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# Spontaneous polarization of vapor-deposited 1-butanol films and its dependence on temperature

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Films of 1-butanol were vapor deposited under vacuum conditions at cryogenic temperatures on a polycrystalline platinum foil. Kelvin probe measurements showed the generation of a large negative voltage on the vacuum side of the film relative to its back side in contact with the platinum foil. Voltages across vapor deposited films, which are known to require molecules with an electric dipole moment, were confirmed to be proportional to the amount of gas deposited at a given temperature. Voltages of several hundreds of volts were recorded for films that were a few thousand monolayers thick. As deposition temperature was reduced from 120 K, the film voltage was found to increase almost linearly from 0 V until a little below 38 K, where the trend was reversed. Ramping up the sample temperature after deposition at 15 K/min exhibited an initial increase in absolute magnitude and then a gradual elimination of the voltage as the temperature of 120 K was reached. Both the initial increase and the subsequent decrease were found to be irreversible and indicate structural changes in the amorphous film. The elimination of the film voltage is associated with small rearrangements of the deposited molecules which are facilitated by the gradual increase of the temperature and the cumulative electric field of the surrounding molecules. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4978239>]

## I. INTRODUCTION

Polar molecules impinging on a cold surface from the gas phase stick on the surface and pile up in such a way that their dipole moments, just like miniscule batteries connected in series, add up to tens of volts. This phenomenon was first reported in 1969,<sup>1</sup> yet it is far from common knowledge even today. Over the decades, few studies<sup>2–8</sup> had tried to quantify and explain the phenomenon. In recent years, interest has grown and several publications<sup>9–19</sup> have attempted to provide a mechanism for the generation of this astonishing result. The phenomenon has been studied more extensively for water.<sup>1–3,5,7,8,10,12,19</sup> The consensus is that measured voltages of fixed sign scale with the amount of material deposited and are substrate independent. It is also understood that substrate temperature affects the voltage created, with the general trend being that the lower the temperature, the higher the voltage established, although deviations from this trend were known from very early<sup>2</sup> on. The sign of the voltage depends primarily on the nature of the molecules deposited and on the substrate temperature, but there is no simple guide to predict it. Water and alcohols give rise mostly to films with the negative end on the vacuum side, while ketone or ether films have their positive end towards the vacuum. Similar behavior has been observed in films deposited at room temperature using tris(8-hydroxyquinolino) aluminum (III),<sup>20–30</sup> 4,4'-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl,<sup>28</sup> 1,3,5-tris(1-

phenyl-1H-benzimidazol-2-yl)benzene,<sup>28</sup> 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline,<sup>28</sup> 1,3-bis[2-(4-tertbutylphenyl)-1,3,4-oxadiazol-5-yl]benzene,<sup>28</sup> tris(7-propyl-8-hydroxyquinolinolato) aluminum(III),<sup>31,32</sup> and bathocuproine.<sup>33</sup> One recent publication<sup>19</sup> appears to provide some convincing explanation regarding water films based on previous simulations<sup>34</sup> and recent data. There has been no theoretical work addressing the creation of polarized films upon vapor condensation at low or high temperatures.

Voltage build-up is a peculiar phenomenon worth studying, but there is at least one more aspect to these systems which is also intriguing. Most experiments benefit from the fact that the deposited films can be removed easily by increasing the substrate temperature causing sublimation, evaporation, and, eventually, desorption. If temperature ramping is done under controlled conditions, information collected during thawing allows quantification of the film mass, e.g., by means of a mass spectrometer detector. By monitoring the film voltage during thawing, one can associate its changes with structural and electrical alterations. One can expect collapse of the voids leading to compacting of the film, followed possibly by crystallization before the disappearance of the film in the gas phase. It might not be easy to interpret such observations in detail, but they offer interesting information in itself.

In this paper, we present information on the behavior of 1-butanol, a small organic molecule bearing a hydroxyl group, which in a way resembles water. Our results are quantitative; they show a very large film voltage, which corresponds to a large fraction of deposited molecules having their dipoles oriented parallel to the substrate normal. Of great interest is the initial increase of the film polarization at the beginning

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of a temperature ramp. All voltage variations are found to be irreversible.

In Secs. II–V of the paper, we will give a brief description of the experimental apparatus, provide information on all the steps encountered during data collection and consolidation, enumerate the results depending on deposition and thawing conditions which pertain to 1-butanol films, and, finally, offer the most plausible picture of butanol deposition and film transformations as a function of temperature, both deposition (initial) temperature and ramped film temperature, along with brief comments on consequences of spontaneous polarization in various systems.

## II. EXPERIMENTAL

The experiments presented in this paper were performed in a stainless steel, triple cross, high-vacuum chamber with six 15 cm diameter ports and three 7 cm diameter ports, evacuated by a turbomolecular pump. The main components of this chamber are a 38 mm × 19 mm × 0.09 mm polycrystalline platinum foil attached to the end of a He closed cycle refrigerator mounted on a rotatable top flange, an 11 mm diameter tube doser connected to a gas handling manifold, a Kelvin probe with an 8 mm diameter tip, and a quadrupole mass spectrometer. The refrigerator can reach 17 K causing the chamber pressure to drop from  $0.6 \times 10^{-8}$  mbar without cooling to  $0.1 \times 10^{-8}$  mbar due to condensation of H<sub>2</sub>, CO, and H<sub>2</sub>O.

