

Real-time observation of oxidation and photo-oxidation of rubrene thin films by spectroscopic ellipsometry

M. Kytka

Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany
and Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in Bratislava, Ilkovičova 3, 812 19 Bratislava, Slovak Republic

A. Gerlach and F. Schreiber^{a)}

Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany

J. Kováč

Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in Bratislava, Ilkovičova 3, 812 19 Bratislava, Slovak Republic

(Received 12 January 2007; accepted 23 February 2007; published online 29 March 2007)

The authors follow in real time and under controlled conditions the oxidation of the organic semiconductor rubrene grown on SiO_2 using spectroscopic ellipsometry. They derive the complex dielectric function $\epsilon_1 + i\epsilon_2$ for pristine and oxidized rubrene showing that the oxidation is accompanied by a significant change of the optical properties, namely, the absorption. The authors observe that photo-oxidation of rubrene is orders of magnitude faster than oxidation without illumination. By following different absorption bands (around 2.5 and 4.0 eV for pristine rubrene and around 4.9 eV for oxidized rubrene) they infer that the observed photo-oxidation of these films involves non-Fickian diffusion mechanisms. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2717561]

Many organic materials with delocalized π -electron systems exhibit significant potential for electronic and optoelectronic applications.¹ But despite progress in the development of encapsulation strategies² one of the important issues in this area remains the change of the electronic properties upon exposure to ambient gases. Rubrene ($\text{C}_{42}\text{H}_{28}$, 5,6,11,12-tetraphenylnaphthalene, see inset of Fig. 1) belongs to a group of small organic molecules with promising properties which found use in organic light emitting diodes (as a red dopant)³ and organic field effect transistors.⁴ However, as also other molecules,⁵ rubrene exhibits strong reactivity and affinity to (photo-)oxidation which reduces the stability and lifetime of devices. While it is well known that rubrene tends to undergo (photo-)oxidation,⁶ the understanding and control of degradation due to oxidation of these materials still are key challenges in organic electronics. For this purpose we studied in real time and under controlled conditions the kinetics of oxidation of rubrene thin films using spectroscopic ellipsometry.

The rubrene material used was purchased from Acros and purified by gradient sublimation. The Si(100) substrates with ~ 20 nm thermal oxide were cleaned with acetone and propanol in an ultrasonic bath, transferred into the vacuum chamber (base pressure $p=3 \times 10^{-8}$ mbar), and heated at temperatures $T \geq 400$ °C for several hours. The rubrene films were grown with the substrate at room temperature by evaporation from a Knudsen cell with a typical growth rate of 0.85 nm/min. The experimental data were acquired *in situ* using a spectroscopic ellipsometer (Woollam M-2000) with a broad band 75 W Xe lamp (250–1000 nm) and CCD based detection system with a spectral resolution of about 1.6 nm. The light spot on the sample was $\sim 2 \times 6$ mm². The light

source and detector were mounted to the vacuum chamber which provides a pair of strain-free windows at a relative angle of 120°.

After growing the film in high vacuum the oxidation experiment was performed in the same chamber. For this purpose we admitted 40 mbar air using a leak valve. To distinguish oxidation and photo-oxidation effects we studied two separate spots on the sample. The first spot (A) was investigated in high vacuum and yields the spectrum of the pristine rubrene. After 870 min exposure to air without illumination with the Xe lamp, we switched to a different spot (B) which was illuminated continuously during the photo-oxidation. Ellipsometry scans with 100 compensator revolutions were taken every 0.2 min at the beginning and every 2 min later.

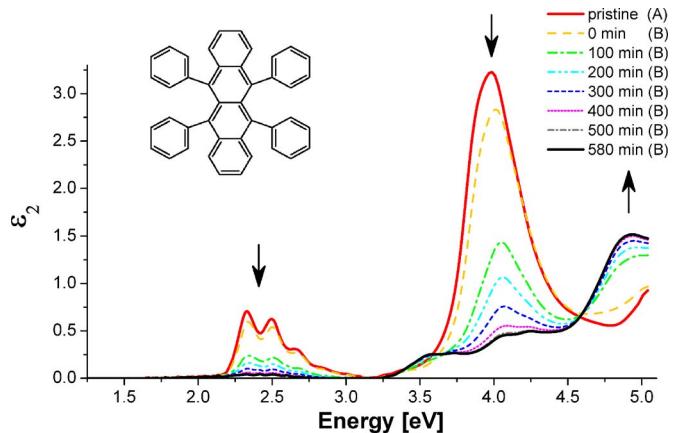


FIG. 1. (Color online) Dielectric function ϵ_2 of the rubrene film before and during photo-oxidation (initial film thickness is 25.1 nm). The absorption bands around 2.5 and 4.0 eV correspond to pristine rubrene, whereas the feature at 4.95 eV originates from oxidized rubrene. The relatively small difference between the pristine and “0 min” spectra shows the effect of exposure to air after 870 min without illuminating the sample.

