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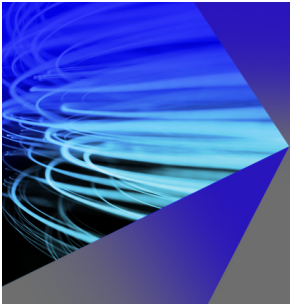
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Interpretation of permittivity values in vapor deposited thin films of organic glasses

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ABSTRACT

Permittivity values of thin glassy films obtained by physical vapor deposition onto interdigitated electrode cells have been reported to increase considerably after annealing the sample above its glass transition temperature, which cannot be explained by effects of density. While such a change might be interpreted as a transformation to a different structure or altered dynamics, we employ a nonpolar molecular liquid to demonstrate that the apparent permittivity derived from impedance experiments can increase without changes in properties inherent in the sample material. More specifically, it is shown that annealing induces surface flattening that leads to material relocating from on top of the metallic electrode digits to between these digits. For films of thicknesses below 10% of the digit spacing, we demonstrate that the impedance measurement senses predominantly the material located between electrode digits, while being blind to the part of the sample deposited onto the digits. This implies that the apparent permittivity can increase without a change in material properties. A relation that determines film height and deposition rate from the observed capacitance increment is provided.

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I. INTRODUCTION

Glasses of organic molecular materials prepared by physical vapor deposition (PVD) have been the subject of intense research in recent years, especially after was observed that deposition onto a substrate at a temperature somewhat below the glass transition, $T_{\text{dep}} \approx 0.85T_g$, leads to material properties that cannot be achieved otherwise.^{1,2} Among these properties are high kinetic stability, high density, low entropy, and low energy, all at levels that could be reached by a glass cooled from the liquid via aging only after thousands to millions of years.³ Numerous techniques have been employed to characterize glassy and liquid films obtained by PVD,⁴ including calorimetry,^{5,6} nanocalorimetry,⁷ ellipsometry,^{8,9} and dielectric relaxation experiments,^{10–14} as well as molecular dynamics simulation studies.¹⁵ Dielectric techniques have provided *in situ* access to the bulk and surface dynamics during film growth, to the transition regarding kinetic stability, and to the properties of the liquid state after warming the as-deposited glass to above T_g .^{16,17}

A common approach to dielectric measurements of films prepared by PVD is to deposit onto a substrate equipped with interdigitated electrodes, which facilitate dielectric relaxation experiments

during and after film growth.^{18–20} In many cases, the film thicknesses remain below a micrometer and, therefore, do not fill the entire volume covered by the electric field. As a result, absolute values of the dielectric permittivity ϵ are obtained only if the film thickness h is known. In studies of glasses obtained by vapor deposition, the thickness may be estimated using the permittivity of the bulk glass cooled from the melt as a reference if associated with the same temperature and frequency as in the PVD case. When depositing a glass at $T_{\text{dep}} \approx 0.85T_g$, the permittivity in this solid state is often near ϵ_∞ , the high frequency limit of permittivity at which the contribution from dipole reorientation is negligible. This value of ϵ_∞ may be assumed to serve as a robust reference because density varies only a few percent when comparing a vapor deposited glass with a glass obtained by cooling the melt.²¹ On the other hand, the permittivity of thin glassy films has been observed to change after annealing above T_g , and the change amounts to a factor beyond what can be explained by density alone.^{22–24}

In this study, we employ the nonpolar glass forming liquid 3-methylpentane (3MP) to explore the potential difference in the glassy state permittivity (ϵ_∞) between as-deposited and annealed films obtained by vapor deposition. This molecular glass former is

chosen because the contribution of dipole reorientation to permittivity is practically negligible, even in the equilibrium liquid state. The experimental data for thin PVD films suggest that the value of ϵ' observed for the as-deposited glass reflects the true value of ϵ_∞ that corresponds to the permittivity of the melt-cooled bulk glass, while annealing the film above T_g results in an apparent increase of ϵ_∞ due to additional sample material being moved into the active capacitance volume.

II. EXPERIMENT

The main sample material, 3-methylpentane (3MP, 99+%, distilled twice),^a has been purchased from Sigma-Aldrich, while methyl-*m*-toluate (MMT, 99%, distilled) has been obtained from Acros Organics. The sample material was vapor deposited within a vacuum chamber onto a temperature controlled substrate, using a Leybold RDK 12-320 closed-cycle helium refrigerator with a Lakeshore Mod. 340 temperature controller. A 1 l reservoir of vapor was held at a pressure of 1 mbar, and the deposition rates and times were determined, respectively, by a needle valve and toggle valves. The details of the deposition chamber have been provided previously.²² Samples were deposited onto a microlithographically fabricated interdigitated electrode (IDE) cell with a Schott D263 borosilicate substrate (ABTECH IME 1050.5-FD-Au).²⁵ The capacitor structure consists of $n = 100$ gold fingers (thickness $g = 110$ nm, length $l = 5$ mm, width $w = 10$ μm , and digit spacing $s = 10$ μm). Using conformal mapping, the geometric capacitance $C_{\text{geo}} = 2.19$ pF is given by²⁶

$$C_{\text{geo}} = \epsilon_0 \times \frac{L}{2}, \quad (1)$$

where $L = (s + w + l) \times (n - 1) = 49.55$ cm is the serpentine length of the structure and ϵ_0 is the permittivity of vacuum. Note that the relation between C_{geo} and IDE geometry in Eq. (1) is valid only for cells with $s = w$ (see the [supplementary material](#)). The periodicity of the IDE structure is $\lambda = 2(s + w) = 40$ μm , and the average electric field extends $\lambda/2 = 20$ μm away from the substrate,²⁷ implying that a sample thickness $h > \lambda/2$ is required to fill the capacitor completely.

