Sub-nanometer thin Conformal Aluminum Oxide Coating Created by Interconversion of SiO$_2$ via Hydrogen Plasma-assisted Atomic Layer Deposition

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ABSTRACT We present a route towards ultrathin and continuous aluminum oxide (AlO$_x$) coatings on silicon substrates for the spatial control of the charge density. X-ray photoelectron spectroscopy provides strong indication for the chemical reduction of SiO$_2$ and its transformation into AlO$_x$ following exposure to trimethylaluminum and hydrogen plasma. Tailoring the growth parameters of plasma-assisted atomic layer deposition allows to achieve partial conversion of SiO$_2$, resulting in ~0.4 nm thin continuous AlO$_x$ coatings that can be deposited at low-temperatures (70°C) in selected regions defined by lithographic patterning. We envision applications for local gating, carrier selective contacts in silicon solar cells and selective surface functionalization.

INTRODUCTION

Atomic layer deposition (ALD) of amorphous alumina (AlO$_x$) is widely applied in silicon (Si) technology, including for the dielectric and chemical passivation, carrier-selective charge transfer at the interfaces in Si solar cells, as a gate dielectric in non-planar field-effect transistors, as well as a diffusion barrier and protective coating. ALD AlO$_x$ introduces a high density of negative fixed charges in the range of $10^{12}$–$10^{13}$ cm$^{-2}$, which repel electrons from the silicon surface, suppressing surface recombination via field-effect and improving the efficiency of Si solar cells. More recently, ultrathin AlO$_x$ has been implemented as an interlayer for hole-selective tunnel contacts in p-doped Si further improving the performance of Si solar cells.

Notably, it has been demonstrated that several ALD AlO$_x$ monolayers have the same potential for field-effect passivation as thicker AlO$_x$ films on p-doped Si. Other related studies unveiled that the coordination and bonds at the SiO$_x$/AlO$_x$ interface predominantly govern interface state density and negative charges, whereas the coordination remains unchanged away from the interface. Thus, a sub-nanometer thin AlO$_x$ coating that introduces fixed charges and...
enhances charge carrier tunneling can further reduce impedance and improve carrier selectivity at p-doped Si contact interfaces. However, up to date, sub-nanometer thin and conformal ALD coatings are challenging to achieve due to steric effects and available binding sites, leading to three-dimensional island growth during the nucleation regime. In fact, it has been shown that a significantly lower negative fixed charge is introduced at the Si/SiO$_2$/AlO$_x$ interface for few cycle ALD processes because the synthesized AlO$_x$ films are likely discontinuous.

Here we applied plasma-assisted ALD for the growth of ~0.4 nm thin conformal coatings via oxide conversion, to define smooth dielectric environments for the control of the surface charge density. Thereby, the surface oxide on Si provides the oxygen atoms for the growth of AlO$_x$ following alternating exposure to trimethylaluminum (TMA) and remote hydrogen (H$_2$) plasma. By omitting the use of a gas-phase oxidant during ALD, we show that the SiO$_2$ layer thickness decreases, whereas it increases for standard ALD AlO$_x$ processes using H$_2$O and oxygen-plasma, the latter of which generates defects and introduces detrimental interface states. Therefore, by applying the TMA/H$_2$ process, ultrathin (and high-quality) SiO$_2$/AlO$_x$ dielectric layers in the regime of electron tunneling are achieved. Moreover, the TMA/H$_2$ process is compatible with temperatures below 100 °C and thus with lift off processing. The demonstrated AlO$_x$ charge density micropatterns provide an intriguing possibility for carrier selective contacts in Si solar cells, selective surface functionalization and local gating.

