

## Flip chip lamination to electrically contact organic single crystals on flexible substrates

M. Coll,<sup>1</sup> K. P. Goetz,<sup>2</sup> B. R. Conrad,<sup>1</sup> C. A. Hacker,<sup>1</sup> D. J. Gundlach,<sup>1</sup> C. A. Richter,<sup>1</sup> and O. D. Jurchescu<sup>2,a)</sup>

<sup>1</sup>Semiconductor Electronics Division, Physical Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

<sup>2</sup>Department of Physics, Wake Forest University, Winston-Salem, North Carolina 27109, USA

(Received 9 February 2011; accepted 23 March 2011; published online 20 April 2011)

The fabrication of top metal contacts for organic devices represents a challenge and has important consequences for electrical properties of such systems. We report a robust, low-cost and nondestructive printing process, flip chip lamination, to fabricate top contacts on rubrene single crystals. The use of surface chemistry treatments with fluorinated self-assembled monolayers, combined with pliable substrates, and mild nanoimprint conditions, ensures conformal contact between ultrasmooth metal contacts and the organic crystal. Space-charge limited current measurements point to better interfacial electrical properties with the flip chip lamination-fabricated contacts compared to the analog architecture of e-beam evaporated top contacts. © 2011 American Institute of Physics. [doi:10.1063/1.3580610]

The field of organic electronics has witnessed significant progress lately in material synthesis, device architecture, and measured performance. However, the choice of processing methods, device geometries, and contact materials presents severe limitations given the fragility of organic materials. One challenge is the formation of electrical top contacts on organic semiconductors. Conventional metal deposition methods (e.g., thermal or e-beam evaporation) yield insufficient reproducibility in device performance as they cause considerable damage at the surface of the fragile organic semiconductors.<sup>1</sup> Organic semiconductors have considerably lower bonding energies (e.g., van der Waals) than covalent and ionic inorganic semiconductors<sup>2,3</sup> resulting from the co-operation and competition between  $\pi$ - $\sigma$  and  $\pi$ - $\pi$  interactions, thereby rendering organic materials susceptible to damage when exposed to direct metal evaporation. Defects can easily be created at the metal-organic interfaces, which can severely hamper charge injection and extraction. For example, de Boer *et al.* have demonstrated that the current measured when injecting from the top electron-beam deposited Au contact is about five orders of magnitude lower than from the bottom-bonded Au contact in an organic single crystal.<sup>1</sup> They have concluded that exposure of the crystal surface to high-energy electrons generated by the electron-beam during the evaporation process induces damage in the organic crystal. Several approaches were proposed to develop soft methods for contact deposition such as ink-jet printing,<sup>4</sup> spray-coating,<sup>5-7</sup> or nanotransfer printing (nTP).<sup>8-11</sup> While these approaches worked well in thin-film device fabrication, a reliable, low-cost fabrication method for top contacting organic single crystals is still lacking. Organic semiconductors in single crystal form are particularly attractive as they offer a well-defined structure where the molecular long-range order can serve as a model system for investigation of the mechanism of charge transport in organic semiconductors.<sup>12-16</sup> Impressive properties such as high mobilities (on the order of 20–40 cm<sup>2</sup>/V s),<sup>17</sup> metallic-like

behavior,<sup>18</sup> and long-range exciton diffusion were reported in organic single crystal rubrene.<sup>19</sup>

In this article we demonstrate the nondestructive deposition of top contacts on organic single crystals by using flip chip lamination (FCL). FCL is a nTP-based technique that combines specifically tailored surface adhesion with mild conditions of pressure and/or temperature to laminate the ultrasmooth patterned metal contacts to organic materials.<sup>20</sup> We describe the FCL of top contacts on rubrene single crystals and demonstrate the effectiveness of this technique by comparing the results with e-beam evaporated top contacts and bonded-bottom contacts.

Figure 1 illustrates the steps we employed to prepare the top metal contacts on rubrene single crystal by FCL. First,