The complex capacitance, $C = C' + iC''$, has been measured during and after deposition using an ultraprecision capacitance bridge, Andeen-Hagerling AH-2700A, at a fixed frequency of $\nu = 1$ kHz, applying a voltage of 15 V ($E = 15$ kV cm⁻¹). Accessing the capacitance increment originating from the material being deposited, ΔC , is achieved by subtracting the capacitance C_{sub} of the empty cell, i.e., $\Delta C = C - C_{\text{sub}}$. During deposition, ΔC increases as a function of time. The value of ΔC after deposition had terminated is referred to as ΔC_{dep} . For vapor deposited films with $h \ll \lambda/2$, the IDE capacitor is not completely filled, implying that the susceptibility measured via $\chi = \Delta C_{\text{dep}}/C_{\text{geo}}$ remains a filling factor of γ below the actual susceptibility of the material. With the exception of a 70 μm thick film deposited at a high rate, all films were below 500 nm in thickness and prepared with deposition rates r_{dep} between 0.31 and 0.35 nm s⁻¹.

Bulk dielectric spectra of 3MP have been measured with the AH-2700A using a vacuum sealed cell mounted onto the cold-finger of a Leybold RDK 5-320 closed-cycle helium refrigerator and temperature controlled with a Lakeshore Mod. 340. The spacer free cell has two stainless steel parallel disks of 16 mm diameter, which are

held by 4 mm thick sapphire disks at a distance of 53.3 μm ,²⁸ leading to a capacitance of $C_{\text{geo}} = 33.4$ pF at $T = 300$ K. The effect of temperature on C_{geo} has been corrected for by recording the empty cell capacitance for each temperature and thermal history for which the sample was measured.

III. RESULTS

To characterize the dielectric permittivity of bulk 3MP cooled from the melt, values for $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ have been measured from ambient temperature to below the glass transition temperature, $T_g = 77$ K. The temperature dependence of $\epsilon'(\nu = 1$ kHz) between 63 and 295 K is shown in Fig. 1, with the practically linear change in ϵ' from 1.89 to 2.25 being dominated by the high frequency limit of permittivity, ϵ_∞ , and its change with density ρ . The loss profile $\epsilon''(\omega)$ in the viscous regime of 3MP is depicted in the inset of Fig. 1 and is consistent with a relaxation amplitude $\Delta\epsilon = \epsilon_s - \epsilon_\infty = 0.02$, where ϵ_s is the low frequency limit of permittivity. The very low relaxation amplitude is due to the minute dipole moment of 3MP, implying that the reorientation of permanent dipoles has a negligible impact on ϵ' relative to that of ϵ_∞ , regardless of frequency and temperature.

A film of 3MP has been vapor deposited at a deposition temperature $T_{\text{dep}} = 63$ K = $0.82T_g$ for a duration $t_{\text{dep}} = 1600$ s at a high rate of 43 nm s⁻¹, leading to a film thickness of 70 μm . The first 525 s of $\Delta C'(t)$ are shown in Fig. 2, and the capacitance leveled off at $\Delta C'_{\text{max}} = 2.71$ pF for $t > 1200$ s. This thickness $h \gg \lambda/2$ guarantees a completely filled capacitor ($\gamma = 1$) so that the permittivity of this glass can be determined via

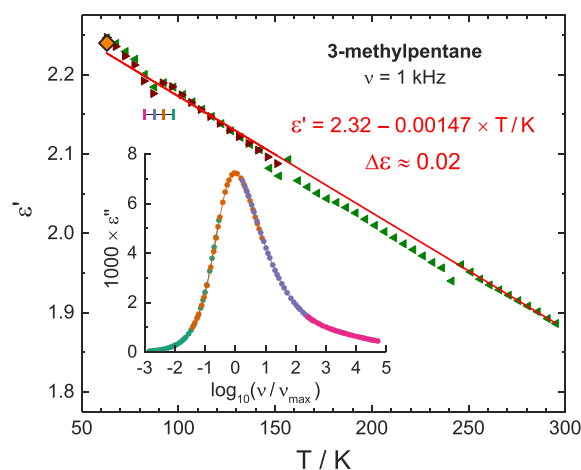


FIG. 1. Real part of dielectric permittivity, ϵ' , of bulk 3MP measured at $\nu = 1$ kHz. Symbols represent data for temperatures between 295 and 63 K on cooling (triangles pointing left) and for the range 63–151 K on warming (triangles pointing right). The small relaxation amplitude of $\Delta\epsilon = 0.02$ leads to the barely resolved step from ϵ_∞ to ϵ_s upon heating near 90 K. The line represents a linear fit to the data, with parameters given in the legend. The larger diamond represents $\epsilon_s = 2.24$ at 63 K obtained for an IDE completely filled with vapor deposited 3MP (see Fig. 2). The inset depicts the loss spectrum on a reduced frequency scale, combined from four temperatures indicated with the color-matched bar above.

