

Robust functionalization of amorphous cadmium sulfide films using z-lift amplitude modulated atomic force microscopy-assisted electrostatic nanolithography

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A robust technique, based on vertical (z-lift) manipulation of a negatively biased oscillating atomic force microscope cantilever, is developed which creates raised columnar nanostructures with high aspect ratios (up to 40 nm high/150 nm wide) on amorphous CdS thin films. The nanostructures' height (8–40 nm) is proportional to z-lift of the tip and correlates with CdS film thickness. An in-house modified electric force microscope is used to record the associated surface charge distribution which is found to be opposite to that of the tip. *2007 American Institute of Physics*. [DOI: [10.1063/1.2742910](https://doi.org/10.1063/1.2742910)]

CdS has been widely used in photovoltaic device appli-

EFM images from the same location indicates that the charge deposited on the CdS surface remains there for 5–10 min before it finally drains via the conductive substrate. However, AFM imaging of the nanostructures 7 days later showed no structural changes. EFM measurements indicated that the sign of the charge at the CdS surface was positive, i.e., opposite to that of the negatively biased AFM tip. It is well known that a weakly biased AFM tip forms a thin water bridge under 20%–40% ambient humidity.¹⁵ Electric breakdown in water occurs in the presence of an electric field whose magnitude approaches 10^9 – 10^{10} V m⁻¹, which is the case for the present 10–20 V biased AFM tip separated from the surface by a distance of 0.5–2 nm. It has been reported recently¹⁶ that electric breakdown inside the water bridge initiates field-induced water ionization producing free carriers (electrons) as follows: $\text{H}_2\text{O} = \text{H}^+$

tric breakdown in water is common and takes place in a variety of the systems involving high magnitude electric field and dielectric, or in semiconductor substrates and we anticipate this to be the case in the present CdS work.

The large dc electric field due to the biased AFM tip in proximity to the grounded CdS film may exceed 10^8 – 10^9 V m⁻¹ because of local structural variations of the tip and CdS surface; this field is sufficient to break Cd–S bonds and trigger ionized mass transport through the CdS films. However, electrochemical reactions at the CdS/water interface which may also produce Cd ions cannot be ruled out. For example, it has been proposed that photocorrosion of CdS occurs in the presence of dissolved oxygen in aqueous solution.^{17,18} In this photocorrosion process light is essentially an initiator which generates electron-hole pairs in the CdS films. After a series of reactions involving the CdS film, holes, and oxygen in the aqueous solution, the net result is that SO₄²⁻ and Cd²⁺ ions are the main photoproducts. In the present work we propose that the large electric field close to the biased AFM tip provides the energy required to create the electron-hole pairs in the initiation step. Then, once Cd ions have been created, oxidation mechanisms and/or mass transport of the Cd ions are possible causing deposition of oxide products and/or Cd ions at the CdS surface creating the observed nanostructures. This suggests transport of material vertically from below the nanostructures towards the surface along electric field lines. Clearly, further work is required to determine the exact nature of the mechanisms leading to nanostructure formation. A useful starting point would be the investigation of the following observations in support of a mass transport mechanism: