Spatially-Modulated Silicon Interface Energetics Via Hydrogen Plasma-Assisted Atomic Layer Deposition of Ultrathin Alumina

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1. Introduction

Atomic layer deposition (ALD) is a key technique for the continued scaling of semiconductor devices, which increasingly relies on scalable processes for interface manipulation of structured surfaces on the atomic level. While ALD allows the synthesis of conformal films with utmost control over the thickness, atomically-defined closed coatings and surface modifications are challenging to achieve because of 3D growth during nucleation. Here, a route is presented toward the sub-nanometer thin and continuous aluminum oxide (AlOx) coatings on silicon substrates for the spatial control of the surface charge density and interface energetics. Trimethylaluminum in combination with remote hydrogen plasma is used instead of a gas-phase oxidant for the transformation of silicon dioxide (SiO2) into alumina. Depending on the number of ALD cycles, the SiO2 can be partially or fully transformed, which is exploited to deposit ultrathin AlOx layers in selected regions defined by lithographic patterning. The resulting patterned surfaces are characterized by lateral AlOx/SiO2 interfaces possessing 0.3 nm step heights and surface potential steps exceeding 0.4 V. In addition, the introduction of fixed negative charges of 9 × 10¹² cm⁻² enables modulation of the surface band bending, which is relevant to the field-effect passivation of silicon and low-impedance charge transfer across contact interfaces.
high fixed negative charge density ($10^{12} \sim 10^{13} \text{ cm}^{-2}$), which repels electrons from the surface and suppresses surface recombination via the field-effect, thereby improving the efficiency of Si solar cells.\cite{2a,6,7} Recently, ultrathin AlO$_x$ has also been implemented as an interlayer for hole-selective tunnel contacts to $p$-doped Si, which has been shown to further improve the performance of Si solar cells.\cite{3c,8}

Chemical bonding directly at the SiO$_2$/AlO$_x$ interface predominantly governs the negative charge and interface state density, whereas the bond coordination within the dielectric film remains unchanged away from the interface.\cite{6,9} As a consequence, relatively thin ALD AlO$_x$ layers (several monolayers) can be used for field-effect passivation of $p$-doped Si, with such thin films exhibiting a similar impact as much thicker AlO$_x$ films.\cite{2b,8c,10} However, sub-nanometer thin and conformal ALD coatings are challenging to achieve due to precursor steric effects and non-uniform distributions of available binding sites on the sample surface, which lead to 3D island growth during the nucleation regime.\cite{2b} Therefore, significantly lower fixed negative charge is introduced at the Si/SiO$_2$/AlO$_x$ interface for few-cycle ALD processes\cite{8c} since the deposited AlO$_x$ films tend to be discontinuous.\cite{10s} Beyond field effect passivation, the challenge of creating sub-nanometer thin and continuous ALD layers limits the ability to engineer semiconductor interfaces at this length scale, which is of critical importance for future device downscaling and low-impedance tunnel contacts.

In this work, we demonstrate an alternative approach to engineer Si surface energetics via ALD of ultrathin and conformal AlO$_x$ coatings formed during cyclic exposure to remote hydrogen (H$_2$) plasma and trimethylaluminum (TMA). Importantly, by using H$_2$ plasma instead of a gas-phase oxidant during ALD, AlO$_x$ formation is governed by the solid-state chemical reduction of the underlying SiO$_2$, resulting in an interconversion of the terminal oxide from SiO$_2$ to AlO$_x$. Here, in situ spectroscopic ellipsometry (SE) and quadrupole mass spectrometry (QMS) were used to elucidate the dominant growth mechanisms in both the few cycle limit and after extended ALD cycles, while X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and surface photovoltage (SPV) measurements were used to characterize the AlO$_x$-terminated Si substrates. With the insights gained from in situ techniques, we demonstrate control of the AlO$_x$ thickness on a sub-nanometer level, resulting in significant modulation of the surface band bending (SBB) through the introduction of fixed negative charge relevant to the field-effect passivation of Si. Moreover, the presented TMA/H$_2$ process can be performed at temperatures below 100 °C and, thus, is compatible with lithographic patterning. Taking advantage of this feature, we demonstrate smooth charge density patterns via spatially selective exposure of Si/SiO$_2$ surfaces to successive cycles of TMA/H$_2$ plasma. The resulting patterned surfaces are characterized by lateral AlO$_x$/SiO$_2$ interfaces possessing step heights as small as 0.3 nm, surface potential steps in excess of 0.4 V, and in-plane electric field strengths of $\approx 3 \times 10^5 \text{ V cm}^{-1}$. The ability to realize smooth dielectric and charge density patterns by low-temperature (LT) ALD in combination with lithographic techniques, provides an intriguing possibility for creating carrier-selective contacts in Si solar cells and local gate structures in advanced transistors, as well as for spatially-defined surface functionalization\cite{11} of relevance for area-selective deposition\cite{12} and chemical sensing.\cite{13}

### 2. Results and Discussion

For the case of native oxide-terminated III-V semiconductors, the application of TMA or of TMA/H$_2$ plasma cycles prior to deposition of dielectric coatings has been demonstrated to reduce the density of interface states.\cite{14} These so-called oxide clean-up processes rely on ligand exchange between the metalorganic precursor and the oxidic surface, which is promoted by the strong electropositivity of TMA. However, to the best of our knowledge, analogous processes have not been investigated for the case of oxide-terminated Si, despite its prominent importance in semiconductor technology.

To gain mechanistic insights into the growth of AlO$_x$ on Si via successive exposure to TMA and remote H$_2$ plasma without the use of a gas-phase oxygen source, we tracked the ALD film thickness and reaction products in real-time by in situ SE and QMS, respectively, and assessed the surface chemical composition by XPS. The evolution of the AlO$_x$ growth, derived from SE (Figure 1a), reveals a steep decrease in the growth-per-cycle (GPC) during the initial $\approx$10 cycles (at 200 °C), followed by a relatively slow decay of the growth rate during subsequent cycles. The decay in the growth rate throughout the deposition is well approximated with a bi-exponential function, suggesting two concurrent processes with distinct reaction rates. As such, we distinguish two AlO$_x$ growth regimes (denoted as (i) and (ii) in Figure 1a), in which different surface chemical reactions dominate. The rapid decrease of the GPC during the initial cycles within regime (i) is consistent with a substrate-enhanced mechanism, and the consumption of the available binding sites (i.e., Si-O-H and Si-O groups) on the native SiO$_2$ terminated Si substrate,\cite{15} while the formation of AlO$_x$ during growth regime (ii) is governed by diffusion-limited mass transport of oxygen from the underlying solid, as discussed in detail below.

Before film deposition, the Si substrate surface was cleaned in the growth chamber with a low-intensity remote H$_2$ plasma treatment (Figure 1b; Figure S1, Supporting Information), resulting in a more hydrophilic (hydroxylated) surface (Table S1, Supporting Information).\cite{16} Subsequent exposure to TMA is known to lead to self-limiting adsorption of TMA according to the following reaction:\cite{17}

$$\text{Si} - \text{OH} + \text{Al(CH}_3)_3 \rightarrow \text{Si} - \text{O} - \text{Al(CH}_3)_2 + \text{CH}_4$$

(1)

Reaction 1 is one of several possible chemical routes for the adsorption of TMA on a hydroxylated surface.\cite{17} For the case of traditional AlO$_x$ ALD processes, subsequent exposure of $\text{Si-O-Al(CH}_3)_2$ to H$_2$O leads to the regeneration of a hydroxyl-terminated surface in the form of $\text{Si-OH}$, onto which TMA can bind in a subsequent half cycle.\cite{17} However, in the present work, the surface is exposed to a remote H$_2$ plasma rather than a gas phase oxidant. Nevertheless, in situ QMS (Figure 1c) indicates the evolution of CH$_4$, consistent with the following proposed sequential reaction within growth regime (i):\cite{18}

$$\text{Si} - \text{O} - \text{Al(CH}_3)_2 + 4\text{H}_2 \rightarrow \text{Si} - \text{O} - \text{AlH}_2 + 2\text{CH}_4$$

(2)
Despite the lack of reactive gas species, in situ SE reveals an increase of film thickness with cycle number (Figure S1, Supporting Information). Although the apparent alumina growth rate is larger for the Ar plasma process than for H₂ plasma process, subsequent O₂ plasma exposure (Figure S1, Supporting Information) leads to a significant reduction of the film thickness for the TMA/Ar plasma process. Moreover, in situ QMS reveals a threefold reduction in the amount of methane (CH₄) released during the plasma step of the TMA/Ar process in comparison to the TMA/H₂ process (Figure S2, Supporting Information). These findings suggest that the TMA/Ar plasma process results in significant carbon incorporation due to physical decomposition of adsorbed TMA, with subsequent O₂ plasma exposure leading to volatilization of carbon impurities. In contrast, no such decrease in film thickness upon O₂ plasma exposure was observed for the AlOₓ film grown by the TMA/H₂ process (Figure S1, Supporting Information), indicating formation of AlOₓ with minimal carbon impurities, as confirmed by XPS (Figure S3a, Supporting Information). Thus, we conclude that Reaction 2 is a critical step for ligand removal during ALD alumina growth in the absence of a gas-phase oxidant.

XPS provides additional insight into the nature of deposited AlOₓ films, as well as their mechanism of formation. Prior to ALD, the surface of the Si substrate is terminated by a native SiO₂ layer (Figure 2a). In addition to the dominant silicon oxide component at a binding energy (BE) of ≈103.3 eV, which is characteristic of SiO₂ (Si⁴⁺), additional spectral contributions at lower BEs indicate the presence of sub-stoichiometric SiOₓ, which has previously been associated with the Si/SiO₂ interface.[19] The XPS derived thickness of the SiO₂ layer (≈1.7 nm) agrees with the result obtained by SE (Table S1, Supporting Information), and was calculated with the model proposed by Hill et al.[20] using the integrated intensities of the silicon oxide components, Iox, and silicon component, Isi, of the Si 2p core level spectrum (Figure 2a; Figure S3, Supporting Information). Following 20 cycles of TMA and remote H₂ plasma, the intensity ratio, Iox/Isi, decreased (Figure 2b), indicating a partial reduction of the surface SiO₂, which is consistent with the thermodynamically favored solid-state redox reaction of TMA with SiO₂ (ΔG = −235 kcal mol⁻¹ at 300 °C).[21] Indeed, the calculated SiO₂ layer thickness decreased by ≈0.9 nm after the TMA/H₂O process. In contrast, application of conventional ALD of AlOₓ with TMA and H₂O at 200 °C reveals an increase of the SiO₂ thickness of ≈0.1 nm (Figure 2c; Table S1, Supporting Information). This result confirms the fundamentally different mechanism of AlOₓ growth using H₂ plasma compared to a gas phase oxidant (H₂O₂). In the former case, oxygen is supplied from the underlying SiO₂, resulting in its partial reduction.

In addition to the changing ratios of oxidized and elemental Si, the overall photoemission intensity from the Si 2p spectral region decreased following 20 TMA/H₂ plasma cycles due to attenuation by the overlayer (Figure S4, Supporting Information). Concomitantly, an additional O 1s component appeared (Figure S3b, Supporting Information) together with an Al 2p component at the characteristic BE of ≈75.5 eV for Al-O[22] (Figure 2b, inset). The resulting spectra are similar to those obtained from the conventional thermal TMA/H₂O process, thus confirming the formation of alumina on Si after the
TMA/H$_2$ plasma process. Here, we note that the sample was transferred from the ALD system to the XPS chamber through ambient air, which resulted in the oxidation of initially generated *Si-O-AlH$_2$ or *Si-O-Al(CH$_3$)$_2$H sites. Notably, the presence of AlO$_x$ alters the surface chemistry of Si, resulting in a more hydrophilic surface, as indicated by the decrease in the static water contact angle from 64° for the bare Si substrate to 25° for the TMA/H$_2$ plasma-treated Si (Table S1, Supporting Information). In this way, the oxide conversion process can be exploited for subsequent (area-selective) chemical functionalization of the AlO$_x$-terminated surface, as recently reported by our group.[14e,23]

We next turn our attention to growth regime (ii) (Figure 1a), during which film deposition proceeded at a slow but nearly constant rate ($\approx$0.05 Å/cycle), despite the absence of a gas-phase oxygen source. Importantly, X-ray photoelectron spectra from samples exposed to 100 cycles of the TMA/H$_2$ plasma process, which is well within regime (ii), indicate that the native SiO$_2$ layer on Si was fully reduced to elemental Si, leaving a Si substrate coated with AlO$_x$ (Figure 2d). We note that other constituents, such as AlSi$_x$O$_y$, may be present,[29] but were not detectable with the XPS system used in this study. Such complete transformation of the $\approx$17 Å thick SiO$_2$ layer (Figure 1a), composed of several monolayers, implies the solid-state transport of atomic or molecular oxygen through the SiO$_2$ and AlO$_x$ layers to the surface during the AlO$_x$ growth process. This is confirmed by XPS analysis of a quartz substrate after TMA and H$_2$ plasma treatment, which reveals the presence of Si$^0$ (Figure S5, Supporting Information) and thus confirms the complete reduction of SiO$_2$ to elemental Si. The activation energy for the diffusion of molecular oxygen through SiO$_2$ has been predicted by density functional theory to be 0.3 eV,[24] which is lower than the reported activation energy of aluminum diffusion in amorphous SiO$_2$ of 0.73 eV.[25] Although the thermal energy at the growth temperature of 200 °C ($k_BT = 0.041$ eV) is significantly below the diffusion activation energies of both elements, it is far more likely for oxygen than for Al to diffuse within SiO$_2$.

In addition to the above considerations, a small shoulder indicative of aluminum carbide (AlC$_x$)[26] appears at low binding energies of the Al 2p core level region following 100 cycles of TMA/H$_2$ plasma (Figure 2d, inset). Based on these observations, we infer that oxygen extraction is facilitated by a strongly oxidizing surface layer (adsorbed TMA), and that complete depletion of the solid-state oxygen source after extended cycling leads to increased carbon contamination in the form of AlC$_x$ due to the absence of an external oxidant. Thus, from the combined insights gained by QMS, SE, and XPS, we conclude that hydrogen plasma and TMA chemically react with the oxidized Si surface until there is a saturation of bindings sites (regime (ii)) and subsequently until complete depletion of the oxygen (regime (iii)) from the native silicon oxide layer, thereby transforming the SiO$_2$ into Si capped with AlO$_x$.
While the surface oxide is reduced for the TMA/H₂ plasma process, it is oxidized for standard ALD AlOₓ processes using water (H₂O) or oxygen plasma, [10b,27] the latter of which generates defects and introduces detrimental interface states in Si. [28] Moreover, for LT ALD processes involving water as the oxidant source, condensation hampers self-limiting deposition and can reduce the film quality. Owing to the high vapor pressure and reactivity of TMA, as well as the self-limiting nature of the reactions of TMA and hydrogen radicals with the sample surface (Reaction 1 and 2), the ALD process can be performed at temperatures below 100 °C and is thus compatible with lithographic processing. Here, we exploited this feature to create dielectric micropatterns comprising distinct regions terminated with SiO₂ and AlOₓ.

Scanning electron microscopy (SEM) and scanning photoelectron microscopy (SPEM) depict the AlOₓ pattern on a Si substrate (Figure 3). The SEM image (Figure 3a) shows a strong contrast between the two materials, AlOₓ and SiO₂, and confirms lithographic pattern fidelity after the lift-off process. Such a strong contrast in the SEM image, despite a sub-nanometer step height, can be explained with Dionne’s model that predicts a larger secondary electron yield for ALD alumina than for SiO₂ (and Si) because of the higher material density, as well as the lower conductivity and electron affinity, of the former. [29] From the elemental map of the Al 2p region obtained by SPEM (Figure 3b), it is evident that alumina is deposited in spatially selected regions as no alumina signal (Al 2p) was detected within the Si/SiO₂ region.

To assess the uniformity and thickness of the AlOₓ coating on a nanometer-scale, we characterized the surface morphology and potential landscape of the AlOₓ patterns by AFM and Kelvin probe force microscopy (KPFM), respectively (Figure 4). Both the topography and the simultaneously acquired contact potential difference (CPD) maps are uniform within each region, demonstrating a continuous AlOₓ coating. The profile extracted from the AFM topograph (Figure 4c, top) shows a height difference between the uncoated and AlOₓ-covered Si region of only 2.9 ± 0.3 Å, which is thinner than previously demonstrated for conformal ALD AlOₓ coatings on Si. Notably, both surfaces are smooth, exhibiting a root mean square (rms) roughness (Rₓ) of 0.18 nm (Figure 4a,c). The fact that the surface remains

Figure 3. a) Secondary electron SEM image of an AlOₓ pattern on Si substrate following 20 cycles of TMA and H₂ plasma at 70 °C. The bright regions correspond to AlOₓ-terminated surfaces. The scale bar corresponds to 8 µm length. An electron acceleration voltage of 2.0 kV was used. b) Synchrotron-based SPEM map of the Al 2p core level. Each pixel (150 × 150 nm²) represents a spectrum in the Al 2p core level spectral range of BEs from 79 – 73 eV. The sample was excited with photons of 638 eV energy. The photoelectron core level spectra (bottom) were retrieved from the marked square regions in the SPEM image. We note that the spectrum is shifted towards higher BE due to differential charging of the insulating AlOₓ layer.

Figure 4. a) Intermittent contact mode AFM topography and b) frequency modulation KPFM image of the AlOₓ pattern on p-doped Si substrate. c) Topography and CPD profiles were taken along the lines, as indicated in the images of (a) and (b). While a step height of less than 3 Å exists across the lateral interface between AlOₓ and SiO₂ terminal surfaces, a surface potential step of 0.42 V arises due to fixed charge introduced by the TMA/H₂ ALD process (10 cycles).
smooth after the TMA/H₂ plasma process is an essential criterion for its implementation in Si semiconductor technology.

Importantly, application of the TMA/H₂ plasma process for the formation of a sub-nanometer thin AlOₓ coating on Si substantially reduces its work function, as determined by KPFM. As such, this process provides opportunities to tune the energy band alignment at the Si interfaces, as discussed below. In particular, a similar decrease in the CPD of 0.4 V was measured for both p- and n-doped Si substrates following deposition of the AlOₓ layer of different thicknesses (Figure 4; Figure S6, Supporting Information) and can be explained by the formation of a microscopic surface dipole, whose negative charges at the SiO₂/AlOₓ interface⁶ are compensated by the positive charges from the AlOₓ-terminated surface in ambient. Thus, a microscopic dipole layer with its positive pole pointing outward leads to a decrease in the effective electron affinity, and the observed reduction of the CPD and work function of the AlOₓ coated Si. Moreover, the potential profile across the patterned region reveals an abrupt potential step of ≈0.42 V, yielding an electric field of ≈3 × 10⁴ V cm⁻¹ at the lateral interface between bare and AlOₓ-coated p-doped Si (Figure 4c, bottom), whose magnitude is determined by the photolithography process and is experimentally underestimated due to the finite tip radius of the platinum-iridium-coated Si tip of about 30 nm. Notably, the CPD is maintained over several months in ambient air as the same potential step has been repeatedly measured throughout this time.

The observed reduction of the work function after alumina deposition on Si and the introduction of negative fixed charges is consistent with prior investigations of conventional ALD using TMA and H₂O, which has shown that AlOₓ deposited on Si introduces negative fixed charge that is beneficial for the field-effect passivation of p-doped Si.⁷ Therefore, we investigated how the ultrathin AlOₓ coatings, synthesized via the TMA/H₂ process, affect the SBB of moderately doped Si substrates of relevance for Si photovoltaics. SPV measurements were conducted using a Kelvin probe that was coupled to a light source for above band gap illumination using an 880 nm light emitting diode. As shown in Figure 5a, these measurements reveal a significant increase (decrease) of the SBB of a moderately n-doped (p-doped) Si substrate after 20 cycles of the TMA/H₂ process. These observations confirm the presence of considerable negative charge density introduced by the AlOₓ. For the case of p-type material, holes are attracted to the surface by the fixed negative oxide charge, resulting in an accumulation layer and the complete elimination of a SPV (Figure 5b).

