

Low-Temperature Synthesis of a TiO₂/Si Heterojunction

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S Supporting Information

ABSTRACT: The classical SiO₂/Si interface, which is the basis of integrated circuit technology, is prepared by thermal oxidation followed by high temperature (>800 °C) annealing. Here we show that an interface synthesized between titanium dioxide (TiO₂) and hydrogen-terminated silicon (H:Si) is a highly efficient solar cell heterojunction that can be prepared under typical laboratory conditions from a simple organometallic precursor. A thin film of TiO₂ is grown on the surface of H:Si through a sequence of vapor deposition of titanium tetra(*tert*-butoxide) (**1**) and heating to 100 °C. The TiO₂ film serves as a hole-blocking layer in a TiO₂/Si heterojunction solar cell. Further heating to 250 °C and then treating with a dilute solution of **1** yields a hole surface recombination velocity of 16 cm/s, which is comparable to the best values reported for the classical SiO₂/Si interface. The outstanding performance of this heterojunction is attributed to Si–O–Ti bonding at the TiO₂/Si interface, which was probed by angle-resolved X-ray photoelectron spectroscopy. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) showed that Si–H bonds remain even after annealing at 250 °C. The ease and scalability of the synthetic route employed and the quality of the interface it provides suggest that this surface chemistry has the potential to enable fundamentally new, efficient silicon solar cell devices.

Thin layers of titanium dioxide, a stable, low cost, wide band gap material of interest for TiO₂/Si heterojunction solar cells,^{1–3} are typically grown by atomic layer deposition (ALD), chemical vapor deposition (CVD), or sol–gel type processes.^{4–9} We recently reported that thin layers of TiO₂ can be grown on hydrogen terminated silicon (H:Si) and can enable an efficient TiO₂/Si heterojunction based solar cell.^{10–13} In particular, we showed^{10–13} that this coating, when used in conjunction with an electron blocking PEDOT-terminated anode, effectively blocked minority carrier holes in the silicon from recombining at the cathode contact. We found that the TiO₂ layer reduced dark current, increased open circuit voltage (*V*_{OC}), increased quantum efficiency at longer wavelengths, increased stored minority carrier charge under forward bias, and yielded excellent hole lifetimes. Whether speciation at the Si/TiO₂ interface affected

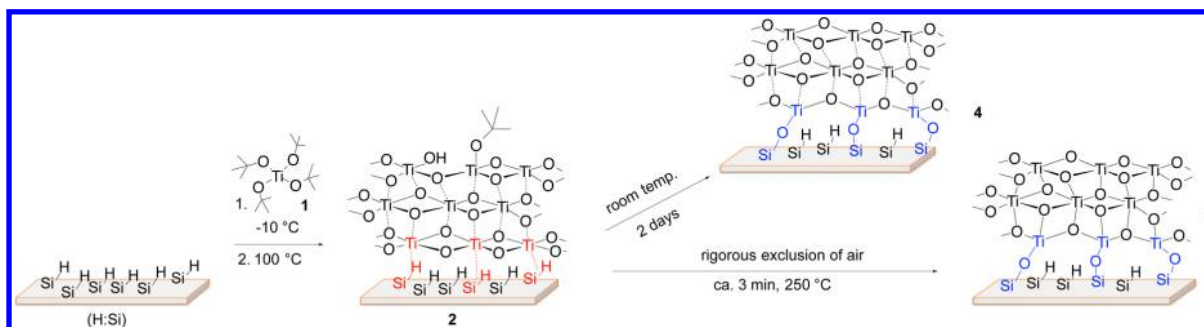
device performance, in particular with regard to hole-blocking, was thus of fundamental importance, which could best be addressed through careful interfacial chemical analysis.

Our solar cells had been constructed on hydrogen-passivated (100)-oriented silicon wafer surfaces that were prepared with minimal exposure to air. The TiO₂ layer was synthesized (Scheme 1) by vapor phase deposition of titanium tetra(*tert*-butoxide) (**1**) onto the externally cooled substrate at 10^{–3} Torr; it was then heated to 100 °C, briefly exposed to air at room temperature, and then used (as **2**) for device fabrication. To understand at the molecular level the role played by the TiO₂/H:Si interface in our devices, we examined speciation for **2** and its thermal evolution products **3** and **4** by angle-resolved X-ray photoelectron spectroscopy (XPS). Our efforts might have been compromised, however, by the possible formation of silicon oxide (SiO_x) formed during the brief periods of air exposure attendant to our procedures. To obviate SiO_x in order to unambiguously identify interfacial speciation, we repeated our synthesis procedures, but with rigorous exclusion of air.

