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Ethanol-Mediated Metal Transfer Printing on Organic Films

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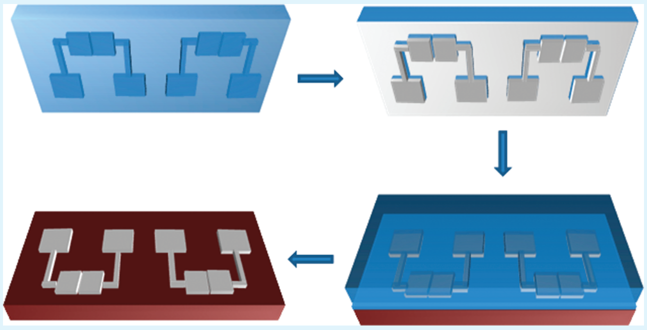

ABSTRACT: Ethanol-mediated metal transfer printing (mTP) is a soft method, which allows to efficiently deposit metals onto various organic surfaces for applications in organic electronics. This simple approach in based on the stronger adhesion of the metals to the organic materials in the presence of thin ethanol layer between the metallized PDMS and the substrate due to the capillary action. Patterns with a resolution of at least 20 μm have been obtained on organic polymeric materials and photoresists without heating or applied pressure. Compared to other methods ethanol mediated mTP is considerably faster and has smaller limitations on the stamp depth. Residual silicone layer detected on the metal surface after the transfer by XPS studies has been mostly removed by UV/ozone treatment. Organic field-effect transistors (OTFTs) based on the metal electrodes deposited by mTP have been successfully fabricated and tested.

KEYWORDS: metal transfer printing, PDMS, OTFT, metal surface, XPS

1. INTRODUCTION

Unconventional fabrication and patterning of nano- and microscale devices proposes various improvements to the classical photolithographic approach.[1] One of the central and most promising methods of such fabrication is soft lithography,[2] which uses poly(dimethylsiloxane) (PDMS) stamps for the replication of given patterns and encompasses several techniques such as microcontact printing (μCP), soft contact lamination, micromolding, and metal transfer printing (mTP). Soft lithography becomes especially important for the fabrication of devices in organic electronics because classical lithographic methods are often not compatible with the materials used in such devices.[3] Thus, direct metal evaporation and etching can be damaging for organic surfaces which is a serious fabrication issue taking into account the primordial role of interfaces in such electronic devices. In mTP method the metal is evaporated on the PDMS stamp, which is eventually brought in contact with the substrate, thus bypassing the incompatibility issues. In addition, the patterning step is done only once during the stamp fabrication, which allows for the repetitive utilization of the same stamp.

The driving force of mTP is the higher adhesion between the metal and the substrate compared to the metal adhesion to PDMS. Taking into account the very small surface energy of PDMS (19.8 mJ/m^2),[4] which is lower than for many other substrates, the transfer should proceed smoothly. However, if the difference of adhesions is too small, or if external factors such as surface roughness or residual contamination take the lead, mTP is less efficient. In order to improve the effectiveness of mTP onto various substrates, several strategies based on surface modification have been proposed. One of the most efficient approaches aims at increasing the surface energy of the metal in order to enhance the metal/substrate adhesion by evaporating a thin layer of high energy metals such as Ti or Cr.[5−9] An alternative approach takes advantage of the poor adhesion on the metal/stamp interface resulting from lowering the PDMS surface energy by its modification with fluorinated molecules.[6,10,11] Another group of methods is based on treating the substrate surface by bifunctional molecules that are capable of forming chemical bonds with the metal during the mTP.[11−14] This approach works particularly well for metallic or silicon surfaces because of their easy modification; however, the transfer on organic surfaces either requires their modification with very specific agents, or is virtually impossible in the case of the transfer on inert polymers.

When surface modification is not sufficient, the mTP efficiency was shown to be further improved by applying elevated temperature and/or high pressure.[8,9,15−19] These methods may work well for the transfer itself but they can turn out to be damaging for the substrates, especially when mTP is one of the last steps of the device integration process. For example, during the fabrication of organic transistors (OTFT) or organic light-emitting diodes (OLEDs), the substrate already contains previously deposited thin layers of organic materials. Such materials are typically extremely sensitive and even mild heating or pressure can significantly deteriorate their performance.

