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Structure and sublimation of water ice films grown in vacuo at 120–190 K studied by positron and positronium annihilation

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Abstract

The crystalline structure of $\sim$5–20 μm water ice films grown at 165 and 172 K has been probed by measuring the fraction of positrons forming ortho-positronium (ortho-Ps) and decaying into three gamma photons. It has been established that films grown at slower rates (water vapour pressure $\geq$ 1 mPa) have lower concentrations of lattice defects and closed pores, which act as Ps traps, than those grown at higher rates (vapour pressure $\sim$100 mPa), evidenced by ortho-Ps diffusion lengths being approximately four times greater in the former. By varying the growth temperature between 162 and 182 K it was found that films become less disordered at temperatures above $\sim$172 K, with the ortho-Ps diffusion length rising by $\sim$60%, in this range. The sublimation energy for water ice films grown on copper has been measured to be 0.462(5) eV using the time dependence of positron annihilation parameters from 165 to 195 K, in agreement with earlier studies and with no measurable dependence on growth rate and thermal history.

Keywords: water ice, positron, positronium, thin film growth

(Some figures may appear in colour only in the online journal)

1. Introduction

The region in the water phase diagram between 140 and 230 K at low pressures is considered a 'no-man's land' because it is inaccessible to most experimental procedures studying the structure of liquid water. Below the homogeneous nucleation temperature of 235 K supercooled water will freeze almost instantaneously, while above the glass transition temperature ($\sim$136 K) crystallization cannot be avoided for long [1]. An additional complication in experiments performed above $\sim$160 K under vacuum conditions is that the ice sample will sublime appreciably during the course of the measurement. Consequently, there have been very few studies of the atomic-scale structural features of μm ice films grown in vacuo in the temperature range 150–190 K, where polycrystalline ice preferentially results [2–5].

There is much current interest in studies of ice grown under these conditions, where there continues to be widespread debate about a variety of topics, from the nature and temperature of the glass transition, to the presence of pockets of supercooled water in the matrix, and to the lattice structure of one of the most abundant phases of ice in the universe—cubic ice, I_c [6–10]. Recent work has suggested that what has traditionally been designated cubic ice may be made up of disordered cubic and hexagonal stacking sequences [9, 11], and that the balance between cubic and hexagonal ice may be determined by the nature of growth spirals [5, 12]. In order to probe the structure and sublimation of water ice films grown by vapour deposition on a copper surface at temperatures above 140 K we have employed variable-energy positron annihilation spectroscopy (VEPAS).

2. Experimental method and procedure

VEPAS has been shown to be an effective probe of ice film structure [13, 14] and well-suited to growth temperatures

at which significant sublimation is also occurring. The Doppler-broadened annihilation lineshape parameter S is used to identify the positron annihilation sites (i.e. film versus substrate). S is a measure of the sharpness (linewidth) of the 511 keV gamma annihilation line measured by a germanium detector and is sensitive to the average momentum of electrons at the annihilation sites. About 75% of positrons thermalized in pure water ice form the positron–electron bound state positronium (Ps) [15]. The fraction F of the incident positrons which form the longer-lived triplet state, ortho-Ps, and decay with the emission of three gamma photons—either in the vacuum above or within pores in the ice—is determined by the quality of the as-grown crystalline film, in which atomic-scale defects serve to reduce diffusion and decrease F via trapping [16]. F was found to have a maximum at ∼0.75 keV of ∼50% [16].

F is obtained from the excess annihilation count rate in the 'valley' region of the germanium detector spectrum (395–505 keV) relative to the total count rate in the 511 keV photopeak when no Ps is formed. Details of the procedure for determining absolute values for F in this way are to be found in [17]. By varying the incident positron energy E one can measure F as a function of mean penetration depth and thereby estimate Ps migration/diffusion lengths.

Most laboratory-based experimental studies on water ice films vapour-deposited in vacuum have been on substrates held at temperatures below 130 K; such films are overwhelmingly amorphous solid water (ASW) [18]. In the present study 5–20 μm ice films were grown by increasing the water vapour pressure in the sample chamber (base pressure ∼20 μPa) to a predetermined value; due to the large volume of the sample chamber (∼0.02 m^3) the ambient pressure is reached after 2–3 s, and pump-down takes a similar time. The machine-polished copper substrate was held between 120 and 190 K, in which range one can grow films with structures varying from compact ASW to crystalline ice [14]; growth times ranged from ∼30 to 10^4 s, and growth rates—estimated by measuring film thickness after a known growth time using $S(E)$ as described in section 3—from 2 to 500 nm s^{-1}. For a general description of the positron beam apparatus used for these measurements, see [19].

