Electron beam effects on oxide thin films – Structure and electrical properties

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# Supplementary information

# Experimental

## Deposition of silicon oxide – magnetron sputering

The SiOx thin films were deposited by pulsed DC reactive magnetron sputtering from a Si target (Goodfellow GmbH, 99.999 %, 2 inch diameter) in a reactive Ar/O2 atmosphere. The magnetron source (Thin Film Consulting, ION’X-2UHV) was mounted in a custom-built vacuum chamber at a distance of 70 mm from the substrate position. Prior to deposition, a vacuum of least 10-4 Pa was reached by a turbo molecular pump (Pfeiffer Vacuum, TMU 262) and a dry scroll pump (Agilent Technologies, SH-110). The reactive gas atmosphere was supplied by a flow of 48 SCCM Ar (purity 99.999%, gas regulating valve: Pfeiffer, EVR116 with attached hot ion cathode IMR 285) and 10SCCM of O2 (purity 99.999%, mass flow controller Alicat, H-MC-100SCCM-D / 5M). For pulsed reactive sputtering, the DC power (supplied by Advanced Energy, MDX 500) was pulsed by a high power MOSFET (Behlke Power Electronics, HTS 31 CF I), that was triggered by a frequency generator (PeakTech, DDS Function Generator 4025, rectangular 0-5 V signal, 80 kHz, 35 % duty cycle). Prior to every deposition process, the target was cleaned and conditioned for a sufficient time (at least 60 s) to reach stable deposition conditions.

## Deposition of Titanium oxide – pulsed laser deposition

TiO2 thin films with a thickness of about 30 nm were grown via pulsed laser deposition using a KrF excimer laser (λ = 248 nm) with a fluence of ~2 J cm−2 and a repetition rate of 1 Hz. The target to substrate distance was maintained at 50 mm. The deposition process was carried out at room temperature and a background oxygen pressure of 0.05 mbar.

# Characterization

### XPS

X-ray photoelectron spectroscopy (XPS, Omicron Nano-Technology GmbH, operating with an Al-anode at a power of 240 W) was used to investigate the chemical composition of the oxide thin films. The recorded spectra were charge referenced by using aliphatic carbon C-1s at 285.0 eV using the software CasaXPS (version 2.3.16). For the quantification of the chemical composition of the oxide thin films, Cr (using Cr-2p lines), O (using O-1s line), Si (using Si-2p line) and Nb (using Nb-3d lines) were used respectively.

# Discussion

## XPS results of SiOx

In Figure S1 the XPS spectra of a SiOx thin film (overview spectrum and high-resolution spectrum of Si-2p line) and a NbOx thin film (overview spectrum and high resolution spectrum of Nb-3d lines) are shown. The overview spectra were analysed for elemental composition and the respective characteristic peaks were marked in the spectra. For the SiOx thin film the elements O, C, Cr and Si and for the NbOx thin film the elements O, C, Cr and Nb were detected. The occurrence of Cr originates in the chromium coated sample holder. Carbon containing surface contamination, such as carbohydrates, result in the presence of carbon in the spectra.

The peak position of the Si-2p line, as shown in Figure S 1b, is at around 103.3 eV, which correlates well with the chemical shift of the line from pure Si at 99.3 eV to SiO2 at 103.3 eV[1]. The ratio of oxygen to silicon was quantified based on the peak area in the XPS spectra. However, the amount of oxygen signal from SiOx was corrected by assuming fully oxidised Cr2O3 on the sample holder. In agreement with the observed chemical shift of the Si-2p line, the quantification yields an O/Si ratio of roughly 1.96, underlining that the investigated thin film is quasi stoichiometric SiO2.

## XPS results of NbOx

Figure S1d shows peak position of Nb-3d lines at 209.6 eV (3d3/2) and 206.8 eV (3d5/2). The splitting of both lines correlates well with the literature value of 2.7 eV[1]. Compared to the position for metallic Nb at 202.4 eV[1], the 3d5/2 line is shifted by approximately 4.6 eV, which is typically interpreted as oxidation to Nb2O5 with a Nb-3d5/2 line at around 206.5-208.2 eV[2,3] or NbO2 with a Nb-3d5/2 line at around 205.2-207.6 eV[3]. However, the quantification based on the assumption of fully oxidized Cr2O3 on the sample holder leads to an O/Nb ratio of roughly 1.9, which is close to the ratio for NbO2.

