Supporting Information for

Observation of Hydrogen-Ordered Cubic Ice Thin Films on the Surface of Ice Ic Nanocrystals upon Coarsening

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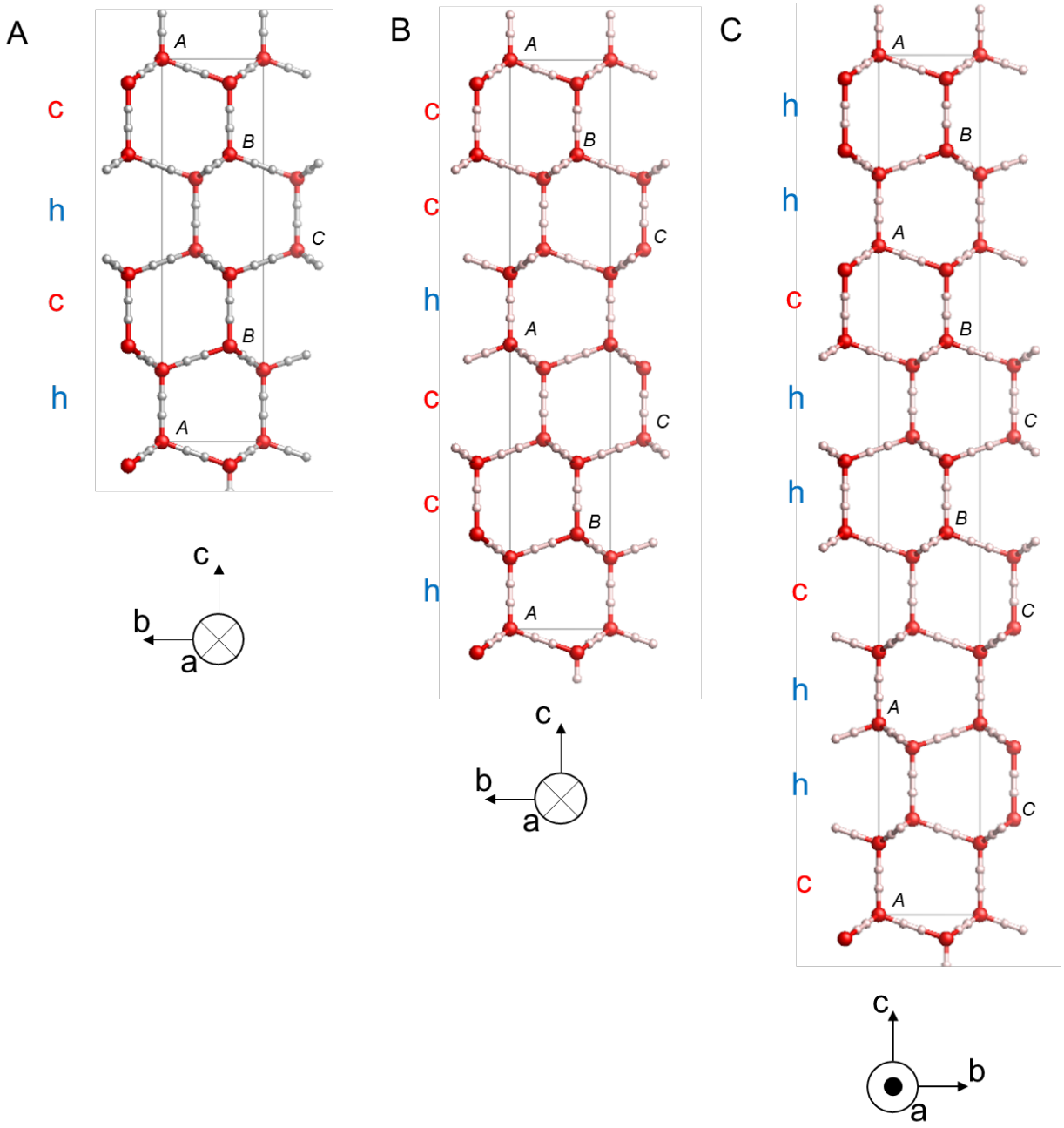
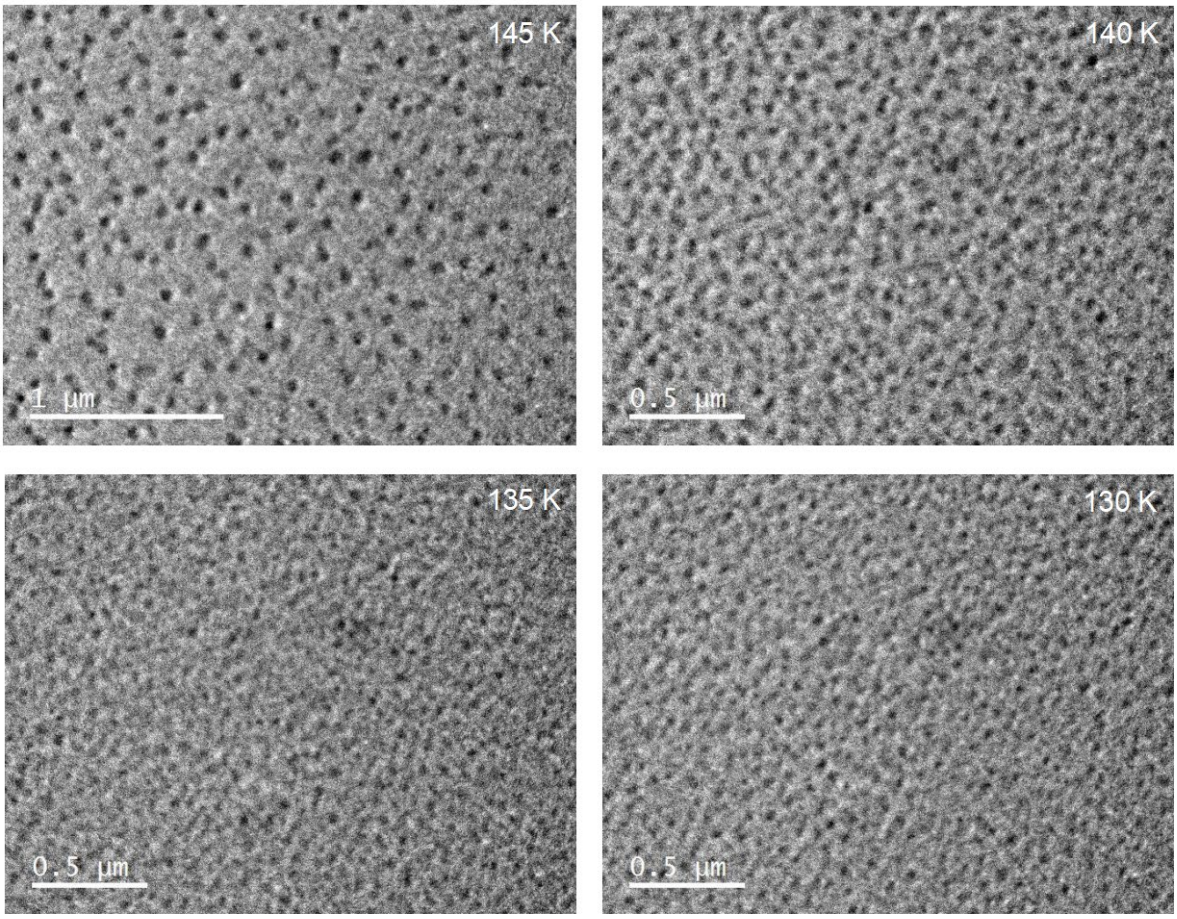


