Electronic Supplementary Information

β-Ketoiminato-based Copper(II) Complexes as CVD Precursors for Copper and Copper Oxide Layer Formation

Elaheh Pousaneh[a], Marcus Korb[a], Volodymyr Dzhagan[b,c], Marcus Weber[d], Julian Noll[a], Michael Mehring[d], Dietrich R. T. Zahn[b], Stefan. E. Schulz[e,f], Heinrich Lang[a*]

a) *Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry, Inorganic Chemistry, D-09107 Chemnitz, Germany*

b) *Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Physics, Semiconductor Physics, D-09107 Chemnitz, Germany*

c) *V. E. Lashkaryov Institute of Semiconductors Physics, National Academy of Sciences of Ukraine, 03028 Kyiv, Ukraine*

d) *Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry, Coordination Chemistry, D-09107 Chemnitz, Germany*

e) *Technische Universität Chemnitz, Center for Microtechnologies, D-09107 Chemnitz, Germany*

f) *Fraunhofer Institute for Electronic Nano Systems ENAS, Technologie-Campus 3, D-09126 Chemnitz, Germany*

[*]Corre*sponding author: Email: heinrich.lang@chemie.tu-chemnitz.de; Phone: +49 (0)371-531-21210;Fax.: +49-(0)371-531-21219*

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Table S1. Crystal and structural refinement data of **4a**,**b**, **5** and **6**.

Complexes	**4a**	**4b**	**5**	**6**
Empirical formula	$C_{22}H_{40}Cu_2N_4O_6$	$C_{32}H_{46}Cu_2N_4O_7$	$C_{20}H_{34}Cu_2N_2O_8$	$C_{26}H_{50}Cu_2N_4O_7$
Formula mass (g/mol)	583.66	725.81	557.57	657.78
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2$_1$/*n*	*P2/n*	*P*2$_1$/*c*	*C2/c*
a (Å)	11.0854(10)	12.9343(7)	8.8928(3)	22.4102(19)
b (Å)	10.0289(5)	9.8945(4)	7.2198(2)	12.7485(9)
c (Å)	11.5267(10)	13.0557(6)	18.5441(6)	11.2535(8)
β (°)	99.229(8)	92.231(4)	91.554(3)	94.524(7)
V (Å^3)	1264.89(17)	1669.58(14)	1190.17(6)	3205.1(4)
Z	2	2	2	4
D_{calc} (Mg·m^{-3})	1.532	1.444	1.556	1.363
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Temperature (K)	115.00(10)	115.00(10)	115.5(4)	116(1)
Absorption coefficient (mm^{-1})	1.725	1.325	1.833	1.372
F(000)	612	760	580	1392
Reflections collected	4887	6711	4581	10414
Reflections unique / R_{int}[a)]	2221/0.0314	2940 / 0.0274	2093/ 0.0245	2816/0.0750
Goodness-of-fit on F^2 [b)]	1.040	1.021	1.072	0.957
Data / restraints / parameters	2221 / 0 / 159	2940 / 2 / 210	2093 / 0 / 149	2816 / 2 / 236
θ range for data collection (°)	3.119 to 24.995	2.995 to 25.000	3.132 to 24.997	3.168 to 24.996
Limiting indices	−10 ≤ *h* ≤ 13, −7 ≤ *k* ≤ 11, −13 ≤ *l* ≤ 10	−15 ≤ *h* ≤ 12, −11 ≤ *k* ≤ 10, −15 ≤ *l* ≤ 12	−10 ≤ *h* ≤ 10, −7 ≤ *k* ≤ 8, −22 ≤ *l* ≤ 20	−26 ≤ *h* ≤ 26, −15 ≤ *k* ≤ 14, −13 ≤ *l* ≤ 13
Final *R* indices [*I* > 2*σ*(*I*)][c)]	R_1 = 0.0367, wR_2 = 0.0869	*R_1 = 0.0300, wR_2 = 0.0676*	*R_1 = 0.0296, wR_2 = 0.0673*	*R_1 = 0.0452, wR_2 = 0.0943*
R indices (all data)[c)]	R_1 = 0.0525, wR_2 = 0.0943	*R_1 = 0.0397, wR_2 = 0.0706*	*R_1 = 0.0420, wR_2 = 0.0715*	*R_1 = 0.0708, wR_2 = 0.1033*
Largest diff. peak/hole (e·Å^{-3})	0.493 /−0.542	0.380 / −0.240	0.336 /−0.279	0.581 / −0.379

[a)] $R_{int} = \sum \left| F_0^2 - F_0^2(\text{mean}) \right| / \sum F_0^2$, where F_0^2 (mean) is the average intensity of symmetry equivalent diffractions. [b)] $S = [\sum w (F_0^2 - F_0^2)^2] / (n-p)^{1/2}$, where *n* = number of reflections, *p* = number of parameters. [c)] $R = [\sum(\| F_0 | - | F_0 |) / \sum | F_0 |)$; $R[\sum(w(F_0^2 - F_0^2))^2 / \sum(w F_0^4)]^{1/2}$.

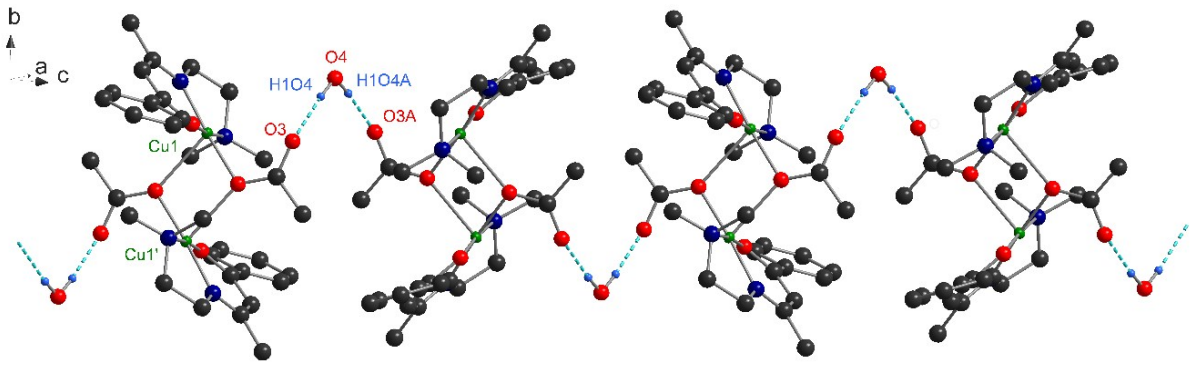

Figure S1. The 1D chains formed by **4b** in the solid state, due to hydrogen bond formation, indicated as dotted lines. All carbon-bonded hydrogen atoms are omitted for clarity. O3···O4 2.820(2) Å, H1O4–O4 0.87(2), O3···H1O4 1.95 (3), O3···H1O4–O4 173.8(19)°. Symmetry code – x + 1, – y, – z + 1.

