

NANOGRAMMETRIC AND PHOTOELECTROCHEMICAL STUDY OF SILICON PASSIVATED BY ULTRATHIN HAFNIUM OXIDE LAYER

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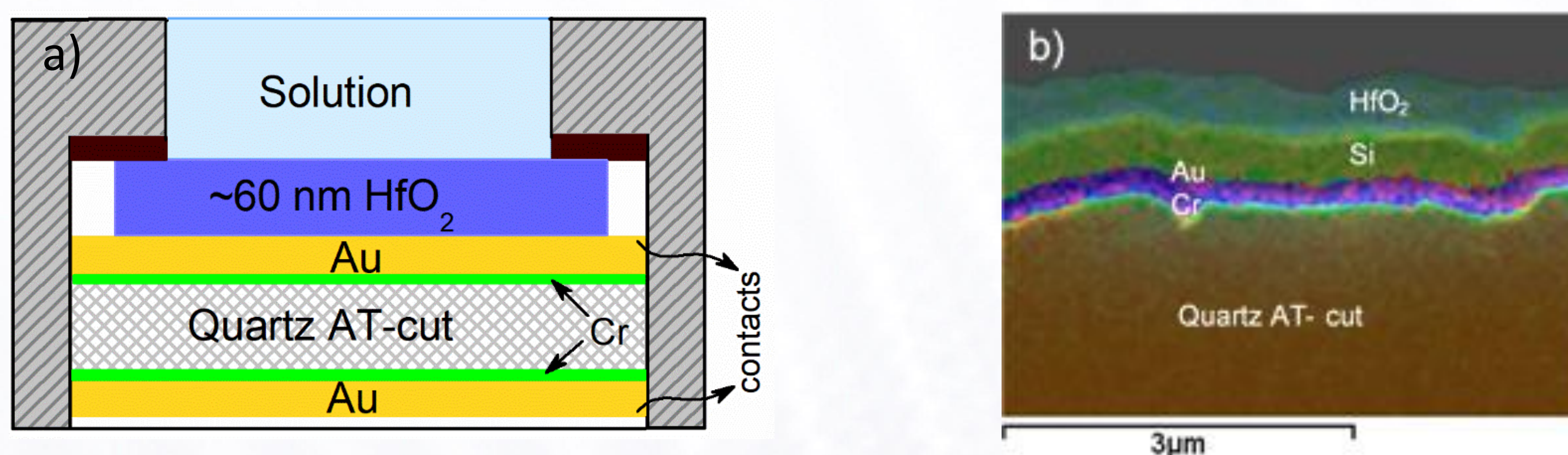
INTRODUCTION

Hafnium oxide due to its good optical transparency, wide band gap, photoluminescence, high dielectric constant, considerable chemical stability is widely applied in various fields: capacitors, switching memories, field effect transistors, heat mirrors, biomedical sensors.

