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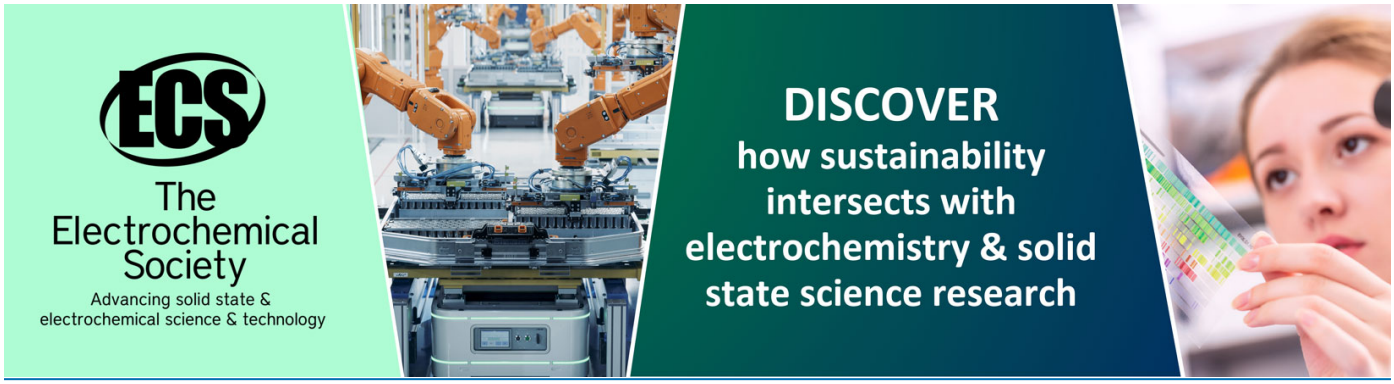

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Observations of the growth and sublimation of water ice films by variable-energy positron annihilation spectroscopy

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Abstract. The near-surface structure of thin vapor-deposited water ice films during formation and sublimation in vacuum has been probed using in-situ positron annihilation spectroscopy. While amorphous solid water films prepared at 120K are highly dense with low porosity micro- and interconnected meso-pores have been observed in the top few tens of nm of ice films prepared at temperature of 170 - 180K as the films are forming and during sublimation. Responses to these near-surface pores are much more pronounced in films grown at 170 - 180K than in those grown at lower temperatures.

1. Introduction

The sublimation of ice is a fundamental phenomenon with relevance to the understanding of many astrophysical phenomena such as the outgassing of volatiles from cometary systems [1]. Sack and Baragiola studied the dynamics of sublimation of water ice grown under different conditions, quoting relevance not only to cometary activity but also to the evolution of the surfaces of particles in Saturnian rings, satellites in the outer solar system and interstellar grains [2]. Recently Gundlach et al. [3] made laboratory measurements of the sublimation of hexagonal water ice and diffusion through a dust layer to allow more realistic modelling of cometary activity.

With the aim of providing new information on the near-surface structure of water ice films during sublimation in vacuum conditions, a study has been carried using in-situ variable-energy positron annihilation spectroscopy (VEPAS). This method has recently been shown to provide unique depth-dependent information on the phase of thin ice films [4] extended to the measurement of the probability of positronium (Ps) formation and decay into three gamma photons, which yields direct information on the formation and collapse of micro- and meso-pores (diameter > 2nm) [4,5].

Positrons of energies E between 0.25 and 30 keV (± 1eV) were implanted into water ice films and the annihilation parameters S and F obtained from gamma ray energy spectra recorded by a Ge detector. S is the fraction of the annihilation line between two pre-set energies symmetrically on either side of 511 keV – this is a measure of the extent of the Doppler broadening of the line, being particularly sensitive to annihilation with low-momentum electrons, and thus to the phase of the ice and/or the presence of vacancy clusters or small closed pores [4]. S, which also reflects the formation and decay of para-positronium (p-Ps) because its two-gamma decay contributes a narrow component to the annihilation line, is normalized to the bulk value for the copper substrate. F, determined from

the ratio of annihilation events in the gamma energy range 475-505 keV to those in the 511 keV annihilation line, is a measure of the ratio of 3γ:2γ annihilations, and thus of the fraction of implanted positrons which are annihilated as triplet, or ortho-positronium (o-Ps), which decays in vacuum overwhelmingly via 3γ emission. F = 1 refers to the maximum o-Ps fraction observed in the current measurements, and F = 0 to zero o-Ps formation (from data for the copper substrate at E = 30 keV). F – here a relative rather than absolute value for the o-Ps fraction - is an excellent measure of the size and concentration of large pores in materials, especially of their interconnectedness [5-7].