RESULTS AND DISCUSSION

I. Native SiO$_2$ conversion to AlO$_x$ following exposure to H$_2$ plasma and trimethylaluminum. To gain mechanistic insights into the growth of AlO$_x$ on Si with TMA and remote H$_2$ plasma without the use of a gas-phase oxygen source, we tracked the ALD film
thickness in real-time by \textit{in situ} spectroscopic ellipsometry (SE) and assessed the chemical composition by X-ray photoelectron spectroscopy (XPS). The evolution of the AlO$_x$ growth, derived from SE (Fig. 1a), reveals a decrease in the growth rate after \textasciitilde 20 cycles (at 200 °C), indicating consumption of the available binding sites (\textit{i.e.}, Si-O-H and Si-O groups) on the moderately hydrophilic silicon surface covered by a \textasciitilde 16 Å thick native SiO$_2$ (Table S1). In this regard, the inflection point of the growth rate, which is derived from the thickness change, corresponds to the minimum number of cycles required to achieve a complete surface coverage. The different growth rates suggest distinct growth regimes (denoted as i and ii in Fig. 1a), in which different surface chemical reactions dominate. X-ray photoelectron spectra confirm the presence of a native SiO$_2$ layer on the silicon substrate prior to ALD (Fig. 1b). Following 5 cycles of TMA and H$_2$ plasma (100 W power), the component of the Si 2p core level spectrum at a binding energy (BE) of \textasciitilde 103 eV, attributed to SiO$_2$ (Si$^{4+}$), decreased in intensity while additional spectral features at relatively lower BEs (<103 eV) emerged, revealing the formation of a SiO$_x$ (x<2) sub-oxide on the substrate surface during the TMA/H$_2$ plasma process (Fig. 1b). We note that sub-stoichiometric transition layers are commonly present at Si/SiO$_2$ interfaces;\textsuperscript{17} however, we focus our analysis on changes in the SiO$_x$ sub-oxide species following ALD. Concomitantly, the overall intensity of the emitted photoelectrons from the Si 2p spectral region decreased, while simultaneously an aluminum (Al 2p) component at the characteristic BE of Al-O environment (\textasciitilde 75.5 eV) emerged (Fig. 1b, inset). Thus, XPS confirmed the formation of an alumina layer on Si substrate after the TMA/H$_2$ plasma process. In addition, the appearance of sub-stoichiometric SiO$_x$ after the ALD process indicates a reduction of the surface SiO$_2$. The concurrent appearance of sub-stoichiometric SiO$_x$ (Fig. 1b) and an alumina component (Al 2p) at a relatively low peak BE of \textasciitilde 75.0 eV following 5 cycles TMA/H$_2$ plasma (Fig. 1b, inset) suggest the formation of a mixed phase (\textit{i.e.},
Si-O-Al bonding), although the creation of oxygen-deficient SiOₓ with oxygen vacancies cannot be excluded from the XPS spectra. From the combined insights gained by SE and XPS, we infer that hydrogen plasma and TMA chemically react with the oxidized substrate surface until saturation of bindings sites (and depletion of surface oxygen), thereby partially transforming the native SiO₂ into AlOₓ, which is consistent with previously predicted redox reaction of TMA with SiO₂ based on thermodynamic considerations (ΔG = −235 kcal/mol at 300 °C). Notably, the ultrathin alumina coating that formed after several cycles substantially reduced the work function (Fig. S1) and altered the surface chemistry resulting in a more hydrophilic surface, as indicated by the reduction in the static water contact angle from initially 64° for the bare Si substrate to 25° for the TMA/H₂ plasma treated Si (Table S1). This can be exploited for subsequent chemical functionalization of the AlOₓ-terminated surface, as recently reported by our group. We next turn our attention to growth regime (ii) (Fig. 1a), in which film deposition proceeded at a constant rate despite the absence of an oxygen source. After 200 cycles of TMA and H₂ plasma, the native SiO₂ layer on Si is reduced to SiOₓ suboxides, leaving a surface coated with AlOₓ, and a top layer consisting of aluminum carbide (AlCₓ) (Fig. S2). We note that the formation of an AlSiₓOᵧ interfacial layer has been reported for the direct deposition of ALD AlOₓ on Si, albeit for annealed samples. In this study, we found no clear evidence for AlSiₓOᵧ.
**Figure 1.** (a) Evolution of the AlO$_x$ thickness, derived from *in situ* SE is shown for 100 cycles of consecutive exposure to TMA and H$_2$ plasma (100 W) and 200 °C. (b) AlO$_x$ created by TMA/H$_2$ plasma process on a Si substrate with native SiO$_2$. XPS shows that the ratio between elemental Si, denoted as Si(0), and SiO$_2$ (Si$^{4+}$) decreased already after 5 cycles of TMA and H$_2$ plasma. The spectra were recorded at a pass energy (PE) of 20 eV.