3. Results and discussion

The parameters S and F are shown in figure 1 as a function of time t after growth, at selected positron energies E, for a 20 μm crystalline ice film subliming at 165 K following growth at the same temperature at a vapour pressure of 10 mPa for 1500 s. S in bulk crystalline ice was measured repeatedly (at high E) to be 0.514, being only slightly affected by Ps annihilation; S increases linearly with F. S in bulk copper is 0.426, rising to ∼0.476 as E decreases and positrons increasingly diffuse to the surface. The key here is that S values for ice and copper are measurably different and distinguishable.

It is clear from figure 1 that initially, when all positrons are stopped in the ice film, S is largely insensitive to E (i.e., penetration depth) whereas F increases significantly at lower E, as a result of migration to the vacuum as described above.

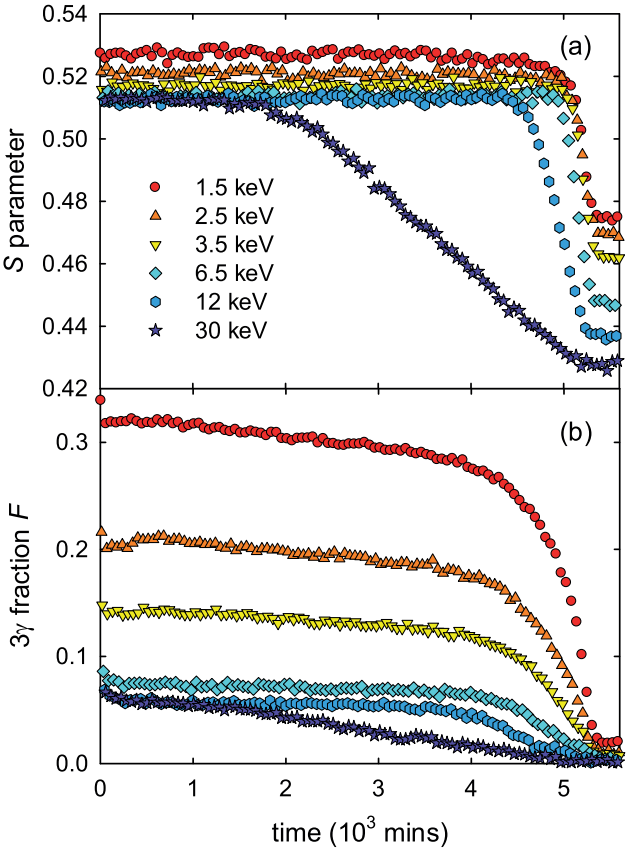

Figure 1. (a) $S(E)$ as a function of time for a 20 μm crystalline ice film grown at 100 mPa for 1500 s at 165 K with sublimation measured at the same temperature. The mean positron implantation depths (in μm) corresponding to their energies shown (in keV) are: 0.08 (1.5), 0.19 (2.5), 0.32 (3.5), 0.53 (4.75, in figures 3 and 4 only), 0.87 (6.5), 2.3 (12), 10.0 (30). (b) The 3γ yield F for the film of figure 1(a).

For positrons implanted to a mean depth of ∼ 10 μm all three-gamma annihilation occurs within pores in the ice film; for example, for a 165 K-grown film F (bulk) ∼6%.

For freshly grown films F is significantly higher, especially at low E, for a short time after growth ends (as illustrated in figure 1 for a fixed temperature of 165 K), even when the temperature is low enough to limit sublimation heavily. A similar short-lived increase is seen if the temperature of a subliming film is raised later in a run; this feature is ascribed to low-pressure growth of a thin surface ice layer, either as vapour is pumped out or released near the heating element.

Over longer time scales $F(t)$ generally exhibits a downward trend, as in figure 1. While this is true for all films studied, those grown more rapidly exhibit a higher slope. This is consistent with the near-surface temperature of the film increasing during growth, resulting in a film quality (and thus F) profile. Results for films grown at the same temperature and rate, but to different thicknesses, suggest that the slope in $F(t)$ is not related to ageing or annealing effects during the measurements.