2. Experimental procedure

Water ice films were grown to thicknesses of ~ 10 μm by bleeding pure water vapor through a needle valve into a chamber evacuated to 1.3 μPa and condensing on to a copper finger cooled by a closed-cycle He refrigerator to pre-set temperatures in the range 50 – 180K. At 50K amorphous solid water (ASW) is formed; at 120K a compact film results, with very few pores; and at 150K or above crystalline films are grown. At the highest temperatures the growth rate has to exceed that for sublimation. For example, at 170K S and F were measured as a function of time at E = 1 and 30keV, for different background vapor pressures P (i.e. varying growth rates). For P = 20 μPa, no growth was observed after 10h; for P = 130 and 1300 μPa, a 10 μm film was grown in ~ 7 and 0.6h, respectively.

Data for individual points were typically collected over 1000 seconds. For temperatures up to 150K the ice is effectively steady state on these timescales, though this is not valid for higher temperatures.

3. Results

For measurement temperatures at or above 170K a 'peak' appears in $S(E)$ and an enhanced peak in $F(E)$ at E ~ 1.5keV (equivalent to a mean positron implantation depth of ~80nm in a solid of unit density), as shown in Fig.1. The behavior of S and F at E < 1.5 keV is probably a result of incomplete

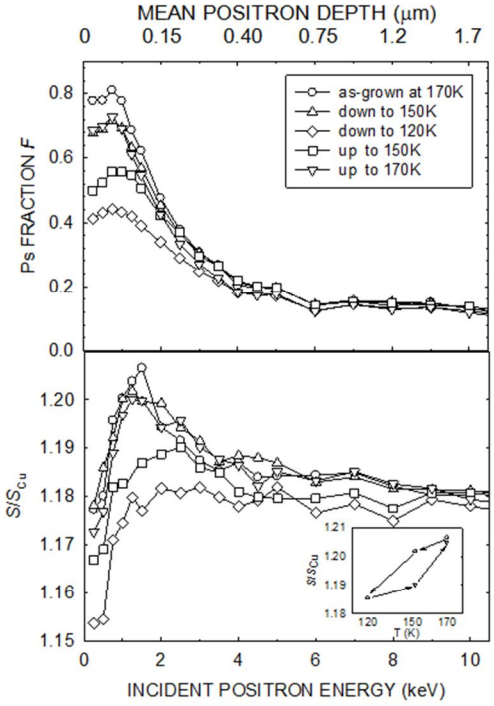

Figure 1. The Ps fraction $F(E)$ and $S(E)$ for ice film grown at 170K, measured at 170, 150 and 120K. The inset shows the hysteresis in the peak S value as the temperature is cycled.

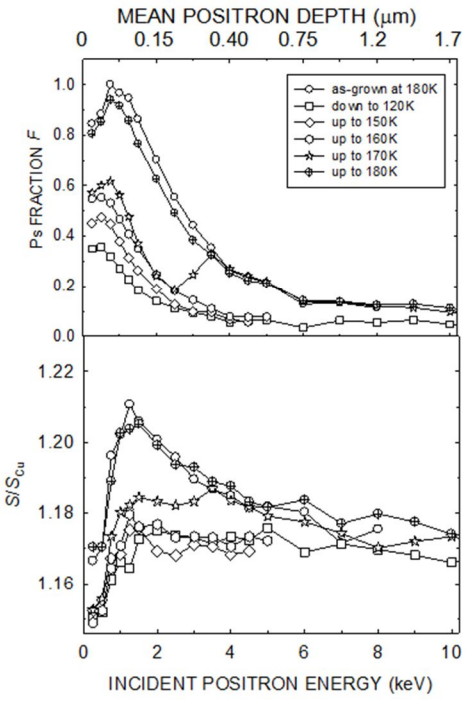

Figure 2. $F(E)$ and $S(E)$ for ice film grown at 180K, measured at 180, 170, 160, 150 and 120K. Note the jump from low to high parameter during the second 170K run.

positron thermalization; thus, the increases in *S* and *F* should be considered to be a result of Ps escape into the vacuum from depths of up to a few hundred nm. As a greater proportion of the o-Ps escapes to vacuum and is lost, the increase in *S* results from an increased contribution from p-Ps decay, verified by fitting the annihilation line as a combination of Gaussian curves and observing changes in the intensity of the narrowest (p-Ps) component.

Fig. 1 shows *S* and *F* for *E* up to 10 keV for a film grown at 170K; the parameter values remain effectively constant at higher values of *E* and suggest that the film is largely crystalline [4]. The high values of *S* and *F* at ~1.5 keV suggest the presence of interconnected pores leading to the surface of the ice, which is subliming during the measurement. The reversibility of this effect as the measurement temperature was cycled down to 120K and back to 170K, is shown in the inset in Fig.1, demonstrating hysteresis. Whereas it takes only timescales on the order of tens of minutes for the enhanced surface response to appear in a film grown at 170K, it takes two orders of magnitude longer for the response to disappear when the temperature is dropped to 120K.

Fig. 2 shows data similar to those in Fig.1, but for a film grown at 180K. Here the differences between measurements is even more marked than in Fig.1; and the rapid change can be directly seen after the first eight measurements at 170K (as the temperature is being increased from 120 to 180K).