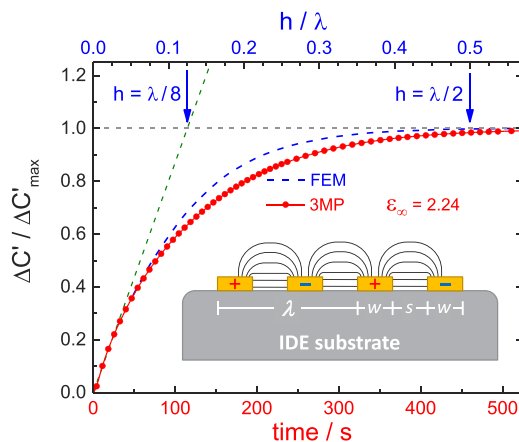


FIG. 2. Normalized capacitance increment $\Delta C'(t)$ recorded at $\nu = 1$ kHz (red dots) vs time during vapor deposition of 3MP at a rate of $r_{\text{dep}} = 43 \text{ nm s}^{-1}$ until $\Delta C' = \Delta C'_{\text{max}} = 2.71 \text{ pF}$ ($T_{\text{dep}} = 63 \text{ K}$, $t_{\text{dep}} = 1600 \text{ s}$, $h_{\text{dep}} = 70 \text{ }\mu\text{m}$). With $\chi_{\infty} = \Delta C'_{\text{max}}/C_{\text{geo}}$, this leads to $\epsilon_{\infty} = 2.24$, the value indicated in Fig. 1 at $T = 63 \text{ K}$ by a diamond. The dashed line indicates the finite element method (FEM) result by Igraja and Diaz (Ref. 27) for a similar IDE cell vs reduced film height h/λ . Note that both the FEM result and the 3MP experiment are consistent with the initial slope $\partial C/\partial h = C_{\text{max}}/(\lambda/8)$ and with near saturation at $h = \lambda/2$ (see top arrows). The inset shows a schematic partial cut view of the IDE cell, with the periodicity λ indicated as a bar.

$$\epsilon_{\infty} = \chi_{\infty} + 1 = \frac{\Delta C'_{\text{dep}}}{C_{\text{geo}}} + 1, \quad (2)$$

which yields $\epsilon_{\infty} = 2.24$ at $T = 63 \text{ K}$. This result is represented as a diamond in Fig. 1 and is consistent with its melt-cooled 3MP counterpart.

A deposition curve typical for thinner films ($h \leq 500 \text{ nm}$) is depicted in Fig. 3, showing $\Delta C'(t)$ and $\Delta C''(t)$, i.e., the time dependent real and imaginary parts of the capacitance increment due to the growing 3MP film during deposition. The deposition at a temperature $T_{\text{dep}} = 63 \text{ K}$ started at $t = 0$ and ended at $t_{\text{dep}} = 1170 \text{ s}$. The linearity of the $\Delta C'(t)$ curve indicates a time-invariant deposition rate r_{dep} . The noise is due to instrument resolution regarding $\tan \delta$, leading to standard deviations of 5×10^{-8} before and after deposition and 1×10^{-7} while ΔC is changing during vapor deposition.

The effect of temperature excursions beyond T_g on the measured susceptibility, $\chi'_{\text{dep}} = \Delta C'_{\text{dep}}/C_{\text{geo}}$, relative to its value right after deposition at $T_{\text{dep}} = 63 \text{ K}$ is depicted in Fig. 4. The curve shows the heating segments from 30 K to T_{max} using a common rate of 3 K min^{-1} , where T_{max} is increased from 86 to 100 K in steps of 1 or 2 K . Two heating scans have been performed for each T_{max} , and the temperature remained at T_{max} for 15 min the first time and for 1 min the second. The cooling segments to 30 K at -3 K min^{-1} (not shown for clarity) include a 5 min equilibration time at 30 K . For this graph, the data have been rescaled so that the as-deposited film corresponds to a permittivity $\epsilon_{\infty} = 2.24$ at $T_{\text{dep}} = 63 \text{ K}$, the value obtained from the thick ($h = 70 \text{ }\mu\text{m}$) film and consistent with bulk 3MP cooled from the melt (see diamond in Figs. 1 and 4). Clearly, each excursion to a higher temperature increases the χ'_{dep} level irreversibly, with the first annealing at $T_{\text{max}} = 86 \text{ K}$ having the largest impact on χ'_{dep} with an increase of 40% . Moreover, after the first