To increase the growth rate and deposit thicker films on Si substrates during growth regime (ii) (Fig. 1a), we used a higher plasma power (300 W) (Fig. 2). XPS analysis revealed the deposition of elemental aluminum (Figs. 2a and S3) after prolonged exposure to TMA/H$_2$ (200 cycles, 300 W plasma power), consistent with a previous report.$^{21}$ Concurrently, an aluminum carbide component at a BE characteristic of Al$_4$C$_3$ appears in the core level spectra of Al 2p (Fig. 2b) and C 1s (Fig. S4).$^{22}$
In addition, X-ray photoelectron spectra demonstrate that the native SiO$_2$ layer on Si was entirely reduced to elemental Si after 200 cycles of the TMA/H$_2$ plasma process at 300 W plasma power (Fig. 2b). Such complete transformation of the ~16 Å thick SiO$_2$ layer into AlO$_x$ (and potentially AlSi$_x$O$_y$), as well as the observed decrease in the XPS intensity ratio, I(Si 2p):I(Al 2p), of both elements (Fig. 1b) imply transport of oxygen through the SiO$_2$ film to the surface or interface. The activation energy for the diffusion of molecular oxygen through SiO$_2$ has been predicted by density function theory to be 0.3 eV,\textsuperscript{23} which is lower than the reported activation energy of aluminum diffusion in amorphous SiO$_2$ of 0.73 eV.\textsuperscript{24} Although the growth temperature of 200 °C (0.041 eV) is below the diffusion activation energies of both elements, it is far more likely for oxygen than for Al to diffuse within SiO$_2$. We hypothesize that the oxygen in the SiO$_2$ layer is extracted by the strongly reducing Al or AlC$_x$ surface layer that is likely formed following reduction of the surface oxides (SiO$_2$, AlSiO$_x$, AlO$_x$) by TMA and the reactive species (e.g., H$^+$) of the H$_2$ plasma. The gradient in the reduction potential facilitates the migration of oxygen to the surface, where it reacts to AlO$_x$. Cyclic exposure to TMA and remotely generated H$_2$ plasma perpetuates the repetitive surface layer reduction and oxidation. By increasing the plasma power, increases the fraction of ionized species reaching the sample surface and enhances the formation rate of the reduced surface layer, which can explain the relatively stronger reduction of SiO$_2$ and deposition of elemental Al (Fig. 2). According to the proposed growth model, the extent of the “oxygen reservoir” of the substrate is expected to affect the growth behavior. Indeed, we observed a faster growth rate with a slower decay on a Si substrate coated with thermal SiO$_2$ (Fig. S5) than on a Si substrate with native SiO$_2$ (Fig. 1a).
Figure 2. XPS spectra of (a) the Al 2p and (b) Si 2p spectral regions of a Si substrate before and after treatment with 200 cycles of the TMA/H$_2$ plasma process at 300 W plasma power and 200 °C.

