An Alternative Route Towards Metal–Polymer Hybrid Materials Prepared by Vapor-Phase Processing

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Dedicated to the late Prof. Ulrich Gösele

Transition metals incorporated into polymers lead to unusual or improved physical properties that significantly differ from those of purely organic polymers. A simple and practicable incorporation of diverse transition metals into any available polymer would make an important contribution to overcome some of the synthetic difficulties of metal-polymer hybrid materials. Here, it is demonstrated that atomic layer deposition (ALD) can be a promising means to resolve some of those difficulties. It is found that even polytetrafluoroethylene (PTFE) with its great physical and chemical stability can be easily transformed into a transition metal–PTFE hybrid material simply by applying a metal-oxide ALD process to PTFE. Upon metal incorporation into the PTFE, the molecular structure as well as mechanical properties (tensile behavior) of PTFE were observed to significantly change. For a better understanding of the changes to the material, experimental investigations using Raman spectroscopy, attenuated-total-reflection Fourier-transform infrared spectroscopy, wide-angle X-ray diffraction, and energy-dispersive X-ray analysis were performed. In addition, with density functional theory calculations, potential bonding states of the incorporated metal into PTFE were modeled and predicted. The ALD-based vapor-phase approach for metal incorporation into a polymer could bring about rapid progress in the research area of metal–polymer hybrid materials.

1. Introduction

The basic idea behind the development of organic–inorganic hybrid materials is the combination of inorganic and organic substances on a molecular scale to achieve a synergetic combination or compromise of each constituent’s properties. The resulting hybrid materials have neither a purely organic nature nor purely inorganic nature. Control of the ratio and type of the organic and inorganic constituents allows an intentional tailoring of properties between purely organic and purely inorganic materials. Therefore, organic–inorganic hybrid materials do not only represent a creative alternative to design new functional materials in academia, but also their improved or unusual features could bring immense innovation in industrial applications.[1,2] The development of polymer-based new hybrid materials is of steadily growing technological and academic importance due to the high cost effectiveness and the promising properties of the resulting polymeric materials. It has been already recognized for a while that incorporation of transition metals into synthetic polymers can lead to unique physical/chemical properties and promising applications in many areas: mechanics, optics, electronics, etc.[1–5] Incorporating metals into polymers, therefore, clearly shows a considerable potential for the preparation of processable materials with properties significantly differing from those of conventional organic polymers.[3] However, synthetic difficulties in the incorporation of metals into organic polymers have so far impeded progress in hybrid metal–polymer materials research, although substantial advances have been achieved toward the preparation of those hybrid materials.[1,6–9] Here, we demonstrate that the atomic layer deposition process (ALD), conventionally used for thin-film deposition, can become a straightforward and promising alternative to overcome those synthetic difficulties by means of direct metal infiltration into polymers. Namely, we exposed PTFE (polytetrafluoroethylene) to vaporized precursor pairs commonly used for metal-oxide ALD (ZnO, ZrO2, and Al2O3), like diethylzinc (DEZ, Zn(C2H5)2)/water (H2O), zirconium(IV) tert-butoxide (Zr(OC(CH3)3)4)/H2O, and trimethylaluminum (TMA, Al(CH3)3)/H2O at a temperature of 70 °C and a pressure of 10−1 torr in a ALD chamber. We observed that the high reactivity of the ALD precursors can lead to an incorporation of transition metals (Zn, Al, and Zr) even into PTFE, which
usually shows a high physical and chemical stability under very harsh environmental and experimental conditions. Among those three processes, the Zn infiltration based on an adapted ZnO–ALD process was found to lead to the most significant physical-property changes. Hence, herein, we focus on this process.