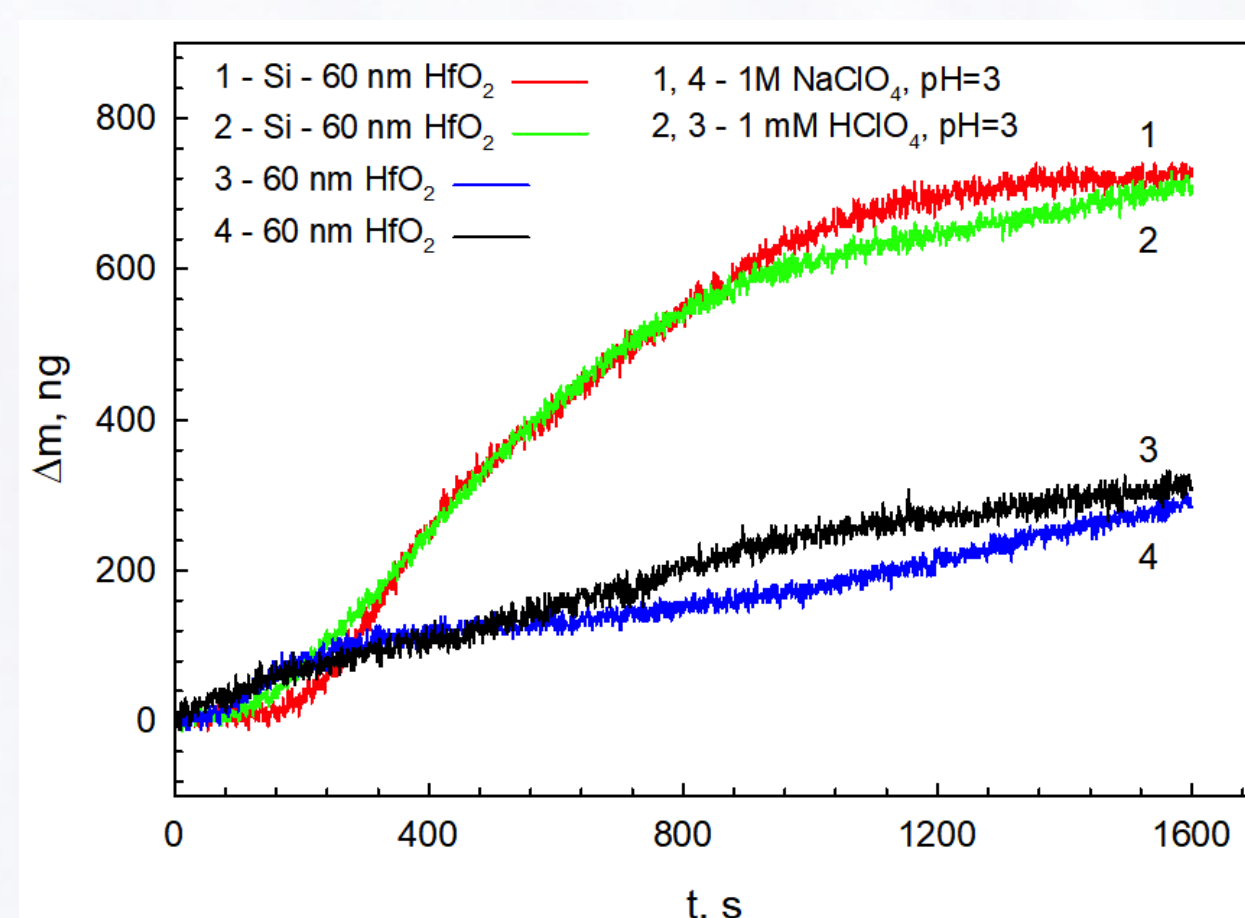
Recently ultrathin HfO₂ layers were studied as promising material to enhance efficiency and stability of organic solar cells. However, a photoelectrochemical (PEC) properties of Si-HfO₂ system are known insufficiently. This study is focused on PEC behavior of p-Si with ultrathin ALD HfO₂ layers in acid perchlorate solution. The quartz crystal nanobalance (QCN) and PEC measurements (illumination: $\lambda = 505 \text{ nm}$ and $N = 50 \text{ mW cm}^{-2}$) at open circuit were used to assess the dynamics of the electrode mass and photocharging in real time.

