Control of SrO buffer-layer formation on Si(001) using the pulsed-laser deposition technique

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– Supplementary Information –

The experimental conditions for SrO deposition

The experimental conditions for SrO deposition used in different segments of the deoxidation process (as schematically shown in Figure 1) are as follows:

- Batch mode, 40 pulses (Part I, Figure 1): the fluence, repetition rate, ablated area and target-to-substrate distance were kept constant at 1.3 J/cm^2, 0.1 Hz, 2.31 mm^2 (mask 16×5 mm^2), and 5.5 cm, respectively. The deposition temperature was always set to 650 °C, where the depositions were performed in vacuum (2×10^{-8} mbar), Ar and O_2 (both at 1.2×10^{-2} mbar). After the deposition all the samples were annealed in vacuum until the characteristic RHEED patterns occurred.
- Batch mode, 1-250 pulses (Part II, Figure 1): the fluence, repetition rate, ablated area and target-to-substrate distance were kept constant at 1.3 J/cm^2, 0.1 Hz, 2.31 mm^2 (mask 16×5 mm^2), and 5.5 cm, respectively. The deposition temperature was always set to 650 °C, where the depositions were performed in vacuum (2×10^{-8} mbar). Only in the case of 10 pulses of SrO was the deposition performed in Ar and O_2 (both at 1.2×10^{-2} mbar). After the deposition all the samples were annealed in vacuum until the characteristic RHEED patterns occurred.
- Pulse-by-pulse mode (Part III, Figure 1): the target-to-substrate distance and temperature of the SrO deposition were kept constant at 5.5 cm and 750 °C, respectively. All the depositions were performed in vacuum (2×10^{-8} mbar). The parameters such as mask size (16×5 mm^2, 8×2.5 mm^2, 4×1.25 mm^2) i.e. ablated area (2.31 mm^2, 0.58 mm^2 and 0.14 mm^2)*, deposition rate and fluence were varied as described in the paper.

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* The ablated area for 4×1.25 mm^2 mask decreases to 0.082 mm^2, for 4 J cm^{-2} and 4.4 J cm^{-2} due to readjustment of optics.

X-ray reflectivity analysis of film thickness (Figure 1, Part I)

In order to determine the thickness of the SrO film used in the deoxidation process, the samples were prepared under conditions matching the ones used in *batch mode* (Figure 1, part I). The experimental conditions are given in Table S1.

Table S1. The experimental conditions used for the preparation of TiO_2 and SrO films.

Sample	Description of experimental conditions
A0	1000 pulses of TiO_2 (1 Hz, 1.3 J/cm^2, T_{room}, 0.012 mbar Ar) on Si/SiO_2 substrate
A1	1000 pulses of SrO (0.1 Hz, 1.3 J/cm^2, T=650 ^{o}C, ~4 ×10^{-8} mbar) on Si/SiO_2 substrate + 2400 pulses of TiO_2 [a)]

[a)] The conditions of TiO_2 deposition were the same as in the case of sample A0.

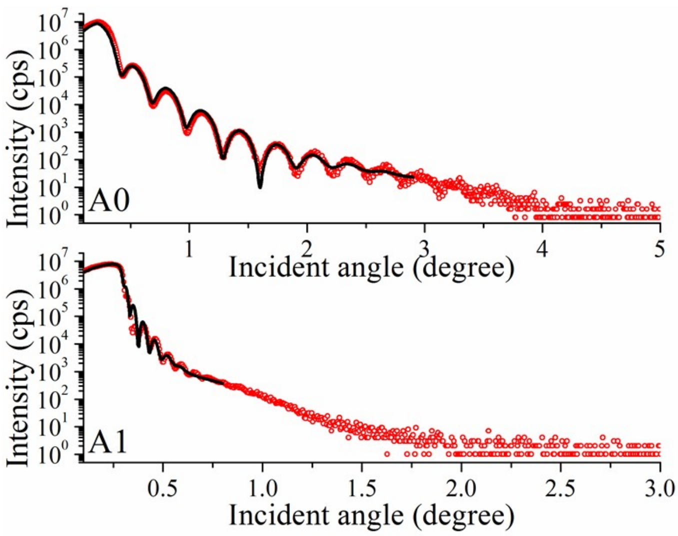

Figure S1. X-ray reflectivity curves of TiO_2 (A0) and SrO/TiO_2 (A1) films deposited on Si/SiO_2. See Table S1 for deposition conditions.

