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Langmuir–Blodgett films of polyethylene

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The possibility to obtain surface layers on water and prepare solid multilayer Langmuir–Blodgett films of medium-density polyethylene is shown. The polymer film on water is stable, demonstrates a reversible surface pressure-area isotherm up to 15 mN/m, and can be deposited onto a substrate using the Langmuir–Blodgett technique in a wide range of surface pressures. The thickness of a single deposited layer is 5.1 nm on average. The dielectric and optical constants of multilayer films are near their bulk values. The films exhibit high dielectric strength of at least 200 MV/m. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1513201]

I. INTRODUCTION

Polyethylene (PE) is a commonly known polymer with a simple chemical formula $-(CH_2-CH_2)-_n$. Depending on the polymerization process, it may have linear or branched chains and density ranging from 0.915 to 0.965 g/cm^3, the lower values for more branched polymers.[1] Polyethylene, with its simple structure, serves as a model polymer. Because of excellent dielectric and tribologic properties, PE thin films have many current and potential applications. Methods of PE thin film preparation include molding, solution casting[2] or dipping,[3] direct[4] or ionization-assisted[5] thermal evaporation in vacuum, synchrotron radiation ablation,[6] and radio-frequency magnetron sputtering.[7] In most reported thin film work, films were 100–1000 nm thick.

The Langmuir–Blodgett method allows one to produce thin ordered organic films by repeated transfer of a monomolecular layer, preformed on a water surface, onto a solid substrate.[8] The thickness of Langmuir–Blodgett (LB) films is determined by the number of transferred monolayers and can be precisely varied from a few nanometers to several microns. To form a good Langmuir monolayer, substance molecules should be amphiphilic, i.e., possess both hydrophilic and hydrophobic groups, and be insoluble in water. Unlike low molecular weight substances, strong amphiphilic character is not strictly required for polymers; macromolecules without pronounced amphiphility, and even water-soluble polymers, can form a distinct surface layer on liquids.[9] Not all polymers produce true Langmuir monolayers, where the polymer chains lie flat at the air–water interface, but may extend partially into the water.[10] As for their low molecular weight analogs, polymer surface films (even if not true monolayers) under certain conditions can be deposited layer-by-layer onto a solid support.

Polymer LB films, in general, have much greater thermal, chemical, and mechanical stability than LB films of low molecular weight compounds. Because of this, polymer LB films are good candidates for capacitor-like applications, metal-insulator-semiconductor devices and various sensors, and may be used as a high resolution electron beam lithography resists.[11] The minimum thickness of a film is a question of special interest. If a polymer forms a true monomolecular surface layer, which may be transferred intact onto a substrate, then the minimum thickness of a single deposited layer is determined only by the geometry of a polymer chain. For example, poly(vinyl acetal) polymers form good LB films, whose thickness is close to the length of alkyl chains attached to a polymer backbone (0.7–1.7 nm per deposition step).[12] In the same way, as in low-molecular weight compounds like stearic acid, these hydrophobic chains facilitate spreading and formation of the true monolayer, but also increase the thickness and reduce the stability of the film on a substrate. Therefore, for the purpose of the fabrication of the thinnest possible stable LB films, the side alkyl chains are undesirable. For example, Kakimoto *et al.*[13] removed them from a LB film of polyamic acid salt by a chemical treatment, leaving a very stable insoluble film of polyimide with the thickness of 0.4 nm per single deposition step and excellent dielectric properties.[14] Another approach is the use of polymers with as small as possible side groups. Weakly amphiphilic syndiotactic poly(methyl metacrylate) has no alkyl chains, but forms good LB films with the thickness of 0.9 nm per deposition step.[10,15] In the ultimate case of a polymer chain without any side groups the successful fabrication of LB films is not easy, but still possible, as has been demonstrated for nonamphiphilic copolymer of vinylidene fluoride and trifluoroethylene,[16] which is a partially fluorinated linear polyethylene. The 1.7 nm thickness of the single deposited layer, however, is greater than the expected geometric value of $\sim$0.5 nm, indicating the more complex nature of the surface layer than just chains lying flat.[17]

Application of the LB technique to polyethylene creates another way to make very thin ordered films of the material, with potential application in molecular nanoelectronic devices for, e.g., building ultrathin insulating barriers. Nevertheless, there are no published reports of successful creation

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of PE surface films on liquids. This is most likely because PE tends to form three-dimensional aggregates rather than to spread on water surface, as was noted in Ref. 18. Although we did observe aggregation with low density PE, our tests revealed the ability of high-density polyethylene (HDPE) to form good surface layers on water without aggregation. Poor solubility of HDPE in organic solvents requires large amount of a solution to be dispersed on a water subphase, a procedure that may take many hours. Fortunately, medium density polyethylene (MDPE) has better solubility and also spreads without aggregation.