II. AlO$_x$ can be conformally deposited with sub-nanometer thickness and introduces negative charges at the SiO$_x$/AlO$_x$ interface. Owed to the high reactivity of both TMA and H$_2$ plasma, the ALD process is compatible with temperatures below 100 °C and thus with lithographic processing, which we exploited to create a micropattern (Fig. 3). Scanning electron microscopy (SEM) and scanning photoelectron microscopy (SPEM) depict the AlO$_x$ pattern on the doped Si substrate (Figs. 3 a,b).
Figure 3. (a) Secondary electron scanning electron microscopy image of an AlO$_x$ pattern on Si substrate following 20 cycles of TMA and H$_2$ plasma at 70 °C. (b) Synchrotron-based scanning photoelectron microscopy map of the Al 2p core level. Every pixel ($150 \times 150$ nm$^2$) represents a spectrum of the kinetic energy in the range from 559 – 565 eV corresponding to a 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 determined the AlO$_x$ thickness and the surface potential on both surfaces from the atomic force microscopy (AFM) and Kelvin probe force microscopy maps of the AlO$_x$ pattern on the Si substrate (Fig. 4). Both the topography and the simultaneously acquired contact potential difference (CPD) maps are uniform within each region, demonstrating a continuous AlO$_x$ coating. The profile extracted from the AFM topograph (Fig. 4c, top) shows a height difference between the uncoated and AlO$_x$-covered Si region of $4 \pm 0.3$ Å, which is thinner than previously reported for conformal ALD AlO$_x$ coatings on Si. Notably, both surfaces are smooth exhibiting an rms roughness ($R_{\text{rms}}$) of 0.18 nm (determined from a $2 \times 2$ µm$^2$ scan, 512 points sampling, $\sim$10 nm tip radius of Si tip) (Fig. 4a, c). The fact that the surface remains smooth after the TMA/H$_2$ plasma process is an important criterion for its implementation in semiconductor technology processing. The potential profile across the patterned region reveals an abrupt potential step of $\sim$0.42 V,
yielding an electric field of ~3 V/µm at the lateral interface between bare and AlOₓ-coated p-doped Si (Fig. 4c, bottom) whose magnitude is determined by the photolithography process and experimentally underestimated due to the finite tip radius of the platinum-iridium-coated Si tip of about ~30 nm. Importantly, the surface potential difference is maintained over several months in ambient (Fig. S5).

The measured decrease in the CPD following deposition of the 0.4 nm thin AlOₓ layer can be explained with the formation of a microscopic surface dipole, whose negative charges at the SiO₂/AlOₓ interface⁶ are compensated by the positive charges from the AlOₓ coated surface (Q_{surface} = Q_{interface}). Thus, a microscopic dipole layer with its positive end pointing outwards leads to the observed decrease in the CPD and work function. For comparison, we also characterized n-doped Si and observed a similar potential step (i.e., ~ -0.4 V CPD decrease after the TMA/H₂ plasma process), indicating that the surface band bending of highly doped Si remains greatly unchanged after ALD. This observation is consistent with earlier reports revealing Fermi level pinning of doped Si by interface and surface states.²⁵ We conclude that the observed CPD decrease after formation of the ultrathin AlOₓ layer is mainly caused by charge redistributions in the surface oxide layers.
Figure 4. (a) Intermittent contact mode AFM topography and (b) frequency modulation KPFM image of the AlOₓ pattern on Si substrate. (c) Topography and CPD profiles were taken along the lines as indicated in the images of a and b.
CONCLUSION

In summary, we presented an ALD process based on TMA and remote hydrogen plasma for the realization of sub-nanometer thin continuous AlO\textsubscript{x} coatings on silicon. The conformal AlO\textsubscript{x} layer can be lithographically patterned to locally modify the dielectric environment and surface chemistry. We envision that the presented gas-phase processing concept finds application for the surface functionalization of (bio)chemical sensors, reduction of the contact resistance of hole-selective Si contacts, the field-effect passivation of Si and defining spatially controlled gates.

MATERIALS AND METHODS

**Si Substrate properties.** Highly \( n \)-doped (Arsenic) and \( p \)-doped (Boron) Si substrates (Siegert Wafer, Germany) with a \(<100>\) crystal orientation and a resistivity of \( \sim 0.005 \, \Omega \, \text{cm} \) were used. The surfaces were chemo-mechanically polished on one side by the manufacturer. Silicon substrates with a \( \sim 1.8 \, \text{nm} \) thick native silicon dioxide layer or with a 270 nm thick thermal SiO\textsubscript{2} were analyzed. The thicknesses of the oxide layers were determined by SE.

