

On the origin of leakage current reduction in TiO₂ passivated porous silicon Schottky-barrier diode

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Significant reduction by 40 times was achieved in the leakage current of TiO₂ passivated porous silicon (PS) Schottky-barrier diode, compared to that of as-grown PS one. It was found that the imperfect native oxide, nonstoichiometric Si-suboxide (SiO_x) and Si-O bond with nonbridging oxygen, and highly chemically reactive Si-H₂ species are the issues of leakage current. These issues can be drastically suppressed and replaced by a stable stoichiometric SiO₂ and Si-OH bond on the TiO₂ passivated PS surface. The enriched OH formation will favor the growth of TiO₂ and passivate the surface states of PS, hence reducing the leakage current. © 2010 American Institute of Physics. [doi:10.1063/1.3309717]

Possible applications in Si-based integrated circuits have stimulated research on porous silicon (PS) photodetector due to it contains light scattering voids which enhance the optical absorption.¹ However, the optic property of PS degrades as a result of absorbing oxygen and hydrogen on the surface of PS layer due to its internal surface is passivated by hydrogen but remains highly chemically reactive.^{2,3} Thus a good passivation for the PS is crucial in order to fabricate a stable and a reliable device with well-defined characteristics.

Titanium dioxide (TiO₂) is a high dielectric-constant material and therefore has less carrier tunneling,⁴ being suitable for a passivation layer in PS devices. Previously, TiO₂ thin films were prepared by sputtering,⁵ plasma-enhanced chemical vapor deposition,⁶ and sol-gel coating.⁷ These methods are either high-temperature process or need a high-temperature post-treatment, which may recover PS. However, liquid-phase deposition (LPD) has advantages of room-temperature and selective growth, hence can be employed on PS to overcome the above drawbacks.

In this work, a passivation layer of TiO₂ was grown on PS using LPD and a Schottky-barrier diode was fabricated with a much low leakage current by about 40 times than the Schottky-barrier diode without TiO₂ passivation. Fourier-transform infrared (FTIR) and x-ray photoelectron spectroscopy (XPS) were investigated to explain this behavior.

N-type silicon (100) wafers with 3–40 Ω cm resistivities were etched by (1:1:2) HF: DI water: ethanol electrolyte in a Teflon electrochemical etching cell with an illumination of 50 W halogen lamps. During etching, a constant current density (5 mA/cm²) was applied on these wafers for 15 min. After that, Au and Al electrodes were evaporated onto this in PS layer as Schottky and Ohmic contacts, respectively. To avoid the metals punching through the PS and contacting with silicon substrate, not any anneal was employed in our experiment. Subsequently, the passivation layer of TiO₂, with a dielectric-constant of 39, was selectively grown on the exposed PS using LPD method maintained at room temperature for a thickness of 20 nm. The deposition solution was prepared with a 0.2 M, 20 ml am-

monium hexafluoro-titanate [(NH₄)₂TiF₆] aqueous solution mixed with 1.2 g TiO₂ powder. Current-voltage (*I*-*V*) characteristic was measured by an HP-4155B semiconductor parameter analyzer.

Cross-section scanning electron microscopy (SEM) of the fabricated as-grown PS is inserted in the inset of Fig. 1, which shows the porosity of 52%, pore-size of about 1 μm, and depth of 5.3 μm. Figure 1 shows the *I*-*V* curves of PS Schottky-barrier diode with and without TiO₂ passivation layer. As compared to the samples without TiO₂ passivation, the leakage current is significantly decreased by about 40 times for the one with TiO₂ passivation. Such an improvement indicates a good passivation is formed on PS surface as a result of surface defects and dangling bonds are dramatically suppressed. Barrier-height of both samples, with and without TiO₂ passivation, is 0.71 and 0.7 eV, respectively. Such a difference is very small due to the barrier-height is only determined by the interface of Au/PS, and is independent with passivation. To understand the chemical states upon TiO₂ passivation, FTIR spectra of as-grown PS and PS with TiO₂ passivation are shown in Fig. 2 with wavenumber ranging 400–1200 cm⁻¹. In Fig. 2, the intensity is normalized to the as-grown PS. In Fig. 2(a), the Si-Si stretching mode is seen at 621 cm⁻¹, which comes from the PS bulk and also observed in XPS data.⁸ Peak located at 663 cm⁻¹ is attributed to a deformation mode of Si-H₂ species, and

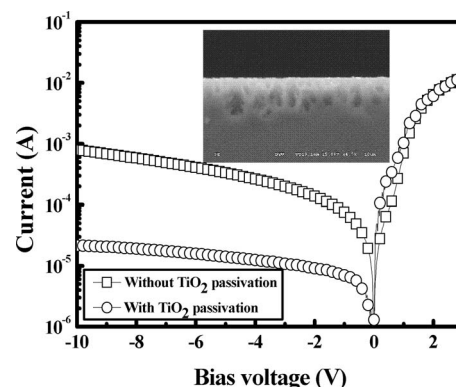


FIG. 1. *I*-*V* curves of the PS Schottky-barrier diode with and without TiO₂ passivation; inset is the cross-section SEM of as-grown PS.