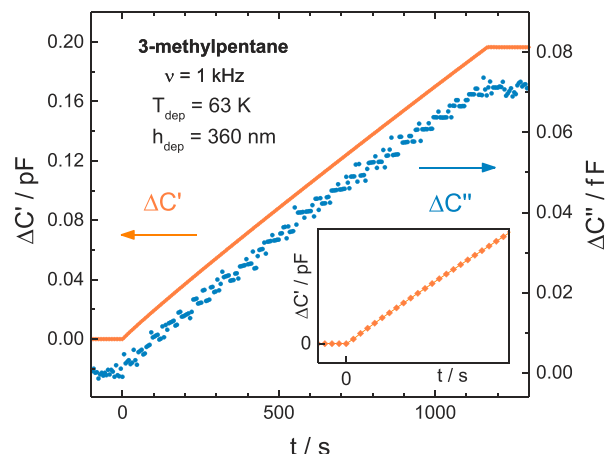


FIG. 3. Typical evolution of the capacitances $\Delta C'$ and $\Delta C''$ measured at $\nu = 1$ kHz during the vapor deposition of 3MP. These curves are for a deposition at $T_{\text{dep}} = 63 \text{ K}$ ($=0.82T_g$) with duration $t_{\text{dep}} = 1170 \text{ s}$, leading to a film of $h_{\text{dep}} = 360 \text{ nm}$ thickness. The linearity of $\Delta C'(t)$ indicates a time invariant deposition rate, $r_{\text{dep}} = 0.31 \text{ nm s}^{-1}$. The inset zooms in on the first 10% of deposition time, equivalent to the first 36 nm (1.6 nm per point).

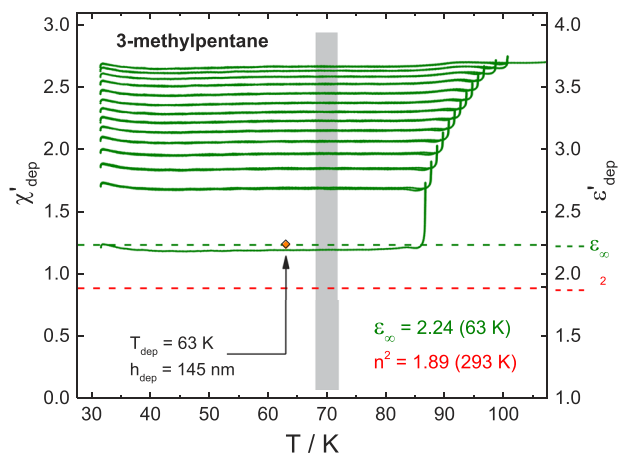


FIG. 4. Real part of susceptibility, $\chi'_{\text{dep}} = \epsilon'_{\text{dep}} - 1$, for a 3MP film of thickness $h_{\text{dep}} = 145 \text{ nm}$, vapor deposited at $T_{\text{dep}} = 63 \text{ K}$ using a rate $r_{\text{dep}} = 0.32 \text{ nm s}^{-1}$, and subject to temperature excursions of stepwise increasing peak temperatures. The original $\Delta C'_{\text{dep}}$ data are normalized such that a level of $\epsilon'_{\text{dep}} = 2.24$ at $\nu = 1 \text{ kHz}$ is obtained directly after deposition at $T = 63 \text{ K}$ (orange diamond). The dashed lines indicate the values of $\epsilon_{\infty} = 2.24$ at 63 K and $n^2 = 1.89$ at 293 K .

annealing step at each T_{max} , χ'_{dep} remains constant during subsequent cooling and heating cycles in the $30 \text{ K} < T < T_g$ range. In the case of Fig. 4, the overall change of χ'_{dep} amounts to an increase by a factor of about two. For thicker films, however, the increase of capacitance $\Delta C'_{\text{dep}}$ from such an annealing process is practically independent of film thickness (see below) so that the effect on χ'_{dep} will diminish with increasing film thickness h_{dep} .

The temperature protocol of Fig. 4 has been applied to numerous other films, and selected results are reported in Fig. 5 in terms

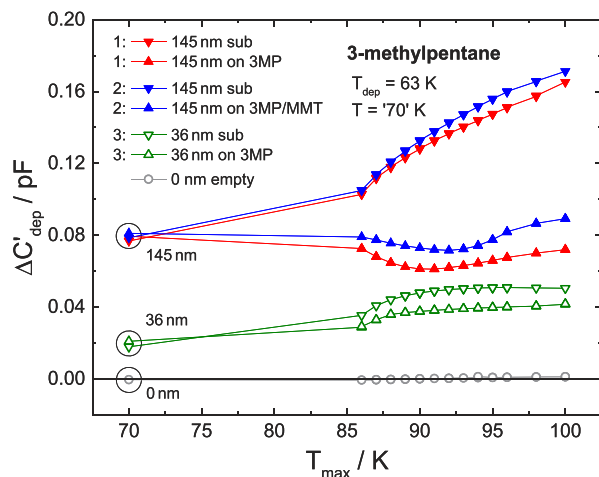


FIG. 5. Real part of the capacitance increment at $\nu = 1$ kHz, $\Delta C'_{\text{dep}}$, originating from vapor deposition of 3MP at $T_{\text{dep}} = 63$ K using rates r_{dep} between 0.32 and 0.35 nm s⁻¹, with $h_{\text{dep}} = 0, 36$, or 145 nm as indicated in the legends. The data are recorded at a nominal temperature of $T = 70$ K but after excursions to different peak temperatures, T_{max} . Data labeled “sub” are deposited onto the substrate and eventually annealed at $T_{\text{max}} = 100$ K (solid triangles down, open triangles down). Data labeled “on 3MP” (solid triangles up, open triangles up) are for films deposited onto the annealed 3MP underlayer, while those labeled “on 3MP/MMT” (solid triangles up) are for a film deposited onto a 130 nm layer of MMT, which had been deposited on top of the annealed 3MP underlayer.