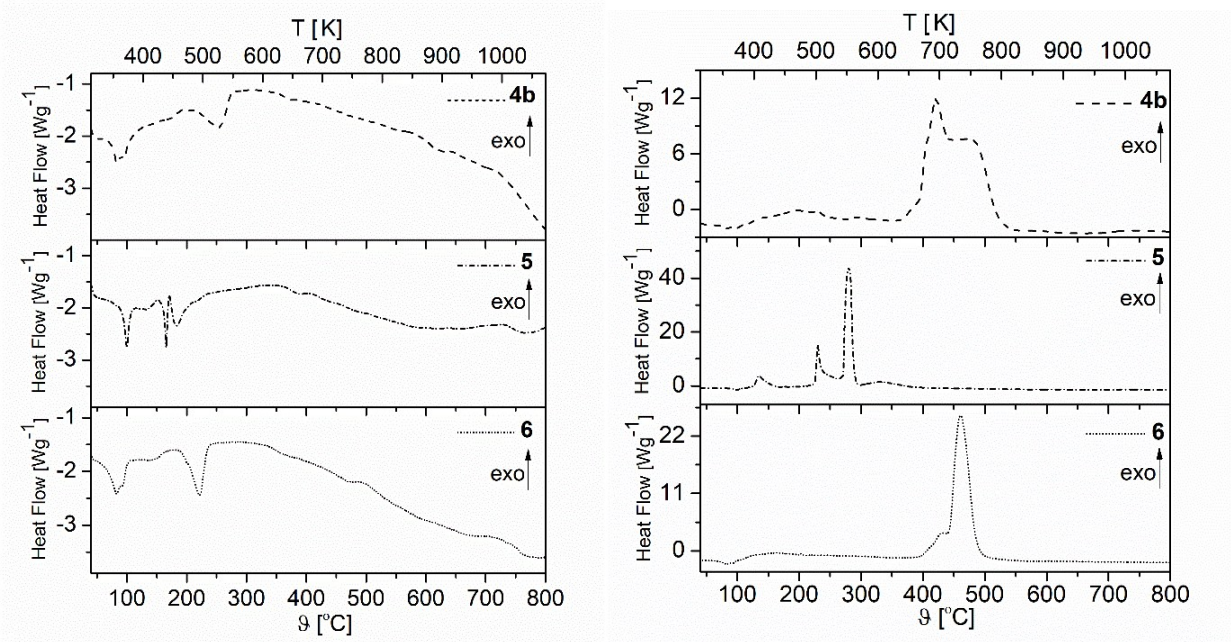

Figure S2. DSC traces of **4b**,**5**, and **6** under argon (left) (gas flow, 20 mL min^{-1}) and oxygen (right) (gas flow, 20 mL min^{-1}; argon carrier gas flow, 40 mL min^{-1}) (heating rate 10 °C min^{-1}).

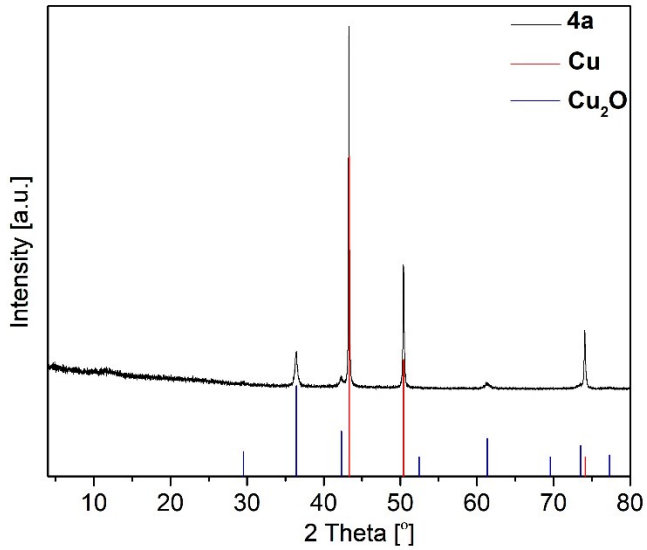

Figure S3. PXRD pattern of the TG residues obtained from **4a** under argon, for comparison Cu (ICDD 00-04-0836) Cu and Cu_2O (ICDD 00-005-0667).

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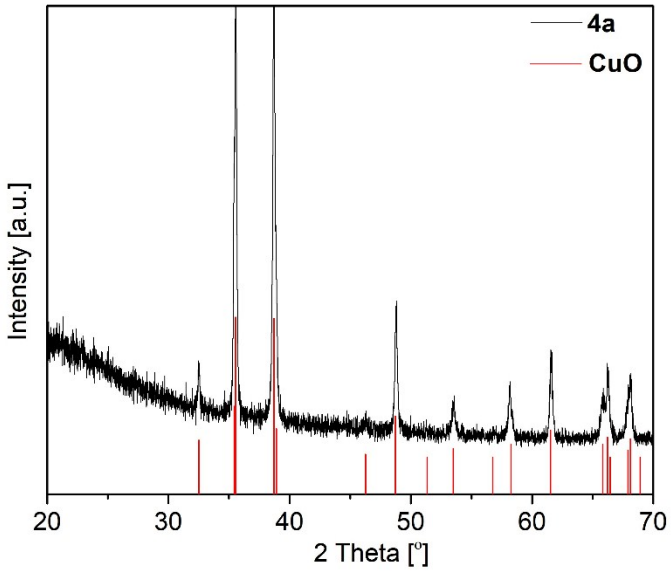

Figure S4. PXRD pattern of the TG residues obtained from **4a** under oxygen, for comparison CuO (ICDD 01-073-6023).

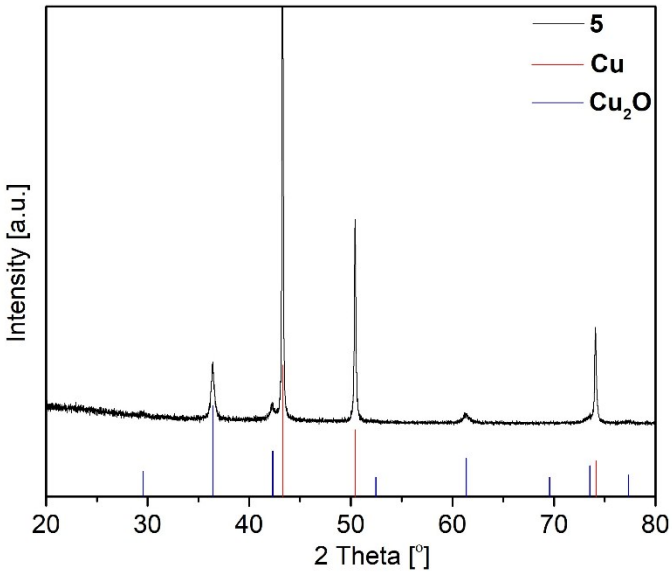

Figure S5. PXRD pattern of the TG residues obtained from **5** under argon, for comparison Cu (ICDD 00-04-0836) and Cu_2O (ICDD 00-005-0667).