1-Butanol vapor is delivered to a reservoir at a pressure of a few mbar (monitored with a Baratron gauge) and a fraction of that is allowed to condense on the cold sample without escaping into the chamber owing to the close proximity of the tube doser to the sample. Sample temperature can reach about 32 K; it is monitored with a platinum sensor and controlled with a thermostat powering a resistive heater mounted at the end of the refrigerator.

The operating range of the commercial Kelvin probe was expanded with the use of a manually adjusted additional bias on the tip to allow measurements of several hundreds of volts.

A personal computer recorded mass spectrometer ion signals, gas manifold and main chamber pressures, and sample temperature. Kelvin probe voltage (also known as contact potential difference, cpd) was recorded on a separate computer and data from the two computers were merged offline based on their time stamps. Typical data collection rates were one point per 2 s for both computers. Data collection and analysis was performed by means of custom procedures written for a commercial graphing and analysis software environment (Igor by Wavemetrics).

The essential components of the experimental apparatus are shown in Fig. 1 with their relative positions indicating their function during the main stages of an experiment. Liquid 1-butanol (CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH, 99.5% Panreac Quimica) was pumped on at 0 °C and maintained at that temperature to fill the gas manifold. A controlled amount of gas at room temperature was deposited on the platinum foil. Then, the sample was rotated by 90° to face the Kelvin probe. After optimizing the distance of the probe from the sample and selecting the appropriate voltage offset, the refrigerator was turned off to eliminate vibrations detrimental to the voltage measurement

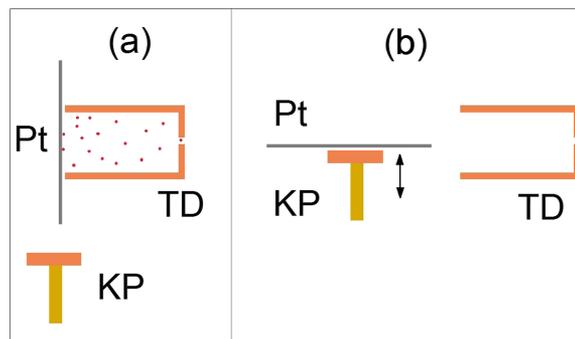


FIG. 1. Sketch of the experimental setup (top view). (a) Tube doser (TD) in close proximity to the platinum foil (Pt) during gas deposition at cryogenic temperature. (b) Oscillating Kelvin probe (KP) almost as close during non-contact, film voltage measurement.

and the sample temperature was ramped up to 270 K usually at a rate of 15 K/min. During the ramp, it was necessary to adjust the voltage offset whenever the determined voltage would go beyond the  $\pm 10$  V range. After the completion of the ramp, the refrigerator was turned on again to recool the sample for the next run.

## III. RESULTS

### A. Data manipulation

Each run consisted of three data sets. The first one was collected during the film deposition, while the other two were recorded simultaneously on separate computers during the temperature ramp.

For the first data set, we recorded sample temperature, backing pressure of the deposited gas in the gas manifold, and mass spectrometer signal for a major mass fragment of the gas deposited as a function of time at constant sample temperature. One example is shown in Fig. 2. The goal was to cause a predetermined drop in the manifold pressure. With finite accuracy, we maintained the rate of pressure drop, hence the deposition rate, constant, by adjusting the starting pressure and the opening of the leak valve to similar values from run to run. Both the total pressure drop ( $\Delta P$ ) and the rate of the pressure drop ( $dP/dt$ ) can be calculated from the data.

Notice the small rise in the sample temperature during deposition, which is caused by the gas condensing on the Pt

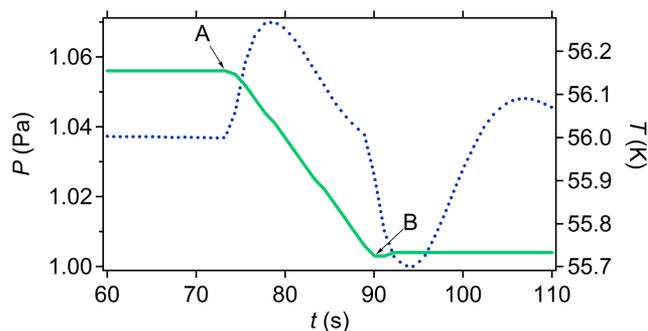


FIG. 2. Gas deposition. Gas manifold pressure (green solid line) is recorded as a function of time. The mini leak valve to the main chamber is opened at point A and is closed at point B. Small fluctuations of the Pt foil temperature (blue dotted line) are observed during the deposition because of the impinging gas molecules and the finite thermal conductivity of the sample mount.

foil and the finite heat conductivity of the sample mount. Subsequent ringing is due to the response time of the feedback loop of the thermostat, because the heating rate needed to maintain the selected temperature is reduced during deposition.

From the pressure drop, we calculated the number of molecules deposited using the equation of state for ideal gases, which is perfectly adequate given the low pressures involved. A common dose was delivered by a  $\Delta P$  of 0.05 mbar, which for a manifold volume of 682.5 cm<sup>3</sup> corresponds to approximately 10<sup>18</sup> molecules. Then, the total surface density of deposited molecules is the latter number divided by the cross section of the doser tube, which is 0.866 cm<sup>2</sup>. Typical deposition rates were  $7 \times 10^{16}$  molecules cm<sup>-2</sup> s<sup>-1</sup>.