**Optical lithography.** Lithographic lift-off processing was combined with low-temperature plasma-assisted ALD to define a micropattern of AlO\textsubscript{x} on a Si substrate. A resist double layer consisting of poly-dimethyl glutarimide (PMGI SF3, Microchem) and ma-P 1205 (micro resist technology) was patterned with a maskless aligner (Heidelberg, MLA100) and developed in tetramethylammonium hydroxide (TMAH, micro resist technology). Lift-off was performed by ultrasonication (10 min, 40 °C) in n-methyl-2-pyrrolidone (NMP, micro resist technology).

**Atomic layer deposition.** Plasma-assisted ALD was carried out in a hot wall reactor (Fiji G2, Veeco) at either 200 °C or 70 °C using argon (99.9999 %, Linde) as the carrier and purge gas. A
~0.4 nm thick aluminum oxide film was formed on the Si substrate following 20 cycles of sequential exposure to TMA (Strem) and remote hydrogen plasma (100 W, 2 s) that was generated with a sapphire-based inductively coupled plasma source. The purge times in argon (110 sccm, 0.09 Torr) after every half-cycle were 15 s. Because the native SiO₂ layer of the silicon substrate served as the oxygen source the growth rate decreased exponentially.

We note that cleaning Si surfaces with hydrogen plasma (100 W, 20 sccm, 0.3 Torr) removes adventitious organic contamination and activates the surface. However, hydrogen ions generated from a remote plasma may also increase the number of interface states in Si(100).

**Spectroscopic ellipsometry.** We obtained the thickness of the SiO₂ layers and the ALD AlOₓ film by analyzing the ellipsometry spectra with established optical models for silicon and SiO₂ and by using a Cauchy model for the AlOₓ layer.

**X-ray photoelectron spectroscopy.** XPS measurements were performed with a custom-built system utilizing components from SPECS Surface Nano Analysis GmbH (Germany), a twin (Al and Mg) non-monochromatic X-ray tube anode, a PHOIBOS 100 concentric hemispherical analyzer, and a MCD-5 detector. Measurements were performed at a base pressure below 7×10⁻⁹ mbar. The Al X-ray source (Al Kα = 1486.6 eV) was operated at an emission current of 20 mA with a voltage of 12.5 kV. XPS spectra were recorded with a pass energy of 20 eV or 10 eV in normal emission (90° ± 2° relative to the surface) in medium area mode (circular electron collection area of 2 mm diameter). Measurement parameters are transmission optimized, resulting in an acceptance angle up to ± 7°. With these settings an instrumental resolution of 1.2 eV was determined by measuring the full width at half maximum (FWHM) of a gold (Au) 4f7/2 XPS spectrum recorded on a 100 nm Au layer evaporated on a Si(100) wafer die. The binding energy
of the hemispherical analyzer was calibrated with silver and gold standard samples. Thereby, the kinetic energies of the Ag 3d (1118.51 eV), Au 4f (1402.73 eV) and Cu 2p (554.07 eV) core levels were referenced to the known peak values. XPS spectra were recorded with SpecsLab (SPECS Surface Nano Analysis GmbH, ver. 2.85).

**Scanning photoelectron microscopy (SPEM).** Synchrotron-based SPEM measurements were performed at the ESCA microscopy beamline at the Elettra synchrotron (Trieste, Italy). Technical details of the SPEM setup is described elsewhere. The X-ray photon energy was set to 638 eV with a (Gaussian) X-ray focal radius of ~150 nm and a pass energy (PE) of 20 eV, resulting in an instrumental broadening of 0.35 eV determined by the Au 4f 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.
ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

Supporting static water contact angle measurements. Additional AFM and XPS data (PDF)

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Supporting Information

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S1. Static contact angle measurements of Si substrates

Static contact angle (SCA) measurements were performed with the contact angle system OCA 15Pro (DataPhysics Instruments GmbH, Baden-Wuerttemberg, Germany) on Silicon substrates under ambient conditions (27.3 °C, 32.7 % relative humidity). Data were acquired and evaluated with the basic module SCA 20 - contact angle (DataPhysics Instruments GmbH, Baden-Wuerttemberg, Germany, ver. 2.0). To estimate an average Young-LaPlace contact angle, 1 μl of deionized H₂O (18.2 MΩ·cm at 25 °C, Merck Millipore) was dispensed with a rate of 1 μl/s from a high-precision syringe (Hamilton, DS 500/GT, gas-tight, 500 µl) on the sample surface and after ~3 s (reaching equilibrium) the side profile of the droplet was taken for further processing. SCAs from at least three different spots were determined to calculate a standard deviation (Table S1).

Table S1. Static water contact angle measurement on Silicon substrates before and after treatment (20 cycles TMA and H₂ plasma) in a plasma-enhanced ALD reactor. The thickness of the native oxide layer was determined by spectroscopic ellipsometry (SE).

| substrate       | SiO₂ thickness by SE | process details         | water CA / ° |
|-----------------|----------------------|-------------------------|--------------|
| Si/SiO₂/AlOₓ    | /                    | 20 cycles TMA/H₂ plasma process | 24.7 ± 0.7   |
| Si/SiO₂         | 16 Å                 | Solvent-cleaned         | 64.0 ± 0.5   |
S2. Contact potential difference of Si substrates

Figure S1. The TMA/H$_2$ process leads to a decrease in the contact potential difference (CPD) of the $p$-Si substrate, presumably due to an increase in the density of negative fixed charges at the SiO$_2$/AlO$_x$ interface. The average CPD values were measured by Kevin probe force microscopy and extracted from averaging 2×2 µm$^2$ (512 points sampling) images.
S3. X-ray photoelectron spectroscopy measurements of Si substrates

**Figure S2.** Carbon 1s core level spectra of solvent-cleaned bare *p*-doped Si (top, black squares), and *p*-Si substrates after exposure to 5 cycles (middle, blue squares) and 200 cycles (bottom, red squares) of TMA and H$_2$ plasma.
To provide further support for the presence of elemental aluminum on the surface of the Si substrate after ALD, we measured the Al KL$_{2,3}$ L$_{2,3}$ Auger spectrum using a magnesium X-ray source (Mg K$_\alpha$ = 1253 eV) with the XPS system described in the methods section of the main manuscript. Two main spectral features can be identified in the Al KLL Auger spectrum at kinetic energies of ~1386 eV and ~1393 eV (Fig. S3) and are attributed to aluminum oxide and elemental aluminum, respectively.\(^1\) The peak energy separation of ~7 eV corresponds to reported binding energy separation between AlO$_x$ and Al on aluminum foil.\(^1\)

**Figure S3.** Corresponding Al KL$_{2,3}$ L$_{2,3}$ Auger spectrum of a Si substrate after TMA and hydrogen plasma treatment (200 cycles). The spectral feature at a kinetic energy of ~1393 eV and its separation from the dominant spectral feature at ~1386 eV indicate the presence of elemental aluminum.

**Figure S4.** XPS spectra of the C 1s core level of a Si substrate after treatment with 200 cycles of the TMA/H$_2$ plasma process at 300 W plasma power and at 200 °C.
S4. Spectroscopic ellipsometry of Si substrates

We considered a three-layer model structure to analyze the SE spectra of a AlO$_x$ film on a SiO$_2$-coated Si substrate. To obtain the thickness of the SiO$_2$ layer, we first characterized a Si/SiO$_2$ substrate without MoS$_2$ by SE. A temperature-dependent library model and the Sellmeier model were used to describe the optical properties of the silicon substrate and the SiO$_2$ layer, respectively.

**Figure S5.** Thickness of AlO$_x$ as a function of time plot obtained from *in-situ* SE on a *p*-doped Si substrate with a 270 nm thick thermal SiO$_2$ layer during 40 cycles of the TMA/H$_2$ plasma process at 200 °C and 100 W plasma power.

**REFERENCES**

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