EXPERIMENTAL

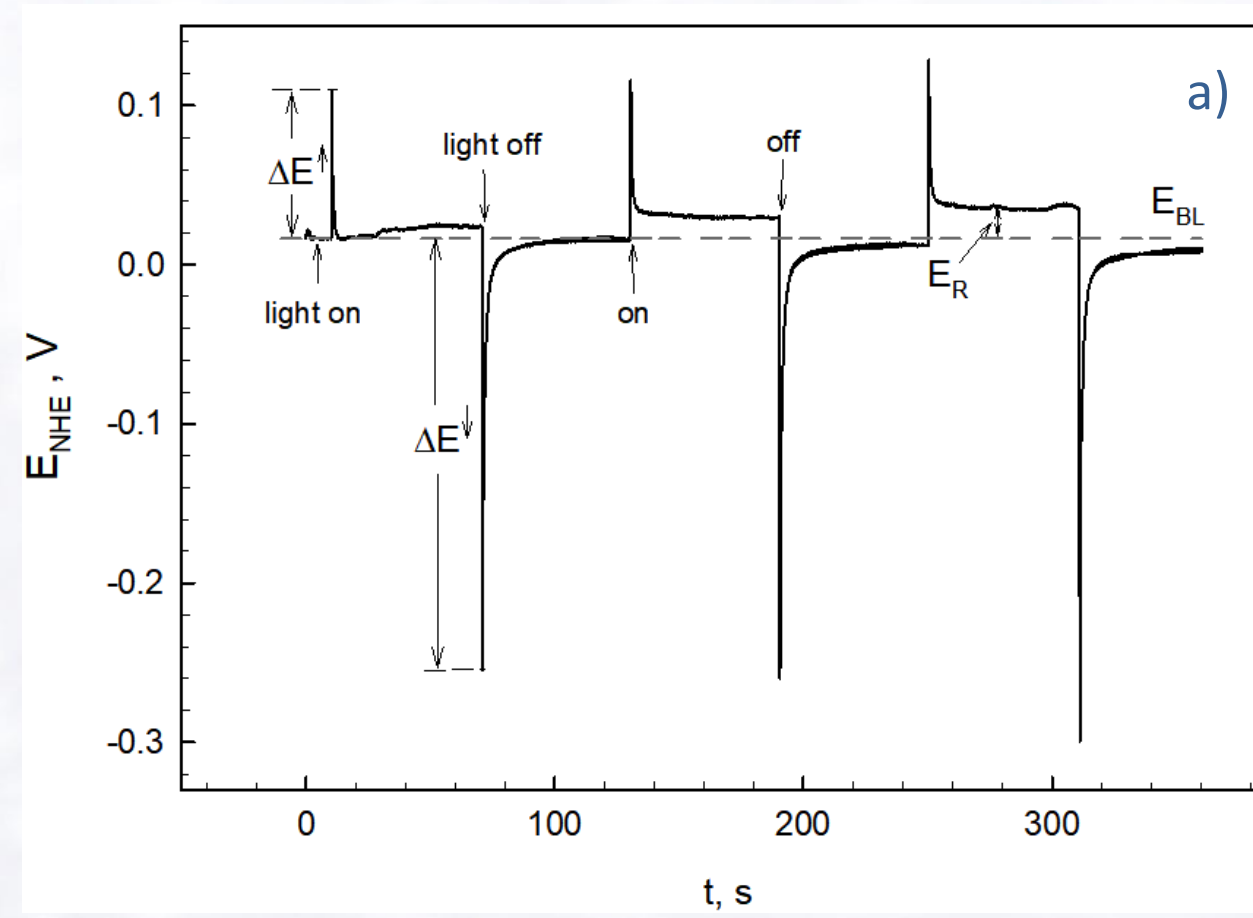
Principal configuration (a) and SEM image of the cross-section (b) of the QCN sensor. The sensor is composed of Cr/Au/Si/HfO₂ layers on quartz. Silicon layer was formed by RF magnetron sputtering and HfO₂ layer was formed by Atomic Layer Deposition (ADL).