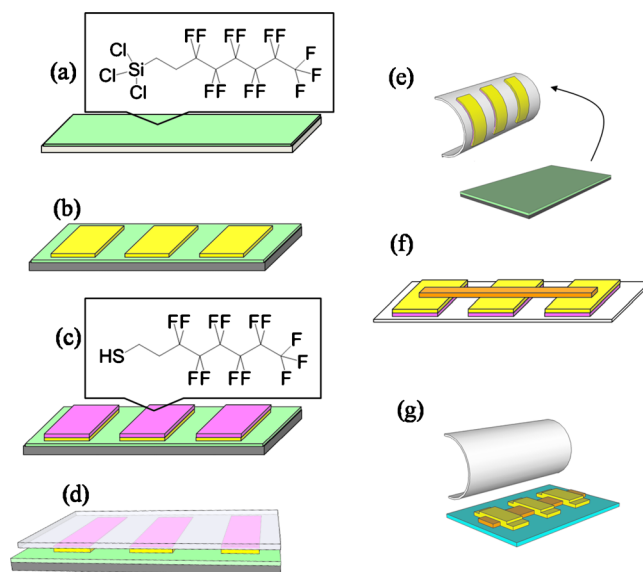


FIG. 1. (Color online) Schematic of the FCL process. (a) Preparation of the fluorinated silane SAM, RL1, on the silicon wafer. (b) Evaporation of the metal patterns. (c) Preparation of the fluorinated-thiol SAM, RL2, on Au/RL1/Si substrate. (d) Contacting the plastic substrate (PET) to the RL2-Au/RL1-Si substrate. (e) Peeling off the PET with the Au pattern adhered. (f) Lamination/Bonding of the organic single crystal onto the Au/PET. (g) Transfer of the crystal with top metal contacts onto a flexible substrate.

<sup>a)</sup>Electronic mail: jurchescu@wfu.edu.

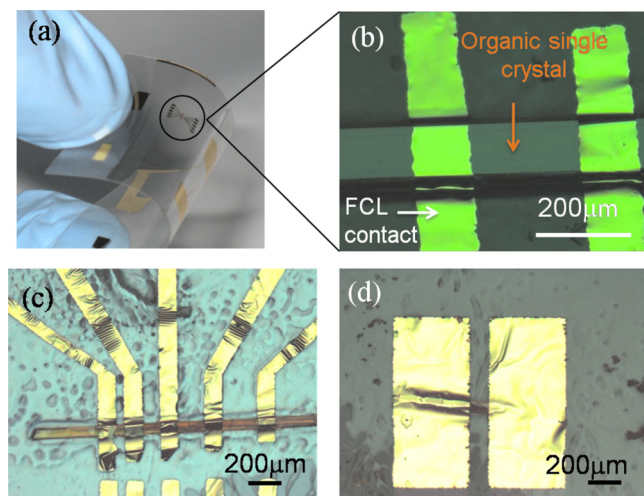


FIG. 2. (Color online) (a) Rubrene device fabricated on a flexible substrate after FCL the top metal contacts. (b) Optical micrograph of a rubrene single crystal with laminated top metal conformal contacts. [(c) and (d)] FCL top metal contacts of different shapes and sizes on rubrene needlelike single crystals.

we prepared a fluorinated silane self-assembled monolayer (SAM), tridecafluoro-1,1,2,2-tetrahydro-octyltrichlorosilane (RL1) [see chemical structure in Fig. 1(a)] on a silicon wafer, as described in detail elsewhere.<sup>21</sup> This chemical surface treatment lowers the free energy ( $\gamma$ ) of the silicon surface<sup>22</sup> and is needed to decrease the work of adhesion ( $W_a$ )<sup>23,24</sup> between the silicon and gold surfaces. During the second step, we evaporated 100 nm thick gold electrodes on the RL1-Si substrate through a shadow mask, Fig. 1(b). Then, we treated the weakly adhered gold electrodes with a fluorinated-thiol SAM (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octanethiol), RL2, Fig. 1(c). In this case, the RL2 allows the transfer of the Au layer onto a plastic substrate (i.e., polyethylene terephthalate, PET),  $W_a(\text{Si}/\text{Au}) < W_a(\text{Au}/\text{PET})$ , but have the Au adhered weakly enough to assure subsequent transfers of this Au layer, Fig. 1(d). Note that the surface energy of a  $\text{CF}_3$ -terminated surface is lower ( $\gamma \approx 15 \text{ mJ/m}^2$ )<sup>25</sup> than bare Au ( $\gamma \approx 1.5 \text{ J/m}^2$ ).<sup>26</sup> Thus, transfer of the RL2/Au from Si to PET, Fig. 1(e), required the application of 90 °C and 250 psi for 5 min by using a commercial nanoimprint tool. These sequential steps produce an ultrasoft Au surface,<sup>20</sup> which ensures conformal contact with the rubrene single crystal.<sup>27,28</sup> AFM measurements performed on the surface of the transferred Au pattern show a surface roughness  $\sim 0.5 \text{ nm}$ .<sup>20</sup> Once the smooth contact is obtained, single crystals are placed by hand onto the Au contact. Rubrene crystals uniformly adhere to clean metal surfaces, further referred to as laminated,<sup>15,29,30</sup> Fig. 1(f). In the last step of the process, the rubrene/Au system is transferred to any device substrate, Fig. 1(g). Note that the use of release layers and mild transfer printing conditions described in steps Figs. 1(a)–1(d) are critical and guarantee complete transfer of rubrene/Au bilayer and easy peel off of the PET substrate without exposing the rubrene to solvents or sacrificial resists.

