Supporting Information

for

A Facile Room-Temperature Layer-by-Layer Deposition Process for the Fabrication of Ultrathin Films with Noncentrosymmetrically Oriented Azobenzene Chromophores

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Fabrication of (PAC-azoBNS/PDDA)*n films

The cleaned quartz wafer was immersed in poly(diallyldimethylammonium chloride) (PDDA) aqueous solution (1.0 mg/mL) for 20 min to obtain a cationic ammonium-terminated surface. Then the PDDA-modified substrates were alternately immersed in aqueous solution of PAC-azoBNS (0.5 mg/mL) and PDDA (1.0 mg/mL) for 10 min, with intermediate water rinsing and N2 drying. Multilayer films can be fabricated by repeating these two steps in a cyclic fashion.

Characterization of the films (UV-vis, QCM, AFM, SEM)

UV-vis absorption spectra were recorded with a Shimadzu UV-3100 spectrophotometer. QCM measurements were taken with a KSV QCM-Z500 using quartz resonators with both sides coated with Ag (F_0 = 9 MHz). Atomic force microscopy (AFM) images were taken with a Nanoscope IIIa AFM Multimode (Digital Instruments, Santa Barbara, CA) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si_3N_4 cantilevers (Nanoprobes, Digital Instruments). Film thicknesses were measured with a SEM (JEOL JSM-6700F field emitting environmental scanning electron microscopy) at 3.0 KV. Samples were sputtered with a layer of gold prior to imaging. Fourier transform infrared (FT-IR) spectra were collected on a Bruker IFS 66V instrument. ^{1}H NMR spectra were determined on a Bruker Avance-500 500 MHz NMR spectrometer.

Second harmonic generation (SHG) measurements

Transmission SHG measurements were carried out using the 800-nm output of a regeneratively amplified Ti:sapphire laser operating at 1000 Hz. The laser light was collimated to a beam diameter of ~3 mm. The typical pulse energy value was 0.4mJ pulse^{-1}. The laser was directed onto the sample at a 45° angle of incidence. The SH signal at 400 nm was collected by a spectrograph(Chromex precision: 0.1nm)&CCD. A 1.30-mm-thick quartz crystal was used as a reference SH signal. The signal from the multilayer films was calibrated to this reference signal from quartz crystal.

To calculate second-order susceptibility of the ZrO_2/PAC-azoBNS/PDDA film materials, we applied the following procedure. When the film thickness is much less than the SHG coherence length (typically a few microns), the SHG should have a quadratic dependence on the film thickness, so there is the following simplified equation:[1]

$$\frac{\chi_{eff}^{(2)}}{\chi_{q}^{(2)}} = \frac{2L_q n_{\omega(film)}}{\pi L_{film} n_{\omega(q)}} \sqrt{\frac{I_{2\omega(film)} n_{2\omega(film)}}{I_{2\omega(q)} n_{2\omega(q)}}} \quad (1)$$

where $\chi_{eff}^{(2)}$ represents the effective second order susceptibility; $\chi_{q}^{(2)}$ is the second order susceptibility of quartz with value of 1.92×10^{-9} esu; L_q is the quartz thickness (1.30 mm); L_{film} is the film thickness; $n_{\omega(film)}$ and ($n_{2\omega(film)}$) are the refractive index of the film at the fundamental and second harmonic frequency, respectively ($n_{\omega(film)}$ = 1.5494, $n_{2\omega(film)}$ = 1.4675); $n_{\omega(q)}$ and ($n_{2\omega(q)}$) are the refractive index of the quartz at the fundamental and second harmonic frequency, respectively ($n_{\omega(q)}$ = 1.54789, $n_{2\omega(q)}$ = 1.56843); $I_{2\omega(film)}$ is the intensity of the second harmonic beam in the film(time of exposure is 0.05 second, cumulate 10 time), $I_{2\omega(q)}$ is the intensity of the second harmonic beam for quartz (time of exposure is 1 second, no cumulate). When the frequencies involved are far from resonances, Kleinman's symmetry condition can be applied to further reduce the number of independent components to two: $\chi_{zxx}^{(2)} = \chi_{xzx}^{(2)} = \chi_{yzy}^{(2)} = \chi_{xxz}^{(2)} = \chi_{yyz}^{(2)} = \chi_{zyy}^{(2)}$ and $\chi_{zzz}^{(2)}$. Therefore, when the fundamental beam is *s*-polarized, the second harmonic beam is *p*-polarized,

$$\chi_{eff}^{(2)} = \chi_{zxx}^{(2)} \sin\theta_{2\omega} \quad (2)$$

When the fundamental beam is *p*-polarized, the second harmonic beam is *p*-polarized,

$$\chi_{eff}^{(2)} = \chi_{zxx}^{(2)} (\cos\theta_{2\omega} \sin 2\theta_{\omega} + \sin\theta_{2\omega} \cos^2\theta_{\omega}) + \chi_{zzz}^{(2)} \sin\theta_{2\omega} \sin^2\theta_{\omega} \quad (3)$$

