Atomically Thin Layers For Energy Harvesting And Storage - Project Approval.

Ewan Matheson - 15015778

Northumbria University

E-mail: `ewan.matheson@northumbria.ac.uk`

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1. Literature review

Thanks to significant cost reductions in the production of renewable energy, H_2 is becoming easier to decarbonise, particularly for electricity generation [1]. There are however some challenges due to the complexity and diversity of producing H_2 as well as storing it efficiently at room temperature.

Recently there has been advances in nanotechnological applications for hydrogen storage, namely utilising surfaces for adsorbing hydrogen for improved gravimetric capacity [2], complex and interstitial hydrides for stationary high volumetric capacity storage [3], and chemical storage methods. Solid state absorbers have shown great potential due to their light weight properties relative to complex and interstitial hydrides, making them suitable for vehicular application. Their ability to operate at room temperature with improved densification relative to gas tanks, allows for improved safety in operation.

Densification is they key advantage nanomaterials have over conventional storage solutions. Previous research has shown that optimised nano-porous (< 2 nm) carbon can confine molecular hydrogen such that its accumulation is characteristic of solid hydrogen. In such structures, densification is promoted via enhanced van der Waals interaction between adsorbed H_2 molecules, and was characterised using in-situ inelastic neutron scattering and confirmed by analysis of gas sorption isotherms [4].

Hydrogen storage capabilities of zinc oxide nanowires has also been previously studied whereby hydrogen is reversibly physisorbed on the nanowire surfaces, and allowing for up to 71% of the gas to be released. Due to diffusion, remaining gas is absorbed and contained as impurities within the nanowires. This nanostructure has shown a 0.83 wt% capacity operating at room temperature and at 3 MPa pressure [5].

Sensing is another important consideration when designing a storage device. For solid state adsorption solutions, higher densification of hydrogen on surfaces means a pressure gauge would not reflect the true capacity, however electrostatic sensing has the potential to offer an alternative solution.

For example, previous research has looked at using 2D electron gas sensors with metallic nanoparticles as the enabling material. Using a TiO_2/Al_2O_3 quantum well with Pd nanoparticles, hydrogen forms PdH_x on the surface of the nanoparticles decreasing the work function of Pd (5.4 eV to 4.7 eV), causing increased band bending at the surface of the TiO_2 layer, implying a transfer of electrons through the Al_2O_3 layer. The change in electron density in the 2D electron gas can be monitored by applying a potential bias across side contacts [6].

Alongside experimentally fabricating a hydrogen storage-sensor device, statistical mechanics studies have been useful tools in research for optimising structure and functionality of materials to implement this technology. Previous research has shown that grand cannonical monte carlo (GCMC) simulations are able to provide useful insights into various conditions of H_2 adsorption. This method uses a statistical mechanics approach, in which a rigorous molecular-level model of adsorption is solved exactly. The solution, gives the exact number of moles of a gas, adsorbed into equilibrium. For example, using GCMC, a simulation can calculate adsorption isotherms for various pressures, temperatures and nanostructures (sheets, nanowires and nanopores) which can be used to compare to experimental data. This allows for the optimisation of the nanostructure based on the theoretical framework [7].

2. Research Aims and Objectives

This research will investigate the possibility of fabricating an all in one hydrogen storage-sensor by growing ZnO nanowires with an atomic layer deposited (ALD) or chemical bath deposited (CBD) film of ZnMgO, with a metallic Ag nanowire contact for electrostatic sensing. This will allow in situ sensing for real time monitoring of the capacitance of the hydrogen storage container. This project will investigate various fabrication methods including ALD, CBD and modified inkjet printing with the aim of designing a fabrication process which is both scalable for industry and cost effective for product development. These aims will be achieved by meeting the following objectives:

- Fabricate a ZnO nanowire samples with varying nanowire arrangements (vertical and randomised) and test for hydrogen storage capabilities by comparing PL intensity differences in the charged and uncharged states as well as measuring adsorption isotherms using pressurised volumetric/gravimetric analysis.
- Deposit a layer of ZnMgO as the seed layer before growing the nanowires and test for the formation of a ZnMgO/ZnO/ZnMgO quantum well. Compare performance between ZnO and Al_2O_3.
- Optimise the fabrication parameters by comparing experimental gas adsorption isotherms with calculated isotherms using Grand Canonical Monte Carlo simulations.
- Investigate implementing nanowire structure with hydrogen gas pipelines and investigate on and off state leakage in pipe coupling.

3. Research Methodology

ZnO nanowires will be grown from a ZnO seed layer and synthesised using chemical bath deposition (CBD). The seed layer is placed upside down and is allowed to float on the surface of the hydrothermal solution, containing 19mM zinc acetate dihydrate ($Zn(O_2CCH_3)_2(H_2O)_2$), 1mM aluminium acetate ($Al(C_2H_3O_2)_3$) and 20mM hexamethylene tetramine ($C_6H_12N_4$), and kept at 80°C for 45-180 minutes. The sample is then lifted from the solution and rinsed with deionised water, before drying with N_2 gas. Changing the growth times changes the length of the nanowires, whereas changing the concentration of the hexamethylene changes the rod diameter [8].

Seed morphology plays a crucial role in the orientation of the ZnO nanowire growth. This surface morphology is formed and determined by the granular seeds which vary in size. Various seed layer deposition methods will be examined using AFM, including ALD and Sputtering deposition, to investigate the root mean square (*rms*) roughness and seed density before nanorod growth. The seed layer granules provide nucleation sites for the growth of the nanowires. ALD grown seed layers will present lower surface roughness, however sputtered seed layers, or ALD parameters closer to Chemical Vapour Deposited layers, will present higher surface roughness [9]. H_2 adsorption will be compared between different *rms* values of seed layer roughness, and consequently varying ZnO nanowire orientations.

The ALD seed layer will be made will be done by placing the sample at the target and depositing ZnO alternating between ZnAc and water at high temperatures, or diethyl zinc (DEZ) and water which, although exothermic, can be done at lower temperatures (100-200^oC) [10].

To create the sensor, a ZnMgO seed layer will be deposited on the surface in place of the ZnO seed layer. This will be done by cycling Diethyl Zinc (DEZ) precursor with water vapour, and bis-ethylcyclopentadienyl-magnesium ($Mg(CpEt)_2$) precursor with water vapour for 0.1 and 2s respectively, to create $Zn_{0.8}Mg_{0.2}O$ composition. ZnO nanowires will then be grown from the seed with an ALD ZnMgO barrier deposited, creating ZnO quantum well using the nanowires. Ag or Pd nanoparticles deposited on the surface using the nanoparticle printer will enable the functionality of the sensor. [11] [12] [13].

To test the adsorbance, a Siverts-type Gas Reaction Controller [5], pressure volumetric analyser, or Brunauer–Emmett–Teller (BET) analyser [14] will be used, whereby the sample is placed inside a glass tube and pressurized with H_2 up to 3Mpa at room temperature or higher at lower temperatures. The molar concentration of gas is measured before and after pressurisation, allowing for isothermal characterisation of the gas adsorption.

This fixed gas pressurisation approach will deduce the gravimetric capacity of the ZnO nanowires, however this nanostructure will also be tested with continuous gas flow to determine if pipelines can be made more efficient, such as reducing gas leaks and improving on-off response time.

GCMC simulations will be programmed using Fortran to be compiled with the gfortran compiler. To aid with this, a lib-directory will be used [15], containing random number generators and other functions needed for the calculations. The GCMC module contained in GULP is adopted to simulate the behaviour of hydrogen on the surface of the ZnO nanowires [7]. This will be used initially produce calculated isothermal adsorption data for an ideal gas based on a Lennard-Jones potential, which will be modified to account for van-der-Waals interactions between gas molecules. Parameters for the simulation will be set in accordance with measured characteristics of the ZnO samples (nanorod length, width, operating temperature and pressure) which will result in data which can be compared to experimental measurements of adsorption. The simulated model can then be adjusted to match the experimental data within the limits of uncertainty in the measurements. This will allow for accurate predictions of the behaviour of the gas with variance on the precise values for the previously determined characteristics. New data can then be calculated from the simulations to describe the materials adsorption as a function of nanorod length and width, operating pressures, adsorption temperatures and more, allowing for optimisation of the growth of the nanowires.

4. Research likelihood to contribute new knowledge

The main innovation of this research project is to demonstrate in-situ sensing and storage of low cost and environmentally friendly nanostructured metal oxides. Nanostructured metal oxide hydrogen storage devices have been demonstrated before, such as randomized ZnO nanowire structures, where the dissociated molecular hydrogen is adsorbed onto the ZnO surfaces at active sites [5][16].

Similarly, nanostructured metal oxide sensors have been demonstrated before, for example, previous research [17] has shown that nano-structured metal oxide devices using Pt nano-spheres with NiO coated shell exhibit sensing capability after exposure to oxygen, or as previously discussed, 2D electron gas confined between two metal oxides with Pd nanoparticles function as sensors [6].

This project will look at the technicalities regarding materials and fabrication as well as the design and implementation of the combination of the storage of physisorbed H_2 and sensing with electrostatic interactions with a 2D electron gas sensor. Novelties such as nanoparticle printing and scalability as well as the implementation of the sensing-storage technologies is what this PhD project looks to offer as new insight for the scientific and industrial community.

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