2. Results and Discussion

In Mendeleev’s Periodic Table, fluorine has the highest electronegativity of all elements, also a high ionization energy and high bonding strength with carbon atoms. In a polymeric (–CF₂)n chain, it shields the backbone from external effects. These unique features of fluorine cause polytetrafluoroethylene (PTFE) (–(CF₂)n–) to possess an extraordinary combination of desirable chemical and physical properties, such as excellent high chemical resistance,[10] thermal stability (melting at 320–327 °C and decomposition at 425 °C),[10–12] low dielectric loss,[10,13] attractive antifriction characteristics,[14] and hydrophobicity.[10,15] Although PTFE is very sensitive to radiation, which induces chain scission,[16,17] due to the attractive physical and chemical properties, PTFE has been most widely used in industry and laboratories for various purposes even under very harsh conditions.[18]

In addition, PTFE is a semicrystalline linear polymer with a helical conformation exhibiting an unusual solid–solid phase-transition behavior (Figure 1 and Figure S1 in the Supporting Information).[19,20] PTFE has three solid-state phases changing within a few degrees Celsius (phase II, IV, and I). In addition, substantial molecular motion within the crystal is observed well below the melting point. At temperatures below 19 °C (phase II), PTFE has a well-ordered triclinic unit cell containing two helical chain stems with 13σ symmetry.[21,22] At 19 °C, the first-order transition (from order to disorder) between phase II and IV occurs, which results in an unraveling of the helical conformation from the triclinic cell with 13σ symmetry.[21,24] Further rotational disordering and untwisting of the helices occurs above 30 °C leading to a pseudohexagonal unit cell (phase I) with long-range positional and orientational order as temperature increases. In a high-temperature region of phase I, the 15σ helical conformation changes into a planar zigzag conformation.[25] The driving force of such phase transitions is postulated to be the presence and mobility of a reversal in the helix (or chain defects, the change from a left-handed to a right-handed helix). Such helix reversals are known to rotate around the molecular axes without affecting long-range ordering in the molecule.[26] Moreover, the reversals on neighboring chains are believed to interact and separate into well-defined defect planes within the PTFE crystal. Besides, such defects could travel along the crystal with high mobility, resulting in a rotational disorder and fluctuation in the PTFE helix structure.[20,27] These helix reversal points (point defects), phase transitions, and crystallinity are considered to affect the mechanical properties of PTFE,[27] although this is still not fully clarified.

Some previous results have demonstrated that the temperature plays an important role for the tensile properties of PTFE.[30–34] Namely, in phase IV (19 °C < T < 30 °C), the PTFE shows the highest strength and ductility in tension. Above 30 °C (phase I), high ductility and low strength are observed, whereas, below 19 °C (phase II), the PTFE shows both low ductility and strength.[34] In our experiment, considering the protection...
The cross-sectioned native PTFE, prepared by using the focused ion beam technique, had the elements C, O, and F uniformly distributed over the whole region as confirmed by TEM–EDX point analysis (Figure 3a–Figure 3c). In the case of ZnO–ALD-processed PTFE (PTFE/400), point analysis (Figure 3f) revealed a considerable amount of Zn in the bulk of the PTFE. Bearing in mind the chemical inertness and the shielding effect by fluorine, an infiltration of Zn into the PTFE molecules by ALD is hardly imaginable. However, the results of subsequently performed Raman and attenuated-total-reflection Fourier-transform infrared (ATR–FTIR) spectroscopy (Figure 4) showed that the incorporation of Zn into PTFE leads to serious structural changes of the PTFE, which are presumably dominant at the point defects and chain-end parts composed of –CF₃. More notably the Zn incorporation induces a phase transformation related to a crystallographic change of the PTFE.