However, the *I/V* curves shows an insulating behaviour in the as prepared state and we expect to have a stable oxide phase.

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| Figure S1 XPS spectra of SiOx (blue line, a+b) and NbOx (red line, c+d) thin films; a) and c): overview spectra; b) high resolution spectrum of Si-2p line; d) high resolution spectrum of Nb-3d lines |

### References:

[1] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Physical Electronics Division, 1992.

[2] N. Singh, M.N. Deo, M. Nand, S.N. Jha, S.B. Roy, Raman and photoelectron spectroscopic investigation of high-purity niobium materials: Oxides, hydrides, and hydrocarbons, J. Appl. Phys. 120 (2016) 114902. doi:10.1063/1.4962650.

[3] NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database Number 20, National Institute of Standards and Technology, Gaithersburg MD, 20899 (2000), doi:10.18434/T4T88K, (retrieved 2018-02-08).

## XPS of TiOx thin films

Qualitative assessment of the chemical composition of TiOx thin films was carried out by means of low (Al radiation, 250 W power) and high (Al-Kα radiation, 300 W power) resolution XPS spectroscopy. The drift of about 1 eV observed in the spectra due to charging effect has been compensated by considering the C-1s line at 284.5 eV as a reference. The left panel in Figure S2 shows an overview scan of a representative sample of TiOx thin film. The observed shift of the O-1s line from 531 eV to about 530 eV is within the 528-531 eV range expected for metal oxides1. The presence of the characteristic carbon line (C-1s) is related to surface contamination after air exposure. A high-resolution scan of the Ti-2p lines is depicted in the right panel. The Ti-2p1/2 and Ti2p3/2 lines, which in pure titanium occur at 460 eV and 454 eV, shift towards 464.5 eV and 458.8 eV, respectively, as expected [1,2] for TiO2.

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| D:\XPS.png  Figure S2 XPS analysis of TiO2 thin films. Low resolution overview scan (left panel) and high resolution Ti-2p lines (right panel). |

### References:

[1]J.F. Moulder, W.F. Stickle, P.E. Sobol, and K.D. Bomben,” Handbook of X-Ray Photoelectron Spectroscopy”, Perkin-Elmer Corporation, Physical Electronics Division, 1992.

[2] U. Diebold, and T. E. Madey, “TiO2 by XPS”, Surface Science Spectra, vol. 4, no. 3, pp. 227–231, 1996, http://doi.org/10.1116/1.1247794.

# Supplementary Figures:

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| Figure S3 Diffraction showing amorphous thin films a) PECVD SiO2; b) mSp-SiO2; c) TiOx; d. NbxOy |

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| Figure S4 Comparison of silicon particles formed by the electron beam in SiO2 Simpore chips: the same area was investigated directly after electron beam irradiation and after 4 days when stored in atmosphere. |



Figure S5 *I/V* cycles of electron beam exposed PECVD SiO2 in ref. to Figure 2.



Figure S6: a) *I/V* cycles recorded during reoxidation of the PECVD silicon oxide exposed to the electron beam starting from a semiconductive state after beam exposure to an insulating state when exposed to air. b) Current at 3V vs. time plotted for the reoxidation.

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| Figure S7: a) *I/V* curves of TiO2 after a dose of 2.0E5 e/nm2 with the electron beam off (green) and on (red). b) I/V curves of NbO2 after dose of 9.9E6 e/nm2 with the electron beam off (blue) and on (red) revealing an offset in the measurement due to electron beam induced current. |

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| Figure S8: Impedance measurements showing strong resistivity change of titanium oxide after electron beam exposure. |
| Figure S9: RDF analysis of titanium oxide of the as prepared film.   |  | | --- | | Figure S10: Resistivity vs. Dose of all three oxides | |