Here we report the successful formation of continuous films of MDPE as thin as 5 nm, made by LB deposition. This article is organized as follows. First, we describe the procedure, used to create a surface layer of polyethylene on water, discuss its properties, and propose a model of its structure. Section II is devoted to a characterization of films, transferred onto a substrate. The results are presented and underlying physical mechanisms are discussed in appropriate parts of the section.

II. EXPERIMENT

A. Film preparation

MDPE powder ($0.940\ \mathrm{g/cm^3}$) with unspecified molecular weight, purchased from Aldrich, was added to benzene in the weight ratio of $\sim 1{:}1000$ and kept in a water bath at $80\,^\circ\mathrm{C}$ for 2 h to obtain a clear solution. During cooling at room temperature the solution became cloudy due to reduction of MDPE solubility and precipitation of polymer particles. The solution was stored at room temperature overnight and then twice filtered through Watman qualitative paper filter No. 1, producing a clear, particle-free liquid. No traces of precipitation were observed even after several days at room temperature. The average molecular weight of the dissolved molecules may be lower than in the original powder. The exact concentration of the resulting solution, which typically was close to 0.01%, was determined by evaporating the solvent and precisely (± 100 ng) weighing the residue.

A Nima model 622 Langmuir trough filled with ultrapure ($>18\ \mathrm{M\Omega\ cm}$) water, kept at $25\,^\circ\mathrm{C}$, was used for surface film investigation and for deposition on substrates. For π-A (pressure-area) isotherm study, 0.5 to 1.2 mL of the MDPE solution was injected onto water surface in 20 μL drops at a rate three drops per minute, allowing sufficient time for the solution to disperse. The surface layer was compressed by movable barriers starting from an area of $1200\ \mathrm{cm^2}$ at a rate of $60\ \mathrm{cm^2/min}$.

The pressure-area (π-A) isotherm for the MDPE surface layer is shown in Fig. 1(a). There is no film collapse evident upon compression up to 44 mN/m. The compression–expansion cycle may be repeated many times with negligible hysteresis, if the maximum pressure does not exceed 15 mN/m [Fig. 1(b)]. Above 15 mN/m, significant hysteresis is observed with a lost area increasing with the maximum cycle pressure. This may be treated as the onset of partial irreversible collapse, which occurs in a wide pressure range and is slow near 15 mN/m. The surface layer is sufficiently stable; after stopping the barriers at 15 mN/m, the surface pressure

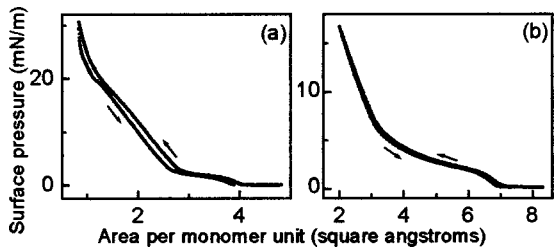

FIG. 1. Pressure-area isotherms of the MDPE surface layer on a water subphase, obtained at $25\,^\circ\mathrm{C}$ after the Langmuir trough was loaded with (a) 1.2 mL and (b) 0.5 mL of a (0.121 ± 0.003) g/L solution of MDPE in benzene. The arrows show the direction of area change.