The second data set recorded was the film voltage, which is the signal of highest interest during a run. It was recorded as a function of time, but change was also effected by changing the sample temperature. The raw signal of one such run is shown in Fig. 3(a) along with its calculated error. The sawtooth appearance arises from the occasional adjustment of the probe bias in 25 V increments. Since these changes in bias were done manually whenever it was deemed necessary, i.e., when the cpd value exceeded the  $\pm 10$  V range, they occurred with random phase difference with respect to the cpd sampling cycle. Consequently, the data points recorded at the time of the switch had to necessarily be discarded. The remaining

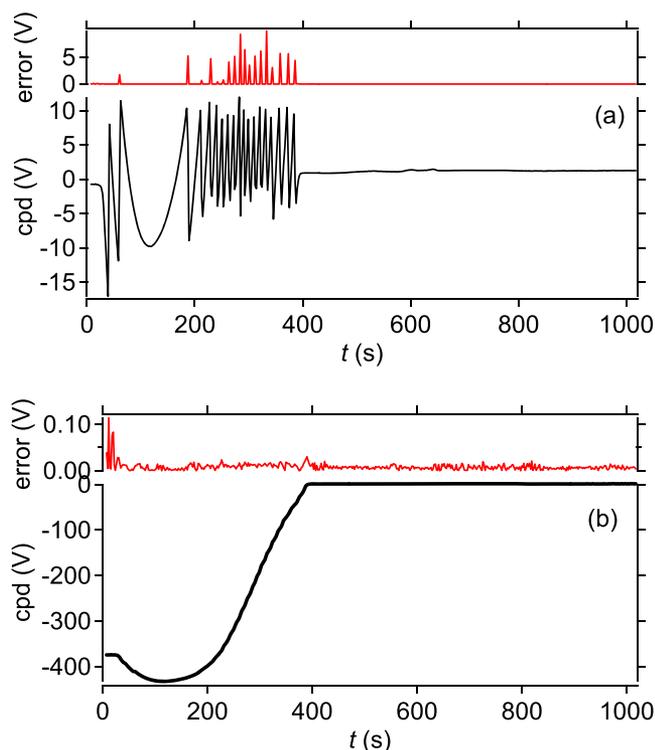


FIG. 3. Film voltage after gas deposition and during temperature ramp. (a) Contact potential difference (cpd) determined by the software provided by the Kelvin probe manufacturer along with associated standard deviation. The sudden steps (associated with huge cpd errors) are caused by manual adjustment (in 25 V steps) of an additional Kelvin probe bias, required to maintain the voltage difference between the Pt foil and the probe within a  $\pm 15$  V interval. (b) After numerical incorporation of the additional bias and elimination of the points affected by the bias switching, the film voltage presents a smooth curve. The relatively large errors persisting at the beginning of the data are due to the vibrations of the refrigerator which is turned off after the start of the temperature ramp at  $t = 19$  s.

points needed to be shifted to actual film values. After these corrections, the signal appears as in Fig. 3(b) with orders of magnitude smaller error values. Upon close inspection, at a detail that is not apparent in Fig. 3(b), one notices that segments recorded at different additional bias values, i.e., between manual bias changes, do not connect very smoothly: on descending sections, segments tend to overlap, while, when the voltage rises, the vertical gap between segments appears excessive. As confirmed through signal simulations, this behavior is due to the incessant and rather fast change of the film voltage in combination with the order in which the three bias voltages, used for the determination of one cpd value, are applied to the probe.

The third data set was similar to the first set with some differences in the channels monitored. We primarily recorded sample temperature and a mass fragment for the compound deposited, viz.,  $m/q = 31$ . In addition, we monitored the overall status of the chamber by recording mass fragments at  $m/q$  equal to 2, 18, and 28, the chamber pressure, and the temperature of the refrigerator cold head. The latter was lower than the sample temperature for most of the temperature ramp.

Merging of the cpd data with temperature readings and mass spectrometer signals results in a plot as a function of time as the one shown in Fig. 4(a). Since for most runs sample temperature changed linearly with time, all the data can be replotted as a function of sample temperature as in Fig. 4(b), with almost no loss of information. This is not true when we chose to employ a non-linear temperature profile, i.e., when the sign or the magnitude of the ramp rate was changed during data collection.