Sublimation rates were measured over a wide range of temperatures and used to determine the energy of sublimation E_{sub}. As figure 1 shows, S decreases when the film thickness

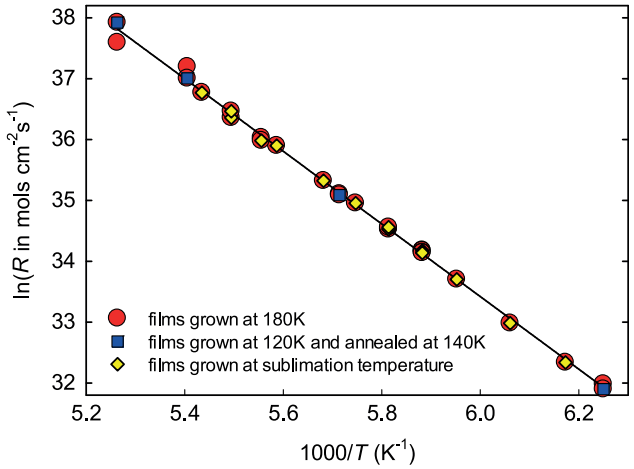

Figure 2. An Arrhenius plot showing the sublimation rate in the range $T = 165$–190 K (mols cm^{-2} s^{-1}) of ice films grown (a) rapidly at 180 K (●), (b) rapidly at the sublimation temperature (◆) and (c) slowly at 120 K with annealing at 140 K (■).

decreases such that positrons start to penetrate into the copper substrate. In a simple model where $S = f_{\mathrm{ice}} S_{\mathrm{ice}} + f_{\mathrm{Cu}} S_{\mathrm{Cu}}$ and both S_{ice} and S_{Cu} are known, f_{ice} and f_{Cu} are the fractions annihilated in ice and copper, respectively, and $f_{\mathrm{ice}} + f_{\mathrm{Cu}} = 1$, then $f_{\mathrm{ice}} = (S - S_{\mathrm{Cu}})/(S_{\mathrm{ice}} - S_{\mathrm{Cu}})$. Combining f_{ice} with the positron implantation profile $P(E, z)$ [20], and neglecting the effects of net positron backscattering from the copper, one can estimate the film thickness d if a constant density is assumed (here taken to be 0.92 gcm^{-3} [21]). Data such as those in figure 1 were only used for $E \geq 9$ keV (mean depth ~ 1.3 μm) for two reasons. First, because data for decreasing E were increasingly sensitive to small variations in ice thickness across the film, which by analysis of $S(t)$ at different E was found to be generally ~4% of the maximum film thickness (prior to sublimation). Second, at higher E the implantation and annihilation profiles are similar, as the depths involved are far greater than expected positron diffusion lengths—which in water ice will be reduced via trapping by OH dangling bonds [3, 22]. The sublimation rate at any given temperature T, $R(T)$, was calculated from $d(t)$ for f_{ice} in the range 7.5–87.5%, as outside this range S is less sensitive to d and more influenced by statistical uncertainty.

To investigate the influence on E_{sub} of growth history and film structure, three series of 20 μm films were grown (a) at 180 K under a vapour pressure of 100 mPa for 90 s (growth rate ~ 0.2 μm s^{-1}), (b) at the sublimation temperature under 200 mPa for 30 s (at over 0.5 μm s^{-1}), and (c) at 120 K under 1 mPa for over 3 h (at ~ 2 nm s^{-1}), then annealed at 140 K for 4 h to obtain a compact, crystalline film.

The sublimation rates are presented on an Arrhenius plot in figure 2. Although it is possible that there are significant differences in morphology between the three sets of films due to their thermal histories, the rate data points for all of them lie essentially on the same line between $T = 165$ and 195 K, consistent with the observations of Sack and Baragiola [23]. Note that any misassignment of film density or the positron profile $P(E, z)$, or surface area factors related to morphology,