dropped by only 2.2 mN/m in 1 h. Comparison of the isotherms reveals some influence of the initial surface concentration of the polymer on the pressure at which apparent phase transitions in the surface layer occur. The expected area per polyethylene monomer unit in a true monomolecular layer with fully untangled and tightly packed polymer chains should be about $5\ \mathrm{Å^2}$. The limiting area, determined from the isotherm by extrapolation to zero surface pressure, is $1.7\ \mathrm{Å^2}$, suggesting that the MDPE surface layer differs from a true monolayer. Analyzing the isotherm, one can conclude, that at 30 mN/m 65%–80% of monomer units in the chain are displaced from the air–water interface. The good compressibility and reversibility in the π-A isotherm allows assignment of the MDPE surface layer to the expanded type, according to Crisp's classification.[19]

To transfer the MDPE surface layer from water onto highly polished silicon wafers or glass slides, we employed the horizontal (Schaefer) variation of the Langmuir–Blodgett technique.[8] The films on the silicon substrates are visible in oblique light after 2–3 deposition steps. The apparent film color changes gradually with increased thickness from a barely visible brown through deep blue and green to yellow and red due to optical interference effects. A microscopic examination revealed that the films are continuous and sufficiently uniform. Local variations of thickness and film quality may be present, but highly homogeneous regions of area $15-20\ \mathrm{mm^2}$ with low scattering are common. We succeeded in transferring the films at surface pressures in the range of 3–20 mN/m. The transfer ratio (area lost from the trough, divided by substrate area) for Si substrates was 120% at 3 mN/m, increasing to 270% at 20 mN/m. Also, films prepared at higher surface pressure are apparently thicker, as their color is shifted toward a long-wavelength spectral region.

B. Film thickness and refractive index

Film thickness was determined using a Variable Angle Spectroscopic Ellipsometer (VASE®, J. A. Woolam Co.) with a rotating analyzer, working in the spectral range from 250 to 1700 nm with 2 nm resolution.[17] For this measurement, a special sample was made at 9 mN/m surface pressure, segmented into pie-shaped wedges with film thickness ranging from 8 to 88 layers, prepared in the same "wipe-and-deposit" process on a 3 in. silicon wafer [see the inset to Fig. 2(a)]. The first VASE polarizer was fixed at 30° from the plane of incidence, and the incidence angle was 55°, 65°, or

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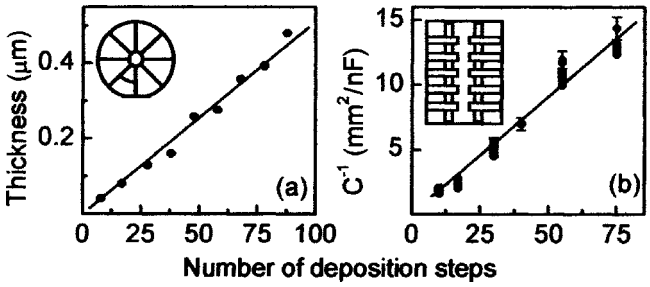

FIG. 2. (a) Thickness, determined by spectroscopic ellipsometry, of the MDPE LB film deposited on a 3 in. Si wafer vs the number of deposition steps. The measurement uncertainty (5 nm) is within a dot diameter. The solid line represents a linear least-squares fit, returning an effective deposition rate of 5.1 nm per transfer. (b) The inverse capacitance per unit area for MDPE LB film samples of different thickness. Data for up to ten spots on each sample are shown. Insets: the schematic layout of the samples.

75° from the sample normal. The film's optical refractive index, attenuation coefficient and thickness were extracted from VASE data using a multisample analysis technique,[20,21] which simultaneously fits the spectra from multiple samples, returning a common set of optical constants and the thickness of each spot.

The analysis yielded 1.51 ± 0.01 for the film refractive index at 546 nm wavelength, in good agreement with literature data for bulk PE, which range from 1.506 to 1.526.[1] Film thickness is linear with the number of deposition steps, as shown in Fig. 2(a), indicating highly reproducible transfer rate and validating the assumption that the optical constants do not depend on sample thickness. The average thickness of a single deposited layer was found to be (5.1 ± 0.3) nm, much higher than could be expected for an ideal monomolecular layer (~ 0.5 nm) from crystal structure data. This fact, along with the increase of the transfer rate and the film thickness with the deposition pressure, suggests that the surface film on water deviates significantly from a true monolayer. This is further supported by analysis of the π-A isotherm, which exhibits low limiting area per monomer unit. Likely, the surface film is built of folded chains, extended into water or air. In this situation not the thickness of the chain, but the length of folds determines the thickness of the film on water. As the surface pressure increases, folds in a flexible chain elongate, accommodating more material per unit area and making the film thicker. The reversibility of this process at high pressures may be hindered by an increasing chain entanglement, leading to the hysteresis in the π-A isotherm.

