Sputter Deposition of Transition Metal Oxides on Silicon: Evidencing the Role of Oxygen Bombardment for Fermi-Level Pinning

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Si/SiO₂ interfaces after hydrogen passivation.\(^{[22]}\) In addition, the addition of alumina on top of the silicon dioxide layer could help to further improve the performance of the device.\(^{[21–25]}\) We therefore studied TMO deposition on top of both hydrogen-passivated n-Si/SiO₂ and n-Si/SiO₂/Al₂O₃ substrates, using X-ray photoelectron spectroscopy (XPS). XPS provides simultaneous information on the chemical nature of the surfaces and of the electronic structure.\(^{[26]}\) It has the advantage that single interfaces can be studied, without the requirement of optimizing a device structure, in which many layers and patterns, e.g., for electrical characterization, are necessary.

Along with this article, we will see that during reactive sputtering of a TMO on silicon, the negatively charged oxygen ions deteriorate the interface. This is indicated by the formation of defect states in the SiO₂ layer, which induce a Fermi-level pinning and limit the band bending in the Si substrate. Defect formation and Fermi-level pinning can be avoided by growing the TMO sequentially using repeated sputtering and oxidation of a very thin metallic layer. We introduce this method as metal layer oxidation (MLO). We take as practical example, the deposition of p-type NiO on n-Si/SiO₂ and n-Si/SiO₂/Al₂O₃ substrates, as NiO could be implemented in numerous applications including silicon-based metal insulator semiconductor structures\(^{[27–30]}\) and photoelectrochemical water-splitting devices.\(^{[31]}\)

2. Results and Discussion

2.1. The Si 2p Spectra

The in situ XPS measurements of the Si 2p region display typically two emission structures, which can be associated to the silicon and the silicon dioxide layer, respectively. As seen in Figure 1, the elemental silicon peak is at lower binding energies. The peak is made of a double feature: a main peak Si₀ and a satellite peak, which are

![Figure 1. Typical XPS spectra of the Si 2p region. Two main features can be identified: the photoemission from the silicon dioxide layer on the surface (SiIV) and the photoemission from the elemental silicon substrate. The elemental silicon is composed of a main peak Si₀ and a satellite peak, which are associated to the spin-orbit split Si 2p₁/₂ and Si 2p₃/₂ components, respectively. The Si₀(meas) arrow indicates the Si₀ peak position.](image)

The evolution of the Ni 2p₁/₂ emission in dependence on NiO film thickness is shown in Figure 3. The spectra are recorded during NiO growth using the MLO process. The spectra of the thickest layer shows the typical features of NiO with a main emission line near 854 eV and a characteristic satellite emission at 1.5–2 eV higher binding energies.\(^{[27,28]}\) Identical spectra are obtained for magnetron-sputtered films. At lower film thickness, the spectra are broadened and have higher binding energies. Such a behavior is frequently observed in dependence on film thickness\(^{[28]}\) and can be associated to the change in the local structure of the NiO layer.\(^{[29]}\) The Si substrate intensity is attenuated exponentially in dependence on NiO film thickness, indicating a layer-by-layer growth and a conformal coverage of the NiO layer.

2.2. Chemical Interface Properties

As observed in Figure 2, after the deposition by sputtering of nickel in oxygen-free atmosphere and before oxidation, the XPS spectra of the Ni 2p region displays a sharp peak which can be associated to elemental nickel Ni₀, and after exposition of the metallic layer in an oxygen-rich atmosphere, the peak is broadened and shifted to higher binding energy as a result of the oxidation of nickel into nickel oxide. No obvious trace of metallic nickel is visible. This result indicates that the metallic nickel layer is totally converted into nickel oxide after oxidation and so that the MLO method is able to produce a metal oxide layer.