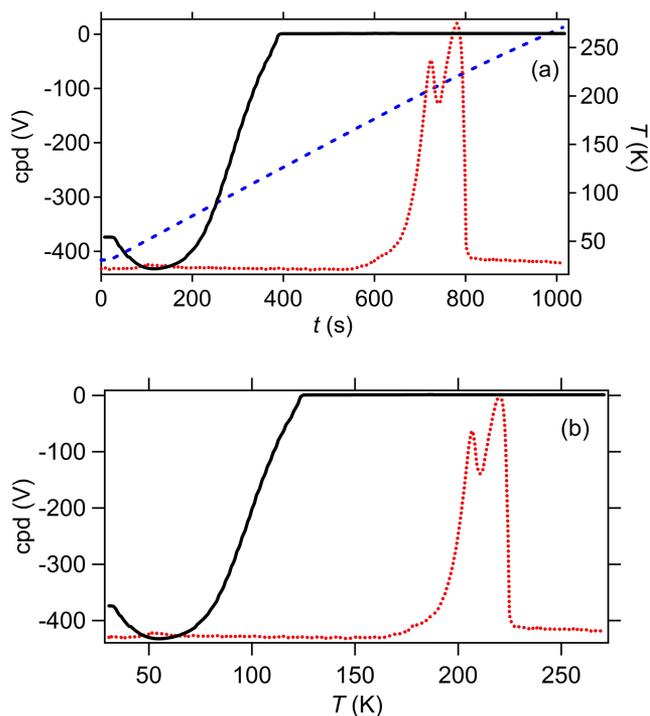


FIG. 4. Film voltage (black solid line) variation with (a) time and (b) temperature during a uniform temperature (blue dashed line) ramp. The major ( $m/q = 31$ ) 1-butanol fragment (red dotted line) in the gas phase, monitored by the mass spectrometer, indicates that film voltage fluctuations occur prior to evaporation of the butanol film.

## B. Sample voltage

A typical set of data is shown in Fig. 4. Notice the negative sign and the magnitude of hundreds of volts of the film voltage at the deposition temperature, in this case 31 K. Second, notice the initial gradual drop to more negative values and the eventual rise to its final value near 0 V. By comparing the mass spectrometer signal with the film voltage, it is clear that the voltage is eliminated long before the evaporation temperature is reached. The mass spectrometer signal appears as a split peak; due to the close proximity of the Kelvin probe, the escape to the gas phase of some of the deposited molecules is obstructed and delayed.<sup>35</sup> A peak at 245 K would correspond to the monolayer desorption of 1-butanol,<sup>36</sup> but it is dwarfed by the multilayer sublimating at a lower temperature.

It is known from the literature that the effect of spontaneous charging of vapor deposited films at low temperatures depends linearly on the amount of gas deposited and does not depend on the nature of the substrate on which the films are grown. First, we confirmed that both statements hold true for 1-butanol by depositing various amounts at 31 K and recording the film voltage and its profile as the substrate temperature was ramped at 15 K/min. Figure 5 shows the film voltage as a function of the number of molecules deposited per unit area. On the same diagram, the second set of points corresponds to the lowermost value recorded during each temperature ramp which appeared at 55.4 K. For both sets we notice that the film voltage,  $V$ , is proportional to the surface density,  $\sigma = N/A$ , of molecules deposited, where  $N$  is the total number of molecules deposited and  $A$  is the doser cross section, while there is no significant offset. This conclusion allows us to present henceforth the data in voltage per surface density of deposited molecules,  $u = V/\sigma$ , thus facilitating comparisons among runs with different amounts of gas deposited.

By depositing 1-butanol at low temperature on top of another film of butanol that has already been annealed and hence its film voltage has been eliminated, we established that the film voltage developed after the second dose was proportional to that dose. Thus, the voltage developed does not depend on the nature of the substrate. This observation made this series of measurements feasible despite the fact that

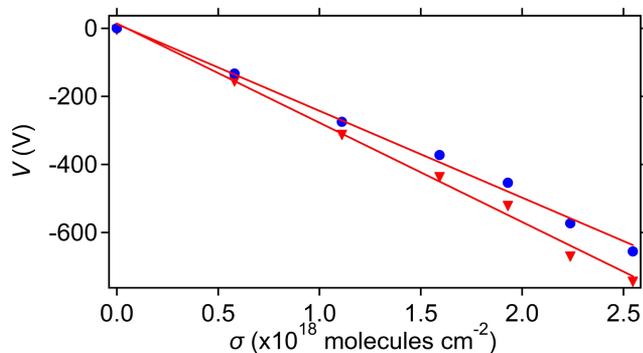


FIG. 5. Film voltage as a function of the number of 1-butanol molecules deposited at 31 K. Initial film voltage (blue dots) and minimum film voltage during the temperature ramp (red triangles) have a magnitude which is proportional to the surface density of the deposited molecules; the proportionality coefficients are  $-2.55(8) \times 10^{-16}$  V cm<sup>2</sup>/molecule and  $-2.92(10) \times 10^{-16}$  V cm<sup>2</sup>/molecule, while the magnitude of each offset is less than its uncertainty.

the metal substrate was not a single crystal of known orientation, nor was the surface cleaned with sputtering and tested for impurities with some surface techniques such as Auger spectroscopy.

1-Butanol films were deposited on the cold platinum foil without special precautions regarding its cleanliness because it is a well-established fact that the nature of the substrate does not affect the film voltage. Furthermore, the sample was held at a temperature that was higher than the refrigerator temperature for all depositions, thus condensable gases would be preferentially cryopumped on the refrigerator surface rather than the warmer platinum foil. Any amounts of oriented contaminant molecules (H<sub>2</sub>, CO, H<sub>2</sub>O) condensed on the sample would give rise to a voltage which we checked before every deposition. These measurements are represented by the point at 0 coverage in Fig. 5. The corresponding voltage is  $-0.05$  V, indicating that, if there is contamination under the film, it is insignificant given that the main signal is tens or hundreds of volts. The duration of the deposition is of the order of 1 min or less (see Fig. 2), so we need not to be concerned about co-deposition. By monitoring contaminants in the gas phase via the mass spectrometer, we know that all of them desorb from the refrigerator as the temperature is ramped, but none of these signals show the characteristic slit peak that is seen for butanol which is obstructed by the Kelvin probe tip. Hence we conclude that no contaminant molecules emerge from under the tip, i.e., they did not come from the sample.