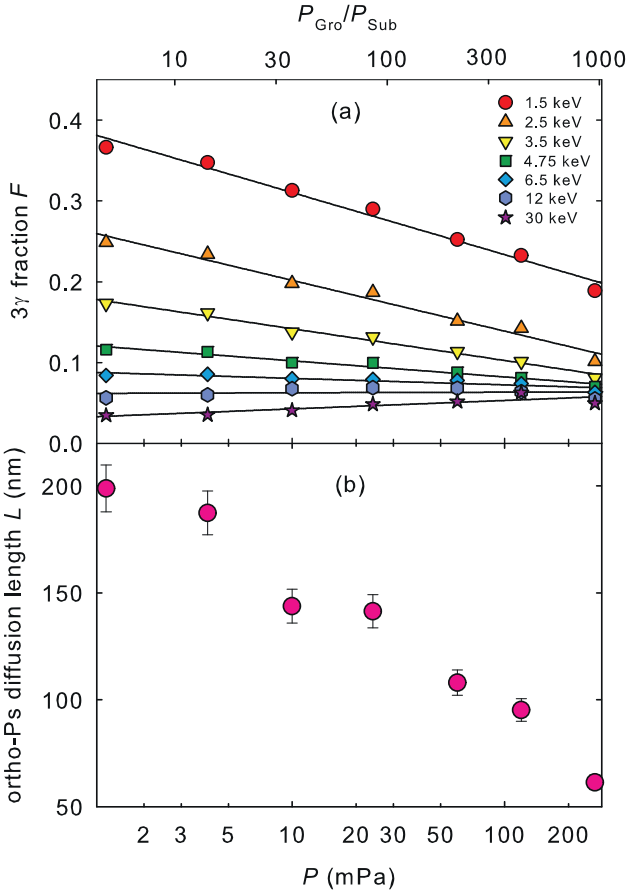

Figure 3. (a) The 3γ yield F for a series of ~ 20 μm crystalline ice films grown at 165 K at deposition pressures in the range 1–100 mPa. The mean positron implantation depths are given in figure 1(a). (b) The effective ortho-Ps diffusion length, obtained by fitting $F(E)$, as a function of deposition pressure.

will have similar multiplicative effects on all rate values and thus the same additive effect on ln R, and E_{sub} is unaffected.

Using the relation $R(T) = A_1 \exp(-E_{\mathrm{sub}}/kT)$ of Haynes *et al* [24] figure 2 yields $E_{\mathrm{sub}} = 0.514(5)$ eV, which agrees well with the value obtained by those authors of 0.516(9) eV. Alternatively, using the relation $R(T) = A_2 T^{3.5} \exp(-E_{\mathrm{sub}}/kT)$ of Sack and Baragiola [23] we obtain $E_{\mathrm{sub}} = 0.462(5)$ eV, again in agreement with their value of 0.44(4) eV.

Figure 3(a) shows that Ps diffusion to the surface (reflected in F) is greater for films grown more slowly (i.e., at lower vapour pressures). Here all films were grown at 165 K, at which the vapour pressure of subliming ice is P_{sub}~0.3 mPa; the lowest growth pressure in figure 3 is 1.3 mPa—i.e., only four times greater than P_{sub}. At lower pressures no films were produced.

Similar trends were seen for growth at 172 K. F values were measured for films of similar thickness (~ 15 μm) at times from 40 to 120 min after growth was completed; data from the first 40 min were excluded for reasons stated above. Note that F was measured for nine values of E throughout this work; the 9 and 20 keV data points are not shown in the figures to aid clarity, but were used in the fitting procedures described below.

The higher values of F for lower growth rates suggests that a more ordered lattice is achieved when the growth

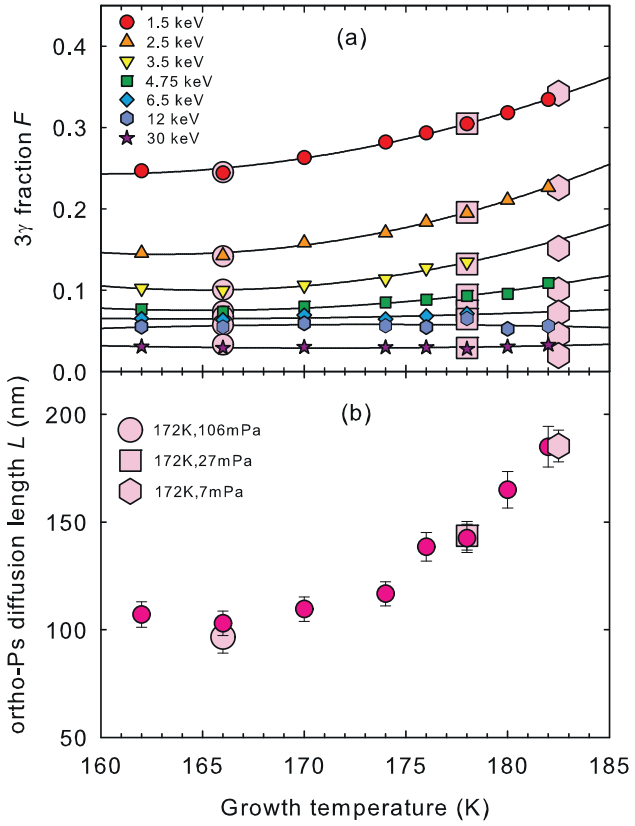

Figure 4. (a) The 3γ yield F for a series of crystalline ice films initially grown to ~ 12 μm from 162 to 182 K at a deposition pressure of 67 mPa. F was measured while the film sublimed from 9 to 7 μm at the growth temperature. Also shown are F for three films grown and measured for the same thicknesses at 172 K at 6.7 mPa (○), 26.7 mPa (□) and 106 mPa (⬡), but plotted at 166, 178 and 182.5 K, respectively, to facilitate comparison. The mean positron implantation depths are given in figure 1(a). (b) The effective ortho-Ps diffusion length, obtained by fitting $F(E)$, as a function of growth temperature.