![Figure 2. XP spectra of the Ni 2p₁/₂ region before and after exposition of a metallic nickel layer to an oxygen-rich atmosphere. The thickness of the final nickel oxide layer is about 0.3 Å.](image)

Photoelectron spectra recorded during stepwise growth of NiO onto Si/SiO₂ are shown in Figure 4. Three different experiments with NiO grown by metal-layer-oxidation, reactive direct current (DC), reactive sputtering, and radio frequencies (RF) sputtering are compared. The spectra are normalized to the Si₀ intensity for better comparison.
The spectra in Figure 4 clearly show that a new emission arises between the $\text{Si}^0$ and the $\text{Si}^{IV}$ peaks when NiO is deposited by reactive DC or RF magnetron sputtering. According to the literature, such intermediate emissions, which are labeled as $\text{Si}^{\text{def}}$ in Figure 4, can be associated with the presence of noncompletely coordinated Si with intermediate oxidation states $\text{Si}^{\text{I-III}}$.\textsuperscript{[30–33]} Contrary to reactive sputtering, no $\text{Si}^{\text{def}}$ emission is observed if the NiO is grown by the MLO method. The results indicate that $\text{Si}^{\text{def}}$ only appears when oxygen is present during sputtering. This suggests that the $\text{Si}^{\text{def}}$ emission is related to the bombardment of the substrate with negatively charged oxygen species formed in the plasma during deposition. For the reactively sputtering NiO films, the $\text{Si}^{\text{def}}$ emissions increase with NiO film thickness, indicating that intensity is proportional to the exposure time of the surface to the plasma.

The maximum of the $\text{Si}^{\text{def}}$ emission occurs at 58% of the distance between the $\text{Si}^0$ and the $\text{Si}^{IV}$ peaks. Therefore, the $\text{Si}^{\text{def}}$ state might correspond to the Si in the oxidation state +III state, which has been reported to occur at 62% of the distance between the $\text{Si}^0$ and the $\text{Si}^{IV}$ peaks.\textsuperscript{[30]}

The $\text{Si}^{\text{def}}$ emissions may have a different origin: 1) they can result from an uncomplete reaction, after diffusion through the $\text{SiO}_2$ layer, of the incoming oxygen ions with the underneath silicon; 2) they could be related to surface etching of the silicon dioxide layer; or finally 3) they could be the fingerprint of the presence of interstitial oxygens in the the $\text{SiO}_2$ layer. The latter case (3) could eventually result in the formation of $\text{Si}^{\text{III}}$ states under X-ray irradiation.\textsuperscript{[34]}

Regarding case (1), it has to be mentioned that we also observed a comparable $\text{Si}^{\text{def}}$ emission next to the $\text{Si}^{IV}$ peak in the course of deposition of barium strontium titanate (BST: (BaSr)TiO$_3$ on thick $\text{SiO}_2$ by RF sputtering in an Ar:$\text{O}_2$ (99:1) atmosphere. In this case, the oxygen source could be the target itself. This result suggests that $\text{Si}^{\text{def}}$ state appears even when no metallic $\text{Si}^0$ is present in the substrate, indicating that the $\text{Si}^{\text{def}}$ state is not related to the reaction of the elemental silicon $\text{Si}^0$ with the incoming oxygen ions. Therefore, case (1) is rather unlikely.

Cases (2) and (3) can be differentiated by comparing the intensity of the oxide emission in comparison with the intensity of the elemental silicon $\text{Si}^0$. For case 2) (etching of $\text{SiO}_2$), a reduction of the $\text{SiO}_2$ thickness has to be expected. Therefore, the intensity of the elemental silicon should increase in comparison with the $\text{Si}^{IV}$ peak. On the contrary, at first sight, no substantial change of that intensity ratio is expected for case (3) (interstitial oxygen). To compare the relative area intensity, the ratio $R_A$ between the area of the oxide ($A_{\text{oxide}}$), which includes the $\text{Si}^{IV}$ and the $\text{Si}^{\text{def}}$ states, and the elemental silicon ($A_{\text{silicon}}$) is introduced

$$R_A = \frac{A_{\text{oxide}}}{A_{\text{silicon}}} \quad (1)$$

The evolution of the ratio $R_A$ with NiO thickness is displayed for the different deposition methods in Figure 5. The result...
clearly indicates that the ratio \( R_A \) increases with NiO thickness for both reactive sputtering methods. This trend discards etching of SiO\(_2\) as origin of the Si\(^{0}\) emission. This is consistent with the relatively high pressure used for the DC and RF sputtering, which favors thin-film deposition in the Keller–Simmon regime, where no etching of the surface is expected.\[^{16}\]