where θ is the angle between the incident beam and the normal line of sample, θ_ω ($\theta_{2\omega}$) is determined by $\sin\theta = n_{\omega(film)}\sin\theta_\omega$ ($\sin\theta = n_{2\omega(film)}\sin\theta_{2\omega}$).[2] After substituting $I_{2\omega}$ values from experiment data into Eq. (1), we can deduce the values of $\chi^{(2)}_{eff}$. Then using Eq. (2) and Eq. (3), we can deduce the values of $\chi^{(2)}_{zxx}$ and $\chi^{(2)}_{zzz}$. The average of the orientation angles (ψ) of the chromophore dipoles with respect to the substrate surface normal was obtained by the following equation:[3]

$$\chi^{(2)}_{zzz} / \chi^{(2)}_{zxx} = 2\cot^2\psi \qquad (4)$$

References:

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3 D. Q.Li, M. A. Ratner, T. J.Marks, C. H. Zhang, J. Yang and G. K. Wong, *J. Am. Chem. Soc.* **1990**, *112*, 7389.

Figure S1. Experimental setup for second harmonic generation measurements.

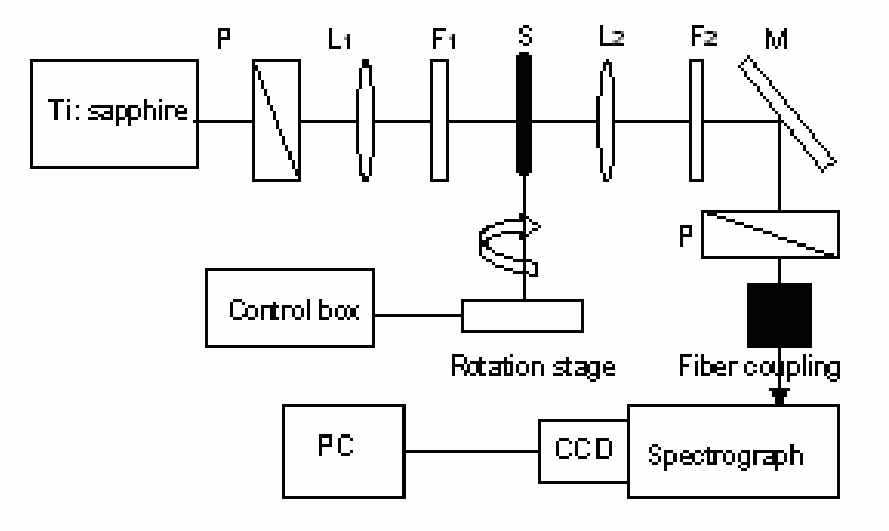

Figure S2. Cross-sectional SEM image of a (ZrO_2/PAC-azoBNS/PDDA)*10 film deposited on silicon wafer. The film thickness is 66.0±3.0, corresponding to an average thickness of ca. 6.6 nm for one deposition cycle of ZrO_2/PAC-azoBNS/PDDA.

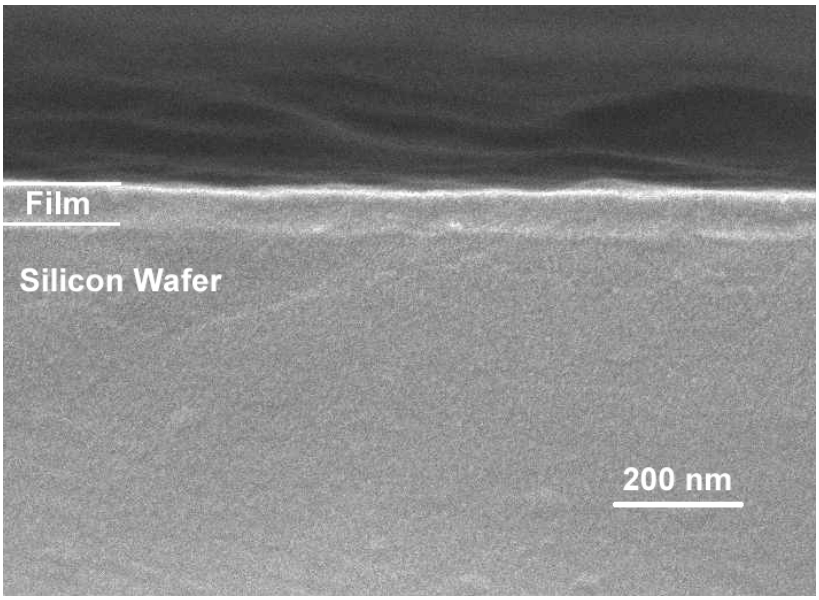

Figure S3. UV-vis absorption spectra of (PAC-azoBNS/PDDA)*n films with different number of deposition cycles. The number of deposition cycles is 3, 6, 9, 12, 15 and 20 from the bottom to the top. The inset shows the absorbance at 472 nm vs the number of deposition cycles.