It is generally accepted in the literature that the film voltage varies with deposition temperature and may be taken as a linear function of the deposition temperature. Figure 6 shows film voltage temperature profiles at a constant ramp rate of 15 K/min for a dense range of deposition temperatures. For all dosing temperatures, each curve displays a minimum at a temperature several kelvins higher than the initial temperature, followed by a gradual elimination of the voltage. The rising parts of the curves appear to line up with each other.

The voltage at the dosing temperature and the minimum value of each curve are summarized in Fig. 7. Both sequences deviate from a straight line (see Fig. 7(a)). At the high dosing temperatures, the voltage was zeroed at the same values as during temperature ramps. At the low temperatures, the initial voltage reaches an extremum near or below 38 K. The difference ( $\Delta T$ ) between deposition temperature ( $T_{\text{dep}}$ ) and the

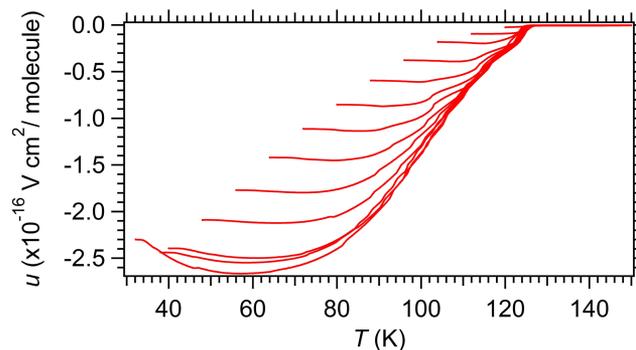


FIG. 6. Scaled film voltage ( $u = V/\sigma$ ) profile of 1-butanol as a function of film temperature and its dependence on deposition temperature. The deposition temperature is the lowest temperature for each curve. After a certain point, all curves follow the same envelope.

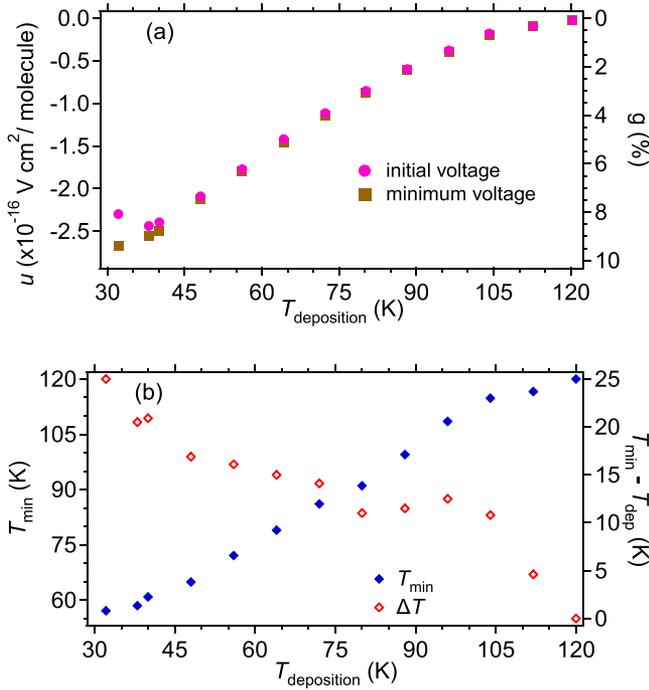


FIG. 7. (a) Scaled voltage of 1-butanol films at the dosing temperature (circles) and at the lowermost point (squares) as a function of deposition temperature. The same points, when projected on the right axis, represent the degree of polarization of each sample. (b) Correlation between dosing temperature and temperature at which the minimum voltage is observed during the 15 K/min ramp (blue solid diamonds), as well as their difference (open diamonds).

temperature with the largest voltage ( $T_{\text{min}}$ ) drops gradually, but it shows a deviation from this trend near  $T_{\text{dep}} = 100$  K.

### C. Sample polarization

Owing to the geometric constrains of the gas deposition and the direct measurement of the total mass deposited, we can quantify the degree of polarization of the deposited molecules. The actual thickness of the film cannot be established without recourse to an interference measurement,<sup>37,38</sup> which is not amenable to this experimental setup due to geometric and financial constraints. The amorphous vapor-deposited film has a density lower than that of crystalline butanol, which in turn is higher than the density of the liquid. Detailed studies<sup>37</sup> done on water, which resembles 1-butanol with respect to thermodynamic values, correlate the deposition temperature to the density (lower deposition temperature corresponds to higher porosity and lower density) and give an indication on how different the densities of crystalline and amorphous solids can be. Hence, as a first order approximation, we use the density of the liquid for the film. It will be shown here that this value is not critical to the calculation of the polarization, and only the film thickness and the electric field intensity depend on this choice.