The Raman spectra (Figure 4a) measured at ambient conditions on native crystalline PTFE (PTFE/N) showed intense peaks at 1385, 1220, 737, 389, and 294 cm⁻¹. Zn–PTFE hybrid showed additional peaks at 1160, 441, and 335 cm⁻¹, which appeared to be not related to the ZnO shell covering the PTFE, as can be seen from the reference Raman spectra of ZnO deposited on a silicon wafer (Si/500). To better understand the possible changes of PTFE in the molecular structure upon Zn infiltration, a molecular model was constructed and possible reaction paths were calculated using density functional theory (DFT) approaches. For modeling of the PTFE, the cyclic molecule of perfluorohexane in a “chair” conformation was used to represent the PTFE polymer. The choice of the cyclic molecule allows adequate modeling of all corresponding valence of the carbon backbone of the PTFE provided by the fluorine (shielding effect leading to chemical inertness), after an ALD process performed at 70 °C, one expects a thin metal-oxide-film deposition on the PTFE and the mechanical properties should be nearly preserved upon heating at 70 °C. However, with extended exposure times to the DEZ during a ZnO–ALD process, the PTFE exhibited considerable mechanical-property change, as shown in the uniaxial tensile-property test curves, which were measured under ambient conditions (Figure 2 and Table S1). The thermal stability of the used PTFE remained preserved, as shown in the tensile behavior of PTFE/H. The tensile test curves of ZnO-processed PTFE show a similar shape (negligible plastic deformation) to a curve measured at a very low temperature (~196 °C, phase I) by Speerschneider and Li. Although a deposited ZnO shell may have a partial influence on the tensile properties such as an increase of the initial Young’s modulus (Table S1), the contribution of the shell to the overall mechanical behavior can be ruled out owing to the inherent brittleness of the oxide materials. Such a considerable property change of PTFE after ZnO–ALD was found to be caused by Zn incorporation into PTFE, as can be conjectured from the transmission electron microscope (TEM)–energy dispersive X-ray (EDX) analysis results (Figure 3).
bonds and angles present in the linear PTFE, and, at the same
time, simplifies the study of the potential-energy surface of the
reacting system, by reducing both the number of atoms and
the number of local minima due to conformational changes.
According to spectroscopic and theoretical investigations,[37]
diethylzinc undergoes thermal decomposition at elevated tem-
peratures, which proceeds typically in the range 300–600 °C, but
starts already at 150–200 °C. The main pyrolysis pathway in this
case is a homolytic fission of the Zn–C bond with a $^{\text{1}}\text{Zn}(\text{C}_2\text{H}_5)$
and $^{\text{1}}\text{C}_2\text{H}_5$ radical formation. The free radicals recombine
after a short time to the dimer $(\text{Zn}(\text{C}_2\text{H}_5))^2$ and alkanes. The
β-elimination mechanism, which leads to hydride formation,
was shown to be not dominant for the pyrolysis of diethylzinc.
Taking into account these literature data, we have concentrated
on the study of possible interactions of intermediate radical
species with perfluoroalkanes under ALD conditions.

The results of our DFT calculations have shown that the
Zn–C bond fission in diethylzinc, which leads to formation of
$^{\text{1}}\text{Zn}(\text{C}_2\text{H}_5)$ and $^{\text{1}}\text{C}_2\text{H}_5$ radicals, is connected with the positive
reaction enthalpy of +59.0 kcal mol$^{-1}$ (Equation 1). This enthalpy
represents the energy barrier for the pyrolysis of diethylzinc
and reflects its relative thermal stability in the ordinary
temperature range of ALD. The hydrolysis of one of the ethyl
groups of diethylzinc is, however, characterized by a negative
reaction enthalpy of −22.4 kcal mol$^{-1}$. An additional amount of
energy is released by the co-condensation of −OH groups in the
hydrolyzed product molecules and clustering of Zn–O fragments
to form a ZnO crystal structure. Thus, in the presence of water
molecules, the energy barrier can be overcome for some Zn–C
bonds at the expense of the hydrolysis enthalpy (Equation 2 and 3).
The fission of some Zn–C bonds is supposed to proceed
concurrently with the diethylzinc hydrolysis at moderate temper-
atures, being the source of the short-lived radical species.