The data in Figure 5 also show that the ratio \( R_A \) does not significantly change when NiO is prepared by the MLO method, contrary to what can be obtained with reactive sputtering. This indicates that the MLO method preserves the Si/SiO\(_2\) interface integrity relatively well. Although a more complicated situation might also account for the Si\(^{0}\) states, our analysis suggests that these states are related to the presence of oxygen interstitial in the silicon dioxide layer (case 3). This proposition is supported by the work of Chen et al.,\[^{34}\] who showed using density functional theory calculations that oxygen interstitials in SiO\(_2\) are the origin of numerous defective structures, which can be stabilized along the oxygen bridging bonded (OBB) structure

\[
\equiv\text{Si} - \equiv \equiv \equiv - \equiv \text{Si} \tag{2}
\]

The OBB structure might convert into a peroxy radical (POR) structure where the bond between the silicon and the oxygen (Si–O) is broken when exposed to irradiation (e.g., X-rays).\[^{34}\]

In the POR structure, the silicon atom would be bonded by three covalent pairs only to the silicon dioxide structure. Therefore, the Si\(^{0}\) state observed in this work may be associated to a POR structure, which should exhibit a binding energy corresponding to Si\(^{III}\) in XPS.

### 2.3. Electronic Interface Properties

Interface experiments such as those shown in Figure 4 aim at determining the built-in voltage (\( V_{bi} \)) in the silicon substrate of the Si/SiO\(_2\)/NiO interface. However, the observed binding-energy shifts of the Si 2p emission do not necessarily correspond to the built-in voltage. The observed shift can be smaller, as a photovoltage \( U_{ph} \) can be induced by the electron–hole pairs generated by the X-ray irradiation.\[^{15}\]

The binding energy of the elemental Si relative to the calculated flat-band position (\( \Delta E_b(Si^0) \)) then corresponds to

\[
\Delta E_b(Si^0) = E_b(Si^0) - E_b(Si^0) = q(V_{bi} - U_{ph}) \tag{3}
\]

where \( q \) is the charge of the electron. Following the calculations described by Schafranek et al.,\[^{16}\] which describe measurements in the same setup, the photovoltage in silicon can be estimated for a built-in voltage \( V_{bi} \) varying from 0 to 0.9 V. In Figure 6, the relationship between the measured peak deviation \( \Delta E_b(Si^0) \) in dependence on built-in voltage is shown. It shows two different regimes: a linear dependence of \( \Delta E_b(Si^0) \) on \( V_{bi} \) for \( V_{bi}<0.6 \) V and a saturation regime where \( \Delta E_b(Si^0) \approx 0.62 \) eV for \( V_{bi}>0.6 \) V. The development of the photovoltage causes a saturation of the observable binding-energy shifts. Consequently, \( \Delta E_b(Si^0) \) measured by XPS is only directly correlated to the built-in voltage if the value is smaller than \( \approx 0.6 \) V. Larger built-in voltages can not be identified any more. Therefore, if the observed binding energy of the Si\(^{0}\) emission is 0.6 eV higher than that of the flat-band position, it can only be said that the built-in voltage is 0.6 V or higher.

The binding energies of the Si\(^{0}\) emission of hydrogen-passivated Si/SiO\(_2\) substrates are shown in dependence on NiO film thickness in Figure 7. After hydrogen passivation, the binding energy of the Si peak \( E_b(Si^0) \) is close to 99.6–99.7 eV (Figure 7). The flat-band position (\( E_b(Si^0) \)), where no charge accumulation (negative or positive) occurs at the silicon surface, is calculated to be 99.57 ± 0.05 eV when the bulk Fermi level and the binding energy of the Si\(^{0}\) emission with respect to the valence-band maximum are taken as 0.83 eV (see Section 2) and 98.74 eV,\[^{17}\] respectively. Therefore, the measurements suggest that passivated Si/SiO\(_2\) samples are slightly accumulating negative charges at the silicon surface (Figure 7). This would imply that not all trapped charges are suppressed after hydrogen passivation. However, the hydrogen passivation step was found to remove contaminants and to reduce substantially the accumulation of charges at the Si/SiO\(_2\) interface (see Supporting Information).
Information, Figure 1). The accumulation of negative charge after the hydrogen passivation step can arise because of the presence of positive trapped charges at the Si/SiO2 interface [38-40] or in the SiO2 layer. [41,42]