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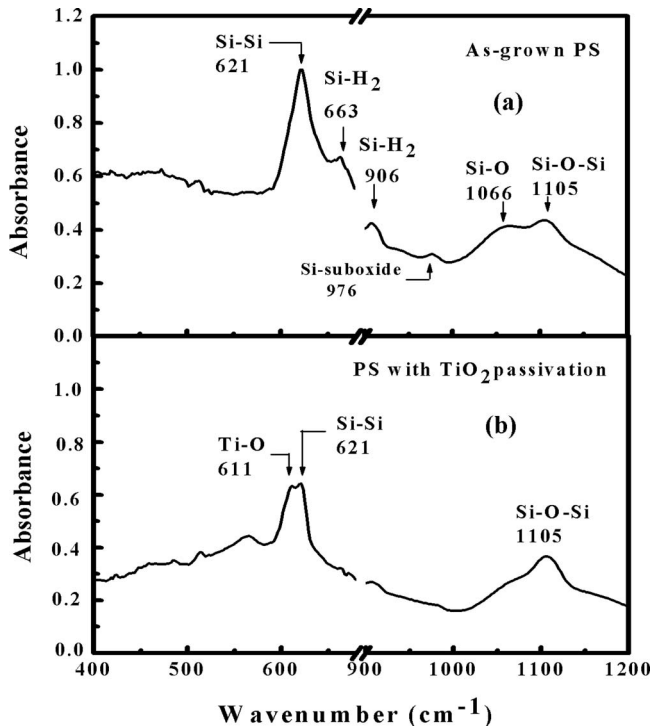


FIG. 2. FTIR spectra of (a) as-grown PS, and (b) PS with TiO_2 passivation with wavenumber ranging 400–1200 cm^{-1} .

906 cm^{-1} is the scissor mode of Si–H₂ species. The Si–H₂ species is due to the PS has hydrogen (H) passivated surfaces. These H atoms come from HF and passivate the dangling bonds that act as nonradiative recombination centers.⁹ The peak at 1105 cm^{-1} is representative for the Si–O–Si asymmetric stretching mode, and 976 cm^{-1} as well as 1066 cm^{-1} are nonstoichiometric Si-suboxide (SiO_x) and Si–O bond with nonbridging oxygen, respectively.^{9,10} It was reported that these imperfect native oxide (Si-suboxide and Si–O bond) and unstable Si–H₂ species provide large amounts of surface states on the surface of PS layer, which are responsible for the large leakage current in PS Schottky-barrier diode.¹¹ Upon TiO_2 passivating, a noticeable contrast is seen in Fig. 2(b). Ti–O bond located at 611 cm^{-1} is found. Moreover, Si-suboxide (976 cm^{-1}) and Si–O bond with nonbridging oxygen (1066 cm^{-1}) are drastically suppressed; however, the perfect oxide (Si–O–Si bond) is still covered on PS surface. Such a phenomenon suggests the SiO_x and Si–O bond are broken and re-constructed into a more stable bond of Si–O–Si on PS surface after TiO_2 passivation. Additionally, the unstable Si–H₂ species (663 and 906 cm^{-1}) are almost undetectable in PS samples with TiO_2 passivation [see Fig. 2(b)]. Where are going of these H atoms?

FTIR spectra of both samples are shown in Fig. 3 with wavenumber ranging 3000–3600 cm^{-1} . In this range, not any peak is observed in the as-grown PS [Fig. 3(a)]. In contrast, a broad-band of 3000–3400 cm^{-1} due to the O–H stretching vibration of Si–OH bond¹² is appeared in PS samples with TiO_2 passivation. Combining Figs. 2 and 3, we know that in the PS samples with TiO_2 passivation, the unstable Si–H₂ species are broken and replaced by a Si–OH bond. The OH enriched surface of PS layer will favor the growth of TiO_2 , as follows:

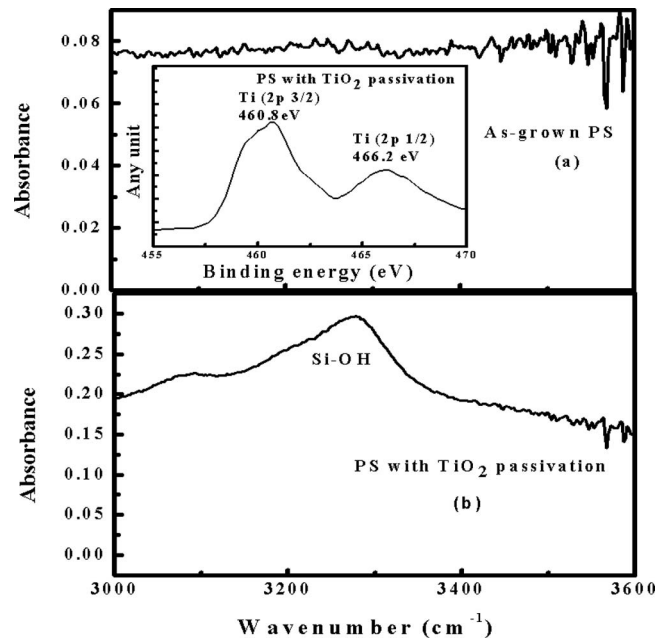
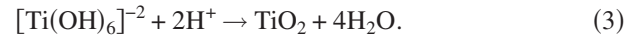
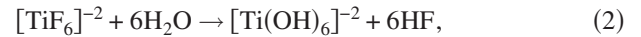


