

# HF-HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O Mixtures for Etching Multicrystalline Silicon Surfaces: Formation of NO<sub>2</sub><sup>+</sup>, Reaction Rates and Surface Morphologies

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The reaction behavior of HF-HNO<sub>3</sub>-H<sub>2</sub>O etching mixtures, which are frequently used for texturing silicon surfaces, is significantly influenced by the addition of sulfuric acid. For high concentrations of sulfuric acid, nitronium ions NO<sub>2</sub><sup>+</sup> ions have been detected by means of <sup>14</sup>N NMR spectroscopy, and results of Raman spectroscopic investigation have allowed the quantification of the nitronium ions. Maximum etching rates of 4000–5000 nm s<sup>-1</sup> are reached for HF (40 %)-HNO<sub>3</sub> (65 %)-H<sub>2</sub>SO<sub>4</sub> (97 %) mixtures with w (40 %-HF)/w (65 %-HNO<sub>3</sub>) ratios of 2 to 4 and w (97 %-H<sub>2</sub>SO<sub>4</sub>) < 0.3. For higher concentrations of sulfuric acid, H<sub>2</sub>SO<sub>4</sub> can be considered as a diluent. In order to investigate the influence of the sulfuric acid at constant HF and HNO<sub>3</sub> quantities, fuming HNO<sub>3</sub> (100 %) was used and the water in the mixtures successively replaced by H<sub>2</sub>SO<sub>4</sub>. A sudden increase of etching rates was found for sulfuric acid concentrations around 6 mol L<sup>-1</sup> correlating with the characteristic color of the etching solutions. Decreased reaction rates at > 7 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> are attributed to high solution viscosities and the formation of fluorosulfuric acid. Generally, in HF-HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O etching mixtures a reduced dissociation of nitric acid, the formation of nitronium ions, the solubility of neutral nitrogen intermediates (*e. g.* NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>), as well as other effects influence the attack of silicon surfaces. The structure of etched silicon surfaces was investigated by means of scanning electron (SEM) and laser scanning microscopy (LSM). The morphologies are influenced most significantly by the relative amounts of sulfuric acid. Unexpectedly, in nitronium ion-containing mixtures rough surfaces with pore-like etching pits are generated.

*Key words:* Acidic Etching, Multicrystalline Silicon, Nitronium Ions, Sulfuric Acid, Solar Cells