The average molecular volume of a hypothetical cubic molecule of side  $a$  is derived from

$$\rho = \frac{m}{a^3} \Rightarrow a = \left( \frac{m}{\rho} \right)^{\frac{1}{3}}, \quad (1)$$

where  $\rho$  is the density and  $m$  the molecular mass. Each layer has thickness  $a$  and surface density per layer  $a^{-2}$  (number of

molecules per unit area). If  $N$  molecules of mass  $M = Nm$  are distributed evenly over an area  $A$ , the film thickness  $L$  is equal to the total volume divided by the area

$$L = \frac{N}{A} a^3, \quad (2)$$

while the total number of layers is given by the ratio of the film thickness to molecular height  $a$ ,

$$n = \frac{L}{a} = \frac{N}{A} a^2. \quad (3)$$

The degree of polarization,  $g$ , is the fraction of the molecules that have their dipole moments aligned parallel to the surface normal; it is calculated as the ratio of the film voltage,  $V$ , to the maximum possible voltage of a hypothetical ferroelectric film. For this simple calculation, we ignore any cooperative effect among dipoles that would affect molecular polarization,

$$g = \frac{V}{nv}. \quad (4)$$

The maximum possible voltage per layer,  $v$ , can be calculated<sup>10</sup> based on the surface density  $a^{-2}$  of a single layer, the molecular permanent electric dipole moment  $\mu$ , and the relative permittivity response at infinite frequency  $\epsilon_{\infty}$ ,

$$v = a^{-2} \frac{\mu}{\epsilon_0 \epsilon_{\infty}}, \quad (5)$$

where  $\epsilon_0$  is the permittivity of vacuum. The degree of polarization  $g$  is then given by the expression

$$g = V \frac{A}{Na^2} \frac{\epsilon_0 \epsilon_{\infty}}{a^{-2} \mu} = \frac{V}{N} A \frac{\epsilon_0 \epsilon_{\infty}}{\mu}. \quad (6)$$

Interestingly enough this result does not depend on the choice of the value for the density. The (homogeneous) electric field intensity is given by the expression

$$E = \frac{V}{L} = \frac{V}{N} \frac{A}{a^3} = \frac{V}{N} \frac{A}{m} \rho. \quad (7)$$

Using the values  $\rho = 0.81$  g cm<sup>-3</sup>,<sup>39</sup>  $\epsilon_{\infty} = 2.2$ ,<sup>40</sup>  $\mu = 1.66$  D,<sup>39</sup>  $1 \text{ D} = 3.335641 \times 10^{-30}$  C m,<sup>39</sup>  $\epsilon_0 = 8.8541 \dots \times 10^{-12}$  C V<sup>-1</sup> m<sup>-1</sup>,<sup>39</sup> and  $A = 0.866$  cm<sup>2</sup>, we get  $a = 5.3$  Å,  $a^{-2} = 3.5 \times 10^{14}$  cm<sup>-2</sup> and  $v = 1.00$  V. For a typical dose of  $N = 10^{18}$  molecules, we have  $L = 1.8$  μm and  $n = 3300$ . A plot of the degree of polarization with respect to time or temperature (point or ramp) is identical in shape with the corresponding plot of film voltage. What is interesting in these calculations is the actual values of the degree of polarization, which are shown in Fig. 7(a) and go almost as high as 10%. The corresponding value for the electric field intensity is  $2.5 \times 10^8$  V m<sup>-1</sup>.

If we assume a substantially lower density due to the high porosity of the film,<sup>41</sup> e.g.,  $\rho = 0.6$  g cm<sup>-3</sup> which corresponds to a porosity of 26%, the numbers that change are  $a = 5.9$  Å,  $a^{-2} = 2.9 \times 10^{14}$  cm<sup>-2</sup>, and  $v = 0.82$  V, which, for  $N = 10^{18}$  molecules, yield  $L = 2.4$  μm and  $n = 4000$ , and  $E = 1.8 \times 10^8$  V m<sup>-1</sup>.

### D. Kinetics information

During heating of a polarized film, the measured voltage goes from its original negative value to more negative values.

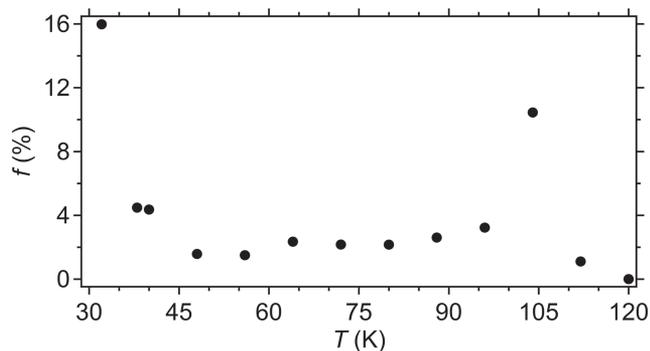


FIG. 8. Fractional absolute increase of film voltage,  $f = \left| \frac{V_{\min} - V_{\text{start}}}{V_{\text{start}}} \right|$ , during temperature ramp as a function of deposition temperature.

The fractional change of this quantity is presented in Fig. 8. The data presented show two maxima, one at lower end of the temperature range and one around 100 K.

Additional information on the nature of the phenomena observed in these systems is derived from runs under modified conditions. We remind the reader that it was not experimentally feasible to start the temperature ramp immediately after the end of the gas deposition. This means that each new film was held at the deposition temperature for a few minutes. During that time, required for the adjustments in the machine, it was observed that the voltage consistently showed a gradual drop to more negative values. Then, all temperature ramps at the beginning showed a brief section of constant film voltage.

Figure 9 shows a slower than usual temperature ramp. The minimum appears at a 53.6 K, a temperature that is lower than the one (55.6 K) observed in a standard, five-fold faster ramp.