That is why alternative "soft" improvement methods have been proposed for mTP. Exposure of polymer-coated

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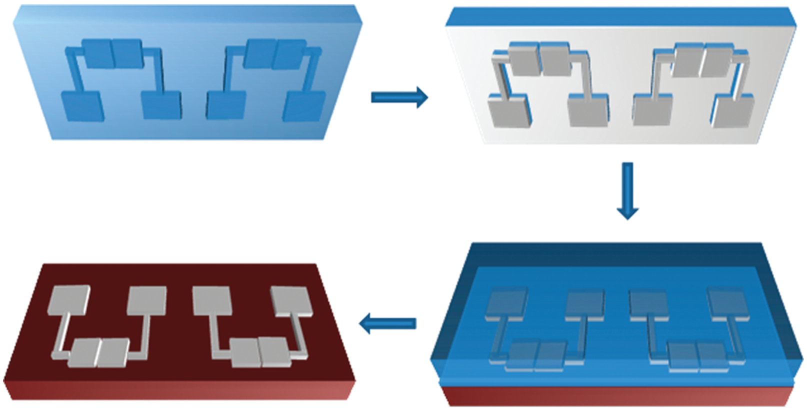

Figure 1. Principle of ethanol-mediated mTP.

substrates to the vapor of a specific solvent was shown to plastify them and improve the adhesion of metals to the so-treated surfaces during mTP.[20] Despite the applicability of this method to a series of important materials, vapor exposure is time-consuming and limited to polymeric surfaces only. In another interesting approach reported recently, a thin layer of water was used as a mediator during the metal transfer.[21,22] As water dries, it pulls the two surfaces together by capillary forces and sticks the metal layer on the substrate. Covalent bonding between the metal and silicon surfaces has even been claimed.[21] Even though this approach can be quite flexible, its major drawbacks include long water drying times even at low humidity as well as potential corrosion effects brought by extended contact with water molecules. Furthermore, we noticed that in water-mediated mTP, the capillary forces developed during water drying are so strong that they cause metal transfer even from the raised regions of the PDMS, which were not initially in direct contact with the substrate. This phenomenon is even observed for stamps fabricated with 10 μm deep patterns, taking into account that the thickness of the transferred metal was only 100 nm. It is referred as sagging and is caused by the stamp deformation because of the high internal stress developing in PDMS upon the strong capillary action of drying water. The sagging may limit the practical applications of water-mediated mTP because of the possible pattern distortion and lack of resolution when the printed regions are situated too close to each other.

In this work, we propose an alternative method for transferring metals by mTP onto various surfaces by using a thin layer of ethanol, and some examples of its utilization for organic electronics applications. Ethanol has a lower boiling point (70 °C vs 100 °C for the H_2O) than water that allows shortening its drying time and therefore speeding up the metal transfer. The capillary force, which is the driving force of liquid-mediated mTP, is a function of the liquid surface energy γ.[23] The surface energy of ethanol ($\gamma_{EtOH} = 23$ mJ/m^2) is almost 3 times lower than that of water,[24] which allows the printing with high resolution using less deeply patterned PDMS stamps.

2. EXPERIMENTAL SECTION

Materials. Sylgard 184 kit (Dow Corning) used for the fabrication of PDMS stamps was purchased from Neyco, France. Pentacene (99.9+% sublimed grade), Mowiol 40−88, absolute ethanol, $NH_4Cr_2O_7$, and [3-(heptafluoro-isopropoxy)propyl]-trichlorosilane (HIPS) were purchased from Aldrich and used as received. Deionized water was purified by Millipore Milli-Q Integral 3 system.

PDMS Stamp Preparation and Treatment. Four-millimeter-thick PDMS stamps were prepared as reported previously.[25] To fabricate masters on silicon wafers, we used photolithographic patterning of 4 μm thick SU-8 resist. Then, the prepared masters were treated by HIPS vapor to decrease PDMS adhesion to the silicon surface. After the stamp fabrication, the PDMS surface was exposed for 10 min to UV/ozone oxidative treatment immediately followed by its modification by HIPS under reduced pressure to diminish its own surface energy. The functionalized PDMS stamps were then placed into the evaporation chamber, and metals (100 nm) were deposited by thermal evaporation under reduced pressure.