^{a)}Electronic mail: frank.schreiber@uni-tuebingen.de

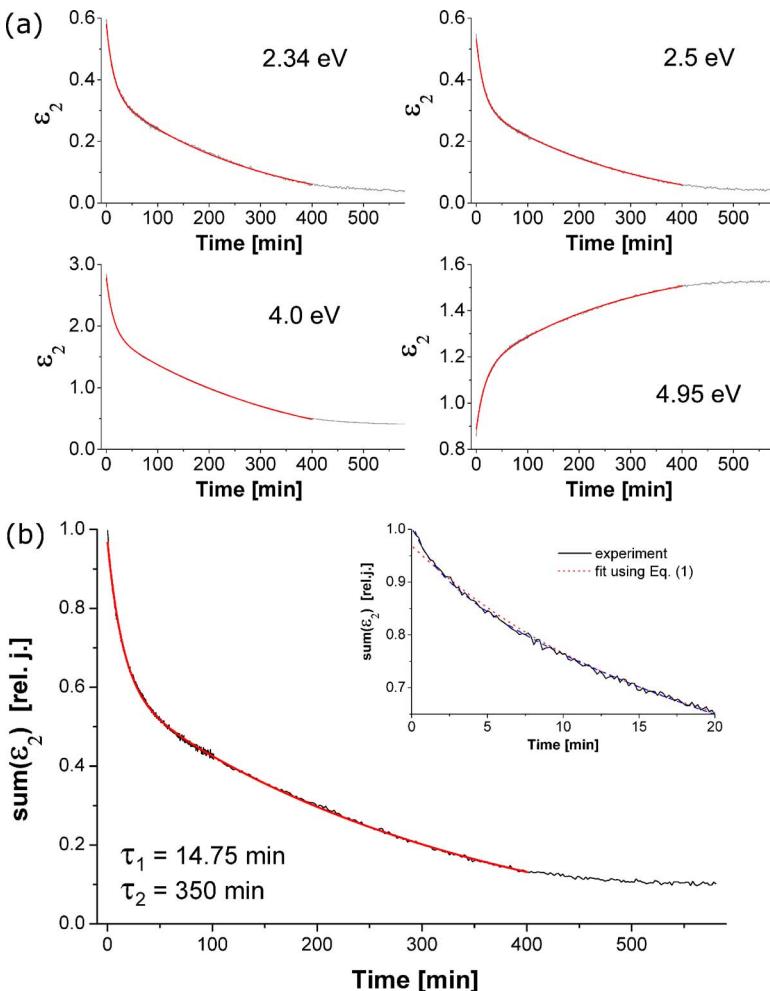


FIG. 2. (Color online) (a) Time dependence of the dielectric constant with a fit according to Eq. (1) for selected energies in the spectra, i.e., 2.34 eV (0–0 transition), 2.5 eV (0–1 transition), 4.0 eV (strongest absorption feature), and 4.95 eV (absorption band of oxidized rubrene). (b) Integral of ϵ_2 over the interval of 1.25–3.17 eV.

Using a commercial software package (WVASE32) we converted the ellipsometric data to the dielectric function $\epsilon_1 + i\epsilon_2$. Since rubrene grows in noncrystalline films on SiO_2 ,^{7,8} we employed an isotropic four-layer model: rubrene- SiO_2 - Si_{int} - Si , with the optical constants of Si, SiO_2 , and Si_{int} (interfacial layer between SiO_2 and Si) taken from Ref. 9. Inhomogeneities of the organic layer during oxidation are neglected in this effective medium approximation. The essential changes of the spectra upon exposure to air, however, were found to prevail regardless of the ellipsometric model used for the analysis. To cross-check our results we verified that both the spectrum of the pristine and that of the fully oxidized film agree with earlier studies on rubrene.¹⁰ Starting with the spectrum of the bare substrate we determined the thickness of the SiO_2 and Si_{int} layers as well as the precise angle of incidence. The optical properties of the organic film were obtained by point-by-point fits and the film thickness was determined by employing a Cauchy model in the transparent region. Consistency checks for pristine rubrene with a general oscillator model gave good agreement over the complete spectral range. A more detailed discussion of the fitting procedure and the optical properties of pristine rubrene will be published elsewhere.¹¹

As shown in Fig. 1 the optical properties change significantly throughout the oxidation process. Since the organic film becomes more and more transparent, even visual inspection reveals the strong effect of oxidation. The spectrum of the pristine rubrene and the spectrum taken after 870 min on the second spot (denoted as “0 min” illumination in Fig. 1)

do not differ strongly. Hence we conclude that oxidation without illumination is relatively slow compared to the subsequent photo-oxidation. While the absorption bands around $E=2.5$ and 4 eV decrease rapidly during oxidation, a feature centered at $E=4.95$ eV appears. We further note that the spectra shown in Fig. 1 exhibit an isosbestic point at 4.59 eV, where the absorption ϵ_2^{iso} remains constant during oxidation. This indicates that the organic film can essentially be regarded as a nonvolatile two component system, i.e., pristine and oxidized rubrene, without noticeable intermediate or products.

Figure 2(a) illustrates the time dependence of the dielectric function for selected energies, i.e., 2.34, 2.5, 4.0, and 4.95 eV, whereas Fig. 2(b) shows the integral of ϵ_2 over the interval of 1.25–3.17 eV. The decrease of the absorption bands around 2.5 and 4.0 eV (pristine rubrene) goes hand in hand with the increase of the high energy feature around 4.95 eV (oxidized rubrene). Apparently, the time dependence of the dielectric constants is nontrivial. While initially the oxidation is very rapid, it slows down after several minutes. Empirically, we find that $\epsilon_2(t)$ can be described by the sum of two exponentials, i.e.,

$$y(t) = y_0 + \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2). \quad (1)$$

Although the absolute values of τ_1 and τ_2 depend slightly on the given sample and experimental conditions, we invariably find two very different time constants [see Fig. 2(b)], i.e., $\tau_1/\tau_2 \ll 1$, indicating that two different mechanisms are involved.

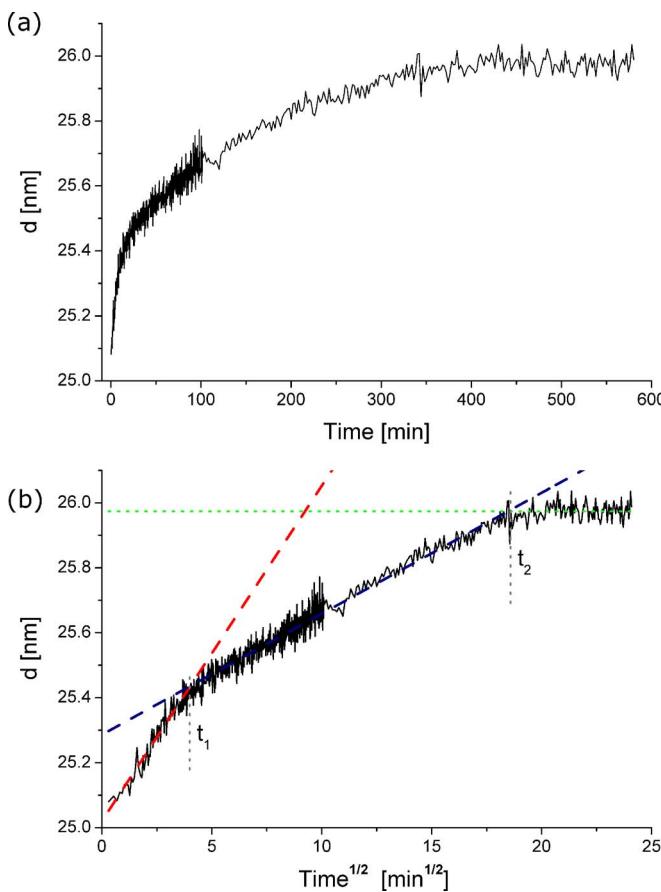


FIG. 3. (Color online) Thickness evolution $d(t)$ of the rubrene film during photo-oxidation. (a) Real-time data derived from ellipsometry measurements exhibiting two regimes. (b) Data on a $t^{1/2}$ axis with a fit according to a non-Fickian model, see Eq. (2).