\begin{align}
\text{Zn(\text{Et}_2)} & \rightarrow \text{Zn} + \text{Et} \quad \Delta H^\circ = +59.0 \text{ kcal/mol} \\
2\text{Zn(\text{Et}_2)} + \text{H}_2O & \rightarrow 2\text{Et} + 2\text{EtOH} \quad \Delta H^\circ = +16.0 \text{ kcal/mol} \\
2\text{Zn(\text{Et}_2)} + \text{H}_2O & \rightarrow 2\text{Et} + \text{EtOH} \quad \Delta H^\circ = -4.0 \text{ kcal/mol}
\end{align}

In contrast to diethylzinc and its hydrolysis products, the
radical species are quite reactive toward perfluoroalkanes. The
ethyl radical can split C–F bonds of perfluoroalkanes to form FC₂H₅ molecules with a relatively low activation-energy barrier (Equation 4). Experimental observations of the C–F bond splitting by different radical species (•H, aromatic radical anions) in PTFE at room temperature were reported in the literature.\(^\text{[38,39]}\)

The C–F bonds of the perfluoroalkanes can be split even more easily by the radicals with an unpaired electron on the Zn atom, like •Zn(C₂H₅), •ZnOZn(C₂H₅), •Zn(OH)₂Zn(C₂H₅), etc. Also, due to the presence of dangling bonds on its surface, the nanoparticulate ZnO is expected to act as a reactive species toward perfluoroalkanes. The calculated activation-energy barrier for the reaction of •Zn(C₂H₅) radical with perfluoroalkanes comprises only +21.1 kcal mol\(^{-1}\) (Equation 5), which can be easily overcome with the energy released by hydrolysis of diethylzinc and by radical-recombination reactions (Equation 6–12). Under ALD conditions, this can thus lead to additional crosslinking of the PTFE chains, by mutual recombination of perfluoroalkyl radicals or by bridging the PTFE chains with the –(Zn–O–Zn)– fragments. During the recombination of the radical species, the highest values of negative reaction enthalpy are achieved by the recombination of two alkyl radicals or alkyl with perfluoroalkyl radicals (Equation 6 and 7). In the case of a recombination of two perfluoroalkyl radicals, the sterical hindrance significantly lowers the energy gain (Equation 12). The high reactivity of alkyl radicals indicates that they may quickly recombine with each other directly after their formation by fission of the Zn–C bond of diethylzinc, so that only Zn-based radical species can further participate in the interaction with perfluoroalkane chains (Equation 5). The part of Zn-based radicals, as well as Zn dangling bonds on the surface of ZnO particles, can recombine with perfluoroalkyl radicals (Equation 8 and 9), which brings significantly more energy gain than the reformation of diethylzinc or formation of (ZnC₂H₅)₂ dimers (Equation 10 and 11). Our calculations also show that the free Zn metal atoms are quite reactive towards perfluoroalkanes and can insert into C–F bonds (Equation 13). This reaction is characterized by a higher activation-energy barrier, but under certain circumstances it may compete with the C–F bond-splitting by ethyl and Zn-based radicals. In this case a small amount of free Zn metal atoms are formed under ALD conditions as a by-product.

To identify the possible presence of the Zn–C bonding to the perfluoroalkane backbone, which results from a recombination of the Zn-based radicals with the perfluoroalkyl radicals or Zn-atom insertion into the C–F bonds of perfluoroalkanes, a simulation of the Raman spectra has been performed. In this study, the perfluoroalkanes were represented by the model molecular structure C₇F₁₆ in helical conformation (Figure 5a), which is close to that experimentally observed for the low-temperature modification of the crystalline PTFE. The –Zn–O–Zn– bridging unit (Figure 5b) or –Zn–F functional group (Figure 5c) have been introduced into the model.