In a typical “no air” experiment Si(100) wafers were cleaned by standard methods¹⁴ and then dipped in a 20:1 deionized water: 48–50% aqueous hydrofluoric acid solution for 45 s to give hydrogen terminated silicon (H:Si). The substrate was rinsed with Milli-Q water, dried, and placed in a glass tube that was connected to both a reservoir of the titanium tetra(*tert*-butoxide) (**1**) precursor of TiO₂ and to vacuum; it was then externally cooled to –10 °C and exposed to vapor of **1** (Scheme 1) for 10 min at 10^{–3} Torr.¹⁵ The substrate was next heated at 100 °C for 10 min to form TiO₂/H:Si (**2**) and was then cooled to room temperature. The TiO₂-coated substrate was then transferred in the sealed deposition chamber into a nitrogen atmosphere glovebox from which it was transferred into the antechamber of the XPS spectrometer via a “vacuum suitcase” that precludes air intrusion. A second sample was heated in the glovebox to 250 °C on a hot plate (to give **3**) and was subsequently transferred into the antechamber, also via the “suitcase.” XPS analysis of **2** showed the binding energy for Ti(2p) (Figure 1b) to be typical of Ti(IV), with no discernible signal for any lower valent Ti species; essentially no peak for Si–O was seen in the angle-resolved Si(2p) XP spectrum (Figure 1a), though the C(1s) spectrum showed some *tert*-butoxy groups are still present (Supporting Information Figure 1). We suggest that the TiO₂ is

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Scheme 1^a

^aNo structure for “Si–H” is implied. Titanium tetra(*tert*-butoxide), 1, is deposited on a cooled ($-10\text{ }^{\circ}\text{C}$) sample of H-terminated Si and then heated at $100\text{ }^{\circ}\text{C}$ to give 2. Preparing 3 from 2 in the absence of air obviates formation of SiO_x and enables identification of Si–O–Ti interfacial species.

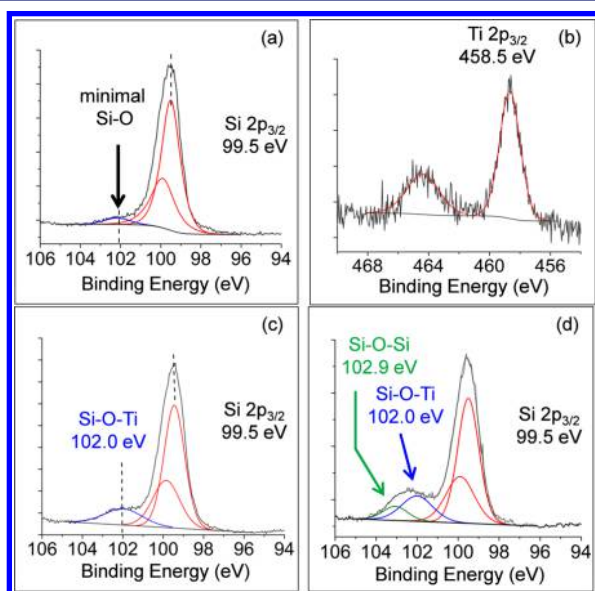


Figure 1. Angle-resolved XP spectra taken at 70° from surface normal (a) Si(2p) for 2; (b) Ti(2p) for 2; (c) Si(2p) for 3; (d) Si(2p) for 2 exposed to air for 30 min and then heated to $250\text{ }^{\circ}\text{C}$. The y-axis scale represents arbitrary counts.

formed by stepwise dehydration at $100\text{ }^{\circ}\text{C}$ in which *tert*-butoxy groups thermolyze to 2-methyl-1-propene with concomitant formation of Ti–OH groups; these condense with elimination of water to give the Ti–O–Ti moieties of 2 (Scheme 2).

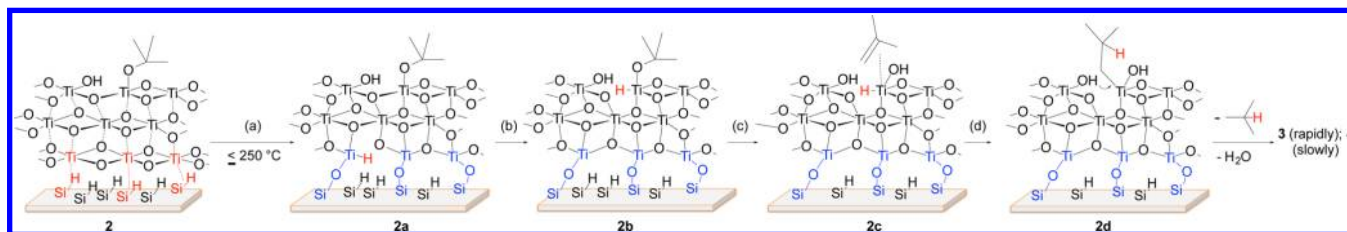
Heating 2 to $250\text{ }^{\circ}\text{C}$ may further cross-link the TiO_2 to give 3; 2 exfoliates in water, but 3 does not.¹⁶ XPS analysis of 3 showed no change in the Ti(2p) spectrum, but a new signal appeared for Si(2p) (Figure 1c). Since 3 had never been exposed to air, this new peak must derive from reaction between a surface Si species