Using FCL, we have established good quality electrical contacts for rubrene single crystals on pliable and transparent substrates, where Au contacts are in intimate contact with the organic single crystal while preserving the crystal integrity, as shown in Figs. 2(a) and 2(b). To demonstrate the viability

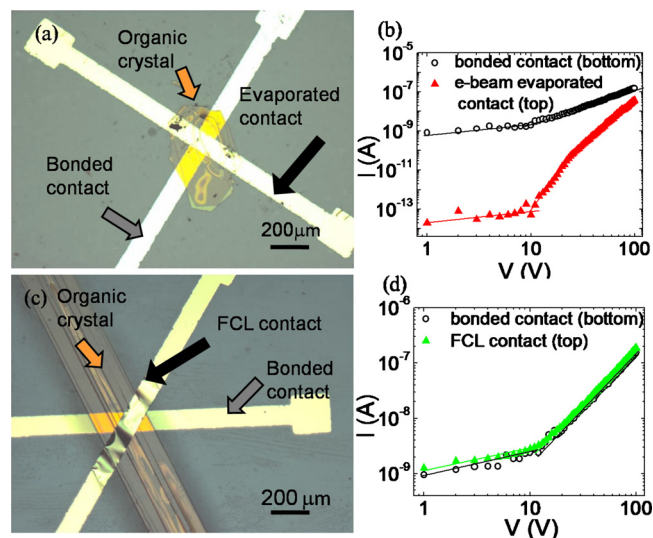


FIG. 3. (Color online) (a) Optical micrograph of a rubrene single crystal device with top-evaporated metal contact and bottom-bonded contact. (b) Current-voltage characteristics showing different behavior for charge injection from the top (e-beam evaporated) and bottom (bonded) contacts. (c) Optical micrograph of a rubrene device after lamination of the top metal contact and (d) the corresponding current-voltage characteristics.

of this approach, we have tested gold patterns of different sizes and shapes. Figure 2(c) shows an optical micrograph of 100 nm thick FCL top contacts on needlelike rubrene single crystals on a pliable substrate. Well-defined narrow top contacts (100  $\mu\text{m}$  width) with varying channel lengths, ranging from 50  $\mu\text{m}$  to 200  $\mu\text{m}$ , are evident. Figure 2(d) illustrates large and wide contacts (0.04 cm  $\times$  0.1 cm) in intimate contact with a rubrene crystal. FCL is thus a very attractive nondestructive approach to fabricating ultrasoft top metal contacts on organic materials facilitating pattern transfer of different sizes on organic single crystals.

In Fig. 3, we present space-charge limited current (SCLC) measurements comparing the electrical behavior of rubrene single crystals sandwiched between two gold electrodes deposited by different methods. In both cases, the crystal is laminated on the bottom gold contact and it spontaneously adheres to this contact, referred to as the “bonded contact.” Several reports have demonstrated that this is an efficient method to fabricate bottom contacts for organic single crystal field-effect transistors.<sup>15,29,30</sup> The two samples differ in the top contact formation. For the first sample, see Fig. 3(a), the top contact is deposited by using e-beam evaporation. For the crystal shown in Fig. 3(c), the top contact is placed on the crystal by using the FCL technique. The current-voltage characteristics, shown in Fig. 3(b), demonstrate orders of magnitude asymmetries when charges are injected from the top e-beam contact compared to charge injection from the bottom-bonded contact. Conversely, Fig. 3(d), shows that charge injection from the FCL top contact is similar to charge injection from the bottom-bonded contact, suggesting comparable organic-metal interfaces. Thus, it is clear that the current-voltage characteristics are very sensitive to the technique used to deposit the contacts.

