Correlation of crystalline and structural properties of C_{60} thin films grown at various temperature with charge carrier mobility

Th. B. Singh[a] and N. S. Sariciftci
Linz Institute of Organic Solar Cells (LIOS) Institute of Physical Chemistry, Johannes Kepler University Linz, A-4040 Linz, Austria

H. Yang
Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York 12180

L. Yang
National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), Upton, New York 11973

B. Plochberger and H. Sitter
Institute of Semiconductors and Solid State Physics, Johannes Kepler University Linz, A-4040 Linz, Austria

(Received 14 February 2007; accepted 3 May 2007; published online 25 May 2007)

Transistors fabricated from C_{60} films grown by hot wall epitaxy at higher substrate temperature, showed an order of magnitude increased charge carrier mobility up to 6 cm^2/V s. In this letter, the authors present an extensive study of morphology and crystallinity of the fullerene films using atomic force microscopy and grazing-incidence x-ray diffraction. A clear correlation of crystalline quality of the C_{60} film and charge carrier mobility was found. A higher substrate temperature leads to a single crystal-like faceted fullerene crystals. The high crystalline quality solely brings a drastic improvement in the charge carrier mobility. A gate voltage independent mobility is also observed in these devices which can be attributed to the highly conjugated nature of the C_{60} thin film.
© *2007 American Institute of Physics*. [DOI: 10.1063/1.2743386]

High performance organic semiconductor devices are nowadays considered for commercial applications.[1] C_{60} with an exceptionally large electron affinity of 2.65 eV (Ref. 2) has been shown to give *n*-channel transistors with high electron mobilities.[3–6] The crystalline structure and the morphology of the organic semiconductor thin film can also be heavily influenced by the surface chemistry of the gate dielectric, the rate, and the temperature (T_D) at which the film is deposited. As an example, pentacene, a planar molecule has been investigated and reported to have crystalline polymorphs even in its bulk phase.[7] Vacuum deposited pentacene thin films, however, differ from the bulk, forming a structure that has been referred to as the "thin film phase."[7] The bulk polymorph is reported to coexist with the thin film phase in evaporated thin films beyond a certain critical thickness, depending on T_D.[7–9] It is also well known that increasing T_D and lowering the deposition rates will decrease the nucleation density, resulting in an increase of the average grain size (G). For a polycrystalline film, most defects are likely to condense in crystal grain boundaries (GBs). A model[10] which assumes a tunneling current due to high charge carrier density at the conducting channel through a back-to-back Schottky barrier induced by GB predicts that (i) the charge carrier mobility μ is proportional to G and (ii) μ is gate voltage (V_{gate}) dependent. When the overall mobility only depends on charge transfer across GB, μ is represented by[10] $1/\mu = 1/\mu_G + 1/\mu_{GB}$. Here μ_G and μ_{GB} are charge carrier mobilities contributed by G and GB, respectively. For asymmetric planar pentacene[11,12] and octithiophene,[10] a G dependent μ has been presented. In the case of spherical C_{60} molecule, high charge transport is not limited by the crystal symmetry as proven in our previous report.[13,14] However, its crystalline nature, degree of order, growth modes, and G dependent μ as well as gate field independent μ are not known in detail until to date.

In this letter, we report that C_{60} layers when hot wall epitaxially grown on various gate dielectrics indicate island growth formation unlike most common organic planar molecules. Strong increases in G and crystallinity of C_{60} with T_D are proven by surface morphology and grazing-incidence x-ray diffraction (GIXRD) studies. The μ increases with T_D and shows an almost independent of V_{gate} behavior due to a higher degree in order of the C_{60} fullerene thin films.

Discrete top-contact transistors were fabricated on quartz glass substrates incorporating a predefined indium tin oxide (ITO) gate. Divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB), Dow Chemicals, was spin coated on top of the ITO/quartz substrate. BCB gate dielectric was cured at 250 °C for 2 h in a vacuum oven. Following the BCB curing, a 300 nm thick film of C_{60} was grown by hot wall epitaxy (HWE) at various T_D in the range from 25 to 250 °C. Finally, top-contact electrodes consisting of LiF/Al (0.6 and 60 nm, respectively) were evaporated under high vacuum ($\sim 10^{-6}$ Torr) through a shadow mask. The channel length (L) and width (W) of the transistor was 30 μm and 1.5 mm, respectively. For a structural characterization of the C_{60} film, heavily *n*-doped Si wafers with native oxide layers on top were also used as a substrate to avoid the large amorphous background scattering of BCB in the XRD spectrum. For this investigation the same growth parameter were used to obtain similar C_{60} films. Electrical measurements were performed at room temperature using an Agilent E5273A with two source-measure unit instruments.