Figure S1. The crystal structures of Isd. The unit cells of Isd of 4H (A), 6H (B), and 9R (C) in the Ramsdell notation were prepared and their diffraction intensities in electron diffraction were calculated. These images were produced by Recipro [S1]. Oxygen and hydrogen atoms are shown as red and white spheres, respectively. Cubic and hexagonal stacking is indicated by 'c' and 'h', respectively. The *ABC*s in the figure indicate a repetition of stacking; for example, that in 4H (A) is *ABCB*. Crystallographic orientations are indicated by 'abc' and arrows.

A



B

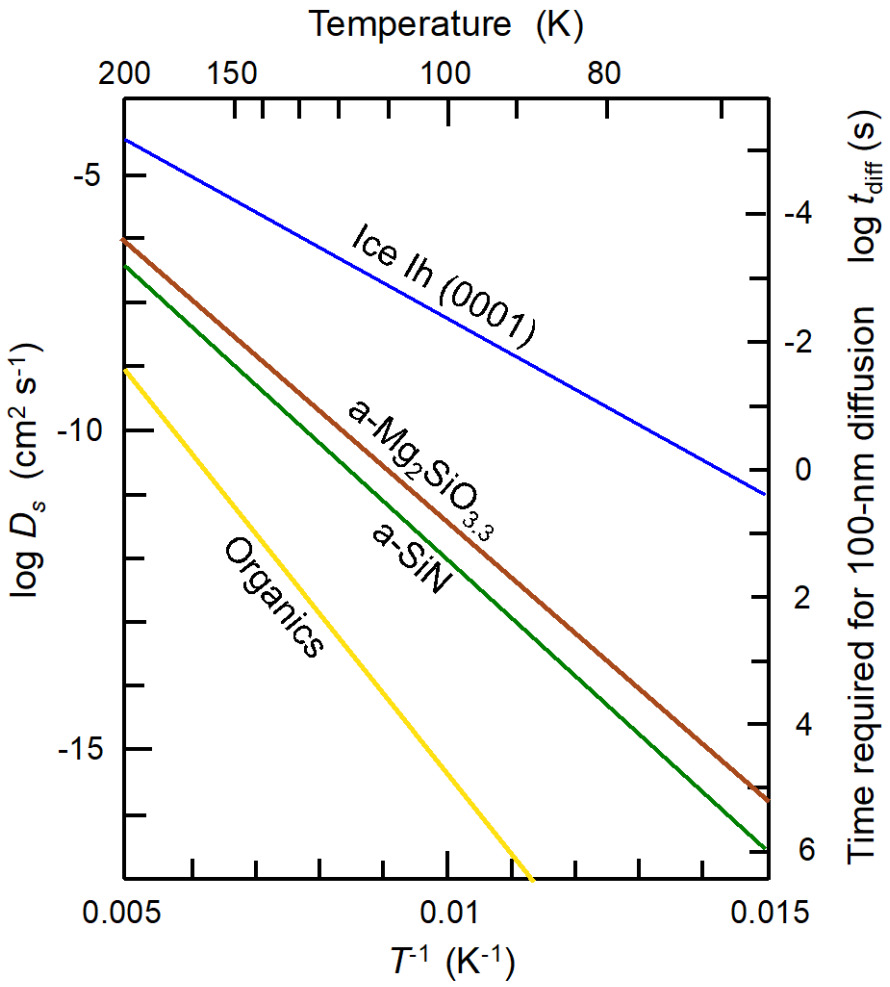


Figure S2. TEM images obtained immediately after saturation of the ice Ic crystal number density during the deposition of H_2O onto a-SiN within 145–130 K (A). Based on the number density of crystals, we followed a reported method [S2] to obtain the activation energy of surface diffusion, E_{sd}, of a H_2O molecule on a-SiN, which was 2080 ± 120 K. Surface diffusion coefficients, D_s, of water molecules on various substrates (B). D_s is expressed as $D_s = D_0\exp(-E_{sd}/kT)$, where D_0 is the preexponential factor, k is the Boltzmann constant, and T is temperature. Thus, we can calculate D_s if D_0 is assumed to be 10^{-3}. The E_{sd} of the (0001) face of ice Ih, identical to the (111) face of ice Ic, was referenced from a previous study [S3], and those of a-$Mg_2SiO_{3.3}$ and organics were referenced from a previous study [S4]. On the right ordinate, the durations required for 100-nm diffusion on the substrates are shown. This figure shows that the water molecules on the a-SiN substrate rapidly diffused between 80 and 130 K. Therefore, the rate-determining step of coarsening was not surface diffusion of water molecules on the a-SiN substrate.