Figure 10(a) displays the film voltage for a sample that has been heated up to 144 K, then cooled down to 31 K, ramped up again to 167 K, once more cooled to 31 K, and finally ramped up again. It is clear that the film voltage has been eliminated. By expanding the voltage scale for values close to 0 (see Fig. 10(b)), it becomes clear that the film is electrically active in a reversible way, albeit with a significant hysteresis.

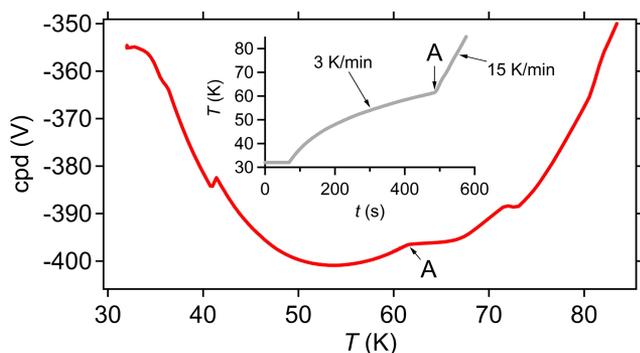


FIG. 9. Film voltage fluctuations during sample temperature ramp; ramp rate was increased 5 times at point A. The inset displays the sample temperature as a function of time. Note that, due to the lower than usual ramp rate, the minimum voltage is reached at a lower temperature than with the usual rate. The kink around 41 K is an artifact caused by the way the cpd is determined when manual adjustments of the Kelvin probe bias are applied (see Sec. II for details).

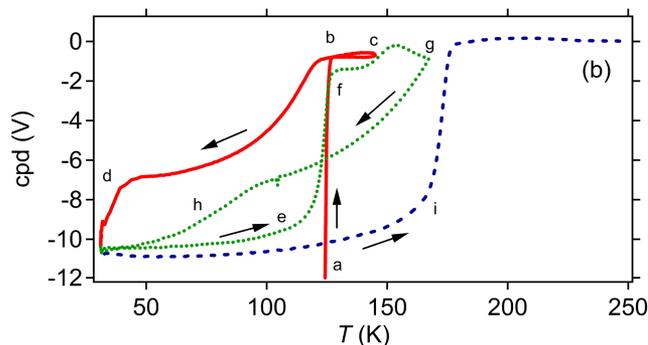
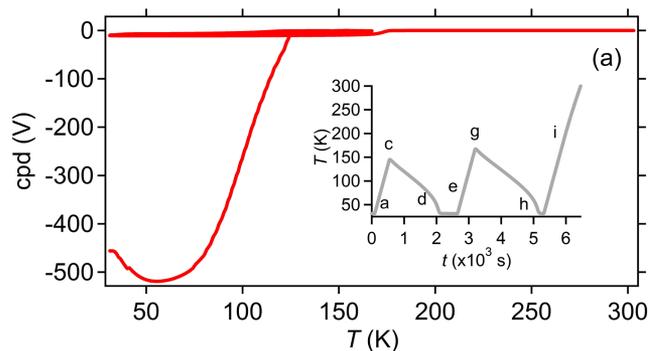


FIG. 10. (a) Film voltage fluctuations during sample temperature variations which are shown in the inset as a function of time. (b) Expanded view of the upper panel. Arrows and letters signify the sequence in which the signal has been recorded. The sample was deposited at 31 K, heated once up to 145 K, cooled down to 31 K (red solid line), ramped up 167 K, cooled again to 31 K (green dotted line), and finally ramped up to 300 K (blue dashed line).

#### IV. DISCUSSION

The data presented here should be able to provide information on two aspects. One is the voltage accumulated during the creation of the film. The other is the variation of the initial voltage upon changing the temperature of the film. The first aspect depends on the mechanism by which individual molecules attach themselves or crash on the cold substrate. The latter aspect gives us a glimpse on the structural changes that occur on the film as time passes and as the temperature is raised.

The present study found that, for the lowest deposition temperature, the equivalent of almost 10% of 1-butanol molecules ended up with their dipole moment parallel to the surface normal (see Fig. 7(a)). The effect of the energy of the impinging molecules has been considered in light of theoretical work that predicts the establishment of an electric field due to a stable temperature gradient in an ensemble of polar molecules<sup>42</sup> or a mixture of nonpolar molecules.<sup>43</sup> We intend to modify the temperature difference between incoming molecules and accommodating surface, not by changing the substrate temperature, but rather by increasing the gas temperature substantially above room temperature. Yet, it is unlikely that the energy of the impinging molecules would have a pronounced effect on the polarization of the deposited film, and, hence, the theoretical work mentioned may have no direct bearing on this phenomenon.

Compared to other molecules deposited at cryogenic temperatures, it appears that 1-butanol gives rise to a rather large degree of polarization. Compared to water, for which much

work has been done in the past, 1-butanol has the same direction of polarization, but clearly has a much larger effect per molecule. The dipole moment for both molecules is similar, yet they differ substantially in size. Very recently, an explanation was offered based on the porosity of the deposited water film and the average orientation of attached molecules.<sup>19</sup> Due to its larger size, 1-butanol would have a higher propensity to create voids, but spectroscopic evidence is lacking to back up the model in this case.