Because of the reactivity of SrO under environmental conditions the deposited films were protected by a TiO_2 layer. Therefore, it was necessary to prepare a TiO_2 film that acts as a reference (sample A0).Thanks to the known thickness of the TiO_2, the information about the film thickness was obtained by fitting experimental reflectivity curves using the previously established model structure i.e. [Si substrate / modified Si / $SrSiO_3$ / SrO / TiO_2].[1] The Figure S1 shows good matching between the experimental and the simulated data. The parameters obtained by the fit are presented in Table S2 and Table S3.

Table S2. The information about the sample A0

Layer Description	Density (g/cm^3)	Min.	Max.	Thickness (nm)	Min.	Max.	Roughness (nm)	Min.	Max.	Delta	Beta
TiO_2	3.753	3.753	4.587	14.147	12	16	0.7723	0.1	4	3.753	3.753
SiO_2	2.3908	2.376	2.904	1.6067	1	3	0.1307	0.1	0.8	2.3908	2.376
Si	2.1925	2.0952	2.5608	1.6574	1	2	0.1803	0.1	0.5	2.1925	2.0952
Sub - Si	2.328			600000			0.05	0.01	0.05	2.328	

Table S3. The information about the sample A1

Layer Description	Density (g/cm^3)	Min.	Max.	Thickness (nm)	Min.	Max.	Roughness (nm)	Min.	Max.	Delta	Beta
TiO_2	4.1784	3.753	4.587	32.7941	29	33	4.2069	0.1	5	128.337	6.6236
SrO	4.6371	4.23	5.17	22.1617	20	30	2.7695	0.1	5	130.76	6.1098
$SrSiO_3$	3.4431	3.303	4.037	1.5445	0.5	5	1.3938	0.1	1.5	102.3572	3.4052
Si	2.5608	2.0952	2.5608	3.5287	0.5	5	1.3835	0.1	1.5	83.2527	1.9025
Sub - Si	2.3	2.3	2.35	600000			0.5236	0.1	4	74.7747	1.7087

From the results of the XRR analysis we can see that 40 pulses of SrO, deposited under conditions described in Table 1, correspond to ~1.7 ML of SrO (1 ML=1 unit cell of SrO). However, since we have also examined a smaller number of SrO pulses (1, 5, etc.) we used the *number of pulses* as a term to describe the amount of material.

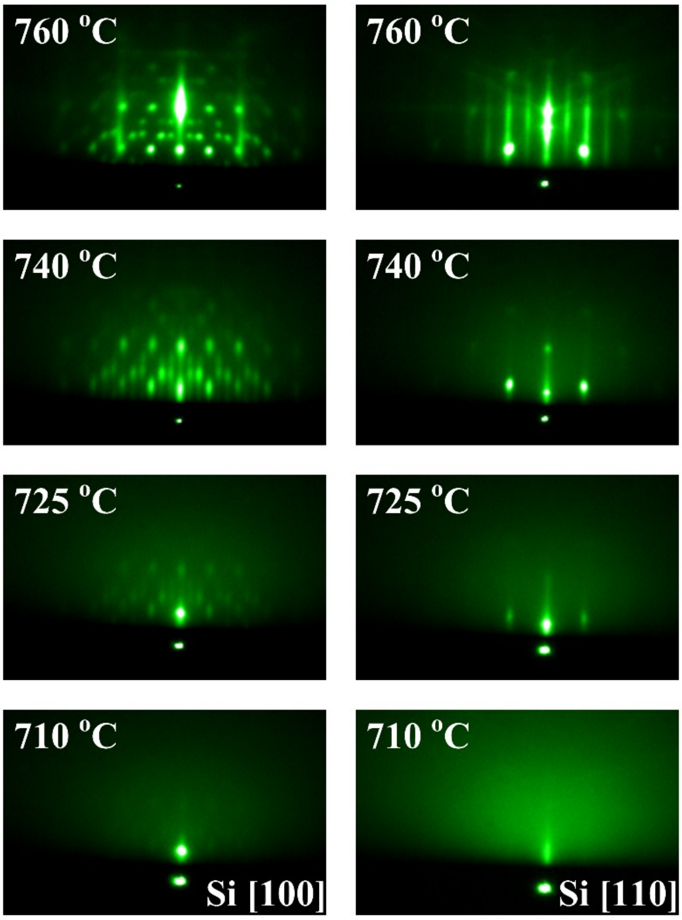

Figure S2. Characteristic RHEED patterns obtained by annealing 40 pulses of strontium oxide deposited on Si/SiO_2. The azimuth direction along which the RHEED patterns were recorded is given in the bottom-right corner.

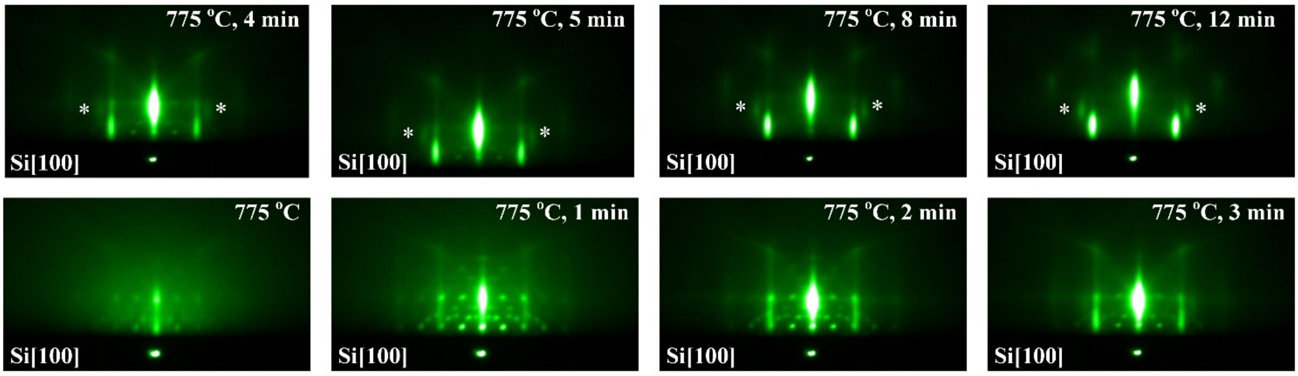

Figure S3. The RHEED images of the spotty 3D structure and the 1× streaks. It can be seen that the length of the 1× streaks decreases gradually as the spotty 3D pattern disappears. After several minutes the SiC phase (marked with *) becomes visible as a consequence of the imperfect vacuum.

The preparation of SrO films using different mask sizes, *i.e.,* different ablated areas (Figure 1, part III)

As in previous cases, in order to perform XRR and XRD measurements in ambient conditions, the SrO thin films were protected by a TiO_2 layer. The deposition procedure can be described in several steps, as follows.

Step 0. Target preablation

Two targets, SrO and TiO_2, were preablated in 1.2×10^{-2} mbar Ar at T_{room} by using 300 pulses with a 1-Hz repetition rate and a 1.3 J/cm^2 fluence. All the preablations were performed using a mask size of 16×5 mm^2 (ablated area of 2.31 mm^2).

Step 1. Initial cleaning of Si/SiO_2 substrate

The 5 mm x 5 mm B-doped Si(100) substrates (Si-Mat, Germany) were ultrasonically cleaned in acetone for 3 min, thoroughly rinsed with EtOH and blow-dried with a N_2 gun. Next, the substrates were glued to the stainless-steel sample plate using silver paste (Leitsilber 200, TedPella, Inc., USA) and heated up in air (~120 ^{o}C) to remove the organic solvent. Subsequently, the sample was inserted into the PLD chamber (Twente Solid State Technology, Netherlands) and degassed at 650 ^{o}C for 1.5 h in vacuum (~2x10^{-8} mbar or lower) followed by a 30-min treatment in 1–1.5×10^{-5} mbar O_2 at 600 ^{o}C in order to minimize the presence of carbon contamination.

Step 2. Deoxidation

The removal of native oxide from a Si/SiO_2 substrate was performed followingthe *batch* mode as described in paper. The temperature of the substrate was increased to 650 °C followed by the deposition of 10 pulses of SrO (0.1 Hz, 1.3 J/cm^2, ablated area 2.31 mm^2, 1.2×10^{-2} mbar Ar). Next, the temperature was increased in vacuum until 2×1 streaks appeared and kept constant for 1–2 min in order to improve the definition of the streaks. Next, the temperature was gradually decreased and the sample was left to cool down in vacuum for 40 min.

Step 3. Deposition of SrO buffer layer (this step is common for all mask sizes, i.e., ablated areas)

Once the sample is cooled to ~T_{room}, the SrO buffer layer was prepared: 50 pulses of SrO were deposited with 0.1 Hz, 1.3 J/cm^2, 2.31 mm^2 ablated area in 1.2×10^{-2} mbar O_2. After the initial deposition of 50 pulses of SrO the temperature was increased in vacuum to 315 °C. The RHEED images of the SrO film during this step are shown in **Figure S4**.