[a]Electric mail: birendra.singh@jku.at

 © 2007 American Institute of Physics
Downloaded 04 Jun 2007 to 140.78.119.119. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

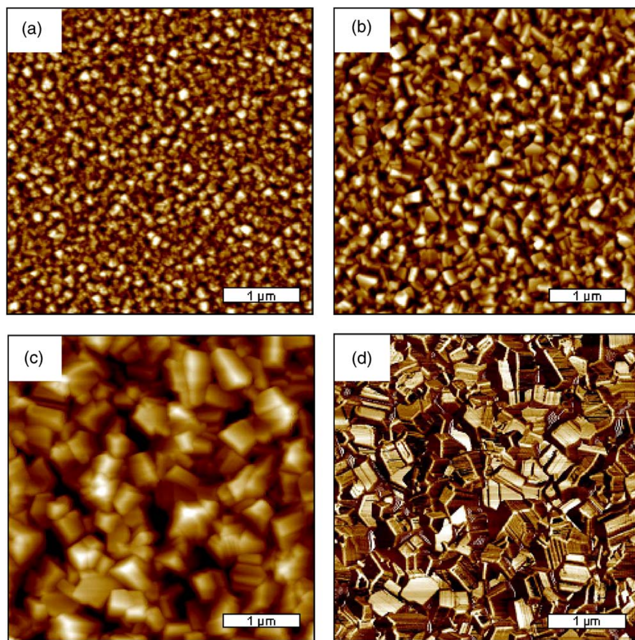

FIG. 1. (Color online) [(a)–(c)] AFM topographic and (d) phase images for 100-nm-thick C_{60} films deposited on SiO_2/Si substrates kept at different T_Ds: (a) 25, (b) 120, and (c) and (d) 250 °C (all scale bars represents 1 μm).

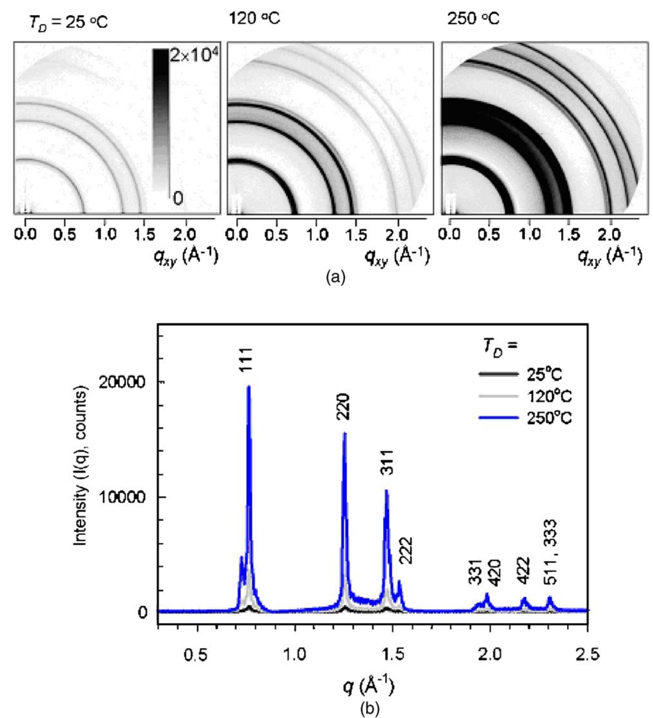

FIG. 2. (Color online) (a) 2D GIXRD patterns and (b) circular average x-ray profiles for 100-nm-thick C_{60} films deposited on SiO_2/Si substrates kept at different growth temperatures (T_D): 25, 120, and 250 °C, respectively.

To study the effects of T_D on the crystallinity of the C_{60}, films were characterized by means of atomic force microscopy (AFM) and GIXRD measurements. Two-dimensional (2D) GIXRD experiments on C_{60} films were performed at beam line X21 of the (NSLS) at (BNL).