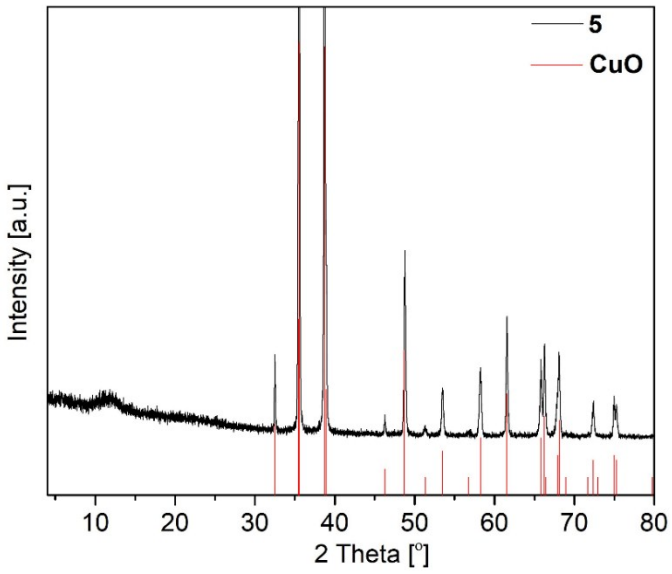

Figure S6. PXRD pattern of the TG residues obtained from **5** under oxygen, for comparison CuO (ICDD 01-073-6023).

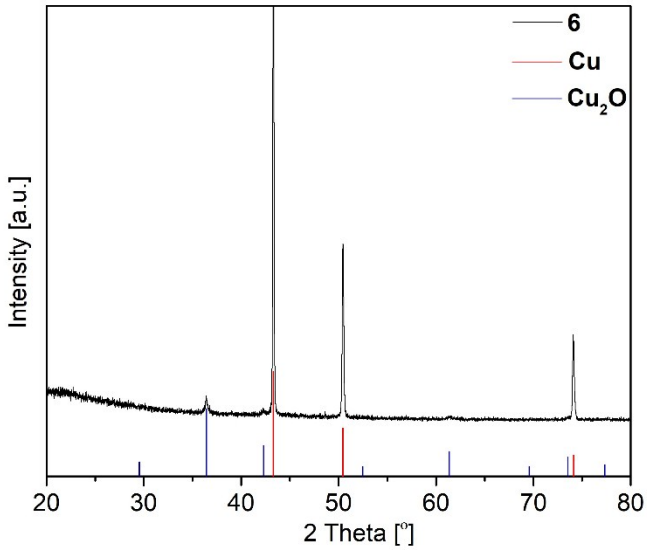

Figure S7. PXRD pattern of the TG residues obtained from **6** under argon, for comparison Cu (ICDD 00-04-0836) and Cu_2O (ICDD 00-005-0667).

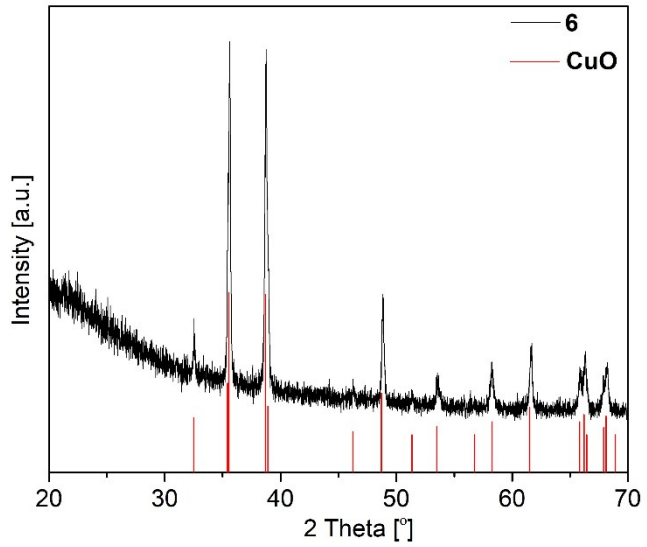

Figure S8. PXRD pattern of the TG residues obtained from **6** under oxygen, for comparison CuO (ICDD 01-073-6023).

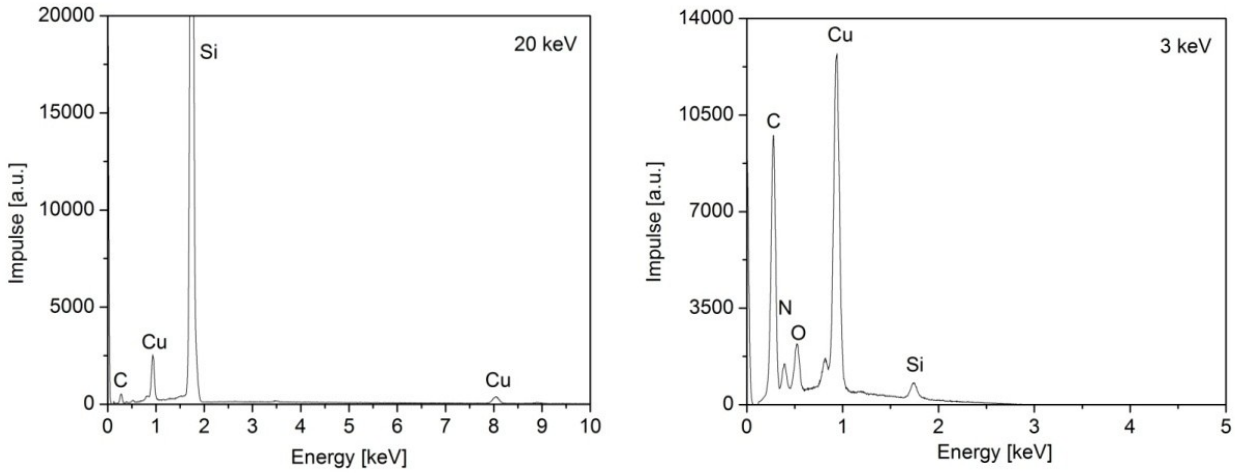

Figure S9. EDX spectra of the films obtained by using **4a** as CVD precursor (layer A) (N_2) (gas flow rate 50 mL min^{-1}, at 20 keV (left) and 3 keV (right), substrate temperature 450 °C).

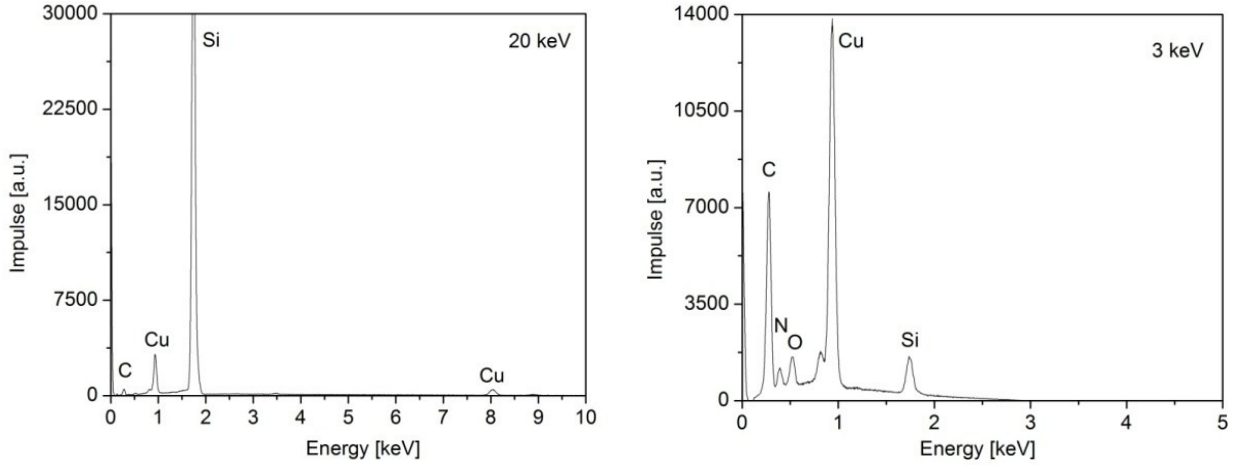

Figure S10. EDX spectra of the films obtained by using **4a** as CVD precursor (layer B) (N_2) (gas flow rate 50 mL min^{-1}, at 20 keV (left) and 3 keV (right), substrate temperature 510 °C).

