# Hydrogen passivation of electronic gap states at the interfaces of ultrathin $SiO_2$ layers on crystalline Si

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Ultrathin $SiO_2$ layers with a thickness of a few nanometers are proposed to act as functional elements in various high efficiency solar cell concepts: (i) A tunnel oxide layer integrated at the interface of a classical c-Si heterojunction with an a-Si:H emitter is proposed to reduce interface recombination due to excellent passivation properties [1]. Normally, these structures suffer from difficulties in the appropriate wafer pre-treatment as well as from controlling the a-Si:H deposition conditions for very low interface defect densities. (ii) Ultrathin $SiO_2$ layers can be applied as barriers in Si-based multi-junction solar cells that consist of stacked quantum wells of different thickness to provide bandgap tunability and thus efficiency enhancement via utilization of quantum size effects [2].

Essential requirement for the realization of such structures is the preparation of uniform ultrathin oxide layers that have ideally structurally abrupt interfaces with very low concentrations of defect states. Interface roughness increases the density of traps and charges, and thereby increases recombination velocities and lowers charge carrier mobilities. Here, we report on the development of a complete *in situ* processing cycle that allows for preparation of ultrathin $SiO_2$ layers, treatment with H plasma as well as interface gap state analysis by near-UV photoelectron spectroscopy without breaking ultrahigh vacuum (UHV). The particular advantages of nearly thermal impact energies ($E_{kin}$ < 1 eV) of (i) neutral O atoms for the formation of chemically abrupt interfaces and (ii) neutral H atoms for significant passivation of dangling bonds at the ultrathin-$SiO_2$/Si interfaces are explored.

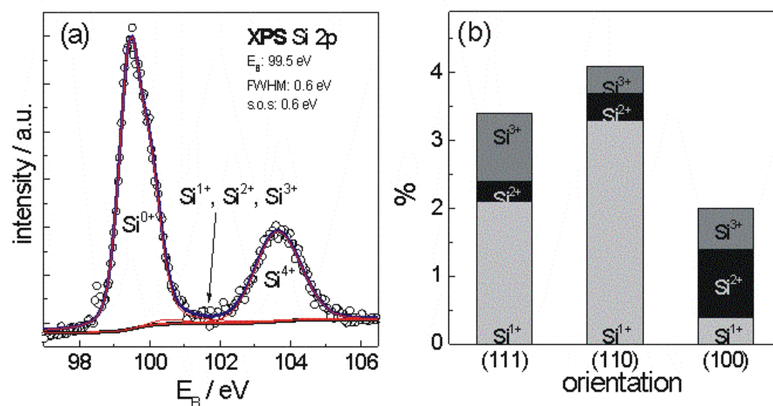


**Fig. 1: (a) Si 2p XPS spectrum and curve analysis of Si(111) after RF plasma oxidation with thermal impact. (b) Amounts of intermediate oxidation states at the interfaces of 2 nm $SiO_2$ on Si(111), (110), (100).**

Fig. 1a shows the x-ray photoelectron spectroscopy (XPS) data of the Si 2p core levels for the ultrathin oxide layers formed by RF plasma oxidation with neutral atomic oxygen at 600°C on Si(111). Analysis of the chemical shift revealed dominant contributions of the oxidation states $Si^{0+}$ and $Si^{4+}$, corresponding to Si and $SiO_2$, and extremely low amounts of the intermediate oxidation states $Si^{1+}$, $Si^{2+}$, and $Si^{3+}$ [3]. Quantitative analysis of the amounts of suboxides at the interfaces of 2 nm $SiO_2$ layers on the low indexed Si(111), (110), and (100) surfaces is given in Fig. 1b. For all three orientations the total suboxide amount is between 2 % and 4 % of the total signal [4]. These are extremely low values, which are

significantly lower than those found for conventional thermal oxidation ranging from 10 to 30%. Thus, high quality ultrathin $SiO_2$/Si interfaces with compositionally abrupt transitions were obtained by UHV plasma oxidation.

The density of interface states at the $SiO_2$/Si transition characterizes the strain and the dangling bond concentration at this interface. Photoelectron spectroscopy with near-UV excitation was applied to map in particular occupied interface defect states within the bandgap. At a first approximation, the number of occupied states $N_{occ}$ is proportional to the internal yield $Y_{int}$, which is determined from the photoelectron signal [5]. In Fig. 2, $N_{occ}$ is plotted for a $SiO_2$/Si interface before and after H plasma treatment. The curve in Fig. 2a corresponds to conventional plasma passivation in a parallel plate source with highly energetic H atoms (>120 eV) normally applied for poly-Si thin film solar cells, whereas Fig. 2b shows the results of the UHV plasma passivation using neutral H atoms with nearly thermal energies. It is found that, that energetic plasma impact leads to an increase of $N_{occ}$, whereas UHV passivation with thermalized neutral atomic H results in distinct decrease of $N_{occ}$ in particular around the midgap, where the dangling bonds are located [6,7]. This interpretation is supported by the results of Si-H bond breaking by thermal annealing of the passivated samples. For the case of energetic plasma impact (Fig. 2a), a further increase of the interface gap state density is found. This effect clearly verifies that upon energetic hydrogen plasma passivation more interface gap states are generated than passivated since large amounts of energy are imparted which deteriorate the electrical properties. Contrary, in case of the thermal plasma passivation in UHV (Fig. 2b) the NUV-PES spectrum after annealing matches the initial state before hydrogen plasma treatment. Accordingly, H is completely removed and no degradation or structural modifications at the interface remain. Thus, significant passivation of dangling bonds at the structurally abrupt interfaces between ultrathin-$SiO_2$ and c-Si is achieved by appropriate H plasma treatment with nearly thermalized atoms.

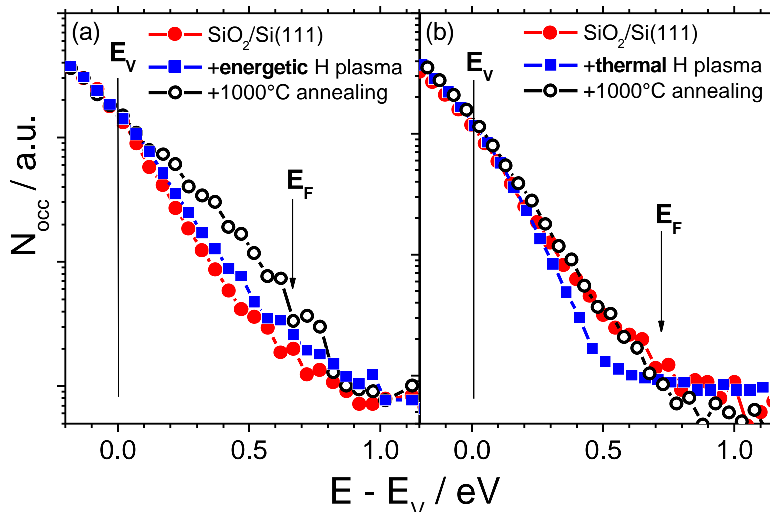


**Fig. 2: Number of occupied $SiO_2$/Si interface states $N_{occ}$ by NUV-PES: (a) conventional energetic H plasma treatment, (b) H plasma passivation at thermal impact energies (UHV). Shown are the spectra before (red) and after H treatment (blue) and after H removal by thermal annealing** (black). **All spectra are aligned at the energy axis according to the position of the valence band maximum ($E_V$). Arros indicate the position of the Fermi energy $E_F$.**

**References:**

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