Fig. 3 shows the much smaller near-surface change associated with a 'compact' film grown at 120K [8] measured at 120 to 170K. No significant effect is seen until the temperature reaches 170K and the film is subliming, when a modest increase in *S* is seen, probably associated with the formation of closed pores near to the surface. Similar results were obtained for films grown at 50 K (amorphous) and 150 K (crystalline).

Fig. 4 shows *S* and *F* measured as a function of time at 170K, both near the surface (*E* = 1keV) and in the bulk (*E* = 10keV) of films grown at 50K. *S* increases steadily throughout the film until, after about 580 mins, the film has completely sublimed and *S* drops to the substrate value. The sublimation rate at 170K has been measured to be ~ 12 nm min^{-1}. Equivalent measurements of *F* exhibit a large absolute increase near the surface compared to the bulk. Larger changes are observed at 180K, at which the sublimation rate is ~ 80 nm min^{-1}.

4. Discussion

We propose a model in which ice grown at high (eg 170-180K) temperatures is characterized by

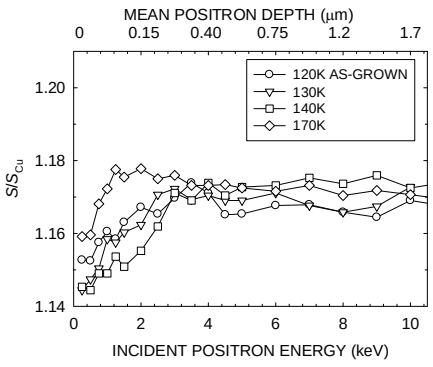

Figure 3. *S*(*E*) for ice film grown at 120K, measured at 120, 130, 140 and 170K.

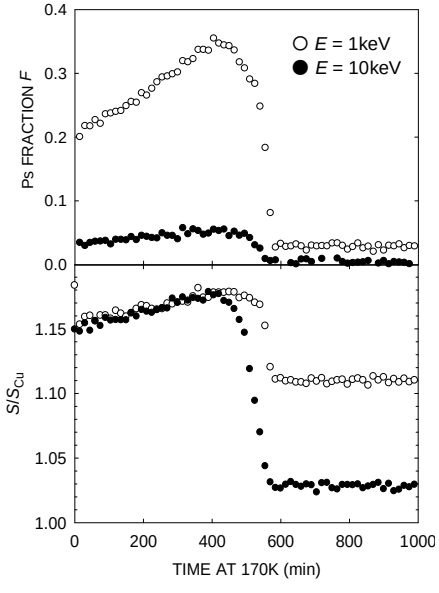

Figure 4. *F*(1,10) and *S*(1,10) for ice films grown at 50K, measured at 170 K as a function of time.

many open, interconnected pores via which o-Ps can escape into the vacuum and decay via 3-gamma emission. As the temperature is decreased to 120 K, water vapor freezes on the topmost surface of the film, closing off the open channels and preventing o-Ps escape. The associated hysteresis (Fig. 1) reflects the time required for the 'ice cap' to form (~ 10h at 120K) and sublime on re-heating. Molecular reorganization at the surface at 120K [9] may also help to form a stable morphology in the near-surface region, which may induce pore closure/collapse.

$F(E)$ in Figs. 1 and 2 were fitted using the standard code VEPFIT [10] to yield effective Ps diffusion lengths L_{Ps}. For films grown at 170K L_{Ps} increases reversibly from ~100 to ~150nm when the measurement temperature is decreased from 170 to 120K, whereas for films grown at 180K L_{Ps} *falls* from ~ 140 to ~ 50nm at temperatures of 180 and 120K. For fast-grown 170K-grown films the bulk F value is always ~ 14%, but for 180K-grown films drops from ~10 to 4% at 120K. In the bulk of the 170K-grown film closed pores hamper Ps diffusion [see 11] - and their thermal contraction at 120K leads to an increase in L_{Ps} without significantly changing F. In the 180K-grown film a larger concentration of inter-connected pores allows Ps to diffuse readily, but on cooling to 120K these shrink and become more isolated, and L_{Ps} falls. Thus the results suggest that the degree of pore interconnectedness in bulk films increases with growth temperature and rate.

The increase of S and F with time at 170K shown in Fig. 4 can be explained in two ways. The first involves the development of a pore structure with time, in which ice films start as 'compact', and transit slowly to porous. This change strongly depends on sublimation rate (which is 7 times greater at 180 than at 170K). The second model is based on crystallization of the whole film; restrained amorphous ice (I_{ar}) can coexist with cubic crystalline ice (I_c) for at least 16h at 178K [12]. Here crystallization of I_{ar} would take more than 10h at 170K. Both crystallization and pore development could be occurring coincidentally, S being more sensitive to the former and F to the latter.

In summary, the VEPAS results indicate the formation of interconnected pores in ice films grown while subliming which provide channels to the vacuum above the surface through which o-Ps can escape and decay. These escape channels are closed on reducing film temperature, and reappear on re-heating. At higher growth temperatures and rates the relative concentrations of open to closed pores in the bulk films increases. Future work will focus on the energetics of these processes.

Acknowledgments

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