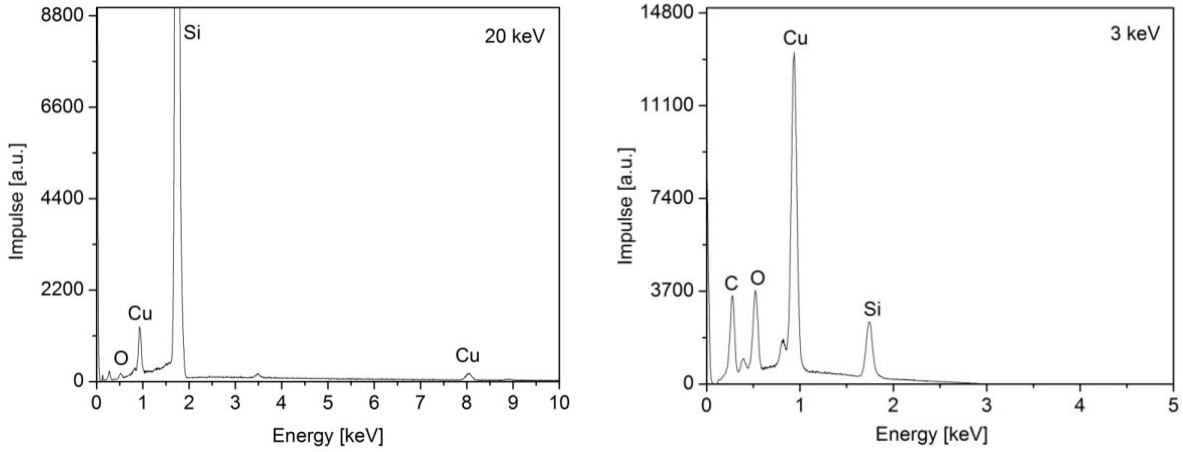

Figure S11. EDX spectra of the films obtained by using **5** as CVD precursor (layer C) (N_2) (gas flow rate 50 mL min^{-1}, at 20 keV (left) and 3 keV (right), substrate temperature 450 °C) for comparison.

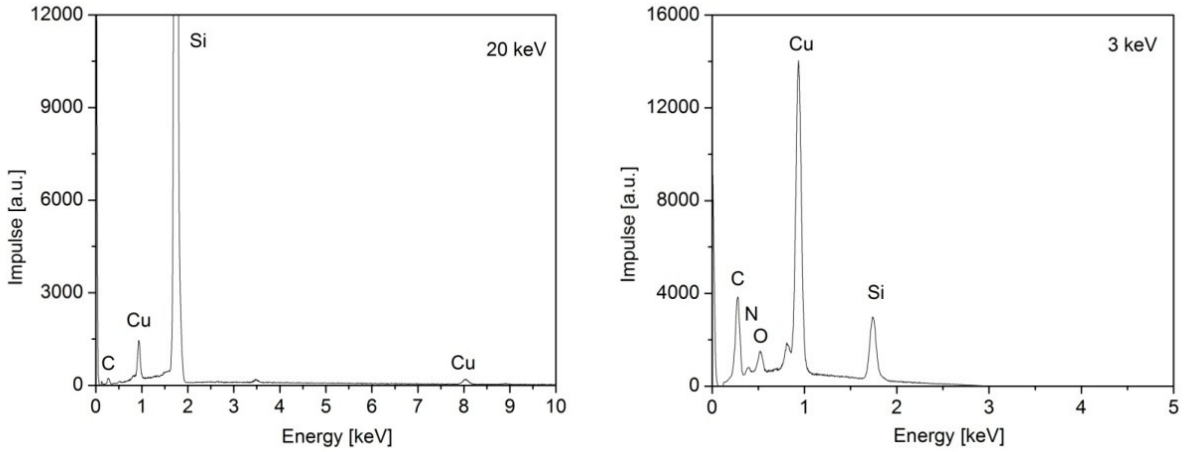

Figure S12. EDX spectra of the films obtained by using **5** as CVD precursor (layer D) (N_2) (gas flow rate 50 mL min^{-1}, at 20 keV (left) and 3 keV (right), substrate temperature 510 °C).

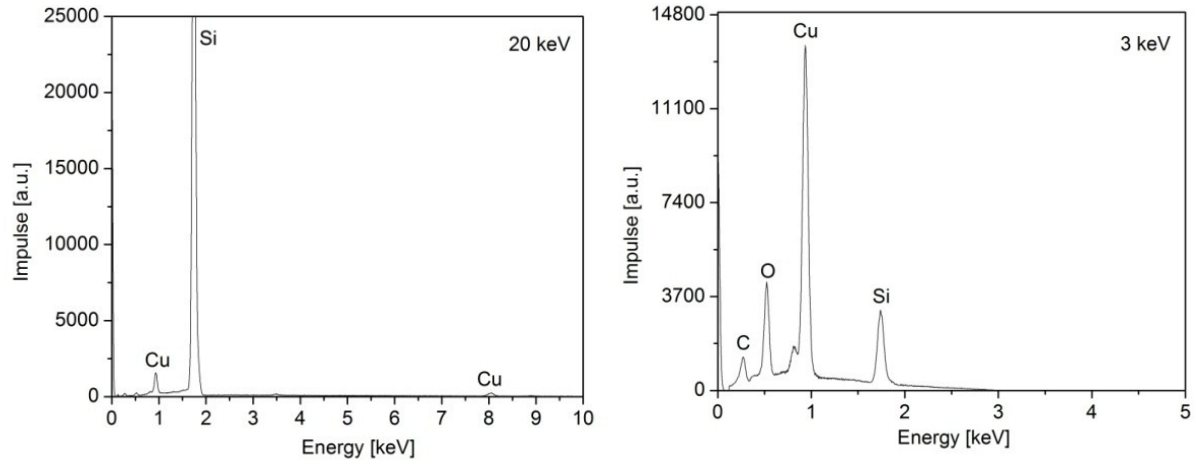

Figure S13. EDX spectra of the films obtained by using **4a** as CVD precursor (layer E) (O_2) (gas flow rate 40 mL min^{-1}, at 20 keV (left) and 3 keV (right), substrate temperature 450 °C) for comparison.