From information gathered from delayed ramps, it is evident that the changes in voltage both in the dropping and the rising part of the curves are under kinetic control; when a ramp is stopped, the voltage does not remain fixed, but rather changes, albeit slowly, in the direction it would go, had the ramp proceeded, and gradually comes to a halt. The situation is similar for the delayed temperature ramp. These observations agree with the notion that the changes in voltage are related to overcoming progressively higher energy barriers. This behavior resembles the effect the ramp rate has on the desorption temperature: a faster ramp yields a peak at a higher temperature than a slower ramp.

The eventual elimination of the film voltage with increasing sample temperature makes sense; the higher the temperature, the easier it is for molecules to overcome rotational barriers and reorient themselves in such a way as to minimize their potential energy within the overall electric field they have created. Given an adequate intermolecular potential, one could simulate the relaxation of this electric field and correlate to a range of barriers. The more settled and more compact the film becomes, the electric field weakens and the harder it is for molecules to change their dipole orientation.

The above discussion does not account for the initial increase (in absolute terms) of the film voltage. One possible explanation may be that the relative permittivity, which is due to the polarizability of the electrons and not nuclear motion, decreases with increasing temperature. This assumption is contradicted by experimental evidence. At all deposition temperatures, recorded cpd values show that there is a small and slow drop during the time it takes the experimenter to start the temperature ramp. Once the ramp starts, the voltage remains constant for a short while. Hence, the first section of the temperature ramps is related to irreversible changes in the films, unlike electron polarizability which would be reversible. Besides, this kind of electrical response is not expected to change with temperature, since it is related to  $\epsilon_{\infty}$ . Another possibility is that at the very low temperatures, molecules, due to their limited mobility, are more sensitive to the local field generated by nearby molecules that are on average aligned along the surface normal. Under such influence, molecules that become labile at the very low temperatures orient their dipoles in the same direction as their neighbors and thus increase the total voltage and the degree of polarization.

If a polarized film is heated up to 144 K, it loses all the film voltage. At that point, the film is above its glass transition temperature (118 K), but below its crystallization temperature (165 K).<sup>44</sup> If it is then cooled back down, the measured voltage remains nearly constant, as seen in Fig. 10(a). Yet, some small voltage fluctuations are observed, which are shown in detail

in Fig. 10(b). The picture seen is that of a reversible behavior with a hysteresis loop and it may be of pyroelectric nature.<sup>45</sup>

Another interesting effect appears around 100 K. Both the fractional increase of film voltage upon heating ( $f$ , see Fig. 8) and the temperature delay for the appearance of the minimum ( $\Delta T$ , see Fig. 7(b)) exhibit a diffuse, but striking variation for deposition at 100 K. This and all other details of these experiments beg the execution of simulations which would explain both the initial film voltage and its variations with temperature.

One further issue that is thought provoking is the following. Most studies have been done at cryogenic temperatures. Is it possible to find a system that would form a polarized film upon deposition at a substantially higher temperature or even above room temperature? What does it take to form such a polarized film? Would a large and rigid, polar molecule form a polarized layer, whose voltage would survive long enough to be measured, or do we have to resort to techniques with a much faster response time? If we could identify systems that show at high temperature the stability seen at cryogenic temperatures for 1-butanol and the like, it would be feasible to create tunable molecular orientation at elevated temperatures<sup>46</sup> from vapor deposition. Incidentally, the question has already been answered to some extent by experiments studying the formation of organic light emitting diodes.<sup>20–33</sup> Polarized films have been deposited at room temperature under vacuum conditions, which were robust enough to retain their voltage in air or allow mechanical manipulations. Heat or visible light was found to eliminate the voltage. Many aspects of these experiments agree with what is known for films deposited at cryogenic temperatures. One difference is that we have not noticed any obvious effect from ambient light on low temperature film voltages.

## V. SUMMARY AND CONCLUSION

In this paper, we describe the deposition of 1-butanol vapor on a platinum foil at temperatures between 32 K and 120 K. We were able to record film voltage as high as 720 V, with the negative end on the vacuum side. This voltage is caused by the non-random build-up of the amorphous film. By monitoring the variations of this voltage, while increasing the substrate temperature after deposition, we followed kinetically driven rearrangements in the solid which resulted in the elimination of the film voltage at temperatures well below the desorption temperature. A similar picture emerged from variation of the deposition temperature. A degree of polarization as high as 9.4% was achieved by depositing at 32 K, but after the sample was heated to 57 K. This increase in absolute voltage is typical of 1-butanol films and may increase (in magnitude) by as much as 16% as the temperature is raised. For the deposition temperature range between 38 K and 120 K, the initial film voltage becomes more negative as the substrates get colder, but the trend is reversed at lower temperatures.

The large voltages generated across 1-butanol films, or on films of any molecule exhibiting the same effect, could play a significant role in experiments involving low-energy ions impinging on such films, either by accelerating or decelerating the approaching projectiles depending on the sign of their

charge. It is also tempting to extrapolate this effect to bodies of astrophysical interest, such as comets or asteroids, but temperatures are not necessarily sufficiently low and time scales are rather long giving sufficient time for the polarization to relax.

We hope that in the near future, there will be enough data available for a variety of systems and at diverse deposition temperatures that will help create a unifying model for this unusual phenomenon.

## SUPPLEMENTARY MATERIAL

See [supplementary material](#) for a detailed description of the apparatus used and the procedures followed in the experiments.

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