IMPROVED PASSIVATION OF THE ANODIC OXIDE / P-SI INTERFACE INDUCED BY ELECTRON INJECTION AT RT

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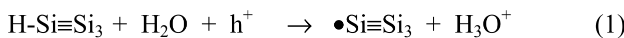
Abstract

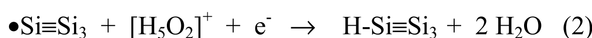
The electronic properties of thin anodic oxide / p-Si interfaces are investigated in-situ by pulsed photovoltage (PV) and photoluminescence (PL) techniques during injection of electrons. A liquid contact of a $(NH_4)_2SO_4$-containing electrolyte is used in the experiments. The surface band bending and the quenching of radiative band-to-band recombination of c-Si by surface nonradiative (nr) recombination are probed stroboscopically (N_2-laser, 100 µJ/cm^2, 10 ns pulses). Fig. 1 shows the potential (a), the current density (b), the PV amplitude (c) and the PL intensity (d) of p-Si(100) in contact with 0.3 M $(NH_4)_2SO_4$ (pH 3) solution. The potential was switched first from 0 V to +8 V to form a thin anodic oxide layer by hole injection into the electrolyte (thickness is about 20 nm) and back to 0 V. The PL intensity is low during the application of the anodic potential and decreases further after switching to zero potential. The corresponding value of the amount of surface nonradiative defects (N_S) is in the order of 10^{12} cm^{-2}. Further, the potential was switched to cathodic values of -1, -2, -3, -4, -6, and -8 V to ensure electron injection into the oxide layer. These injected electrons (from the Si bulk into the oxide layer) lead to a reduction of the PV amplitude (compensation of positively charged species, fig. 1c) and suppress the nr surface recombination by about one order of magnitude, see fig. 1d. The solid and open circles in fig. 1 represent the mean values of the PV amplitude and PL intensity measured at 0 V after the electron injection. Fig. 2 shows the amount of N_S (as obtained from PL intensity) as a function of Q_{ox} (positive charge as calculated from PV). Both values are reduced from 10^{12} to 10^{11} cm^{-2} and $2\cdot10^{11}$ to $2\cdot10^{10}$ q/cm^2, respectively. N_S decreases monotonously with decreasing Q_{ox} and tends to saturate at the lower values of Q_{ox} (N_S^{min} is about 10^{11} cm^{-2}).

The correlation between N_S and Q_{ox} is very similar to the negative-bias-temperature instability (NBTI) of SiO_2/Si interfaces [1] with the following reaction scheme [2]:



$$\text{H-Si}\equiv\text{Si}_3 + \text{H}_2\text{O} + h^+ \rightarrow \bullet\text{Si}\equiv\text{Si}_3 + \text{H}_3\text{O}^+ \quad (1)$$

In accordance to (1), we propose the following reaction for the reduction of Q_{ox} and N_S at the anodic oxide / p-Si interfaces by electron injection:



$$\bullet\text{Si}\equiv\text{Si}_3 + [\text{H}_5\text{O}_2]^+ + e^- \rightarrow \text{H-Si}\equiv\text{Si}_3 + 2\,\text{H}_2\text{O} \quad (2)$$

Reaction (2) is, in principle, the inverse reaction of (1). Reaction (2) is controlled by the number of injected electrons and the amount of water present at the interface. Reaction (1) dominates at anodic potentials while reaction (2) is initiated by injection of electrons at cathodic potentials.

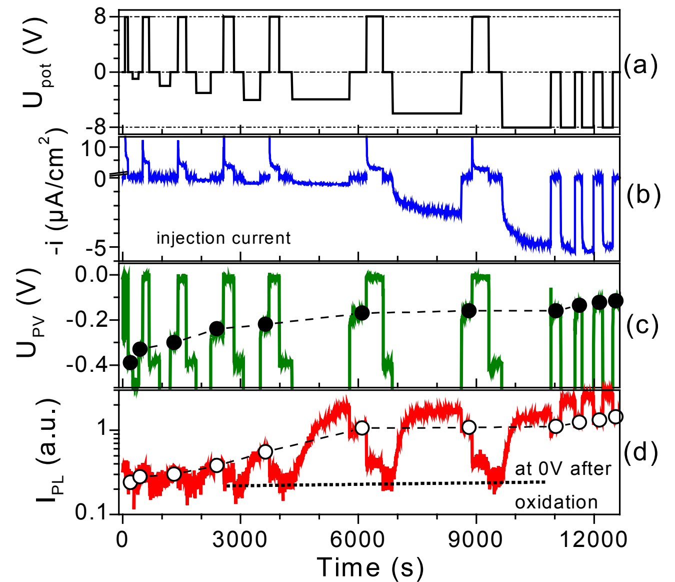


Fig. 1: Potential (a), current density (b), PV amplitude (c) and PL intensity (d) of p-Si(100) in 0.3 M $(NH_4)_2SO_4$ (pH 3) as a function of time.

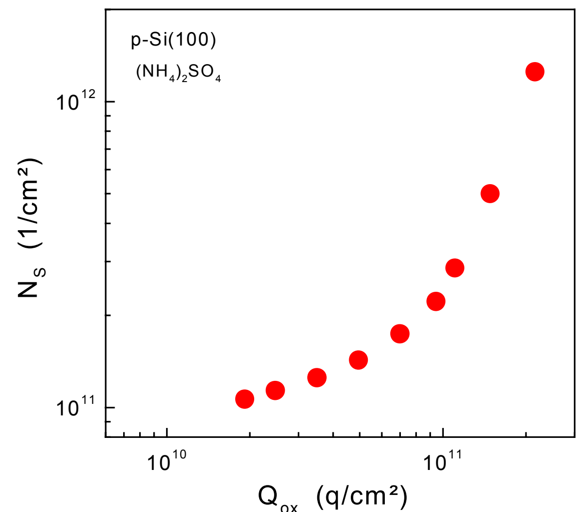


Fig. 2: N_S (as obtained from PL intensity) as a function of Q_{ox} (positive charge as calculated from PV).

1. C. E. Blat, E. H. Nicollian, and E. H. Poindexter, J. Appl. Phys. **69**, 1712 (1991)
2. E. H. Poindexter, J. Non-Crystal. Sol. **187**, 257 (1995); and E. H. Poindexter, Z. Naturforsch. **50a**, 653 (1995)