Supporting Information

Structural Order in Cellulose Thin Films Prepared from a Trimethylsilyl Precursor

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Content:

A) Thin film preparation

Thin films from tetrahydrofuran solutions (in case of $TMSC_S$) or chloroform (for $TMSC_A$) solutions (c = 15 mg ml^{-1} for $TMSC_A$ and 36 mg ml^{-1} for $TMSC_S$) at a = 2500 rpm s^{-1}, v = 4000 rpm, and t = 60 s yielding layer thicknesses in the range of 1400 nm ($TMSC_S$) and 120 nm ($TMSC_A$). The regeneration of the *TMSC* films was performed by placing them in a polystyrene petri dish containing 2 ml of 10 wt% HCl. The dish was covered and the films were exposed to HCl vapor for different time intervals (0, 75, 165, 270, and 700 s) at room temperature to generate partly and fully regenerated films. The removal of trimethylsilyl groups leads to a significant shrinking of the film thickness due to the formation of hydrogen bonding in the cellulose. For the fully regenerated films, 50% shrinkage of the total film thickness was observed so that finally cellulose films with a thickness of ca. 740 nm ($TMSC_S$) and 50 nm ($TMSC_A$) were obtained.

In order to produce even thicker cellulose films (3300 nm and 225 nm), $TMSC_S$ and $TMSC_A$ were processed using different spin coating parameters (a = 1500 rpm s^{-1}, v = 500 rpm, and t = 60 s), followed by conversion with HCl vapors as described above.

The regeneration process of *TMSC* to regenerated cellulose was also performed on powder material without using any dissolution process in solvents. The final fully regenerated cellulose material is denoted as $Cell_S$ or $Cell_A$ depending on the source material.

B) Complementary X-ray diffraction investigations

The used measurements geometries are given in Figure S1. Grazing incidence X-ray diffraction (GIXD) was performed by using synchrotron radiation in combination with a 2-dimensional detector, while in-house X-ray diffraction (on thin films as well as on powder samples) was performed in specular geometry by using a point detector.

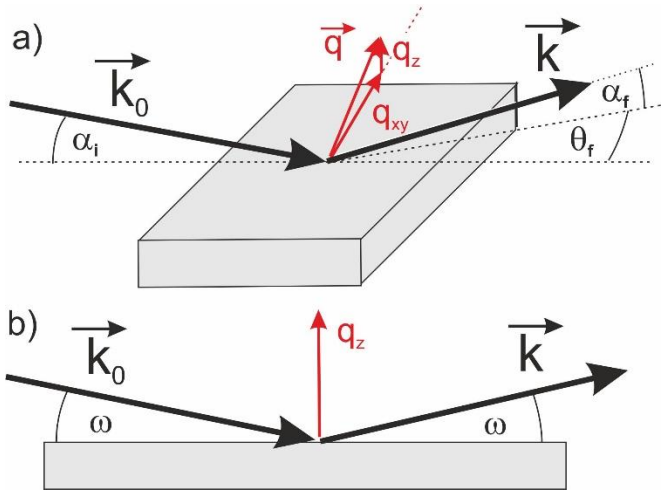

Figure S1: Geometry of grazing incidence X-ray diffraction (a) and of specular diffraction (b) for the investigation of thin films as well as of powder samples.

The reciprocal space map measured by grazing incidence X-ray diffraction of the regenerated cellulose $Cell_A$ is depicted in Figure S2. This measurement is in comparison to the corresponding reciprocal space map of the regenerated cellulose $Cell_S$ given in the main part of the paper (Fig. 3).

Since the GIXD studies cannot give precise information in the specular direction (intensity as a function of q_z with $q_{xy} = 0$), specular X-ray diffraction patterns are taken. The corresponding results are depicted in Fig. S3

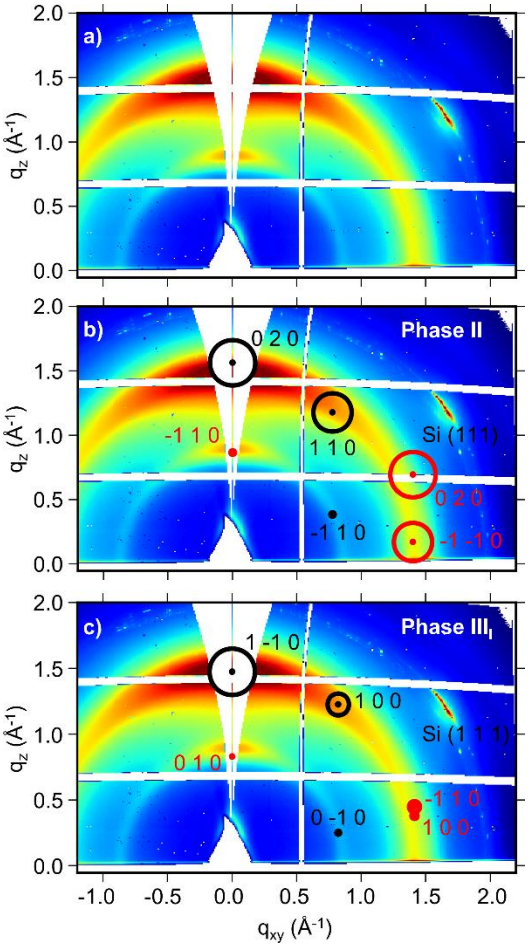

Figure S2. (a) Reciprocal space map of a cellulose thin film with a thickness of 225 nm of *Cell*$_A$. (b) The reciprocal space map together with calculated peak positions (points) and peak intensities (circles) of phase II and (c) of phase III$_I$. In each case, two selected crystal orientations are depicted by black and red circles.

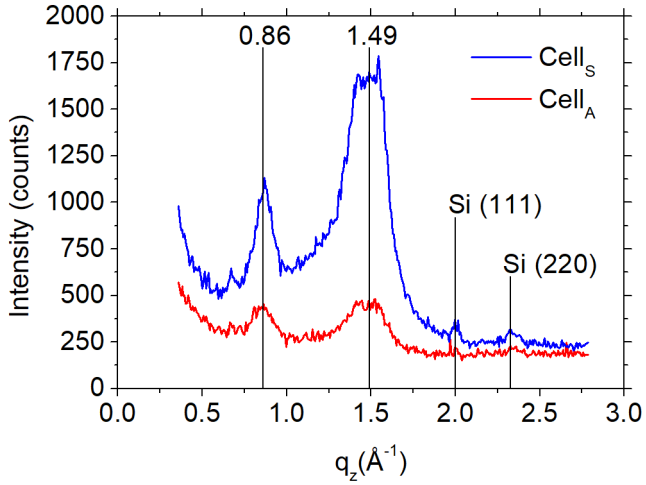

Figure S3. Specular X-ray diffraction patterns (q_{xy} = 0) of two regenerated cellulose films prepared from *Cell*$_S$ and *Cell*$_A$, the corresponding film thicknesses are 740 nm and 225 nm, respectively.