From the AFM micrographs of these C_{60} films, as shown in Fig. 1, it is evident that G increases with increasing T_D. The increase in G with T_D can be attributed to a decrease of the nucleation density at the beginning of the deposition.[7] Interestingly, G scales with T_D which is proven to be more favorable for efficient charge transport.[10–12] Figure 1 shows the GIXRD patterns and profiles for 100-nm-thick C_{60} films grown at T_D=25, 120, and 250 °C, respectively. As T_D increases, the crystallinity in the C_{60} films considerably increases as determined by increasing intensity of the diffraction peaks. As seen in Fig. 2(a), crystal reflections along the debye rings strongly support that all these films have randomly oriented crystals due to irregular stacking of crystal grains as observed by AFM (see Fig. 1), and C_{60} does not form a specific thin film phase induced by the molecule-substrate interaction. One-dimensional circular x-ray profiles of these ring-type crystal reflections [Fig. 2(b)] are in good agreement with the previously published XRD data of a cubic C_{60} crystal.[13,14] However, most striking difference is the comparison of crystalline orientation in C_{60} films with those of other common small molecular organic semiconductors. Compared to terracelike morphology of pentacene,[7] showing preferentially oriented crystals with respect to the substrate, C_{60} films exhibit three-dimensional powder forms of randomly oriented crystals with much smaller G of approximately 150 nm at low T_D=25 °C up to 400 nm for higher T_D=250 °C. The crystal shape converts from irregular to faceted structure with increasing T_D. In the present case, we assume an island growth mode since the interactions between the molecules are stronger than the substrate, forming three-dimensional islands (see Fig. 1). However, although SiO_2/Si substrates were chosen for thin-film characterization, our previous studies have shown that μ of HWE grown C_{60}-based organic field-effect transistors (OFETs) with BCB as dielectric is superior compared to that of SiO_2/Si.[6] Hence we chose BCB as a gate dielectric for OFET fabrication. Glass transition temperature (T_G) of BCB is 360 °C, which allows us to grow the C_{60} film at $T_D < T_G$.

Transistor characteristics of a top-contact OFETs incorporating a C_{60} film grown at 25 °C on BCB gate dielectric are shown in Fig. 3. The device structure is shown in the inset. The output characteristics [Fig. 3(a)] show a linear drain current I_{drain} as a function of drain voltage V_{drain} with almost no sign of contact resistance. A subthreshold characteristics with V_{drain}=2 V is shown in Fig. 3(b). OFETs turn on at around 2 V with a subthreshold slope of 4 V/decade and the linear mobility μ_{linear} of 0.2 $cm^2/V\,s$. Transistor characteristics for OFETs with C_{60} layers grown at three different T_D were reported previously.[6] To investigate the influence of G on the μ, we evaluated the data from our previous report.[6] μ was calculated as a function of V_{gate}. Taking the local slope of the I-V characteristics, the obtained results are shown in Fig. 3(c). The three curves represent the μ of C_{60} layers grown at three different T_D. From the curve, two crucial device parameters can be deduced: (i) μ increases as a function of V_{gate} and is almost independent for a wide range of V_{gate} for films with $T_D \geq 120$ °C; (ii) μ depends on T_D. μ increases from 0.6 $cm^2/V\,s$, for films grown at T_D=25 °C, to 6 $cm^2/V\,s$ for films grown at T_D=250 °C. The strong dependence of μ on T_D and G is in contrast to the findings of Kobayashi *et al.*,[4] where the electron μ did not display a strong correlation with T_D. We note here that in the latter work, measurements were performed on C_{60} films grown on SiO_2 deposited by a molecular-beam deposition technique. An analytical model for polycrystalline film predicts μ(G).[15] In the present case, a single-crystalline-like faceted structured films (for films with high T_D) with a large ratio of

Downloaded 04 Jun 2007 to 140.78.119.119. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