rate is low, resulting in a considerably longer Ps diffusion length L. At higher growth rates, where the structure is grown too quickly to self-organize, a higher concentration of defects results which will trap Ps and prevent diffusion to the surface. This is illustrated in figure 3(b), where L has been deduced by fitting $F(E)$ at each growth rate using the standard code VEPFIT [25], assuming a film density of 0.92 gcm^{-3} [21]. From the only earlier measurement of Ps diffusion in crystalline ice one can deduce a value of $L = 108 \pm 30$ nm [16].

One can discount the alternative interpretation of the results shown in figure 3(a), that when growth and sublimation rates become closer interconnected pores are grown into the film and allow Ps migration to the surface, because measurements on highly porous amorphous films at very low temperatures yielded much greater F values in bulk than those seen here. Additionally, the small increase in F with growth rate for $E = 20$ and 30 keV is attributed to the growth of more, or larger, closed pores within the bulk of the film, allowing more Ps to survive long enough to decay via three rather than prematurely to two gamma photons. The authors have also observed that the open-pore structure of ASW rapidly reconstructs prior to crystallization, so that such channels are not expected to be grown in—or, at least, to survive—at higher growth temperatures.

Figure 4 shows that increasing the growth temperature has effects on F and L similar to decreasing the growth rate. Here a series of crystalline ice films were initially grown on the copper substrate at temperatures in the range 162–182 K to a thickness of ~ 12 μm at a deposition pressure of 67 mPa. The films were left to sublime at their respective growth temperatures and F measured while the films thinned from 9 to 7 μm. Also shown are F values for three ~ 12 μm films grown and measured following an identical procedure at 172 K at pressures of 6.7, 26.7 and 106 mPa.

The latter results are superimposed on the former at 182.5, 178 and 166 K to demonstrate the equivalence of growth rate and temperature; for example, the film grown at 172 K at the lowest pressure here has a similar profile to that grown at 182.5 K at a higher pressure.

Films grown at a high temperature (180 K) showed no change in structure (i.e. in the values of F and L) when subsequently cooled to 160 K. Likewise, films grown and initially measured at 160 K showed no increase in F or L upon heating and measuring at 180 K. This indicates that structural features are essentially frozen in during growth.

The effective ortho-Ps diffusion length, shown in figure 4(b) as a function of growth temperature, again obtained by fitting $F(E)$, exhibits two distinct branches. Below 170–175 K L is essentially independent of growth temperature, but then increases linearly with temperature, from 115 to 185 nm, between 174 and 182 K. This once more points to the growth of a less disordered film at higher temperatures, and the equivalence of growth temperature and rate. It is interesting to note that other researchers have observed structural changes at or about 170 K, frequently associated with the cubic-to-hexagonal ice, or related, transition [9, 12].

The nature of the disorder capable of impairing the diffusion of Ps atoms may take several forms, including pockets of ASW co-existing with crystalline ice [26], crystal grain boundaries and associated open volumes, closed (∼nm) pores, screw dislocations [12], and spaces between disordered cubic and hexagonal stacking sequences [11].

4. Conclusions

In summary, positron and Ps annihilation spectroscopies are ideal *in situ* probes of the evolution and morphology of water ice films at temperatures and under pressures where significant sublimation occurs.

Positrons have been used for the first time to measure the sublimation energy of water ice with higher precision than in earlier measurements [23, 24], with which the value of 0.462(5) eV agrees well. The present work suggests that this energy is not dependent on film growth and history.

Ps formation and decay in vacuum into three gamma photons have been used to study the crystalline structure of water ice films grown under conditions where growth and sublimation compete. It was found that films grown at lower rates and/or higher temperatures had morphologies exhibiting a crystalline structure with less disorder, leading to much longer ortho-Ps diffusion lengths. At higher rates/lower

temperatures the size and/or concentration of nm-sized closed pores and atomic-scale defects increases. Across the chosen ranges of growth conditions, the ortho-Ps diffusion length changes by a greater factor when the growth rate, rather than growth temperature, was varied.

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