**Figure 5.** The molecular models used to simulate the Raman spectra for a) the linear perfluoroalkane and its derivatives, containing b) a –Zn–O–Zn– bridging unit and c) a –Zn–F group.
to estimate the response of the Raman spectral features. The calculated spectra, together with the experimental ones, are presented in Figure 4b. Although the calculated Raman spectra are generally shifted to a higher frequency region ($\Delta \omega = -15 \text{ cm}^{-1}$) than the experimental spectra, they qualitatively show high accuracy. In the calculated spectra, the main differences between the native PTFE and the Zn-infiltrated PTFE were observed in the range of 1050–1200 cm$^{-1}$ (peaks, 1193, 1161, 1114, and 1099 cm$^{-1}$ in the blue box in Figure 4b). In the experimental spectra, this range is completely overlaid, presumably due to the combined spectra from $-\text{Zn-O-Zn-}$ bridging units and $-\text{Zn-F}$ groups. This hypothesis finds support after deconvolution of the curve using Gaussian functions in the region of 1000–1200 cm$^{-1}$ of the PTFE/500 spectrum (Figure 4c). The deconvoluted Gaussian curves appear close to the peaks at 1099 and 1161 cm$^{-1}$, albeit there is a slight discrepancy of the other two peaks. However, a direct comparison of calculated and measured spectra needs to be treated with care.

Additionally, a band at 598 cm$^{-1}$ (Figure 4a) can be observed which is associated with the conformational defect of the helix reversal,[35,40] and a band at 578 cm$^{-1}$ associated with unperturbed helical sequences.[41] Notably, both bands exhibit an evolution of behavior after Zn infiltration. Namely, the intensity of the defect-induced band (598 cm$^{-1}$) decreases after Zn infiltration, whereas the band at 578 cm$^{-1}$ becomes sharper and stronger. This means that the concentration of the helix-reversal defects decreases after Zn infiltration. A similar evolution in the Raman spectra of the native PTFE has been observed in the temperature range, $-10 {^\circ}\text{C} < T < 60 {^\circ}\text{C}$[41] or $9 {^\circ}\text{C} < T < 184 {^\circ}\text{C}$.[28] which accompanies a phase transformation from a 15$_2$-hexagonal (phase IV) to a 13$_6$ triclinic (phase II) phase. The Raman spectra of the Zn–PTFE hybrid are notably similar to the spectra measured at $-10 {^\circ}\text{C}$[41] or $9 {^\circ}\text{C}$,[28] although our Raman measurements were performed at room temperature. In other words, after Zn incorporation, the native PTFE has transformed from the transitional phase II–IV into phase II (see Figure 1), which remains stable even at room temperature, although this phase is expected for native PTFE at much lower temperatures. A comparison of the mechanical properties with the reported data for PTFE at very low temperatures (phase II)[30–34] additionally confirms the phase transformation of PTFE. From the tensile behavior of PTFE/H, pure thermal effects can be assumed to have negligible influence on such a transformation. In this experiment, the ZnO–ALD process for Zn infiltration into PTFE was performed at 70 °C. In addition, it was proposed that increasing torsional oscillations with increased temperatures (twisting and untwisting of the PTFE helix along the chain axes) could be an important factor for such phase transitions.[22] Therefore, the native PTFE (phase II–IV) should be initially transformed into phase I (pseudohexagonal) with an enhanced untwisting and an increasing number of defects in the ALD chamber at 70 °C.[41,42] Subsequently, during the exposure/purge sequences of DEZ and H$_2$O vapor, PTFE appears permanently transformed from phase I into phase II after Zn infiltration into defect sites of PTFE, which thereby decreases the defect concentration of PTFE, as already confirmed from the band decrease at 598 cm$^{-1}$.