FIG. 3. FTIR spectra of (a) as-grown PS, and (b) PS with TiO_2 passivation with wavenumber ranging 3000–3600 cm^{-1} ; inset of (a) is the Ti 2p XPS spectrum of the PS with TiO_2 passivation.



The Ti 2p XPS spectrum of TiO_2 passivated PS sample is shown in the inset of Fig. 3(a), which is fitted by Gaussian function. Two peaks located at 460.8 and 466.2 eV are found, which are representative for Ti 2p_{3/2} to Ti 2p_{1/2} spin orbital splitting.⁶ The Ti 2p spectrum shows no peak at lower energy side of the main peak, i.e., there is no characteristic of metallic Ti.¹³ Si 2p XPS spectra of both samples are appeared in Figs. 4(a) and 4(b). In Fig. 4(a), in addition

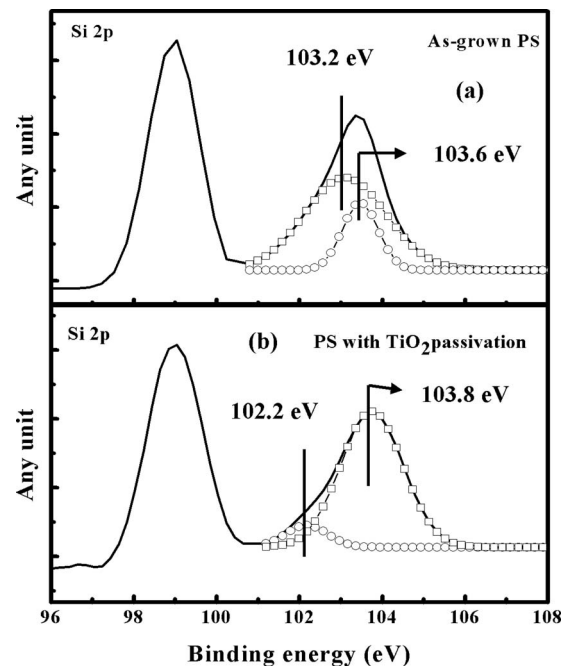


FIG. 4. Si 2p XPS spectra of (a) as-grown PS, and (b) PS with TiO_2 passivation.

to the PS bulk of 99 eV, the silicon dioxide (SiO_2) is also observed at about 103 eV.¹⁴ However, the silicon oxide consists of two peaks located 103.2 and 103.6 eV. The peak located 103.2 eV has a larger area as compared to the 103.6 eV, showing that it contains a larger ratio of less-compact oxide (103.2 eV) on the surface of as-grown PS, such as Si-suboxide (SiO_x), which is well agreement with FTIR results. In contrast, the PS with TiO_2 passivation has a very small area of less-compact oxide (102.2 eV) as compared to the more-compact oxide located at about 103.8 eV, shown in Fig. 4(b). The area ratio of less-compact to more-compact oxide is reduced from 3.14 to 0.13 for the samples without and with TiO_2 passivation. Moreover, the TiO_2 passivated PS shows a stronger binding-energy (103.8 eV) as compared to that (103.6 eV) without TiO_2 passivation, suggesting a more stable oxide layer is associated with TiO_2 passivated PS. Hence, the weaker Si–O bond on the surface of as-grown PS is replaced by a stronger bonding of Si–O–Si in the TiO_2 passivated PS through reconstructing. The stronger bonding forms an effective passivation on the surface of PS Schottky-barrier diode, thus dramatically reducing the leakage current.

Leakage current has been much reduced by about 40 times in TiO_2 passivated PS Schottky-barrier diode, compared to that of as-grown PS one. FTIR and XPS spectra show that the surface of as-grown PS is covered with imperfect native oxides (Si-suboxide and Si–O bond with non-bridging oxygen) and unstable Si– H_2 species, which provide large amounts of surface states on the surface of PS layer, leading to a large leakage current in PS Schottky-barrier diode. However, in the PS with TiO_2 passivation, the Si– H_2

and imperfect native oxide are drastically suppressed and replaced by a Si–OH and stoichiometric SiO_2 , respectively.

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