Substrate Preparation. The substrates (glass or metal-coated glass) were routinely cleaned in the following way: they were immersed into deionized water and placed into an ultrasonic bath for 10 min. Then they were dried under an argon flow, and the procedure was repeated with ethanol and then acetone as solvents followed by their exposure to UV/ozone for 10 min. Commercial photoresist polymers (950-PMMA-A3 and SU-8 2010) were then deposited onto thus prepared surface by spin-coating following the standard procedures. To obtain the DPVA film, ammonium dichromate (0.0014% w/w) was added to aqueous 5% PVA (Mowiol 40−88) solution. After spin-coating, the film was exposed for 10 s to UV light for cross-linking followed by its rinsing with DI water for 1 min and annealing at 120 °C.

Calculation of Surface Energy. The surface energy of DPVA film was calculated using Owens, Wendt, Rabel, and Kaelble (OWRK) method by measuring contact angles of three different liquids, H_2O, DMSO, and DMF and building a graph with the obtained data.

Pattern Transfer. Several drops of absolute ethanol are deposited on the surface of the substrates with organic polymer films and left to spread and cover spontaneously the entire surface. For example, 1 drop of ethanol per 6 cm^2 of surface is required to obtain a continuous thin liquid film on DPVA. Once the film is spread, the metal-covered stamp is carefully placed on the substrate and left to dry spontaneously. Under ambient conditions it takes about 1 h for 25 cm^2 substrates to dry completely. Under dry conditions the transfer is much faster. Finally, the PDMS stamp is slowly peeled off the substrate leaving behind the printed pattern. Used stamps can be recycled by removing the residual metal film, if any, with a Scotch tape and subsequent cleaning for 10 min consequently in ethanol and acetone in ultrasonic bath.

OTFT Fabrication and Characterization. For a typical transistor fabrication Cr gate electrodes (100 nm) were sputtered on Corning glass substrates. Silicon nitride films were deposited in a conventional capacitively coupled PECVD reactor (Nextral ND200) at 250 °C from $SiH_4/NH_3/N_2$ mixture. After insulator and electrode deposition,

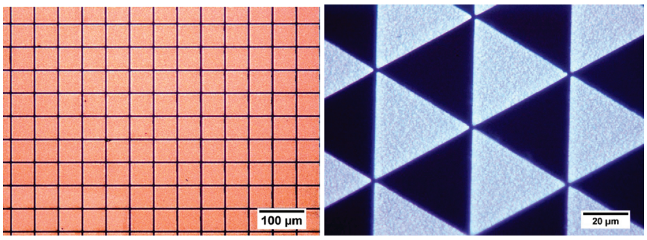

Figure 2. Aluminum patterns on DPVA obtained by ethanol-mediated mTP.

pentacene (50 nm) was thermally evaporated through a shadow mask on the substrate at a slow average deposition rate of 0.1 nm/s.

Instrumentation. The surface rms roughness was determined by AFM analysis on a Molecular Imaging PicoSPMLe (PicoScan 2100 controller, Scientec, France). Contact-angle measurements for the surface energy determination were performed with water (Millipore) on a Krüss DSA 10 contact-angle measuring system, equipped with Krüss drop shape analysis software. XPS spectra were recorded on a KRATOS AXIS ULTRA spectrometer with an Al Kr source monochromatized at 1486.6 eV. Optical micrographs were obtained by a Leica DMLM microscope equipped with a Leica DFC320 digital camera. Photo-cross-linking of DPVA was done by Oriel Mercury Xenon 200W UV lamp. OTFTs were tested on 4-probe Keithley 4200 semiconductor characterization system.

3. RESULTS AND DISCUSSION

Metal Transfer Principle. Figure 1 shows the principle of ethanol-mediated mTP. First, a PDMS stamp is fabricated by using as a master a Si wafer with photoinduced patterns in a photolithographic resin SU-8. Then a thin layer of metal is thermally evaporated on the PDMS surface. Metals like silver or gold exhibit a small adhesion to the stamp with a low surface energy and hence their release onto the substrate surface is relatively easy. However, for metals like aluminum or chromium, their higher affinity to PDMS makes direct mTP rather complicated and requires a special stamp treatment. This is why the inert polysiloxane stamp surface is oxidized by exposure to UV/ozone in order to release free siloxane groups available for subsequent chemical transformation. Then the activated stamp is exposed to HIPS vapors at reduced pressure in order to make the PDMS surface hydrophobic, further decrease its surface energy and significantly lower the metal adhesion to the stamp. That pretreatment of the stamp results in similar metal transfers by mTP for lower surface energy metals (such as silver) and higher surface energy ones (e.g., aluminum).