Aside from the defect sites, we found that Zn infiltration also occurred at terminal groups of the PTFE chain (–CF$_3$) and was accompanied by notable crystallographic changes. This result can be derived from the ATR–FTIR investigations (Figure 4b). The main peaks in the IR spectrum of the native PTFE were detected at 1152 and 1210 cm$^{-1}$, which correspond to the characteristic band of CF$_3$ stretching.[43] A broad peak at ca. 980 cm$^{-1}$ and a peak at ca. 760 cm$^{-1}$ have been reported to be characteristic stretching peaks of CF$_3$ at the chain ends of PTFE and in amorphous PTFE.[44,45] As with the Raman spectra, heating (PTFE/H) the sample had a nearly negligible effect on the chain conformation. However, the spectra of PTFE before and after Zn infiltration differ strongly. For instance, the broad peak (ca. 980 cm$^{-1}$) of the native PTFE indicates that the PTFE has many chain ends, which means that the chain is likely to be short or that serious branching of the chains occurs, which thereby forms amorphous PTFE. This suggestion is also supported by the presence of the peak at around 760 cm$^{-1}$. Notably, after Zn infiltration, the broad peak disappears, which means that the terminal CF$_3$ groups have been modified. This modification may be caused by interconnections of the terminal groups by means of $-\text{Zn-O-Zn-}$ bridges or alternatively a change from $-\text{CF}_2-\text{Zn-F}$ to $-\text{CF}_2-\text{Zn-F}$, both of which manifest a disappearance of CF$_3$. Moreover, the complete vanishing of the peak at about 760 cm$^{-1}$ indicates that the infiltrated Zn leads to a significant reduction of amorphous PTFE, or alternatively creation of additional crystals in PTFE,[46] which was additionally confirmed with wide angle X-ray diffraction (WAXD) by high-resolution transmission electron microscopy (HR-TEM) investigation (Figure 6).

Semicrystalline PTFE in phase IV has a hexagonal unit-cell structure with lattice parameters $a = 5.66$ Å and $c = 19.5$ Å (Figure 1a and Figure S1). The crystal lattice consists of a periodic arrangement of the long axes of the helical-chain repeating unit (15$_2$-helix). Crystal domains are connected by amorphous regions, which have the same repeating atomic structure as the crystalline domains but without short- or long-range ordering. The WAXD pattern of the native PTFE shows an intense peak at a $2\theta$ value of 18.05° (Figure 6a). The position of this peak implies diffraction from (100) planes with a spacing of 4.90 Å in PTFE, which can also be seen in the HR-TEM image (Figure 6b). In the case of the Zn–PTFE hybrid, two new peaks were observed at 2$\theta$$_{PF}$ = 16.62° and 2$\theta$$_{PF}$ = 13.55°. Obviously these peaks E and F do not have any relation to the ZnO shell deposits around the PTFE (Figure S2). In HR-TEM images of the Zn–PTFE hybrid, the plane spacing of some crystal domains was measured to be about 5.30 Å (Figure 6c), which corresponds well to the spacing of the peak E.

Presently, polymers are believed to consist of lamellar crystals, separated from each other by amorphous phases and interconnected by tie molecules through the amorphous phase. A number of scientists have extensively investigated the deformation mechanism of semicrystalline polymers under tensile/compressive force.[47,48] Currently, an accepted mode for deformation is the slip/separation/stack rotation of the amorphous interlamellar regions for elastic deformation and the crystallographic slip of crystalline regions for plastic deformation.[47] Considering the negligible plastic deformation behavior of the Zn–PTFE hybrid, the mechanical
behavior is likely to be related to amorphous regions rather than crystalline ones. The experimental evidence and theoretical models in our work indicate that the infiltrated Zn is likely to build –Zn–O–Zn– bridging units or –Zn–F groups at both defect sites and chain termini, which leads to a permanent phase transformation and serious molecular-structure changes (Figure 7). Therefore, Zn atoms connecting helical chains in the amorphous phase of PTFE presumably function as impurities which can noticeably reduce or hinder the flexibility or mobility of single chains as well as whole chain bundles. Such a significantly reduced flexibility or hindered mobility by Zn infiltration is believed to lead to a considerable mechanical-property change of the resulting Zn–PTFE hybrid under uniaxial tensile force.