Even with this model there still is a discrepancy between the obtained film thickness and the π-A isotherm data, which would imply a surface layer not thicker than 2–2.5 nm. An additional contribution to the thickness may come from the deposition process. This may be, for example, a spontaneous formation of bilayer, the phenomenon, known for LB films of low molecular weight substances. More studies are required to determine the real film structure and all factors influencing the thickness. Nevertheless, the observed dependence of the thickness on the surface pressure makes it possible to control the film thickness and holds out a hope that thinner films may be prepared.

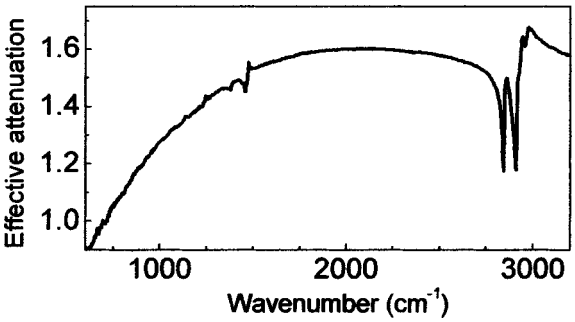

FIG. 3. Infrared reflection spectrum of an 88-layer MDPE Langmuir–Blodgett film deposited on n-doped Si (100).

C. IR spectroscopy

Infrared spectra were measured at multiple incident angles with an Infrared Variable Angle Spectroscopic Ellipsometer (IR-VASE®, J. A. Woolam Co.) system, consisting of a Fourier transform IR spectrometer coupled with a rotating-analyzer VASE. This instrument is capable of determining optical constants of thin films with 4 cm^{-1} resolution over the frequency range 200–7000 cm^{-1}. The input polarizer was fixed at 45° to the incidence plane. Figure 3 shows the IR-VASE spectrum recorded at 55° incidence angle from the 88-layer section of the sample shown on the inset to Fig. 2(a). Strong peaks at 2920 and 2850 cm^{-1} correspond to asymmetrical and symmetrical CH_2 stretching modes,[22,23] respectively. Other peaks (1462 and 1472 cm^{-1}–bending, 1175 cm^{-1}–wagging, 720 and 730 cm^{-1}–rocking modes) are weak. Bending and rocking peaks in highly crystalline bulk PE[23] and in highly oriented orthorhombic PE bulk films[24] are much sharper than in the LB film, and disappear above the melting point.[25] Bands near 1360 cm^{-1} may come from the GG, GTG, and GTTG defects.[25] One can conclude from this that the LB film had low crystallinity, even if weakening the peaks by absorption in the doped Si substrate is taken into account. Preliminary θ-2θ x-ray diffraction studies also failed to reveal any film crystallinity.

D. Dielectric properties

For dielectric measurements, MDPE films were deposited onto glass slides with evaporated Al, Au, or Pd stripe electrodes. After the film transfer, top electrodes were evaporated to form an array of ten 12 mm^2 capacitors on each sample in the arrangement shown in the inset to Fig. 2(b). As is often the case for organic films,[26–29] samples with noble metal electrodes were always short-circuited, presumably due to formation of metallic filaments inside the film. In the case of aluminum electrodes, a 3–5 nm thick native oxide layer prevents shorting the sample, therefore all electrical measurements were made on samples with Al electrodes. More than 90% of such capacitors had high resistance at least 20 MΩ at 1 V.