of $\Delta C'_{\text{dep}}$ evaluated at 70 K for each heating segment (see the gray bar in Fig. 4). The curve for the empty cell in Fig. 5 demonstrates that the borosilicate substrate does not contribute significantly to the enhancement of $\Delta C'_{\text{dep}}$. Three pairs of measurements are presented in Fig. 5, with each curve labeled “sub” representing 3MP deposited at $T_{\text{dep}} = 63$ K onto the substrate. The second curve for pairs 1 and 3 is for 3MP deposited on top of the annealed first 3MP layer. In the case of pair 2, an additional 130 nm layer of MMT was deposited on top of the first, annealed 3MP film, before depositing the second 3MP layer. MMT remains solid during these measurements due to its high $T_g = 170$ K. For the thin films ($h < g$, pair 3), the second layer behaves similarly to the first one. For the thicker films ($h > g$, pairs 1 and 2), the second layers on top of the annealed underlayers show little change in $\Delta C'_{\text{dep}}$ compared with the considerable increases seen for films deposited directly onto the substrate.

To understand the results of Fig. 5, it is important to realize that the rise of $\Delta C'_{\text{dep}}$ is a matter of the annealing history and that all data are measured at the same temperature, $T = 70$ K, i.e., well below T_g . The thinner films increase their $\Delta C'_{\text{dep}}$ by a factor of 2.8, where the level appears to saturate. The values of $\Delta C'_{\text{dep}}$ of the thicker films deposited directly onto the substrate increase by a factor of 2.2, remaining slightly below saturation for $T_{\text{max}} \leq 100$ K. By contrast, the changes of $\Delta C'_{\text{dep}}$ for films deposited onto annealed underlayers do not exceed $\pm 20\%$. We note that this exact behavior was observed for all films with thickness $h_{\text{dep}} > g$ investigated in this study.

The time dependence of the $\Delta C'_{\text{dep}}$ enhancement is explored for two annealing temperatures, 86 and 92 K, in Fig. 6. At $T = 86$ K, where the structural relaxation time is $\tau_\alpha = 1$ ms, the increase of $\Delta C'_{\text{dep}}$ follows an exponential rise with a time constant $\tau = 8000$ s and appears to level off within that 30 ks segment. At $T = 92$ K,

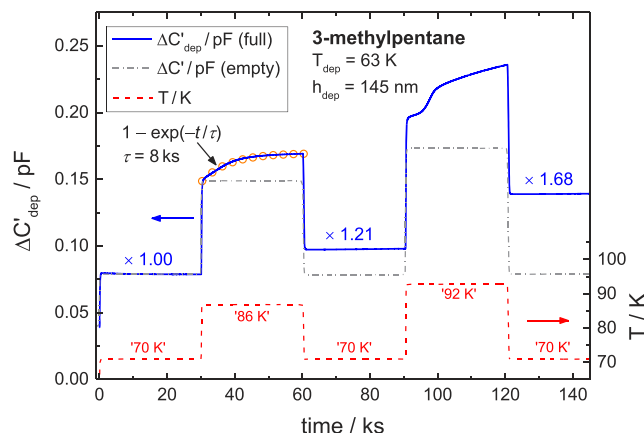


FIG. 6. Real part of the capacitance increment at $\nu = 1$ kHz, $\Delta C'_{\text{dep}}$, originating from vapor deposition of 3MP at $T_{\text{dep}} = 63$ K using a rate $r_{\text{dep}} = 0.34$ nm s⁻¹, with $h_{\text{dep}} = 145$ nm. The solid curve represents $\Delta C'_{\text{dep}}$ vs time recorded over 145 000 s, while temperature is varied stepwise as shown by the dashed curve and indicated by the nominal values for each 30 000 s segment. The dashed-dotted curve represents the concomitant capacitance change of the empty cell, shifted to match the level of $\Delta C'_{\text{dep}}$ in the first “70 K” segment. The relative increase of $\Delta C'_{\text{dep}}$ at $T = 70$ K is indicated above the curve. The exponential rise in the “86 K” segment is consistent with a time constant $\tau = 8000$ s (see open circles).

$\Delta C'_{\text{dep}}$ rises further, but only after a 5000 s induction time. The dashed-dotted curve is for the empty cell subject to the same temperature protocol, indicating again that the borosilicate substrate is not responsible for the time dependent changes, although its permittivity changes reversibly with temperature.