Figure 7 shows that the position of the Si0 peak shifts to lower binding energy for any deposition method, indicating that the deposition of NiO leads to the formation of a depletion layer in the silicon with a built-in voltage $V_{bi} > 0$. The binding energies at the interfaces with RF and DC sputtered NiO saturate at approximately 99.2 eV, corresponding to a built-in potential of 0.4 V. This value is in line with what has been reported in the literature. [11]

In contrast, the binding energies obtained when NiO is deposited by MLO at $T > 100 \degree$ C saturate at approximately 99.0 eV, which is 0.6 eV lower than the expected value for the flat-band condition. As discussed earlier (see Figure 6), it can then only be said that the built-in voltage $V_{bi}$ in the silicon is at least 0.6 eV.

The interface experiments highlight that larger Si0 peak deviation is attained with the MLO method if sufficient temperature is brought to the substrate during the oxidation step (Figure 7). A lower peak deviation, comparable with that for reductively sputtered NiO, is observed when NiO is deposited by MLO with the oxidation step being carried out at room temperature. This lower $V_{bi}$ could be due to an incomplete surface reaction of the metallic nickel with oxygen during the oxidation step or due the formation of a nonhomogeneous material. It is mentioned that $\Delta E_b(Si^0)$ is also approximately 0.6 eV, when a thin ALD Al2O3 layer is inserted between the silicon dioxide and the nickel oxide layer. This can be particularly interesting as it has been reported that tunneling SiO2/Al2O3 structures on top of silicon might provide better device performance. [23-25] In addition, it could be assumed that the alumina layer may be used as a diffusion-blocking layer to avoid degradation over time, by the reaction of hydrogen from the hydrogen-passivated SiO2 layer and the reduction of the NiO layer.

Finally, as depicted in Figure 8, the limited Si0 deviation when NiO is deposited by reactive sputtering could be associated to the presence of oxygen interstitials in the silicon dioxide layer, resulting from the intense bombardment of the surface by energetic ionized oxygen particles during deposition. In comparison with the results obtained by MLO, the defects produced during NiO deposition by reactive sputtering would pin the Fermi energy in a non-desired position. Therefore, to produce a high-quality interface of a TMO by sputtering on Si/SiO2 substrates, the results presented in this article would suggest that it is preferable to start from a metallic target, to sputter, without oxygen, a thin metallic layer (<1 nm), and to oxidize by exposing the metallic layer to oxygen without the plasma. For practical use, this method can be referred as MLO.

3. Conclusion

Along with this article, an alternative to reactive sputtering has been presented to interface thin TMO layers (<5 nm) with Si/SiO2. The deposition consisted of the growth of thin metallic (nickel) layers (<1 nm) in oxygen-free atmosphere followed by a subsequent oxidation step in oxygen without plasma, where the addition of thermal energy during the oxidation process might increase the TMO layer quality. Named MLO, the method has the advantage to avoid direct surface exposition to negative oxygen ion bombardment as for DC and RF reactive sputtering. Thus, the band deviation in silicon has been estimated to be at least 0.6 eV when passivated Si/SiO2 substrate is interfaced with nickel oxide by the MLO method. On the contrary, DC and RF reactive sputtering processes provide a more limited band-bending (≈0.4 eV). The results suggest that reactive sputtering pins the bands in an undesired position as a consequence of the intense bombardment by negative oxygen ions of the Si/SiO2 interface which might implant oxygen interstitial in the SiO2 layer.

4. Experimental Section

Base Substrate: Experiments were realized with n-type float-zone silicon single crystal (100) wafers with sheet resistivity 10.1 $\Omega$ cm determined by...
the van der Pauw method. The doping concentration was estimated to be \(4.4 \times 10^{14} \text{cm}^{-3}\), corresponding to bulk Fermi-level position of 0.834 eV above the valence-band maximum.