3. Concluding Remarks

We found that the incorporation of a transition metal into a polymer can be easily realized simply by applying a metal-oxide ALD process to the polymer. Experimentally we demonstrated that even PTFE, with its high physical and chemical stability, was easily transformed into a Zn–PTFE hybrid material after a ZnO–ALD process. Upon Zn incorporation into PTFE, the molecular structure as well as the mechanical properties (tensile behavior) of PTFE significantly changed. DFT calculations were performed to evaluate possible bonding states of the Zn within the hybrid and corresponding Raman spectra were simulated. A comparison of the experimental and theoretical Raman spectra showed that the existence of –Zn–O–Zn– bridging units

![Figure 6. WAXD pattern and HR-TEM images of PTFE. a) WAXD patterns of PTFE samples in the range of 12° < 2θ < 20°; b–c) HR-TEM images of PTFE/N and PTFE/400, respectively.](image)

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![Figure 7. Proposed model to describe the chemical changes of PTFE after Zn infiltration.](image)

Figure 7. Proposed model to describe the chemical changes of PTFE after Zn infiltration.
or –Zn–F groups at both defect sites and chain terminals is highly probable. Since many transition-metal ALD processes have been developed and many synthetic polymers are available, it can be expected that, by controlling the combination and ratio of transition metals and synthetic polymers, the physical properties of the resulting metal–polymer hybrid materials can be intentionally tuned as the occasion demands. In addition to the known hybrid materials, which are in most cases synthesized by bottom-up approaches, this top-down strategy allows an incorporation of alternative metals to the known ones, greatly expanding the range of combination possibilities. In addition, in the area of protein-based biomaterial research, the ALD approach for developing new types of metal–biopolymer hybrid materials could bring about rapid progress, if processing conditions are well optimized.[9–33]

4. Experimental Section

ZnO–ALD: Commercial PTFE (Teflon) tape (Carl Roth, dimension: 12 m × 12 mm × 0.08 mm) was placed in an ALD reactor (Savannah 100, Cambridge Nanotech Inc) and dried at 70 °C for 200 min in vacuum (1 × 10⁻⁴ torr) with a steady Ar gas stream (20 sccm). For the ZnO deposition, Zn(C₂H₅)₂ (DEZ, Sigma-Aldrich) and deionized H₂O were used as zinc and oxygen sources, respectively. During the deposition process, the PTFE was alternately exposed to/purged from DEZ and H₂O vapor. The detailed processing conditions and sample numberings can be found in Table S4. For the preparation of the PTFE/H sample, the PTFE was annealed without precursor pulse/exposure/purge under identical ALD conditions used for PTFE/400. In the case of Si/500, identical ALD conditions used for PTFE/500 were applied to a silicon wafer.

Uniaxial Tensile Test: For the preparation of PTFE specimens, the PTFE was carefully cut with a knife (12 mm × about 90 mm) and soft tapes were attached to each end of the PTFE specimens for gripping in the ZWICK 1445 tensile-test machine with an extension rate of 50 mm and 25 mm min⁻¹. The tensile test was performed on a ZWICK 1445 tensile-test machine with ORIGIN 7.5, respectively. The tensile test was performed on a ZWICK 1445 tensile-test machine with ORIGIN 7.5, respectively.

DFT Calculation Details: The geometry optimizations and single-point energy calculations were performed in the frames of DFT, using spin-unrestricted self-consistent field (SCF) method and scalar relativistic treatment of electrons (Douglas–Kroll–Hess). The gradient-corrected exchange-correlation functional BP86[54,55] was used for geometry optimizations and numeric calculations of the Hessian matrices. Hybrid functional B3LYP[60–62] partly accounting for exact exchange energy contributions, was used for single-point energy calculations. The contracted Gaussian-like atom-centered basis sets were applied: triple-zeta split valence (TZV) with three sets of first polarization functions for zinc atom and triple-zeta split valence (TZV) with one set of first polarization functions for all other atoms. The speed-up in the calculation of the Coulomb part of energy contributions was achieved using the “resolution of the identity” approach[64,65] by approximating the charge distribution by the linear combination of the auxiliary basis functions.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

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