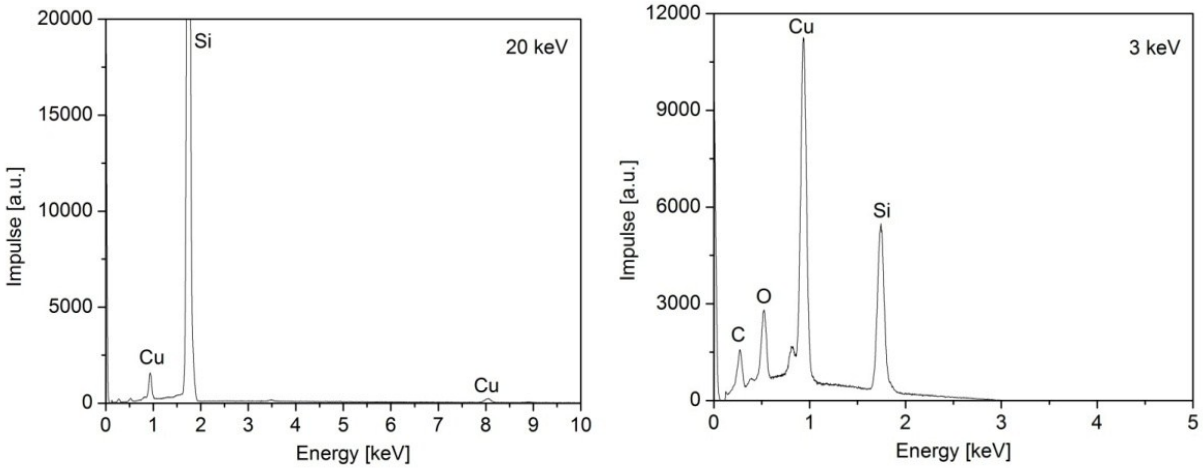

Figure S14. EDX spectra of the films obtained by using **4a** as CVD precursor (layer F) (O_2) (gas flow rate 40 mL min^{-1}, at 20 keV (left) and 3 keV (right), substrate temperature 510 °C).

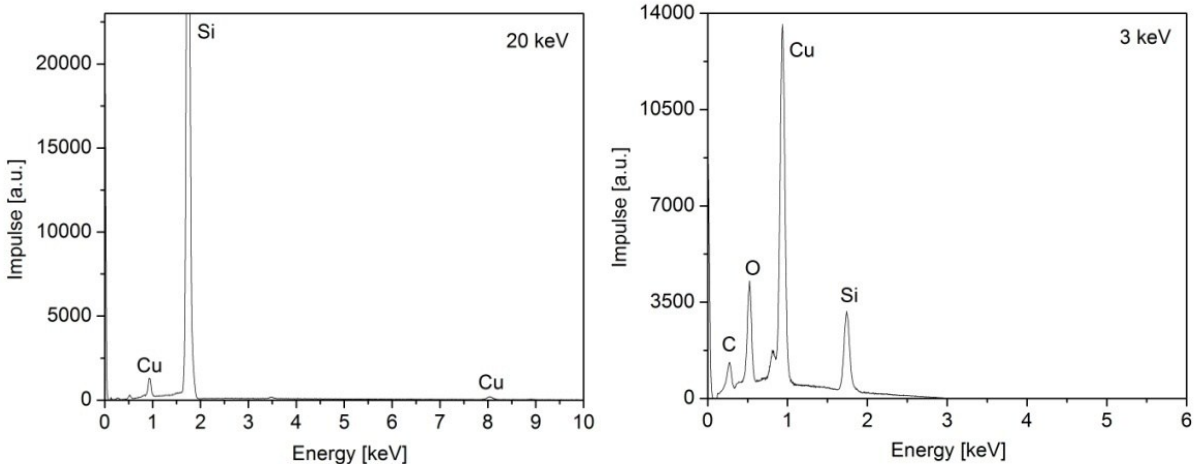

Figure S15. EDX spectra of the film obtained by using **5** as CVD precursor (layer H) (O_2) (gas flow rate 40 mL min^{-1}, at 20 keV (left) and 3 keV (right), substrate temperature 510 °C).

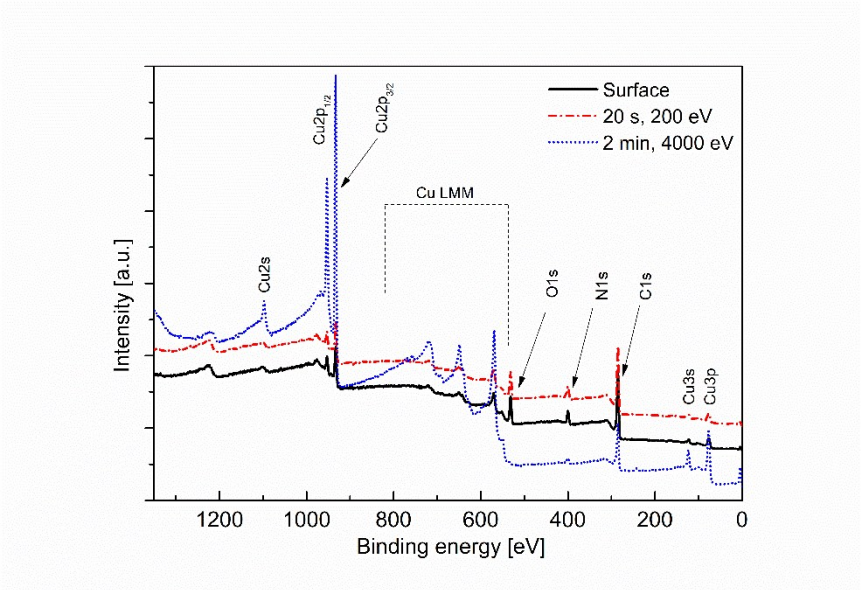

Figure S16. Detailed XPS spectra obtained of layer A (applied parameters are given in Table 4) of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

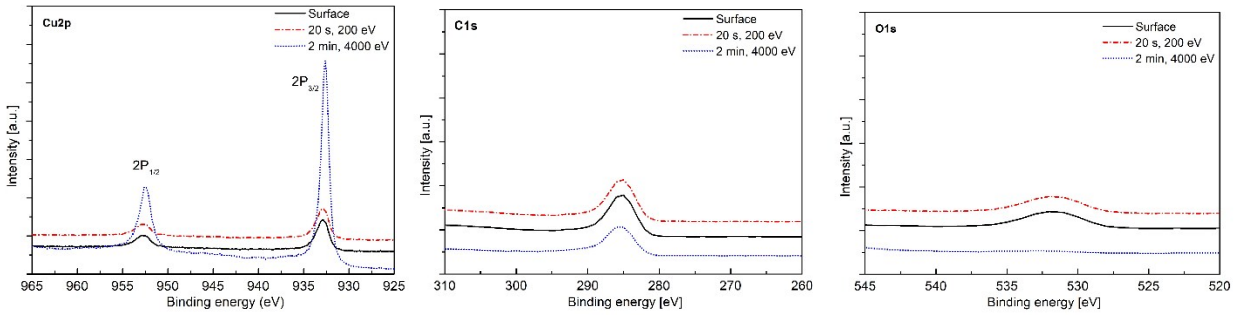

Figure S17. Detailed XPS spectra of the Cu2p (left) peak, C1s (middle) and O1s (right) obtained of layer A from **4a** of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