In Fig. 3, when the charges are injected from the bottom contact (open black circles), the measured  $I$ - $V$  represents typical SCLC characteristics, where at low voltage the current is Ohmic ( $I \propto V$ ), and at higher electric fields it follows the Mott–Gurney law ( $I \propto V^2$ ).<sup>28</sup> On the contrary, when the

injection is done from the top e-beam evaporated contact (full red triangles), Fig. 3(b), the  $I$ - $V$  presents severe deviations from SCLC behavior, in spite of the fact that we measure the same crystal, in the capacitor geometry. This intriguing behavior is consistent with de Boer's model, that describes an increased number of deep trap states present at the surface of the organic crystal, which dominate charge injection and modify the electrostatic profile throughout the thickness of the crystals.<sup>1</sup> While in conventional SCLC models the density of deep traps ( $N_t$ ) is assumed uniform, de Boer's model introduces a dependence on the position of the  $N_t$ , with a larger defect density at the crystal-metal (e-beam) interface than in the bulk. In our experiment, we believe the increased surface trap density originates from crystal damage following exposure of its surface to x-ray and high-energy electrons generated by the e-beam during the evaporation process. The difference in surface trap densities between the bottom-laminated contact and the top e-beam evaporated contact can explain the differences measured in  $I$ - $V$ s for the same crystal. The current is large when the charges are injected from the bottom contact, where the trap density is very low. On the contrary, when injection occurs from the top (i.e., e-beam evaporated) contact, the current is four orders of magnitude lower since the same bias is not sufficient to fill the surface traps present at the interface between the organic crystal and metal contact to create mobile charges. Additionally, the evolution of the current with voltage, at higher voltages follows a power-law behavior  $I \propto V^n$ , with  $n > 2$ , which is usually attributed to a continuous distribution of energies of the trapping states.<sup>31</sup> In our plot, the  $I$ - $V$  at high voltage can be fit with  $n=7.5$  for  $V < 25$  V and with  $n=4$  for  $V > 25$  V. The two different slopes may indicate the superposition of two different continuous distributions, and that the transport is governed by the density of surface traps in the first regime ( $V < 25$  V) and by the density of the bulk traps in the second ( $V > 25$  V).<sup>32</sup> Figure 3(d) shows the SCLC currents when the deposition of the top contact is performed via FCL. The  $I$ - $V$  characteristics are more symmetric in this sample. In the frame of the model described earlier, this translates to comparable and very low surface trap densities at both contacts (bottom bonded and top FCL). The small differences notable from these data may result from different surface trap densities induced during fabrication, and are within the error of the same technique usually encountered for organic semiconductors.<sup>15</sup> This result demonstrates that the FCL method maintains good crystal quality at the interface and excellent electrical properties, and it may represent a viable approach for efficiently fabricating top contacts on organic single crystals compatible with a variety of substrates and free from further chemical processing.

In conclusion, we have demonstrated the formation of high-quality top metallic contacts on rubrene single crystals on flexible plastic substrates by FCL. This soft-contact deposition technique circumvents the mechanical and thermal limitations of the organic semiconductor. The  $I$ - $V$  characteristics suggest that the interface between the organic semiconductor and the FCL top metal is considerably better than the analog fabricated by e-beam evaporation. The ability to tune the surface energy of the materials involved in the transfer process offers a great opportunity to further extend this low-cost approach to a wide variety of organic materials and electrodes for fabricating more complex architectures on

flexible substrates in which the quality of the top contacts to the organic film is critically important such as in organic photovoltaics or organic spintronics.

Research performed in part at nanofabrication facility within the NIST Center for Nanoscale Science and Technology and Wake Forest University Center for Nanotechnology and Molecular Materials.