IV. DISCUSSION

Fabricating materials by physical vapor deposition has attracted considerable interest because glasses can be obtained with properties that differ substantially from the melt-cooled counterparts, e.g., the kinetically ultra-stable glasses achieved with $T_{\text{dep}} \approx 0.85T_g$ and polyamorphism.^{3,22,23,29} Dielectric spectroscopy is a powerful tool for the *in situ* detection of differences between the as-deposited amorphous solid and the glass obtained by cooling the supercooled liquid, i.e., before and after annealing. Observing a rise in permittivity in the glassy state after annealing above T_g could be rationalized by assuming that annealing activates a boson peak or any other fast relaxation process that became frozen by the high kinetic stability or enhanced density.^{30,31} However, in a case like 3MP, dipole reorientation has negligible influence on permittivity, regardless of frequency or temperature, implying that a boson peak would be even smaller. Therefore, density is the only factor expected to influence the level of the dielectric permittivity, ϵ' , in 3MP. In a capacitor that is only partly filled with a given amount of substance, however, ϵ_∞ as inferred from $\Delta C'_{\text{dep}}$ does not scale with density because the number of molecules within the capacitor is not affected by a change of density. The present data support this notion when comparing the slope $\partial\epsilon_\infty/\partial T$ for the bulk experiment (Fig. 1) with that for the thin film (Fig. 4), where the effect of temperature on $\Delta C'_{\text{dep}}$ of the thin PVD film reflects only 1% of the true density effect on ϵ_∞ , which would be observed in a completely filled capacitor.

To rationalize the observed changes in $\Delta C'_{\text{dep}}$, a closer scrutiny of the IDE cell geometry and the inhomogeneous electric field is in order; see also Latimer *et al.* for the agreement between conformal mapping and finite element analysis.³² A schematic representation of the IDE cell with field lines is provided in Fig. 7. The situation of Fig. 7(a) is meant to represent a thin sample deposited as glass ($T_{\text{dep}} < T_g$) that had not been softened by exposure to a temperature above T_g . In that case, the surface of the sample will mirror the square-wave pattern of the $g = 110$ nm thick digits, as indicated. After sufficient annealing of the sample at $T_{\text{max}} > T_g$, any material will tend to minimize the sample/vacuum interface area and flatten, as shown in Fig. 7(b). The question is whether such a redistribution of material will affect the measured capacitance.

In the thin film limit ($h < g = 110$ nm) and assuming that the material is situated *only* between the digits (cross hatched area in Fig. 7), i.e., not on top of gold, the capacitance increment can be calculated as follows. Using $C = \epsilon_0 A/d$, where d is the electrode separation and A the electrode area, the capacitance increment from adding a layer with susceptibility χ and thickness $h < g$ onto the substrate is $\Delta C_{\text{dep}} = \chi \epsilon_0 Lh/s$, with electrode separation (digit spacing) s and area $A = L \times h$ given by the serpentine length L times film height h . In the thick film limit ($h \gg \lambda/2$), the increment regarding C is $\Delta C_{\text{max}} = \chi C_{\text{geo}} = \chi \epsilon_0 L/2$, with C_{geo} taken from Eq. (1); see the [supplementary material](#) for IDEs with $s \neq w$. For the present IDE geometry with $s = w$ and, therefore, $\lambda = 4s$, the normalized capacitance increment for the case of adding material with $h < g$ *only* between digits then becomes

$$\frac{\Delta C_{\text{dep}}}{\Delta C_{\text{max}}} = \frac{\chi \epsilon_0 Lh/s}{\chi \epsilon_0 L/2} = \frac{h}{s/2} = \frac{h}{\lambda/8}. \quad (3)$$

This implies that a curve, as in Fig. 2, i.e., $\Delta C'_{\text{dep}}/\Delta C'_{\text{max}}$ vs h , should have an initial slope of $1/(\lambda/8)$, provided that material is added *only* between gold digits and not exceeding their height. However, this is precisely the slope observed by the vapor deposition

experiment of a thick film shown in Fig. 2 and consistent with FEM calculations for the range $0 \leq h \leq 0.025\lambda$, where the entire IDE area is covered by a sample. It may be inferred that for film thicknesses h up to about 1000 nm ($=0.025\lambda$), the capacitance measurement is sensitive only to material positioned between digits [cross-hatched area in Fig. 7(a)], while being blind to the other half of the sample positioned on top of the gold digits, consistent with theoretical considerations.³² In other words, when a solid film with $h < 1$ μm is vapor deposited, twice the amount of material is deposited onto the IDE surface compared to that contributing to $\Delta C'_{\text{dep}}$ and with a square-wave profile that mirrors the digit height [see Fig. 7(a)].