Thus, ultrathin AlOₓ formed by the TMA/H₂ process can be used for field-effect passivation of p-doped Si. In contrast, the fixed negative oxide charge repels electrons within n-type material, resulting in a significantly larger SBB (Figure 5b), which increased by 340 mV. Applying Poisson’s equation and Gauss’ theorem for the 1D model of n-type Si shown in Figure 5b with the measured SBB (Figure S5, Supporting Information), yields an increase in the fixed negative charge density at the AlOₓ/SiO₂ interface of Qₓ = 9 × 10¹² cm⁻². We note that a similar increase of the SPV and SBB (350 mV) is achieved for n-type Si coated with a 1 nm thick AlOₓ layer deposited with the TMA/H₂O process (Figure S7, Supporting Information). This finding suggests that remote H₂ plasma exposure (and reduction of the SiO₂ layer) during the TMA/H₂ process does not introduce additional electronic defects and that the negative fixed charges are indeed introduced at the SiO₂/AlOₓ interface, in agreement with prior work.⁷ Nanometer-thin alumina films, deposited by TMA and water, provide similar field effect passivation as the ones created with the TMA/H₂ process. However, the comparably thicker layers obtained with the TMA/H₂O process impede interfacial charge carrier transport⁶ and would lead to larger lateral step heights when patterned.

3. Conclusion

In summary, we presented an ALD process based on TMA and remote hydrogen plasma to convert the native oxide on Si into alumina. This gas-phase process is scalable and omits wet-chemical treatments, thus providing a simple path to interface...
engineering in Si electronics. In particular, the sub-nanometer thin continuous AlOx coatings on silicon were demonstrated for field-effect passivation, and can be potentially utilized for carrier-selective transport across contact interfaces. Furthermore, the selective deposition in lithographically defined areas at low temperatures allowed us to locally modify the dielectric environment and surface chemistry of Si substrates. The presented gas-phase processing concept provides new opportunities for engineered interfaces of relevance for surface functionalization of (bio)chemical sensors, control of charge carrier transport and field-effect passivation at Si interfaces, and defining gate structures for local control of charge carriers via field-effect. In addition, the ultrathin AlOx coating can be potentially used as a buffer layer to relax lattice matching constraints in the synthesis of semiconductor heterostructures, as previously shown for gallium nitride.[31]

4. Experimental Section

Silicon Substrates: Moderately n-doped (As) and p-doped (B) Si substrates (Siegent Wafer, Germany) with a <100> crystal orientation and a resistivity of ≈6 Ω cm were used for this study. The frontside surfaces were chemo-mechanically polished by the manufacturer, and were terminated with a 1–2 nm thick native oxide layer. The thicknesses of the oxide layers were determined by SE and XPS.

Ohmic contacts were applied to the backsides of the Si wafers by metal evaporation and annealing. Immediately prior to mounting samples in the evaporator, Si backside surfaces were etched in 5% HF at 200 °C for 5 min in a rapid thermal annealer. For p-type Si, 100 nm of Au was evaporated onto the backside of the wafer before annealing in vacuum (≈10−6 mbar) at 500 °C for 5 min in a rapid thermal annealer. For n-type Si, 100 nm of a Au95Si5 alloy was evaporated and annealed under the same conditions, resulting in the formation of a AuSi eutectic. Following Ohmic contact formation, 10 nm Ti and 100 nm Au were evaporated onto the backside surface to provide a homogeneous and conductive interface. Highly n-doped (As) and p-doped (B) Si substrates (Siegent Wafer, Germany) with a <100> crystal orientation and a resistivity of ≈0.005 Ω cm were used for KPFM.

Optical Lithography: Lithographic lift-off processing was combined with LT plasma-assisted ALD to define a micropattern of AlOx on the substrates (Siegert Wafer, Germany) with a <100> crystal orientation and a resistivity of ≈6 Ω cm were used for KPFM. The thicknesses of the oxide layers were determined by SE and XPS.

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Optical Lithography: Lithographic lift-off processing was combined with LT plasma-assisted ALD to define a micropattern of AlOx on the frontsides of Si substrates. A resist double layer consisting of polydimethyl glutarimide (PMGI SF3, Microchem) and mA-1205 (micro resist technology) was patterned with a maskless aligner (Heidelberg, Microchem). Lift-off was performed by ultrasonication in n-methyl-2-pyrrolidone (micro resist technology). Lift-off was performed by ultrasonication (10 min, 40 °C) in n-methyl-2-pyrrolidone (micro resist technology).

Atomic Layer Deposition: Plasma-assisted ALD was carried out in a hot-wall reactor (Fiji G2, Veeco) at either 200 or 70 °C) in n-methyl-2-pyrrolidone (micro resist technology). Atomic Layer Deposition: Plasma-assisted ALD was carried out in a hot-wall reactor (Fiji G2, Veeco) at either 200 or 70 °C) in n-methyl-2-pyrrolidone (micro resist technology).