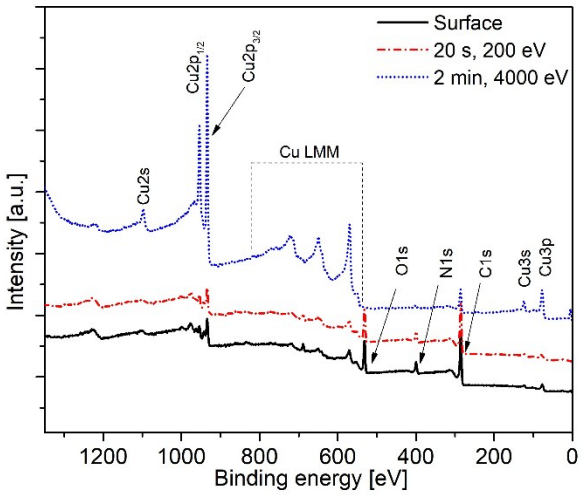

Figure S18. XPS survey spectra obtained of layer B (applied parameters are given in Table 4) of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

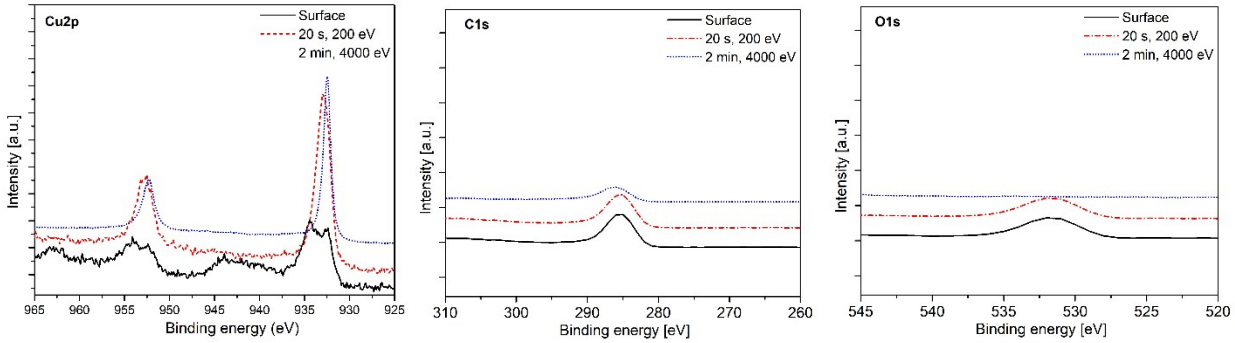

Figure S19. Detailed XPS spectra of the Cu2p (left) peak, C1s (middle) and O1s (right) obtained of layer B from **5** of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

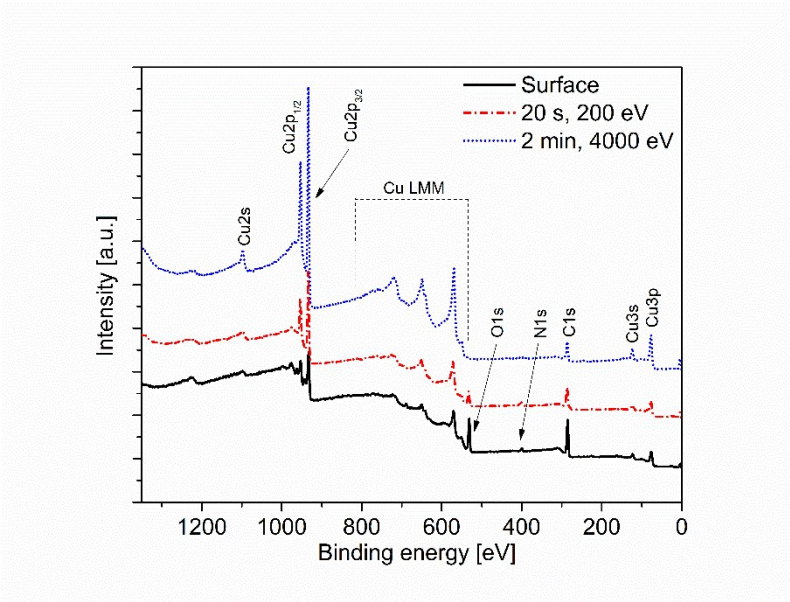

Figure S20. XPS survey spectra obtained of layer C (applied parameters are given in Table 4) of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

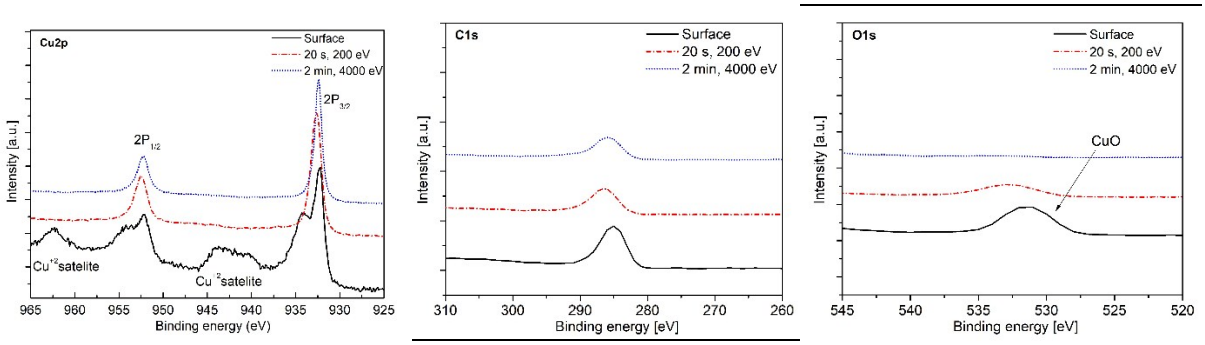

Figure S21. Detailed XPS spectra of the Cu2p (left) peak, C1s (middle) and O1s (right) obtained of layer C from **5** of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

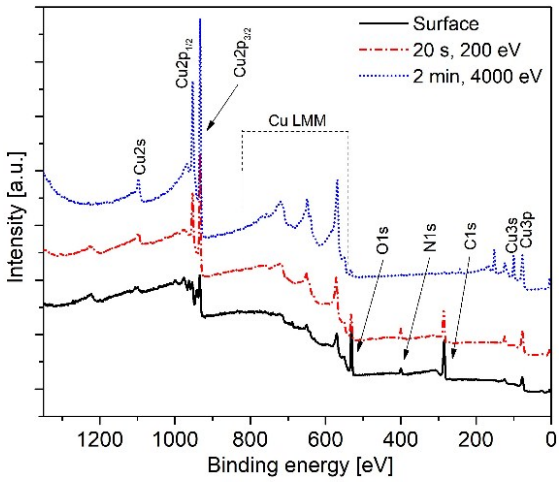

Figure S22. XPS survey spectra obtained of layer E (applied parameters are given in Table 4) of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

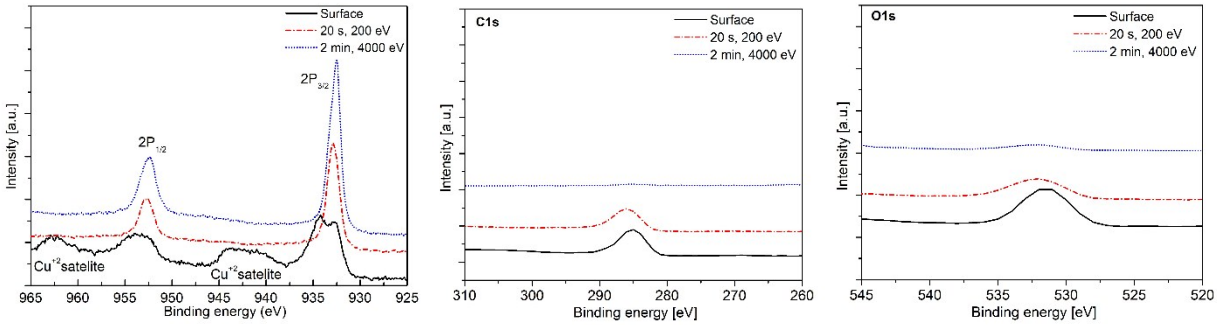

Figure S23. Detailed XPS spectra of the Cu2p (left) peak, C1s (middle) and O1s (right) obtained of layer E from **5** of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