and the TiO_2 overlayer. Angle-resolved XPS showed that this new species is surface-located; the depth of this Si–O layer is $2\text{--}3\text{ \AA}$ ^{17,18} (Supporting Information Figure 2). Its binding energy, $\text{BE} = 102.0\text{ eV}$, is lower than that for SiO_x ($\text{BE} = 102.7\text{--}103.0\text{ eV}$). We assign it to a new interfacial species, Si–O–Ti;^{6,19} this lower BE assignment is consistent with the lower electronegativity of Ti vs Si. This same Si(2p) spectrum was recorded for 2, which was stored under inert atmosphere for 2 days to give 4 (Supporting Information Figure 3). As a control, H:Si was heated at $250\text{ }^{\circ}\text{C}$ for 5 min in the absence of air; no Si–O species were observed in the XPS (Supporting Information Figures 4 and 5).

All Ti and Si peak positions and intensities in XP spectra of 3 remained unchanged after 18 h of ambient exposure. In contrast, when 2 was exposed to air for only 30 min prior to heating at $250\text{ }^{\circ}\text{C}$, Si(2p) XPS showed a broad peak, which could be deconvoluted into a component assigned to Si–O–Ti and a second one to SiO_x (Figure 1d) consistent with some Si–H oxidation.

We propose that Si–O–Ti formation under anaerobic conditions involves σ -bond metathesis between surface Si–H and Ti–O^{20,21} groups of the TiO_2 overlayer, which yields a Ti–H species (intermediate 2a); such ligand exchange is well-established for the titanium alkoxide-activated reduction of organics using polymeric hydrosiloxanes.²¹ Further H–Ti/O–Ti σ -bond metathesis (to 2b), thermal decomposition of *tert*-butoxy ligands to Ti–OH and 2-methyl-1-propene (2c), and finally Ti–OH protonolysis of the (2-methylpropyl)titanium resulting from β -hydride addition²² (2d) gives the observed products (Scheme 2).

ATR-FTIR further probed the effect of TiO_2 film formation on the Si–H surface: Differential absorption spectra of the starting Si–H surface (Figure 2,i) and 3 before (Figure 2,ii) and after 18 h of ambient exposure (Figure 2,iii) were referenced to a clean,

Scheme 2^a

^aProposed formation of Si–O–Ti in the absence of air by a sequence of (a) Si–H/Ti–O σ -bond metathesis, (b) H–Ti/O–Ti σ -bond metathesis, (c) *tert*-butoxy ligand fragmentation, and (d) β -hydride addition and protonolysis by a neighboring Ti–OH moiety.

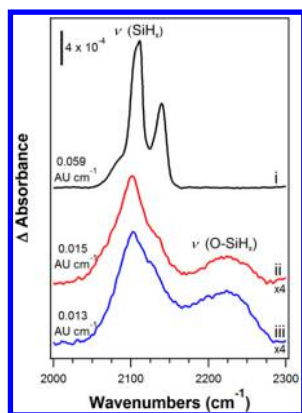


Figure 2. Attenuated total reflectance-FTIR absorption spectra of (i) an H-terminated Si(100) surface; (ii) **3**, with no air exposure; and (iii) **3**, after 18 h air exposure. All spectra were referenced to a clean, chemically grown oxide on Si(100). The area of the SiH_x peaks were integrated over the region from 2040 to 2165 cm⁻¹. Spectra ii and iii are magnified $\times 4$ for clarity.

chemically oxidized surface. About 25% of initial Si–H was found to remain by comparison of peak areas for the SiH_x region (2050–2150 cm⁻¹) after TiO₂ deposition.²³ A small shoulder at ca. 2260 cm⁻¹ appears and is assigned to the stretching mode of Si–H where oxygen is “back-bonded” to Si;²⁴ this shoulder grew with exposure to air. The persistence of Si–H bonds in **3** can be understood by comparing the areal density of Si atoms in the Si(100) plane (ca. 7×10^{14} Si atoms/cm²) compared to that of Ti atoms in a model (rutile) TiO₂(111) plane (ca. 5×10^{14} Ti atoms/cm²). Thus, the Ti in **3** can bond to only about 70% of the Si atoms by this analysis, leaving about 30% of the original Si–H bonds unreacted (Scheme 1), approximating our experimental result. The TiO₂ film of **3** acts somewhat as a protective layer, slowing air oxidation of residual Si–H bonds, consistent with XPS observations.