The film thickness $d(t)$ derived from the ellipsometry data exhibits two regimes, see Fig. 3. Starting at $d_0 = 25.1$ nm we find a rapid expansion at the beginning and a slowly saturating behavior after a thickness increase of 0.9 nm towards the end of oxidation. The similarity with the time dependent absorption at 4.95 eV, i.e., a feature related to the oxidized rubrene, suggests that the thickness increase is caused by the intake of oxygen. Assuming that each rubrene molecule reacts with one oxygen molecule to rubrene peroxide,¹² a volume expansion of 2.1% is expected (assuming a constant density of the organic). For fixed lateral dimensions the thickness would consequently increase by a maximum of 6.5%—an estimate which is compatible with the observed rise by 4.2% and which shows that nearly the entire film can be oxidized.

To explore the kinetics of rubrene oxidation in more detail, we tried several models describing the data. Interestingly, within the given dynamic range a good fit to the thickness evolution can only be obtained not only with an

exponential expression as in Eq. (1) but also with a composite square-root dependence, i.e.,

$$d(t) = \begin{cases} d_0 + at^{1/2} & \text{for } 0 \leq t \leq t_1 \\ d'_0 + bt^{1/2} & \text{for } t_1 < t \leq t_2 \\ \text{const.} & \text{for } t > t_2, \end{cases} \quad (2)$$

with $t_1 \approx 15$ min ($t_1^{1/2} \approx 3.87$ min) and $t_2 \approx 360$ min ($t_2^{1/2} \approx 18.97$ min) for the data presented in Fig. 3(b). Thus the oxidation kinetics do not follow a simple Fickian diffusion model which would result in a continuous $t^{1/2}$ dependence. The underlying reason for this behavior cannot easily be identified, however, there are several possible explanations for this non-Fickian diffusion: for example, (1) a depth dependent diffusivity of oxygen, (2) space charge effects, (3) surface effects influencing the intake of oxygen, or (4) a delay between the diffusion and the oxidation reaction. In order to distinguish these effects and their influence on the oxidation kinetics of rubrene, further studies are required. Complementary techniques and a theoretical description could improve our understanding of the described phenomenon considerably.

In conclusion we have presented real-time ellipsometry data which yield essential information about the optical properties and the reaction kinetics of rubrene. Based on the thickness data we infer that the diffusion of oxygen into the organic follows a non-Fickian law. We hope our study on the oxidation of rubrene will contribute to an improved understanding of degradation mechanisms in organic electronic materials.

The authors thank J. Pflaum for providing the purified rubrene and G. Witte for discussing the results of this work. The authors gratefully acknowledge financial support by DFG and EPSRC.

- ¹F. Schreiber, Phys. Status Solidi A **201**, 1037 (2004).
- ²S. Sellner, A. Gerlach, F. Schreiber, M. Kelsch, N. Kasper, H. Dosch, S. Meyer, J. Pflaum, M. Fischer, and B. Gompf, Adv. Mater. (Weinheim, Ger.) **16**, 1750 (2004).
- ³H. Aziz and Z. D. Popovic, Appl. Phys. Lett. **80**, 2180 (2002).
- ⁴R. W. I. de Boer, M. E. Gershenson, A. F. Morpurgo, and V. Podzorov, Phys. Status Solidi A **201**, 1302 (2004).
- ⁵A. Vollmer, H. Weiss, S. Rentenberger, I. Salzmann, J. P. Rabe, and N. Koch, Surf. Sci. **400**, 4004 (2006).
- ⁶R. M. Hochstrasser and M. Ritchie, Trans. Faraday Soc. **52**, 1363 (1956).
- ⁷S. Kowarik, A. Gerlach, S. Sellner, F. Schreiber, J. Pflaum, L. Cavalcanti, and O. Konovalov, Phys. Chem. Chem. Phys. **8**, 1834 (2006).
- ⁸D. Käfer, L. Ruppel, G. Witte, and C. Wöll, Phys. Rev. Lett. **95**, 166602 (2005).
- ⁹C. M. Herzinger, B. Johs, W. A. McGahan, J. A. Woollam, and W. Paulson, J. Appl. Phys. **83**, 3323 (1998).
- ¹⁰A. Otomo, S. Otomo, S. Yokoyama, and S. Mashiko, Org. Lett. **27**, 891 (2002).
- ¹¹M. Kytka, A. Gerlach, J. Kováč, and F. Schreiber (unpublished).
- ¹²D. Käfer and G. Witte, Phys. Chem. Chem. Phys. **7**, 2850 (2005).