

Metal-Insulator-Semiconductor Photoelectrodes as a Platform for Efficient and Stable Photoelectrochemical Water Splitting

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Photoelectrochemical (PEC) water splitting is a promising route to solar-driven H₂ production, but the efficiency and stability of semiconducting photoelectrodes must be improved. One potential approach to achieving high efficiency and good electrochemical stability is the metal-insulator-semiconductor (MIS) photoelectrode design. (1,2,3) The MIS arrangement generally consists of catalytic metal structures, or collectors, deposited on an oxide-covered semiconductor as illustrated in Fig. 1. The critical element of this design is the insulating oxide layer, which protects the semiconductor from the potentially corrosive electrolyte while mediating minority carrier tunneling between the semiconductor and collectors. The oxide layer must be ultra-thin (1-3 nm) and exhibit minimal defects at the SiO₂/Si interface in order to facilitate efficient tunneling and maximize photovoltage. Si is a commonly used photovoltaic material that is also attractive for use in MIS photoelectrodes, but Si-based MIS electrodes demonstrated to date have suffered from poor oxide quality, resulting in interfacial trap states that drastically lower photovoltage and overall water splitting efficiency. (2)

In this work, three modifications to Si-based MIS structures are implemented for improved solar-to-hydrogen conversion efficiency. First, SiO₂ tunneling layers with near-optimal thickness are grown by rapid thermal annealing (RTA) on p-Si(100). These thermally-grown SiO₂ layers create a high quality Si/SiO₂ interface that significantly reduces surface recombination and mitigates voltage losses associated with trap states at lower quality Si/SiO₂ interfaces. Additional improvements are achieved through the use of a bilayer

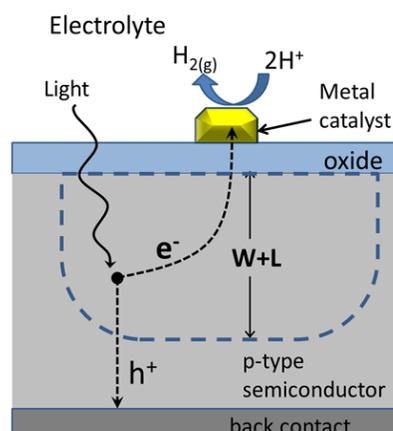


Fig. 1 Schematic side-view of MIS-based photocathode illustrating photo-generation and subsequent collection of charge carriers at metallic collectors used to catalyze the H₂ evolution reaction. According to the conventional view of MIS photoelectrode operation, excitons generated within a distance less than the sum of the depletion width (W) and minority carrier diffusion length (L) may be successfully collected at the catalyst particles.

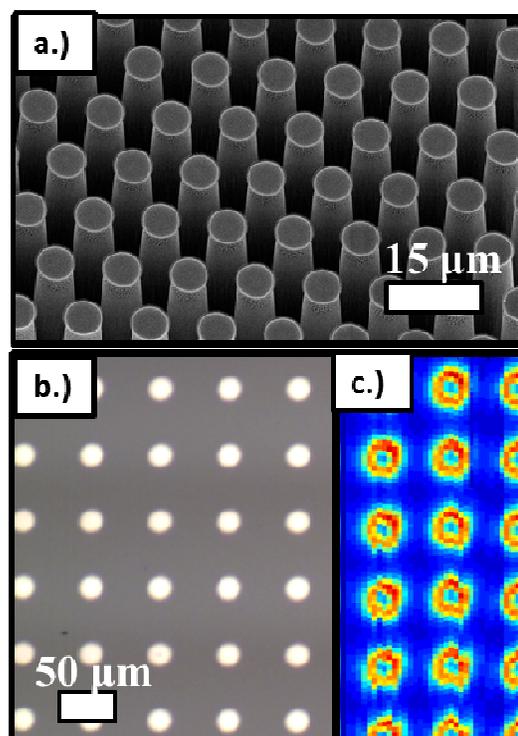


Fig. 2 a.) SEM image of 3D-structured MIS photoelectrode fabricated by reactive ion etching of p-Si(100) substrate. b.) Optical image of planar p-Si MIS photocathode consisting of bilayer PtTi collectors deposited on 2 nm thick thermally grown SiO₂. c.) EQE map of the planar MIS photocathode shown in b.), measured in 0.5 M H₂SO₄ by scanning a focused laser beam ($\lambda=532$ nm, Power=23 μ W) while holding the electrode potential at +0.33 V RHE.

collector structure, allowing for the decoupling of the collector's role as catalyst from its role as the metallic component in the MIS junction. Finally, we explore the use of 3D-structured MIS photoelectrodes (Fig. 2a) as a means to further improve performance through reduced optical reflection and increased catalytically active surface areas for decreased kinetic overpotential losses.

Central to the development of these MIS photoelectrodes has been the use of scanning probe techniques for *in-situ* evaluation of the catalytic and photoelectrochemical properties with high spatial resolution. Techniques include scanning photocurrent microscopy (SPCM, Fig. 2c) and scanning electrochemical microscopy (SECM), used for mapping local catalytic activity and external quantum efficiency (EQE), respectively. By performing these measurements on planar and 3D structured MIS photoelectrodes with well-defined geometries, these tools are shown to be extremely useful for optimizing geometries and elucidating fundamental charge transfer phenomena occurring in these photoelectrodes. This has included the presence of long distance carrier collection through an inversion layer and the observation of H-spillover assisted H₂ evolution off of the SiO₂ surface.

References

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