The capacitance and dielectric loss of samples with Al electrodes were measured at 1 kHz and 0.1 V excitation with a Hewlett-Packard model 4192A impedance analyzer. The dissipation factor ($\tan \delta$) for all the samples was typically 0.005–0.007 and never exceeded 0.01. The reciprocal ca-

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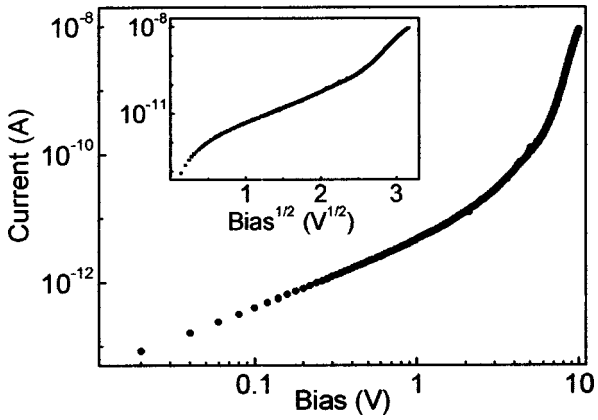

FIG. 4. Current–voltage curve for the 29-layer PE LB film with evaporated Al electrodes. Inset: the same data plotted vs a square root of the bias.

pacitance was linear with the number of layers, as shown in Fig. 2(b), confirming the consistent layer-by-layer transfer, revealed in thickness measurements [Fig. 2(a)]. The average capacitance of a single layer was found to be 0.183 nF/mm^2. With a bulk value of 2.31 for dielectric constant,[1] this corresponds to 3.7 ± 0.3 nm in thickness per single deposited layer, a value compatible with ellipsometric data.

The current–voltage ($I-V$) curve for the 29-layer sample (148 nm) was obtained with a Keithley 6517 electrometer and a Keithley 2400 SourceMeter under ambient conditions (21 °C, 30% relative humidity). The bias voltage was changed in 40 mV steps at a rate of four steps per minute. The $I-V$ curve is symmetric about the origin, its positive part is shown in the Fig. 4. Below 0.5 V the conduction is ohmic with the resistivity of 2.0×10^{13} Ω m. In the range of 0.5–5 V either Shottky or Poole–Frenkel conduction[30] may dominate, as can be seen from the linear part of the curve in the inset to Fig. 4. Since $\log I\sim V^{1/2}$ for both types of conduction, more work is necessary to make an unambiguous conclusion about the actual conduction mechanism. The value of dielectric constant calculated from the slope of the $I-V$ curve corresponds better to the bulk value, if Schottky conduction is assumed.

We compared the results for the LB film with those from an evaporated HDPE film of comparable thickness, also between Al electrodes, as reported in Ref. 31. At 1.5 V, the lowest voltage for which the evaporated film data are available, the HDPE resistivity is 1.7×10^{13} Ω m, while the LB film of MDPE has 1.5×10^{13} Ω m, in excellent agreement. The Poole-Frenkel mechanism appears to dominate the conduction in evaporated films.[31]

The MDPE LB films with Al/Al_2O_3 electrodes have high dielectric strength. Under ambient conditions, a ten-layer sample (51 nm thick) was able to withstand an applied potential of 11 V, which corresponds to an electric field of 2×10^8 V/m. During a 40 h continuous application of this voltage, the initial sample capacitance of 7.3 nF decreased by less than 5%. The dissipation factor increased significantly, from 0.005 to 7.0 during the same period, but slowly decreased down to 0.18 within 3 h after switching the field off. The reduction of the capacitance is due to the partial damage of aluminum electrodes, which is typical for Al–Al_2O_3–polymer LB film–Al structures, subjected to a high electric field. The damage appears to occur at weak spots, where the polymer film and/or underlying oxide layers are thinner than in the rest of the sample, and is visible under an optical microscope as a small transparent patches, scattered over the opaque electrode. By eliminating weak spots, the damage typically increases the resistance of samples. The sharp increase of the dissipation, which mostly recovers after switching the field off, could be due largely to space charge effects.

III. CONCLUSION

In conclusion, the Langmuir–Blodgett method was applied to fabricate thin films of medium-density polyethylene. The polymer forms a stable surface layer on water with a reproducible and reversible pressure-area isotherm below 15 mN/m. The isotherm suggests that polymer chains within the surface layer are not confined to the air–water interface, but form a thicker mat. The surface layer can be transferred by the horizontal LB method onto a solid substrate to form multilayer films with a thickness of 5.1 ± 0.3 nm per single deposited layer. Infrared spectroscopy and x-ray diffraction show low film crystallinity. Films with aluminum electrodes have low dielectric loss and high dielectric strength.

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