If the glassy sample of Fig. 7(a) is then annealed above its T_g , it will minimize the sample/vacuum interface area by flattening, as indicated in Fig. 7(b). Provided $h > g$, this brings material from where it did not contribute to where it does contribute to $\Delta C'_{\text{dep}}$, thus adding to the measured capacitance as observed in Figs. 4–6. With the above-mentioned result, the film height h_{dep} can be determined using

$$h_{\text{dep}} = \frac{\lambda}{8} \times \frac{\Delta C'_{\text{dep}}}{\chi_{\infty} C_{\text{geo}}} = \frac{\lambda}{8} \times \frac{\chi'_{\text{dep}}}{\chi_{\infty}} = \frac{\lambda}{8} \times \frac{\Delta C'_{\text{dep}}}{\chi_{\infty} \epsilon_0 (L/2)}, \quad (4)$$

where $\Delta C'_{\text{dep}}$ refers to the as-deposited value *prior* to annealing and χ_{∞} is the true high frequency limit susceptibility of the material deposited. Equation (4) has been employed to determine all thickness values h_{dep} and deposition rates $r_{\text{dep}} = h_{\text{dep}}/t_{\text{dep}}$ listed, using $\chi_{\infty} = 1.24$, $\lambda = 40$ μm , and $C_{\text{geo}} = 2.19$ pF.

It remains to be seen to what extent the present results are consistent with the above-mentioned rationale for the increases of $\Delta C'_{\text{dep}}$. The effects presented here are not specific to 3MP, as the same features have been observed for 2-methyltetrahydrofuran,^{22,23} *n*-propylbenzene,²⁴ and others, with the increase always being initiated by increasing temperature above the respective T_g (or by transformation from high to standard kinetic stability for films deposited near $T_{\text{dep}} = 0.85T_g$).

Regarding the effect of the electrode profile with height g , it makes sense that films with $h = 36$ nm ($<g$) display different annealing behavior compared with the thicker $h_{\text{dep}} = 145$ nm ($>g$) films (see Fig. 5). Similarly, an annealed underlayer of $h = 36$ nm does not prevent the overlaid 36 nm film of 3MP from displaying the same increase regarding $\Delta C'_{\text{dep}}$, see Fig. 5, because the total height of 72 nm still remains below the digit height g . By contrast, assuming an annealed film of 145 nm ($>g$) has flattened, layers deposited on top of it should not display the square-wave profile of Fig. 7(a) nor the ensuing $\Delta C'_{\text{dep}}$ increase, which is the observation in Fig. 5.

For any film with $h_{\text{dep}} > g$ deposited onto the substrate, complete flattening of the surface by annealing is expected to add the height of $g/2 = 55$ nm to the volume between electrode digits. This is equivalent to an increase by 40% for the $h_{\text{dep}} = 145$ nm cases and corresponds well to the change observed after annealing at $T_{\text{max}} = 86$ K in Fig. 4, but $\Delta C'_{\text{dep}}$ increases further at higher annealing temperatures. No explanation for the latter effect can be given, and it might be specific to the present setup. While tests at ambient conditions did not reveal signs of 3MP dewetting from gold or borosilicate glass, we cannot exclude that it might contribute to the relocation of material at the present low temperatures. Dielectric experiments alone will not distinguish between flattening and dewetting effects.

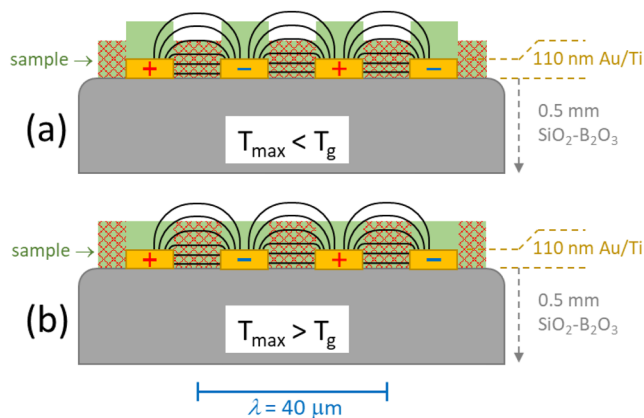


FIG. 7. Schematic cut view of the IDE cell with curves representing the electric field and a thin sample film. The top (a) is for a solid film deposited below T_g and never exposed to a higher temperature, with its square-wave surface profile reflecting the height of the gold digits. The bottom (b) is for the film after being annealed above T_g , resulting in a flattening of its surface. Only the cross-hatched part of the sample contributes to the capacitance increment. Note the difference in vertical and lateral scales.

Given the polar nature of a silicate surface, dewetting may be a more pronounced factor with films of polar materials.

Regarding the time scale of material relocation during annealing, Fig. 6 shows that the time constant for the exponential rise of $\Delta C'_{\text{dep}}$ at 86 K is $\tau = 8000$ s, much longer than the structural relaxation time $\tau_\alpha = 1$ ms of 3MP at that temperature. Assuming that viscous flow is mainly responsible for the flattening effect, the expected time constant of the exponential decay is $\tau_{\text{flat}} = \eta\lambda/\pi\gamma$,³³ with viscosity η , surface tension γ , and $\lambda = s + w$. As detailed in the [supplementary material](#), the values $\eta_{86\text{K}} = 2 \times 10^7$ Pa s and $\gamma_{86\text{K}} = 22$ mN m⁻¹ (see Fig. S1) yield $\tau_{\text{flat}} = 5800$ s at $T = 86$ K, in favorable agreement with the observation of $\tau = 8000$ s in Fig. 6. Based on the deposition temperatures $T_{\text{dep}} = 63$ K ($=0.82T_g$) and rates $r_{\text{dep}} \approx 0.3$ nm s⁻¹ of all thin ($h_{\text{dep}} < 500$ nm) films, these as-deposited glasses are kinetically very stable, i.e., with onset temperatures several K above T_g . In the absence of kinetic stability, the effect of annealing (first large step up in Fig. 4) would begin at a somewhat lower temperature, but the time scale of flattening is not expected to change, as it is only observed after full transformation to the liquid state.

