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# Imaging and Quantification of Hydrogen in Materials: SIMS Based Correlative Microscopy

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Hydrogen alters the properties of materials dramatically. A well-known example of the detrimental influence of hydrogen in materials is the hydrogen embrittlement of steel and other alloys. Hydrogen may also be intentionally introduced into materials to passivate dangling bonds in semiconducting materials and thereby enhance the electronic properties of materials. Furthermore, hydrogen is identified as an important environment-friendly energy source with a potential to replace fossil fuels. Development of a diverse range of materials technologies thus crucially relies on the ability to detect and map hydrogen, and to understand the physical mechanisms by which hydrogen influences the properties of materials.

Transmission Electron Microscopy (TEM) is a powerful tool for high-resolution imaging of materials down to even atomic resolution. However, it is a challenge to directly map hydrogen in materials using analytical techniques typically available in electron microscopes such as Energy-Dispersive X-ray Spectroscopy (EDX) or Electron Energy-Loss Spectroscopy (EELS). Furthermore, the detection limits of EDX or EELS are inadequate to detect trace concentrations (< 0.1 at. %) of elements. In this context, Secondary Ion Mass Spectrometry (SIMS) is suitable to analyze all elements (and isotopes) of the periodic table, including hydrogen. Furthermore, SIMS offers excellent sensitivity and detection limits, enabling the analysis of even dopant level concentrations. However, the lateral resolution in SIMS imaging is fundamentally limited to ~10 nm by the ion-solid interaction volume. Moreover, quantification of secondary ion intensity is not straightforward because of the matrix effect (secondary ion yields depend on the host matrix). Atom Probe Tomography (APT) offers sub-nm chemical imaging of elements, and it can be used to detect and quantify all elements and isotopes. However, variations in field evaporation of different elements and limited mass resolution can result in artefacts. Furthermore, the volume analysed in APT is very small (~ $10^5$ to $10^6$ $nm^3$) and the sample preparation is laborious. While individual techniques have their inherent strengths and limitations, a correlative approach combining these techniques can result in complementary insights about the investigated materials [1].

We have investigated the 3D distribution of hydrogen in (i) passivating contacts in silicon based solar cells, and (ii) hydrogen storage materials based on Ni-Mg alloy. The overarching theme of our investigations was to correlate the microstructure and local chemical composition to the macroscopic properties of the materials.

Using deuterium as a tracer for hydrogen, we performed a correlative SIMS-APT-TEM study to pinpoint hydrogen segregation sites in the passivating contacts in solar cell materials. A method to remove the hydrogen background in APT data originating from the residual gas of the analysis chamber was developed and demonstrated [2]. Subsequently, the concentrations of all elements including hydrogen and deuterium within nanometric thick layers were quantified. These results in turn help to optimize the solar cell fabrication process, improving performance as well as reducing production costs.

In the example of hydrogen storage materials, Ni-Mg alloy thin films were fabricated at different processing parameters to engineer a columnar or equiaxed microstructure. The films were then partially or fully hydrogenated (or deuterated). The nucleation and growth preferences of the hydrogenated phase were then investigated using SIMS based correlative microscopy. The direct 3D SIMS images of partially hydrogenated films revealed that the processing parameters dictate whether the hydrogenated phase nucleates preferentially at the film surface or at the interface with the substrate. These results were then correlated with bright-field and dark-field TEM imaging and diffraction. Understanding the correlation between the processing parameters and the formation mechanisms of the hydrogenated phase helps to design materials suitable for hydrogen storage applications. [6].

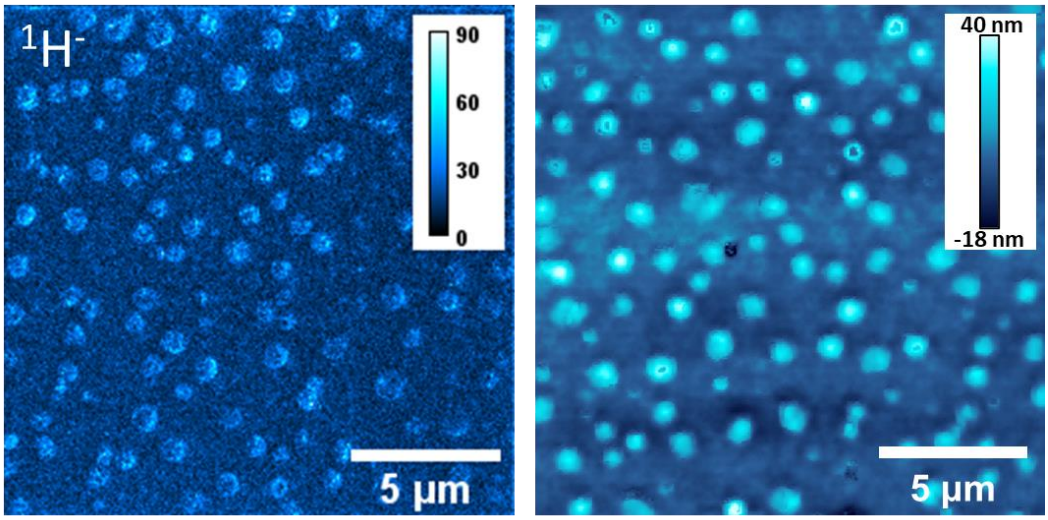


**Figure 1.** Left: SIMS image of hydrogen distribution in a partially hydrogenated Ni-Mg alloy (colorbar indicates measured counts). Right: Height image from confocal microscopy in another location showing topographic changes which can be attributed to the volume expansion associated with hydrogenation.

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