The purpose of TiO₂ films that are grown on n-type Si in a device is to let electrons pass and to reflect photoexcited holes in order to raise the photovoltage of solar cells.^{10–13} The maximum photovoltage is generated when all holes that impact a TiO₂/n-Si interface reflect from it without interacting. At nonideal interfaces some holes do get trapped in interface defect states and then recombine with electrons; the rate of this recombination rises with the areal density of interfacial electronic defects, which are associated with incomplete bonding across the interface. The effective lifetime (τ_{eff}) of holes is reciprocal to the surface recombination velocity (SRV): the lower the SRV, the longer the effective hole lifetime. The τ_{eff} for **2** was measured by the quasi-steady state photoconductance decay (QSSPCD) method²⁵ to be poor, with SRV > 1000 cm/s.²⁶ In marked contrast, τ_{eff} for **4** was measured to yield an SRV as low (good) as 50 cm/s,¹² comparable to lifetimes reported for TiO₂/Si heterojunctions made by low temperature atomic layer deposition (ALD) or sol–gel type processes.^{27–29} The τ_{eff} for **3** also yielded a good SRV (ca. 50 cm/s).²⁶ The excellent diode characteristics (Figure 3) demonstrate the effectiveness of the hole barrier without excessive recombination; omitting the TiO₂ layer resulted in high current in both directions. In short, the hole effective lifetime depends critically on the chemical nature of the TiO₂/Si interface: In the absence of Si–O–Ti bonding (**2**), τ_{eff} is unfavorably short; when Si–O–Ti bonding is present at the interface (**3** and **4**), τ_{eff} can be improved significantly.

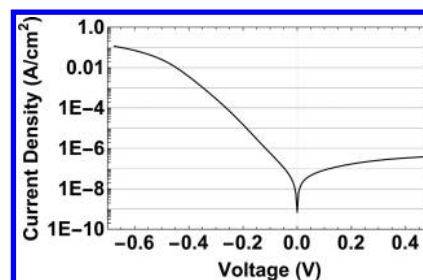


Figure 3. Diode characteristics of **3** equipped with 150 nm Al electrodes on the TiO₂ and Ag electrodes on the p-type substrate. Voltage was applied to the TiO₂ terminal with the substrate grounded.

It is interesting that when **3** was treated with 0.3 mL of **1** in 10 mL of ethanol under inert atmosphere and then exposed to ambient conditions, a strongly passivating interface resulted; the SRV decreased to 16 cm/s, which is comparable to the best reported ones for SiO₂/Si interfaces that are prepared by the classical thermal oxidation process used for silicon integrated circuits.^{30,31} The thickness of the TiO₂ (ca. 6 nm) did not increase measurably by ellipsometry, and angle-resolved XPS showed that the Ti:Si ratio, which was about 0.3 before the “dip,” increased to about 0.55. AFM showed that the TiO₂ layers before and after such treatment remained conformal with the substrate, and roughness of the TiO₂ layer remained essentially constant (Figure 4).

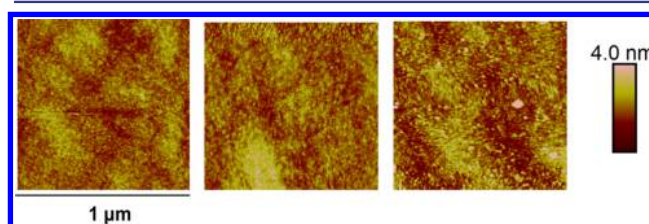


Figure 4. AFM sections ($1 \mu\text{m} \times 1 \mu\text{m}$) of **2** (left [0.43 nm]), **4** (center [0.39 nm]), and **4** treated with Ti tetra(*tert*-butoxide) (right [0.62 nm]); rms roughness is shown for each in square brackets, [].

We have shown that a TiO₂/Si interface that comprises Si–O–Ti bonding is of high electronic quality and can be prepared at surprisingly low temperatures compared to the standards of classical silicon technology. This interface has an extremely low density of electronically active defects, as shown by our measurements of effective lifetimes of holes, which makes it comparable to the highest quality SiO₂/Si interfaces that are typically prepared at high temperatures for use in integrated circuits or high efficiency solar cells. Given the ease and scalability of our synthetic route and the quality of the interface we prepare, our surface chemistry has the potential to enable fundamentally new, efficient silicon solar cell devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b09750.

Five sets of XPS data (PDF)

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Notes

The authors declare no competing financial interest.

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