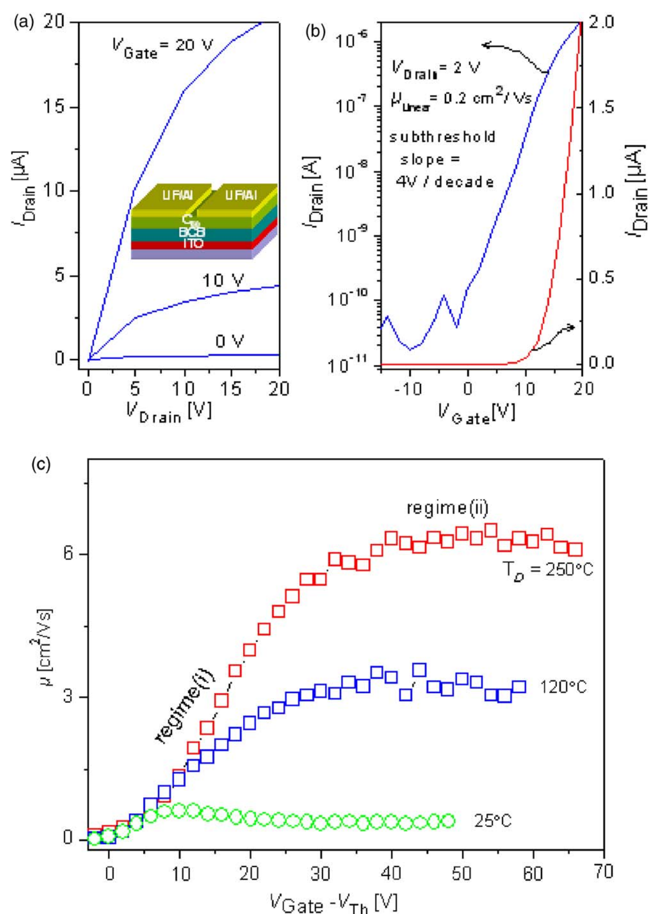

FIG. 3. (Color online) (a) Room temperature output characteristic of the top contact/bottom gate C_{60} OFET based on C_{60} grown at 25 °C with LiF/Al source/drain contact. Inset diagram shows the device architecture employed. (b) Room temperature subthreshold characteristic with subthreshold slope of 4 V/decade and linear mobility μ_{linear} of 0.2 cm^2/V s. (c) Plot of μ vs V_{gate} for C_{60} OFETs fabricated on C_{60} films were grown at different T_D. Transfer characteristics of these devices are shown in Ref. 6.

"bulk phase" to thin film phase is expected to be very large as seen in AFM (Fig. 1). This speculation stems from the fact that experimentally measured μ goes linearly for a wide range of T_D. As T_D increases G also increases. As T_D increases, the bulk phase underneath the "island growth" keeps growing which could lead to reduced GB.

A plot of μ vs V_{gate} [Fig. 3(c)] reveals two distinct regimes: regime I, increase of μ_e with V_{gate} and regime II, μ_e independent of V_{gate}. Regime (I) can be explained using various models[16,17] which is attributed to the defect induced charge traps in the semiconductor film. As the absolute V_{gate} increases, the Fermi level gradually moves towards the band edge as more of the empty traps become filled due to charge injection. Accordingly, the ratio of free to trapped carriers increases, so the effective mobility increases too. Regime II is a rather unusual observation among organic thin films and strongly indicates the presence of smaller trap densities in the C_{60} film grown by HWE specifically at higher T_D. We note here that our devices are designed with a large channel length L and negligible contact resistance. A smaller trap density also implies higher degree order of the C_{60} films with uniform trap distribution approaching monocrystalline properties. Hence most of the defects are not likely to condense in grain boundaries and a uniform distribution of traps might exist in the HWE grown C_{60} film at higher T_D. We note here that HWE is well-known to work under close to thermodynamic equilibrium condition. Although it is rather difficult to compare reports on C_{60} deposited by other technique on bare SiO_2 (Ref. 4) or self-assembled-monolayer modified SiO_2,[18] a strong V_{gate} dependence μ have been observed from all devices, which is also indicated by the deviation from a straight line in $\sqrt{I_{drain}}$ vs V_{gate} curves. A check for the assumption that the V_{gate} independent mobility is related to highly ordered films with reduced trap density is the drop in μ with V_{gate} for C_{60} films with T_D=25 °C, as shown in Fig. 3(c). As T_D increases gradually a transition from weak V_{gate} dependent μ to V_{gate} independent μ is observed.