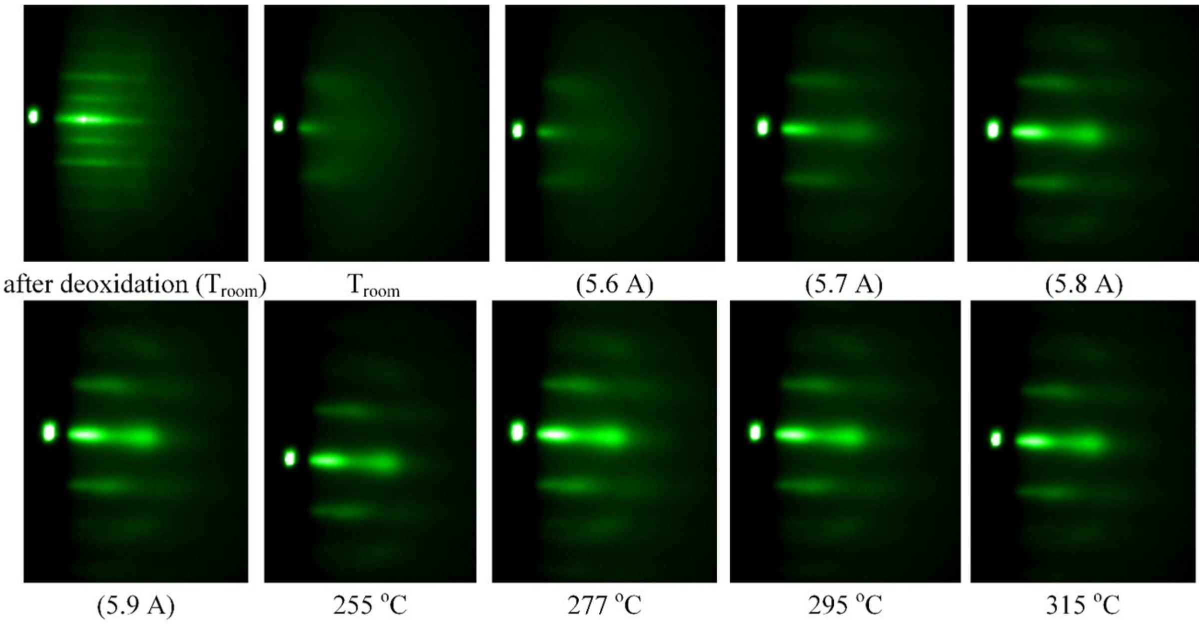

Figure S4. The RHEED images of the SrO buffer layer at different temperatures. The values in parentheses represent current intensity, in amperes, provided to optical fiber of IR laser used for heating (the temperature in this cases were below detection limit of pyrometer, T=250 °C)

Step 4. Deposition of SrO film using different mask sizes i.e. ablated areas

Next, when 315 °C was reached the further deposition of SrO was performed on the SrO buffer, *using different masks*: *16×5, 8×2.5 and 4×1.25 mm²*. The conditions were the same for all the ablated areas: 1800 pulses of SrO, 1 Hz, 1.3 J/cm², T=315 °C, 1.2×10^{-2} mbar O_2. The RHEED image of the SrO film grown by using a mask of 16×5 mm² is shown in Figure S5.

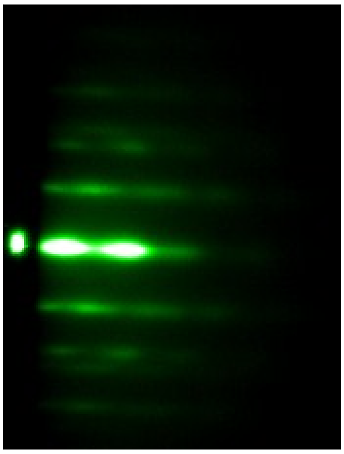

Figure S5. The RHEED image of SrO thin film obtained after the deposition of 1800 pulses of SrO with a mask of 16×5 mm².

Step 5. Deposition of TiO_2 protective layer

Next, the sample was cooled down to ~T_{room}, after which a TiO_2 protective layer was deposited: 1000 pulses of TiO_2, 1 Hz, 1.3 J/cm^2, mask 16×5 mm^2, T<250 °C, 1.2×10^{-2} mbar O_2.

XRR analysis of SrO films prepared using different mask sizes

The XRR curves of the prepared films are given in Figure S6. Thanks to the known thickness of the TiO_2, the information about the film thickness was obtained by applying [Si substrate / modified Si / SrO / TiO_2] model structure*. The parameters obtained with the combined fitting mode are presented in Table S4-S6.