X-ray Photoelectron Spectroscopy: XPS spectra were acquired in the hybrid lens mode at a pass energy (PE) of 10 eV, and a take-off angle of 0° with a Kratos Axis Supra setup equipped with a monochromatic Al Kα X-ray source (photon energy = 1486.7 eV) operated with an emission current of 15 mA. The beam area was set to ≈2 × 1 mm² using the slot collimation mode. The BE was calibrated with respect to the Auger peak positions of Au, Cu, and Ag standard samples. The surface energies of the Al 2p (131.51 eV), Cu 2p (540.73 eV), and Ag 2p (406.71 eV) core levels were referenced with an accuracy of 25 meV to the known peak positions. Charge neutralization was not required, as no BE shifts indicative of (differential) charging were observed for the doped Si substrates. Each sample was measured at three different locations, and the extracted SiOx thicknesses were averaged to obtain a mean thickness and standard deviation for each sample (Table S1, Supporting Information).

Surface PhotoVoltage Measurements: SPV measurements were carried out in ambient air at room temperature using a commercial setup (KP Technology) in a closed faraday cage. The Si substrate was illuminated with a focused light-emitting diode with a wavelength of 880 nm (M340A, Thorlabs) and an intensity of ≈35 mWcm⁻². A piezoelectrically driven gold probe with a tip diameter of 50 μm and a work function of ≈4.9 eV was used as the measurement electrode. The time resolution of the CPD measurements was 1.0 s.

Scanning Electron Microscopy: Sputter-deposited SPEM measurements were performed at the SEM microscope beamline at the Elettra synchrotron (Trieste, Italy). Technical details of the SPEM setup were described in a previous report.[32] In brief, the X-ray photoelectron energy was set to 638 eV with a (Gaussian) X-ray focal radius of ≈150 nm and PE of 20 eV, resulting in an instrumental broadening of 0.35 eV determined by the Au 4f core level emission from an internal gold standard. Maps were acquired by using a multichannel delay line detector, allowing the acquisition of a spectrum in snap-shot mode at every pixel of the map. The X-ray energy was set to 638 eV with a (Gaussian) X-ray focal radius of ≈150 nm and PE of 20 eV, resulting in an instrumental broadening of 0.35 eV determined by the Au 4f core level emission from an internal gold standard. Maps were acquired by using a multichannel delay line detector, allowing the acquisition of a spectrum in snap-shot mode at every pixel of the map. The X-ray energy was set to 638 eV with a (Gaussian) X-ray focal radius of ≈150 nm and PE of 20 eV, resulting in an instrumental broadening of 0.35 eV determined by the Au 4f core level emission from an internal gold standard. Maps were acquired by using a multichannel delay line detector, allowing the acquisition of a spectrum in snap-shot mode at every pixel of the map. The X-ray energy was set to 638 eV with a (Gaussian) X-ray focal radius of ≈150 nm and PE of 20 eV, resulting in an instrumental broadening of 0.35 eV determined by the Au 4f core level emission from an internal gold standard. Maps were acquired by using a multichannel delay line detector, allowing the acquisition of a spectrum in snap-shot mode at every pixel of the map.
Atomic Force Microscopy and Kelvin Probe Force Microscopy: AFM and KPFM measurements were carried out with a Bruker Multimode V microscope (Billerica, MA, USA) in ambient using platinum/rhodium (95/5) coated AFM probes (PPP EFM, NanoSensors) with a nominal tip radius of 20 nm, typical resonance frequency of 75 kHz and force constant of 2.8 N m⁻¹. Height images (12×12 μm²) were acquired at a scan rate of 0.3 Hz with 512 point sampling. High-resolution images were obtained with a 2×2 μm² scan with 512 point sampling using an uncoated Si tip with ~10 nm tip radius. The height and CPD profiles were obtained by averaging over 10 scan lines (each line probed with 512 sampling points) using the software Gwyddion (v. 2.55). The average step heights were determined from AFM measurements of two patterned Si substrates that were manufactured following the same process.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

All authors have given approval to the final version of the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aluminum oxide, atomic layer deposition, field-effect passivation, hydrogen plasma, silicon surface charge density

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