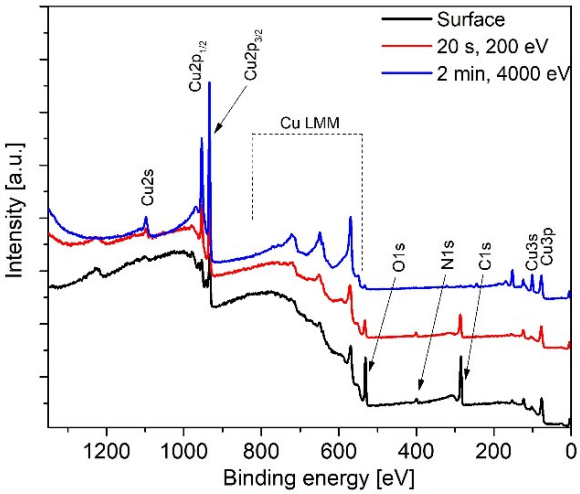

Figure S24. XPS survey spectra obtained of layer F (applied parameters are given in Table 5) of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

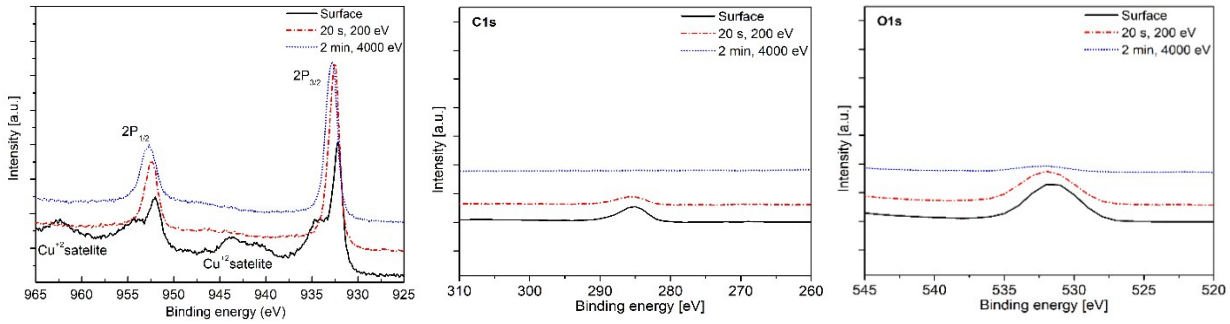

Figure S25. Detailed XPS spectra of the Cu2p (left) peak, C1s (middle) and O1s (right) obtained of layer F from **5** of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

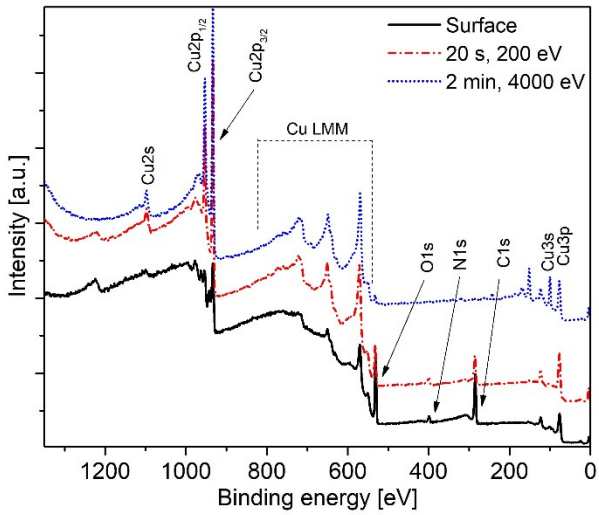

Figure S26. XPS survey spectra obtained of layer G (applied parameters are given in Table 4) of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

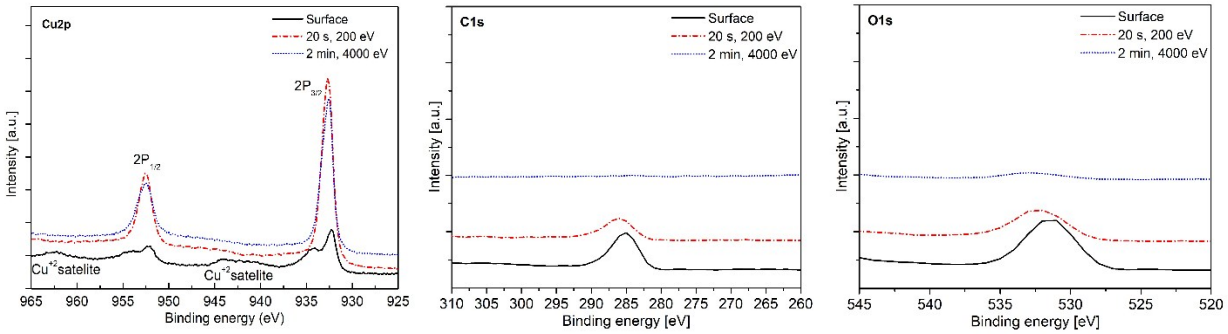

Figure S27. Detailed XPS spectra of the Cu2p (left) peak C1s (middle) and O1s (right) obtained of layer G from **5** of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

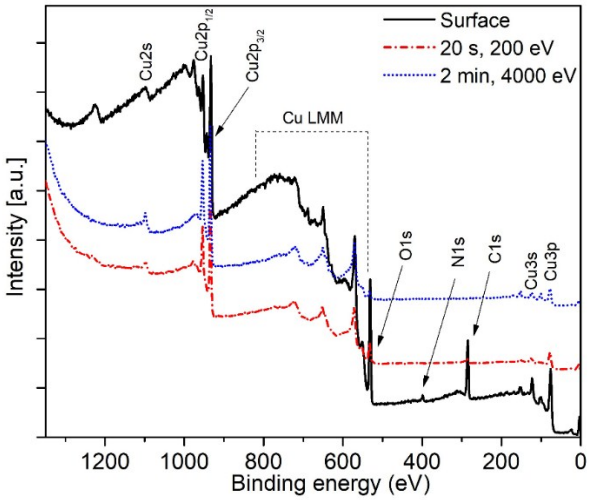

Figure S28. XPS survey spectra obtained of layer H (applied parameters are given in Table 5) of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

