



Behavior of electroless copper deposition onto multi-crystalline silicon in diluted hydrofluoric acid solutions

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The metal-assisted etching of Si is a method which has been studied for many years with regard to the creation of nanoscale surface structures, but much less research was done to elucidate the reaction processes. Most publications argue that either reduction of the metal cation could result in double charge transfer with concomitant hydrogen release or four-fold charge transfer without H₂ formation [1]. Following, SiO₂ is to be formed, which is subsequently converted into H₂SiF₆ by F⁻, HF₂⁻ or HF [2]. Due to the few reliable findings, own experiments were carried out. In this context, the deposition of Cu on multi-crystalline Si at various Cu²⁺ activities and different HF levels was investigated, and the H₂ emission for these processes analysed. The results of the series of experiments indicate a different reaction behavior from the theory described above. Apparently, a slightly higher redox potential of the Cu²⁺/Cu⁺ half-cell compared to 2H⁺/H₂ redox couple is sufficient to initiate the silicon dissolution process. The stoichiometric ratio between Cu deposition and Si dissolution process is strongly affected by the Cu²⁺ activity, but it is obviously not influenced by HF activity. At Cu²⁺ activities of < 2·10⁻⁵ mol/kg less than one electron is nominally exchanged between metal cation and Si, and at activities of approx. 1·10⁻² mol/kg there is an almost four electron charge transfer. At activities > 1·10⁻² mol/kg the stoichiometric ratio and the Cu deposition and Si dissolution kinetics decrease, presumably due to the fact the compact Cu layer inhibits the transition of the dissolved Si into the etching solution. The shift in the stoichiometric ratio suggests the first Cu²⁺ based oxidative attack on Si enables the reaction of a further oxidizing agent. It is likely water will attack the silicon as second oxidant, since there is no dependence between the content of HF species in the etching solutions and the Si dissolution kinetics. This second reaction step seems to be associated with hydrogen evolution. The amount of hydrogen formation indicates that at a Cu²⁺ activity of < 2·10⁻⁵ mol/kg calculative only one electron is transferred from Si to Cu²⁺ and H⁺, and at a Cu²⁺ activity of 1·10⁻² mol/kg four electrons in total. However, HF is necessary to convert the oxidized Si to the supposed formation of H₃SiF, H₂SiF₂, HSiF₃, and SiF₄ and H₂SiF₆ respectively.

[1] M. Jeske, J.W. Schultze, M. Thönissen, H. Münder, *Thin Solid Films* **1995**, 225, 63-66.

[2] H. Morinaga, M. Suyama, and T. Ohmi, *J. Electrochem. Soc.* **1994**, 141, 2834-2841.