In summary, exceptionally high quality films of C_{60} grown by hot wall epitaxy are characterized by AFM and GIXRD. Higher T_D lead to a significant increase in crystallinity as determined by integration of the diffraction peaks. C_{60} does not seem to form a specific thin film phase induced by the molecule-substrate interaction. With increasing T_D, the crystal shape converts from irregular to single-crystalline-like faceted structure. The highly crystalline nature plus excellent transport properties of C_{60} thin films solely brings a drastic improvement in the charge carrier mobility. The gate field independent mobility is also observed in these devices which indicate a highly conjugated nature of our C_{60} thin films.

The Authors acknowledge the financial support from Austrian Science Foundation (FWF), Project Nos. S P16891-N08 and S9706-N08. One of the authors (H.Y.) acknowledges financial support from the National Science Foundation (DMR 0117792). Fruitful discussions with Gilles Horowitz and Thomas Anthoupolos are acknowledged.

[1]Th. B. Singh and N. S. Sariciftci, Annu. Rev. Mater. Res. **36**, 199 (2006).
[2]D. L. Lichtenberger, K. W. Nebesney, C. D. Ray, D. R. Huffman, and L. D. Lamb, Chem. Phys. Lett. **176**, 203 (1991).
[3]R. C. Haddon, A. S. Perel, R. C. Morris, T. T. M. Palstra, A. F. Hebard, and R. M. Fleming, Appl. Phys. Lett. **67**, 121 (1995).
[4]S. Kobayashi, T. Takenobu, S. Mori, A. Fujiwara, and Y. Iwasa, Appl. Phys. Lett. **82**, 4581 (2003).
[5]Th. B. Singh, N. Marjanovic, G. J. Matt, S. Gunes, N. S. Sariciftci, A. M. Ramil, A. Andreev, H. Sitter, R. Schwodiauer, and S. Bauer, Org. Electron. **6**, 105 (2005).
[6]T. D. Anthopoulos, Th. B. Singh, N. Marjanovic, N. S. Sariciftci, A. M. Ramil, H. Sitter, M. Colle, and D. M. De Leeuw, Appl. Phys. Lett. **89**, 213504 (2006).
[7]R. Ruiz, D. Choudhary, B. Nickel, T. Toccoli, K.-C. Chang, A. C. Mayer, P. Clancy, J. M. Blakely, R. L. Headrick, S. Iannotta, and G. G. Malliaras, Chem. Mater. **16**, 4497 (2004).
[8]C. D. Dimitrakopoulos, A. R. Brown, and A. Pomp, J. Appl. Phys. **80**, 2501 (1996).
[9]I. P. M. Bouchoms, W. A. Schoonveld, J. Vrijmoeth, and T. M. Klapwijk, Synth. Met. **104**, 175 (1999).
[10]G. Horowitz and M. E. Hajlaoui, Synth. Met. **122**, 185 (2001).
[11]J. G. Laquindanum, H. E. Katz, A. J. Lovinger, and A. Dodabalapur, Chem. Mater. **8**, 2542 (1996).
[12]R. Ruiz, B. Nickel, N. Koch, L. C. Feldman, R. F. Haglund, A. Kahn, F. Family, and G. Scoles, Phys. Rev. Lett. **91**, 136102 (2003).
[13]D. Stifter and H. Sitter, Appl. Phys. Lett. **66**, 679 (1995).
[14]K. Horiuchi, K. Nakada, S. Uchino, S. Hashii, A. Hashimoto, N. Aoki, Y. Ochiai, and M. Shimizu, Appl. Phys. Lett. **81**, 1911 (2002).
[15]G. Horowitz, J. Mater. Res. **19**, 1946 (2004).
[16]M. Shur, C. Hyun, and M. Hach, J. Appl. Phys. **59**, 2488 (1986).
[17]M. C. J. M. Vissenberg and M. Matters, Phys. Rev. B **57**, 12964 (1998).
[18]S. Kaboyashi, T. Nishikawa, T. Takenobu, S. Mori, T. Shimoda, T. Mitani, H. Shimotani, N. Yoshimoto, S. Ogawa, and Y. Iwasa, Nat. Mater. **3**, 317 (2004).

Downloaded 04 Jun 2007 to 140.78.119.119. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp