made to the refractive index ($n_s$) of the solution, and Eq. 1 was used for the calculation of the sample curvature.

Summarizing the main points of the above considerations the following conclusions can be drawn:

1. If the effect of refraction has been neglected in Refs. 1, 2, the reported $\kappa$ values are too high, and all of them should be corrected for refraction.

2. The schemes of the experimental setup (Fig. 1) in Refs. 1 and 2 are misleading, since the directions of the light beams in the two different media adjacent to the optical window are identical.

In the case of the experimental setup reported in Ref. 3 the above problems are not present, but Fig. 1 is still misleading, since the directions of the incident and reflected beams before and after passing the fused silica wafer/gas boundary are indicated incorrectly (in reality, the direction of the light beam changes as it passes from one material to another). A possible source of error related to the experimental arrangement when the light beam is reflected from the “back side” of the cantilever (that is by the metal surface in contact with the transparent substrate plate) has been discussed in Ref. 7. It has been concluded that in the small-angle approximation (and if the thickness of the transparent substrate is small) the relative error of the deflection angle is negligible. However, in Ref. 3 both the angle of incidence and the angle of refraction are apparently relatively large. The error estimation in this case becomes a more difficult subject, but it should be done in order to check the reliability of the results.

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