**Cleaning:** To ensure a clean surface free of any carbon or oxygen species, the samples were processed in a piranha (\(\text{H}_2\text{O}_2 : \text{H}_2\text{SO}_4 : 5:2\)) bath followed by a fluoridic acid (HF 2%) treatment. The samples were extensively rinsed with DI water between each bath and at the end. After the chemical bath, a hydrophobic silicon surface was obtained, which was a clue of an H-terminated oxide-free silicon surface.

**Silicon Dioxide Growth:** Immediately after the cleaning step, an \(\approx 2.3-2.5 \text{ nm amorphous silicon dioxide layer}\), compatible with electrical tunneling,[25] was thermally grown in a Koyo VP1000 furnace. After purging the chamber with nitrogen, the furnace temperature was cycled from 700 to 1000 °C in dry nitrogen atmosphere (99.9995% purity). It was believed that oxygen participating in the SiO\(_2\) growth process originated from oxygen desorption from the furnace wall during the thermal cycling.

**Hydrogen Cleaning and Surface Passivation:** A hydrogen plasma source (Tectra Gen2 Hybrid Atom/Ion Source) was used for both surface cleaning and passivation of the Si/SiO\(_2\) samples. Atomic hydrogen was obtained by cracking dihydrogen molecules in a plasma chamber set on atomic mode, for which the current was set to 30 mA and the gas pressure was set to 0.2 mbar. The hydrogen cleaning step was performed at \(\approx 250 \text{ °C}\) substrate temperature for 10 min. It allowed to remove efficiently the surface contaminants (hydrocarbons, water, etc.) originating from sample exposure to air during the transfer from the furnace to the vacuum system. Following reports in the literature,[10,14] an additional 45 min hydrogen plasma exposure was carried out at higher temperature (350 °C) for the hydrogen passivation step. To avoid possible hydrogen desorption from the sample, the plasma is maintained until the sample holder temperature reaches 150 °C.

**Alumina Deposition:** ALD-alumina was deposited by the alternative deposition and oxidation by water of TMA at 50 °C.[15] Low-temperature deposition was selected to avoid any SiO\(_2\) depassivation reaction. TMA and water pulses lasted for 80 and 150 ms, respectively, and were separated by an evacuation period of 3 min. The first pulse started with TMA. Overall, ten TMA pulses were realized. After the ALD deposition, another hydrogen cleaning and hydrogen passivation step were processed as previously described.

**Deposition of NIO:** The deposition of nickel oxide on the Si/SiO\(_2\) substrates had been realized by DC and RF reactive sputtering in 5% O\(_2\) and target-to-substrate distance of 13 cm. The pressure was set to 6 and 1 Pa for DC and RF sputtering, respectively. The MLO process had been realized in similar conditions except that a metallic nickel layer was DC sputtered in oxygen-free atmosphere, which was then followed by an in situ post oxidation step without plasma exposure. The oxidation of the metallic nickel in the growth chamber works relatively well for the thickness of less than 1 nm. The oxidation process was tested for gas pressures between 1 and 6 Pa using processing gases with 10% and 100% oxygen content and various temperatures from RT to 200 °C. All conditions provided a fully oxidized NiO layer as confirmed by XPS.

**In situ Analysis:** Interface analysis using XPS was realized in the DAISY-MAT (Darmstadt Integrated System for Materials Research) system in which the electron spectrometer (Physical Electronics PHI 5700) was connected to various vacuum chambers hosting the remote plasma source, the ALD system, and the sputter deposition.[24] Samples can be transferred to the different places without breaking the vacuum, which eliminates any surface contamination during the experiments.

**XPS Measurements:** All XPS measurements were realized with a 1486.6 eV Al Kx monochromatic X-ray and 45° take-off angle to the sample. Binding energies were referenced to the Fermi level, which was calibrated beforehand against a clean silver surface.

### 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.

### Keywords

Fermi-level pinning, interface passivation, NiO, photoemission, Si

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