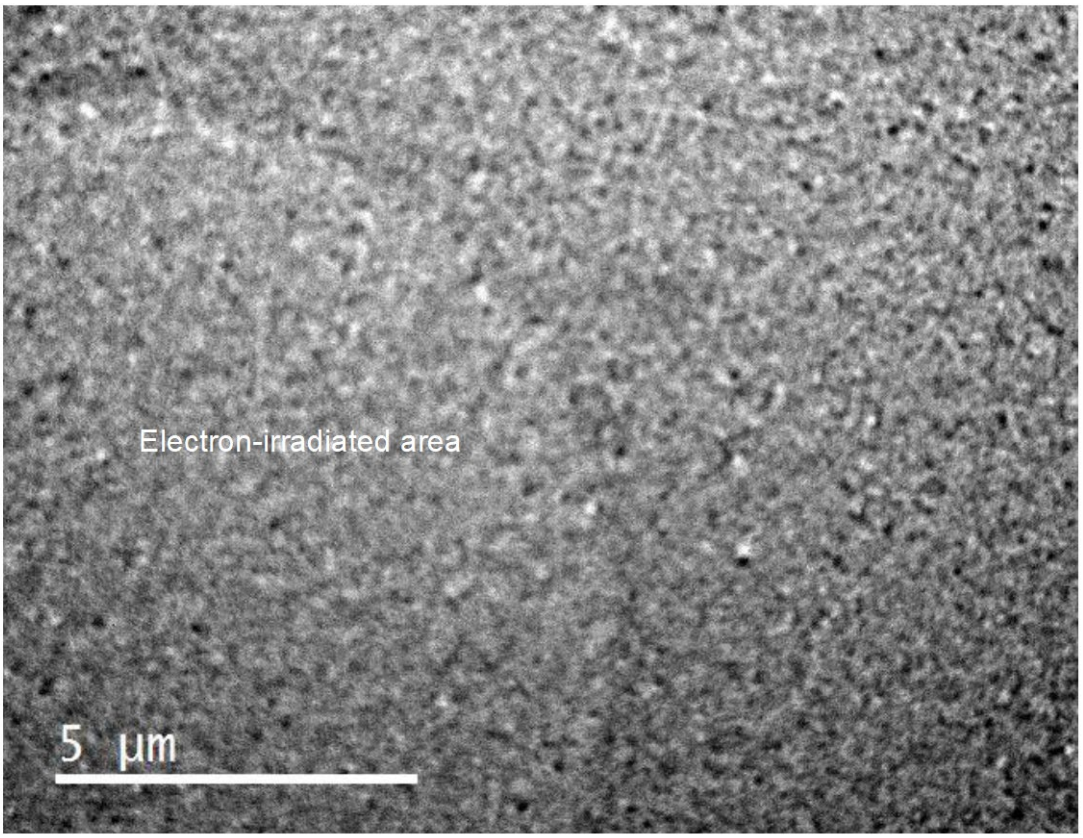


Figure S3. Low-magnification TEM image after 6-h electron irradiation at 120 K. An electron beam ~12 μm in diameter was continuously irradiated at the same position of the ice Ic sample for 6 h. Sputtering of the ice Ic crystals preferentially proceeded. Although measuring the thickness of the sputtered region from this photomicrograph was difficult, we assumed that the thickness of the sputtered region was half that of the unsputtered region (~25 nm) for the estimation of the sputtering rate. We observed that the sputtering rate induced by the electron beam was ~4 nm/h at most. Typically, diffraction spots of crystals appear if the number of crystalline layers exceeds four. The four-layer thickness of ice Ic was 1.2 nm. Therefore, the disappearance of the electron diffraction spots of hydrogen-ordered cubic ice observed after 20 min of electron irradiation (Figure 9) correlated with the estimated sputtering rate. This supported the suggestion that hydrogen-ordered cubic ice was formed on the surface of ice Ic.

Table S1. Lattice constants of each structure of ices used for calculation of relative intensities.

Lattice parameter	C1	C2	C3	C4	C5	C6	C7	C8	C9
a	8.776	8.773	8.778	8.774	8.787	8.771	8.785	8.781	8.782
b	4.385	4.382	4.381	4.389	4.393	4.383	4.392	4.389	4.387
c	6.219	6.236	6.232	6.229	6.217	6.231	6.221	6.222	6.221
α	90	89.999	90.005	89.946	89.975	90.007	90	90.035	89.99
β	90	89.98	89.995	89.978	90	89.956	90	89.93	89.988
γ	90	90	90.007	90.003	90	89.995	89.979	89.982	89.998

Lattice parameter	C10	C11	H1	H2	H3	H4	H5	H6	H7
a	8.78	8.761	4.369	4.417	4.415	4.423	4.424	4.415	4.42
b	4.387	4.386	7.641	7.62	7.617	7.54	7.543	7.619	7.612
c	6.228	6.239	7.184	7.138	7.139	7.188	7.18	7.145	7.134
α	89.963	90.065	90	90	90	90	90	90	90
β	89.937	90.065	90	90	90	90	90	90	90
γ	90.018	90.008	90	90	90	90	90	90	90