- <sup>1</sup>R. W. I. de Boer and A. F. Morpurgo, *Phys. Rev. B* **72**, 073207 (2005).
- <sup>2</sup>M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed. (Oxford University Press, New York, 1999).
- <sup>3</sup>S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
- <sup>4</sup>S. Gamerith, A. Klug, H. Scheiber, U. Scherf, E. Moderegger, and E. List, *Adv. Funct. Mater.* **17**, 3111 (2007).
- <sup>5</sup>Y. F. Lim, S. Lee, D. J. Herman, M. T. Lloyd, J. E. Anthony, and G. G. Malliaras, *Appl. Phys. Lett.* **93**, 193301 (2008).
- <sup>6</sup>N. A. Azarova, J. W. Owen, C. A. McLellan, M. A. Grimminger, E. K. Chapman, J. E. Anthony, and O. D. Jurchescu, *Org. Electron.* **11**, 1960 (2010).
- <sup>7</sup>C. K. Chan, L. J. Richter, B. Dinardo, C. Jaye, B. R. Conrad, H. W. Ro, D. S. Germack, D. A. Fischer, D. M. DeLongchamps, and D. J. Gundlach, *Appl. Phys. Lett.* **96**, 133304 (2010).
- <sup>8</sup>D. R. Hines, S. Mezheny, M. Breban, E. D. Williams, V. W. Ballarotto, G. Esen, A. Southard, and M. S. Fuhrer, *Appl. Phys. Lett.* **86**, 163101 (2005).
- <sup>9</sup>Y. L. Loo, R. L. Willett, K. W. Baldwin, and J. A. Rogers, *Appl. Phys. Lett.* **81**, 562 (2002).
- <sup>10</sup>J. Zausseil, T. Someya, Z. N. Bao, Y. L. Loo, R. Cirelli, and J. A. Rogers, *Appl. Phys. Lett.* **82**, 793 (2003).
- <sup>11</sup>J. B. Kim, S. Lee, M. F. Toney, Z. H. Chen, A. Facchetti, Y. S. Kim, and Y. L. Loo, *Chem. Mater.* **22**, 4931 (2010).
- <sup>12</sup>M. E. Gershenson, V. Podzorov, and A. F. Morpurgo, *Rev. Mod. Phys.* **78**, 973 (2006).
- <sup>13</sup>H. A. v. Laarhoven, C. F. J. Flipse, M. Koeberg, M. Bonn, E. Hendry, G. Orlandi, O. D. Jurchescu, T. T. M. Palstra, and A. Troisi, *J. Chem. Phys.* **129**, 044704 (2008).
- <sup>14</sup>O. D. Jurchescu, D. A. Mourey, S. Subramanian, S. R. Parkin, B. M. Vogel, J. E. Anthony, T. N. Jackson, and D. J. Gundlach, *Phys. Rev. B* **80**, 085201 (2009).
- <sup>15</sup>O. D. Jurchescu, S. Subramanian, R. J. Kline, S. D. Hudson, J. E. Anthony, T. N. Jackson, and D. J. Gundlach, *Chem. Mater.* **20**, 6733 (2008).
- <sup>16</sup>V. Podzorov, E. Menard, A. Borissov, V. Kiryukhin, J. A. Rogers, and M. E. Gershenson, *Phys. Rev. Lett.* **93**, 086602 (2004).
- <sup>17</sup>I. N. Hulea, S. Fratini, H. Xie, C. L. Mulder, N. N. Iossad, G. Rastelli, S. Ciuchi, and A. F. Morpurgo, *Nature Mater.* **5**, 982 (2006).
- <sup>18</sup>V. Podzorov, E. Menard, J. A. Rogers, and M. E. Gershenson, *Phys. Rev. Lett.* **95**, 226601 (2005).
- <sup>19</sup>H. Najafov, B. Lee, Q. Zhou, L. C. Feldman, and V. Podzorov, *Nature Mater.* **9**, 938 (2010).
- <sup>20</sup>M. Coll, L. H. Miller, L. J. Richter, D. R. Hines, O. D. Jurchescu, N. Gergel-Hackett, C. A. Richter, and C. A. Hacker, *J. Am. Chem. Soc.* **131**, 12451 (2009).
- <sup>21</sup>M. Coll, N. Gergel-Hackett, C. A. Richter, and C. A. Hacker, (unpublished).
- <sup>22</sup>S. Perutz, J. Wang, E. J. Kramer, C. K. Ober, and K. Ellis, *Macromolecules* **31**, 4272 (1998).
- <sup>23</sup>D. R. Hines, V. W. Ballarotto, E. D. Williams, Y. Shao, and S. A. Solin, *J. Appl. Phys.* **101**, 024503 (2007).
- <sup>24</sup>J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1991).
- <sup>25</sup>D. A. Lamprou, J. R. Smith, T. G. Nevell, E. Barbu, C. Stone, C. R. Willis, and J. Tsibouklis, *Appl. Surf. Sci.* **256**, 5082 (2010).
- <sup>26</sup>L. Vitos, A. V. Ruban, H. L. Skriver, and J. Kollar, *Surf. Sci.* **411**, 186 (1998).
- <sup>27</sup>P. Cosseddu and A. Bonfiglio, *Appl. Phys. Lett.* **88**, 023506 (2006).
- <sup>28</sup>C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater. (Weinheim, Ger.)* **14**, 99 (2002).
- <sup>29</sup>R. W. I. de Boer, T. M. Klapwijk, and A. F. Morpurgo, *Appl. Phys. Lett.* **83**, 4345 (2003).
- <sup>30</sup>J. Takeya, C. Goldmann, S. Haas, K. P. Pernstich, B. Ketterer, and B. Batlogg, *J. Appl. Phys.* **94**, 5800 (2003).
- <sup>31</sup>A. Rose, *Phys. Rev.* **97**, 1538 (1955).
- <sup>32</sup>O. Zmeskal, F. Schauer, and S. Nespurek, *J. Phys. C* **18**, 1873 (1985).