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# p-(In,Ga)N nanowire photocathodes for solar hydrogen evolution

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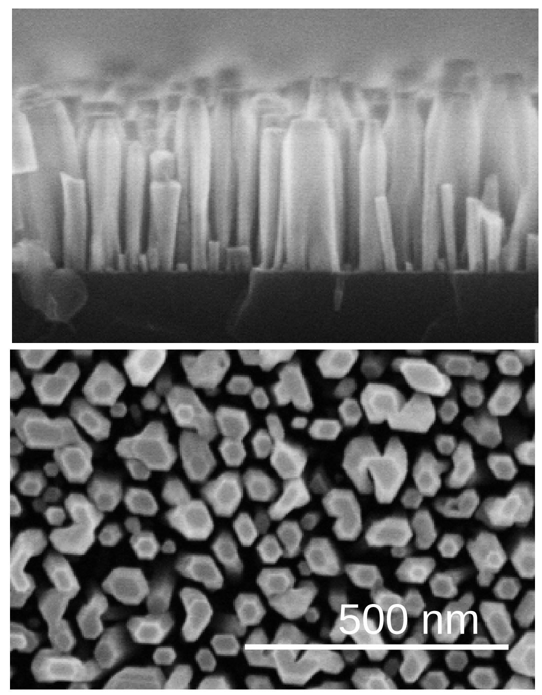
(In,Ga)N alloys are very promising materials for solar water splitting due to their large absorption coefficient for visible light and the possibility to tune the bandgap energy across the entire solar spectrum. In addition, their conduction and valence band edges can straddle the H+/H2 and O2/H2O redox potentials. However, it is difficult to grow (In,Ga)N bulk layers in high structural quality because of the lack of lattice-matched substrates.
In this work, we report solar hydrogen generation using p-(In,Ga)N nanowires which are able to accommodate lattice mismatches by lateral elastic relaxation.
As a photocathode the (In,Ga)N samples were grown on Si(111) substrates by plasma-assisted molecular beam epitaxy without catalysts. There average indium content was around 4%. As a well defined and characterized reference and model material also GaN nanowires onto silicon were prepared.

The samples were electrochemically characterized by cyclic voltametry and differential electrochemical mass spectroscopy (DEMS) in 0.5 M $H_2SO_4$ under illumination with a halogen lamp as well as with light from a solar simulator. DEMS detects volatile products like $H_2$ which are formed at the electrode simultaneous to the photocurrent and allows thereby to distinguish between the hydrogen evolution reaction (HER) and possible corrosion processes.
Under illumination the (In,Ga)N electrodes show only a small photocurrent which is however well correlated to the mass signal m/e=2 of evolved hydrogen. The material reveals a constant photocurrent in potentiostatic experiments for a duration of 60 min., indicating good stability under electrochemical conditions within our experimental time frame.
A significant enhancement of the photocurrent and the corresponding mass signal of hydrogen was observed upon photoelectrodeposition of Pt nano particles onto the NWs. Obviously the efficiency of the electrodes is limited by the low catalytic activity for the HER.
The incident photon-to-current efficiency (IPCE) was around 40% at -0.45 V/NHE in the entire visible wavelength region even though the average In content was only around 4% . For a homogeneous indium distribution in the NWs a bandgap of about 3.25eV would be expected.
Photoluminescence and cathodoluminescence measurements revealed that the NWs emit across the whole visible spectrum, and each NW has its own individual luminescence spectrum. These results are consistent with compositional fluctuations along individual NWs and between different NWs. This could be an advantage for the purpose of solar water splitting, because the compositional fluctuations seem to extend the spectral range for efficient light absorption. In the opposite way the presence of domains with varying compositions could also be responsible for high recombination rates.
As it is difficult to obtain general knowledge upon the limiting factors of such a complicated material. additional studies were carried out on well defined GaN nanowires as a model system. First results concerning the influence of electrodeposited metal nano particles as catalysts for the HER on the obtained photocurrent and photovoltage are presented.




Top view and cross-sectional SEM images of p-$In_{0.04}Ga_{0.96}N$ NWs grown at 640 $^oC$