The annealing induced capacitance increase is also not limited to the ABTECH 1050.5 type cell, as analogous features are observed with a Micrux ED-IDE2 cell (see Fig. S2). The change in $\Delta C'_{\text{dep}}$ is not a matter of creating high kinetic stability at $T_{\text{dep}} = 63$ K ($=0.82T_g$), because it is also observed for $T_{\text{dep}} > T_g$, where the increase occurs already during deposition (see Fig. S3). Consistent with the present rationale is that increasing film thicknesses do not lead to larger increases of $\Delta C'_{\text{dep}}$ by annealing (see Figs. S4 and S5), which is consistent with the annealing induced added height of $g/2$ being independent of h for $h > g$. Moreover, under- and inter-layers of solid MMT have little impact (see Figs. S6 and S7) on the effect of annealing on $\Delta C'_{\text{dep}}$. The idea of material relocation rather than material properties changing is further supported by observing in Fig. S8 that $\tan \delta = \Delta C''_{\text{dep}}/\Delta C'_{\text{dep}}$ is less affected than $\Delta C'_{\text{dep}}$ in the process of annealing, since the amount of material will not alter $\tan \delta$. Moreover, it cannot be excluded that relocation of material from outside the active IDE area or forces due to the electric field impact the observations regarding $\Delta C'_{\text{dep}}$, as demonstrated in Fig. S9 by reducing the deposition to a fraction of the active IDE area and by applying a lowered field (1.5 instead of 15 kV cm⁻¹).

In retrospect, this flattening effect has been observed in several dielectric studies of vapor deposited films.^{22–24} Applying broadband dielectric spectroscopy, Gabriel *et al.*²³ have shown for a thin film that the annealing induced increase of susceptibility is captured by a single factor for the entire spectrum from ϵ_s to ϵ_∞ , as expected for flattening. By contrast, the increase of ϵ_s observed for vapor deposited *n*-propanol is not reflected in ϵ_∞ ,¹⁴ which excludes flattening as an explanation. In studies by Riechers *et al.*, the effect of flattening is observed for 2-methyltetrahydrofuran (2MTHF),²² *n*-propylbenzene (nPB), and *iso*-propylbenzene (iPB).²⁴ These previous studies demonstrate that the effect of flattening occurs equally for glass formers with little (nPB, $\Delta\epsilon = 0.3$; iPB, $\Delta\epsilon = 0.3$; 3MP, $\Delta\epsilon = 0.02$) and with considerable (2MTHF, $\Delta\epsilon = 16$) polarity.

V. SUMMARY AND CONCLUSIONS

Dielectric relaxation spectroscopy is a powerful tool for *in situ* characterization of vapor deposited films when using

interdigitated electrode (IDE) cells. However, the interpretation of the observed impedance is more complex than in the case of the usual planar disk capacitor approach. A nonpolar glass forming liquid, 3-methylpentane, is employed to ensure that the permittivity is the same for the glass produced by physical vapor deposition and that obtained by cooling the melt. It is recognized that the deposition of a molecular glass onto a typical interdigitated electrode cell leads to a square-wave type surface profile that mimics the height of the metallic digits. After annealing such a glass by warming above T_g , the material will flatten this profile via viscous flow, thereby moving the sample from on top of the digits to in between the electrodes.

For films with heights not exceeding 10% of the digit spacing, it is demonstrated that the impedance measurement is predominantly sensitive to material between the electrode digits (see cross-hatched areas in Fig. 7), while being blind to about half of the sample that is situated on top of the metal digits. This implies that annealing induced flattening leads to an apparent increase in sample permittivity, without a concomitant actual change in material properties. A further result is the relation connecting capacitance increment ΔC of a thin glassy film (prior to annealing) to its height h , $\Delta C = \chi\epsilon_0 Lh/s$, where χ is the susceptibility of the glass, L is the serpentine length of the IDE structure, and s is the digit spacing.

While a complete quantitative correction for the flattening effect cannot be provided, it is important to recognize its impact on the observed capacitance so that apparent permittivity changes can be discriminated from actual ones. In particular, the idea that annealing should bring the permittivity closer to the value corresponding to equilibrium may lead to false interpretations when disregarding the effect of surface flattening.

SUPPLEMENTARY MATERIAL

Calculations of the IDE geometric capacitance and of the incremental capacitance in the thin film limit and estimation of the flattening kinetics, as well as further data detailing the capacitance enhancement upon annealing, can be found in the [supplementary material](#).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Erik Thoms: Conceptualization (equal); Formal analysis (lead); Investigation (equal); Writing – review & editing (equal). **Ranko Richert:** Conceptualization (equal); Funding acquisition (lead); Investigation (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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