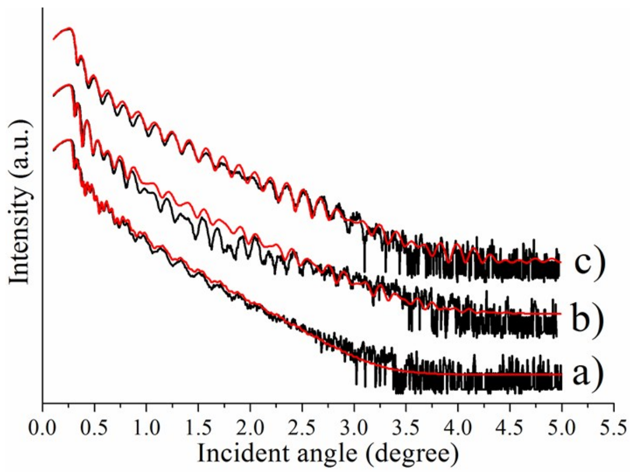

Figure S6. The X-ray reflectivity curves of SrO thin films deposited with different mask sizes [a) 16×5 mm^2, b) 8×2.5 mm^2, c) 4x1.25 mm^2] resulting in the target's ablated areas of 2.31 mm^2, 0.58 mm^2, 0.14 mm^2, respectively .

Table S4. The parameters of SrO thin film prepared with 16×5 mm^2 mask (ablated area 2.31 mm^2)

Layer Description	Density (g/cm^3)	Min.	Max.	Thickness (nm)	Min.	Max.	Roughness (nm)	Min.	Max.	Delta	Beta
3, 0 - TiO_2	3.753	3.753	4.587	23.5045	20	24	0.5031	0.1	5	115.2714	5.9493
2, 0 - SrO	4.7904	4.23	5.17	54.0112	50	60	0.7451	0.1	5	135.0823	6.3118
1, 0 - Si	2.4593	2.0952	2.5608	2.4636	0.5	5	1.4316	0.1	2	79.9539	1.8271
Sub - Si	2.35	2.3	2.35	600000	600000	600000	0.3912	0.05	0.5	76.4003	1.7459

* The model structure is based on XPS results (see Figure 9 in paper).

Table S5. The parameters of SrO thin film prepared with 8×2.5 mm^2 mask (ablated area 0.58 mm^2)

Layer Description	Density (g/cm^3)	Min.	Max.	Thickness (nm)	Min.	Max.	Roughness (nm)	Min.	Max.	Delta	Beta
3, 0 - TiO_2	3.753	3.753	4.587	25.8565	20	30	0.3916	0.1	5	115.2714	5.9493
2, 0 - SrO	4.714	4.23	5.17	8.5749	7	20	0.3624	0.1	3	132.9292	6.2112
1, 0 - Si	2.5288	2.0952	2.5608	1.6484	0.5	6	1.3209	0.1	2	82.2129	1.8787
Sub - Si	2.3	2.3	2.35	600000	600000	600000	0.2912	0.05	0.5	74.7747	1.7087

Table S6. The parameters of SrO thin film prepared with 4×1.25 mm^2 mask (ablated area 0.14 mm^2)

Layer Description	Density (g/cm^3)	Min.	Max.	Thickness (nm)	Min.	Max.	Roughness (nm)	Min.	Max.	Delta	Beta
3, 0 - TiO_2	4.0985	3.753	4.587	23.921	20	24	0.3882	0.1	5	125.8829	6.497
2, 0 - SrO	4.23	4.23	5.17	3.3723	1	5	0.1424	0.1	2	119.2806	5.5735
1, 0 - Si	2.5608	2.0952	2.5608	2.0414	0.5	5	0.4449	0.1	0.5	83.2535	1.9025
Sub - Si	2.3	2.3	2.35	600000	600000	600000	0.1326	0.1	1	74.7747	1.7087

Based on the XRR results and having in mind that the SrO buffer layer is present in the case of all the ablated areas, we can calculate the *thickness of SrO per pulse*. The *thicknesses of the SrO per pulse* deposited in the case of targets with ablated areas of 2.31 mm^2, 0.58 mm^2, 0.14 mm^2 are 0.0292 nm/pulse, 3.953×10^{-3} nm/pulse, and 1.063×10^{-3} nm/pulse, respectively.

References:

1. Jovanović, Z.; Spreitzer, M.; Kovač, J.; Klement, D.; Suvorov, D., Silicon Surface Deoxidation Using Strontium Oxide Deposited with the Pulsed Laser Deposition Technique. *ACS Appl. Mater. Interfaces* **2014,** *6* (20), 18205-18214.