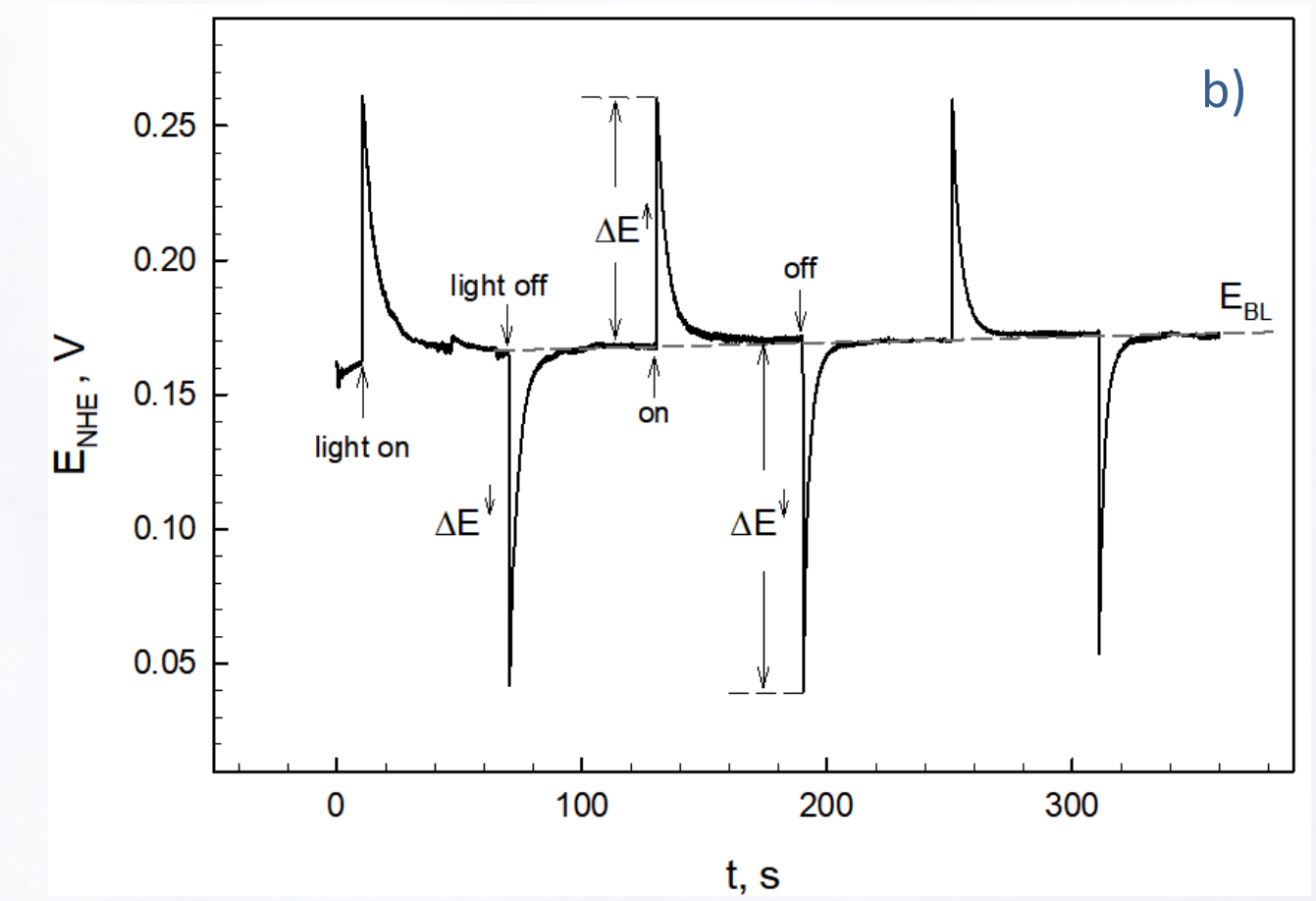
RESULTS



Mass change determined by the QCN of the samples with 60 nm HfO₂ layer on Si (1,2) and on Au (3,4) substrates when exposed in 1 mM HClO₄ (pH 3) and 1 M NaClO₄ adjusted to pH 3



Photopotential variation at open circuit of p-Si coated with HfO₂ in 1 M NaClO₄ (pH 3) when illumination is chopped at 1 min intervals for 10 nm (a) and 60 nm (b) HfO₂ layers on p-Si. Irradiation: $\lambda = 505 \text{ nm}$ and $N = 50 \text{ mW cm}^{-2}$



CONCLUSIONS

- The QCM measurements with HfO₂ film on Si and Au substrates indicated electrolyte intake rate into the oxide film. The mass of the film on Si substrate increases up to $\Delta m \sim 700 \text{ ng cm}^{-2}$ with an average rate of $\Delta m/\Delta t \sim 0.58 \text{ ng s}^{-1} \text{ cm}^{-2}$. The analogous rate for the sample with Au substrate was less: $\Delta m/\Delta t \sim 0.2 \text{ ng s}^{-1} \text{ cm}^{-2}$. The differences in Δm variation of Au and Si based samples could be attributed to different electrochemical potentials of the substrates. Silicon exerts a negative potential bias and this is an accelerating factor for proton migration.
- No indications of the oxide dissolution have been observed. The mass gain effect did not depend on perchlorate concentration: similar mass gain was determined in the electrolytes with 1 mM L⁻¹ and 1 M L⁻¹ NaClO₄.
- The photopotential variation has been studied at wavelength 505 nm for p-Si with 10 nm and 60 nm HfO₂ layers. The studied systems exhibited nearly ideal polarizability, no Faradaic process has been induced during the illumination at open circuit. Origins of the observed photopotential behavior were explained by the photoelectron generation, the positive Si surface charging, and the specific adsorption-desorption of anions. When illumination is terminated, the electron-hole pairs recombine, the photoelectrons no longer exist, and the potential is determined solely by the charge photoattracted from the solution phase. This provides an opportunity to assess the electrode in terms of photoresponsiveness and charge accumulation.