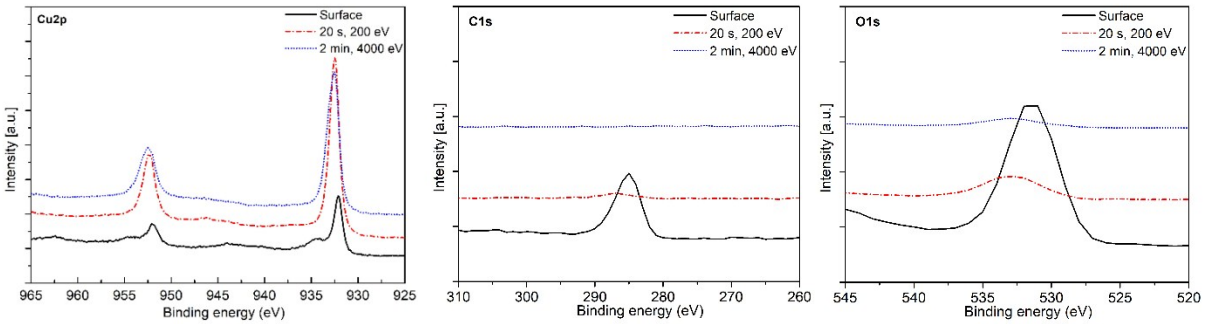

Figure S29. Detailed XPS spectra of the Cu2p (left) peak C1s (middle) and O1s (right) obtained of layer H from **5** of the surface and layer after 20 s (200 eV) and 2 min argon ion sputtering (E = 4000 eV).

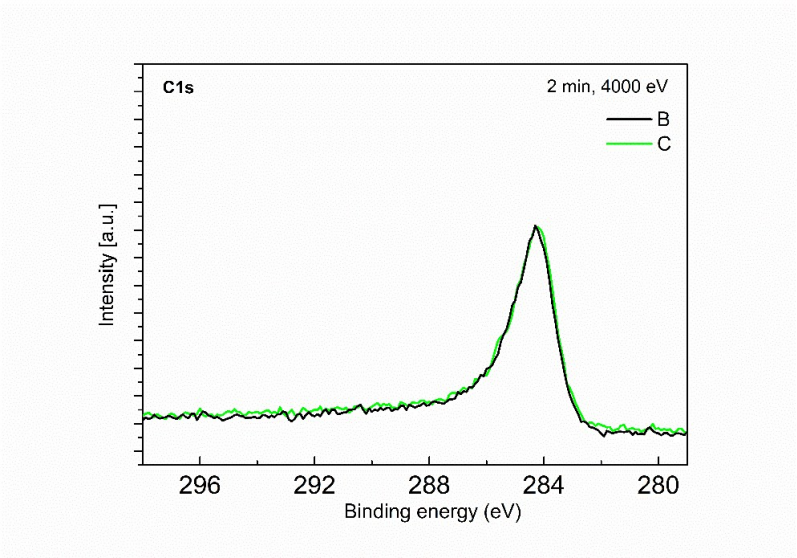

Figure S30. Detailed XPS spectra of the C1s obtained of layers B and C of the layer after 2 min argon ion sputtering (E = 4000 eV).

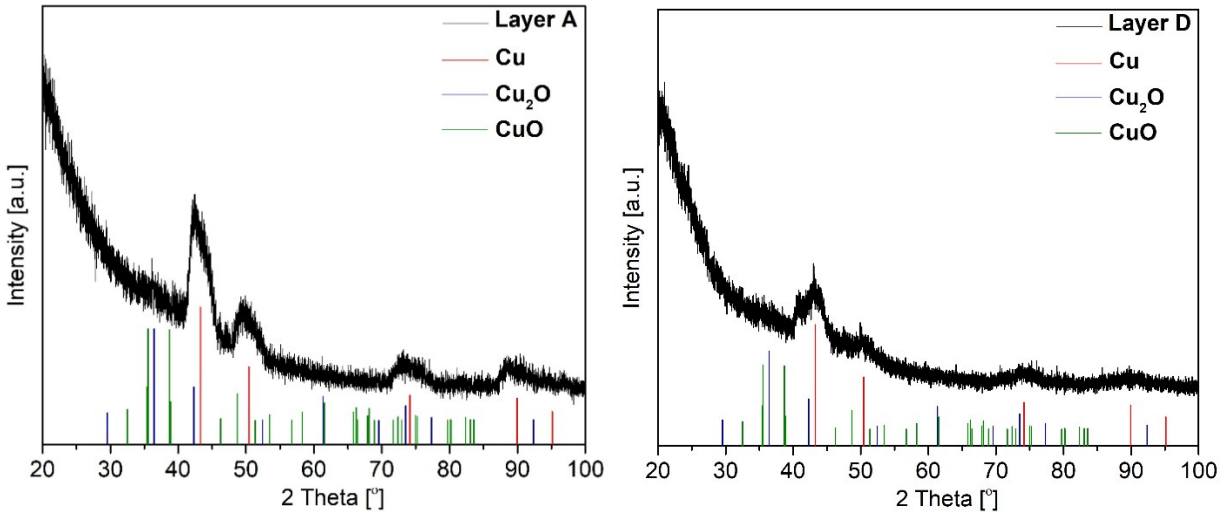

Figure S31. PXRD pattern of the layer A (left) from **4a** and layer D (right) from **5** CVD (N_2) (applied deposition parameters are given in Table 4).

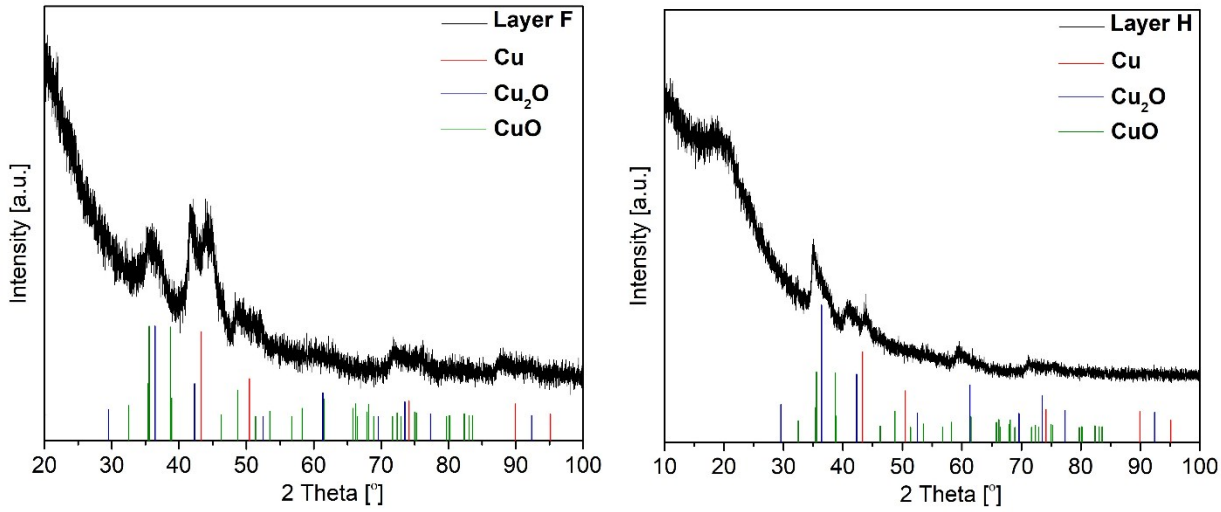

Figure S32. PXRD pattern of the layer F (left) from **4a** and layer H (right) from **5** by CVD (O_2) (applied deposition parameters are given in Table 4).