Lattice parameter	H8	H9	H10	H11	H12	H13	H14	H15	H16
a	4.422	4.395	4.372	4.43	4.417	4.417	4.43	4.372	4.424
b	7.548	7.567	7.641	7.544	7.616	7.616	7.544	7.641	7.544
c	7.183	7.185	7.18	7.174	7.14	7.138	7.169	7.181	7.181
α	90	90.59	90	90	89.953	90.015	90	90	89.974
β	89.991	90	90	89.971	90	90	90	90.022	90
γ	90	90	90.014	90	90	90	90.116	90	89.973

Lattice parameter	4H	6H	9R
a	4.49073	4.49073	4.49073
b	4.49073	4.49073	4.49073
c	14.667	22	33
α	90	90	90
β	90	90	90
γ	120	120	120

Table S2. Calculated relative intensities of hydrogen-ordered ices Ih in electron diffractions.

d (Å)	hkl[a]	Group	C1~11	Structure number, ideal space group							
				H1	H2	H3	H4	H5	H6	H7	H8
				$Cmc2_1$	$Pna2_1$	$Pna2_1$	$Pbn2_1$	$Pca2_1$	$P2_12_12_1$	$P2_12_12_1$	Cc
9.01	100	A	+								
7.81											
6.38	001	B	+								
5.36					+	+			+	+	
5.21	101	C	+								
4.51-4.50	200, 010	D	+					+			
4.03	110		+								
3.92-3.90				+++	+++	+++	+++	+++	+++	+++	+++
3.84							+		+	+	
3.68	011, 201		+++	+++	+++	+++	+++	+++	+++	+++	+++
3.46-3.42				+++	+++	+++	+++	+++	+++	+++	+++
3.41	111		++								
3.33					+	+			+	+	
3.19	210, 002	E	+								
3.01	102, 300		+								
2.95							++		++	+	
2.85	211		+		++	+		++	+	+	
2.74					++	+	+	++	+	+	
2.72	301		++								
2.68				+++	+++	+++	+++	+++	+++	+++	+++
2.60	012, 202		++								
2.50	112, 310		++								
2.45					++	++			++	++	
2.34					++	++			++	++	
2.33	311		++								
2.30					+	+	++	++	++	+	
2.25-2.26	020, 212, 400		+++	+++	+++	+++	+++	+++	+++	+++	+++
2.19	302, 120		++								
2.17							+++	+	++	++	
2.15				++		+	++	++	++	++	++
2.12	401, 003, 021		++		++	++			++	++	
2.08				+++	+++	+++	+++	+++	+++	+++	+++
2.07	103, 121		++								

(*Continued*)

Table S2. Continued

d (Å)	hkl[a]	Group	C1~11	Structure number, ideal space group							
				H9	H10	H11	H12	H13	H14	H15	H16
				Pc	Pc	Pc	$P2_1$	$P2_1$	$P2_1$	$P2_1$	P1
9.01	100	A	+								
7.81				+							
6.38	001	B	+								
5.36						+	+	+	+		
5.21	101	C	+								
4.51-4.50	200, 010	D	+	+							
4.03	110		+								
3.92-3.90				+++	+++	+++	+++	+++	+++	+++	+++
3.84				+	+			+	+		+
3.68	011, 201		+++	+++	+++	+++	+++	+++	+++	+++	+++
3.46-3.42				+++	+++	+++	+++	+++	+++	+++	+++
3.41	111		++								
3.33					++	++	+	+	++	++	
3.19	210, 002	E	+								
3.01	102, 300		+								
2.95				+		+	+	+	+	++	+
2.85	211		+	+	+		++	+	+		+
2.74				+	++	+	+	+	++	+	+
2.72	301		++								
2.68				+++	+++	+++	+++	+++	+++	+++	+++
2.60	012, 202		++						+		
2.50	112, 310		++								
2.45				+	+	+	++	++	+	+	
2.34					++	++	++	++	++	++	
2.33	311		++								
2.30					++	+	+	+	++	+	+
2.25-2.26	020, 212, 400		+++	+++	+++	+++	+++	+++	+++	+++	+++
2.19	302, 120		++								
2.17				++		++	+	++	+	++	++
2.15				+	++	++	+	++	++	++	++
2.12	401, 003, 021		++		+	+	++	++	+	+	
2.08				+++	+++	+++	+++	+++	+++	+++	+++
2.07	103, 121		++								

The diffraction intensities are grouped according to the calculated relative intensities (%) into +++, 1-100; ++, 0.1-1; and +, 0.001-0.1.

[a]Miller indices for orthorhombic cells of C1-C11.

References

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