Indeed, by using ethanol as a mediating layer, we obtained an efficient transfer of silver and aluminum on top of the substrates coated by poly(vinylalcohol) (PVA), poly(methylmethacrylate) (PMMA) and SU-8. Water-soluble PVA was used in its photopatternable form (DPVA) by adding a small amount of ammonium dichromate as a photosensitizer.[26] After the deposition of the organic films (100−400 nm) on the untreated or metal-coated glass, a thin layer of ethanol was evenly introduced on the substrate surface. Immediately after its spreading, a pattern was efficiently transferred from metal-coated-PDMS stamps onto the substrate. mTP mediated with ethanol was found to be about 4 times faster than that mediated with water. Typical result of such mTP is shown on Figure 2 (aluminum) and 5 (silver). One can see fine and precisely reproduced metal patterns on top of the intact organic surface.

Table 1. Surface Energies of the Compounds Used for mTP

surface energy (mJ/m^2)	SU-8[28]	DPVA	PMMA	PDMS[7]	Al[29]	Ag[29]
γ^D	39	21.4	29.6	19	76	n/a
γ^P	9	21.4	11.5	0.8	1060	n/a
γ^{total}	48	42.8	41.1	19.8	1136	1250

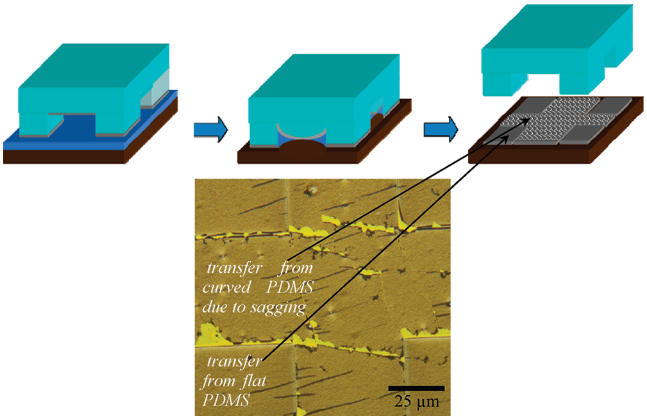

Figure 3. Mechanism of stamp sagging (top) and a typical result of water-mediated mTP onto polymer substrate (bottom). The metal has been transferred even from the raised zones of the stamp.

The metal surface after the transfer was found relatively smooth, as manifested by low values of surface rms roughness, R_{rms} = 1−3 nm, which matches well the roughness of the PDMS stamp before the evaporation, 2.6 nm. If the stamp surface was not treated by HIPS, the transferred metal surface roughness was about ten times higher (25−30 nm), which again corresponds to the untreated PDMS (23 nm). We suppose that UV/ozone exposure used for the stamp treatment removes most reactive surface irregularities and thus smoothes the stamp.

Some liquids other than ethanol have been equally tested as potential mTP mediating layers but none have proved as efficient. Thus, low-boiling-point hexane and acetone do not develop sufficient capillary force for the metal transfer, whereas toluene swells the PDMS stamp and distorts the pattern.

Theoretical Considerations. Theoretical possibility of metal transfer can be estimated by comparing adhesion energies at the interfaces PDMS/metal and metal/substrate. The transfer is energetically favorable when $W_{PDMS/metal} < W_{metal/substrate}$. The adhesion energies can be calculated by using an expression derived[27] from the Dupré equation

$$W_{A/B} = 2\sqrt{\gamma_A^D \gamma_B^D} + 2\sqrt{\gamma_A^P \gamma_B^P} \qquad (1)$$

where $\gamma_{A,B}^D$ and $\gamma_{A,B}^P$ are the dispersive and polar components of the surface energies of the substrates A and B, respectively (see Table 1). Although the γ values for most of the materials used are known, surface energy values for DPVA were calculated on the basis of the contact angle measurements with various solvents.

By putting these values into eq 1, adhesion energies for different materials can be calculated: $W_{PDMS/Al}$ = 134 mJ/m^2; $W_{Al/DPVA}$ = 382 mJ/m^2; $W_{Al/SU\text{-}8}$ = 304 mJ/m^2. The adhesion on the interface metal/substrate is obviously higher than that of PDMS/metal, which means that from a theoretical standpoint, the metal transfer on those surfaces is energetically favorable, in the absence of external forces. Even if we take into account the

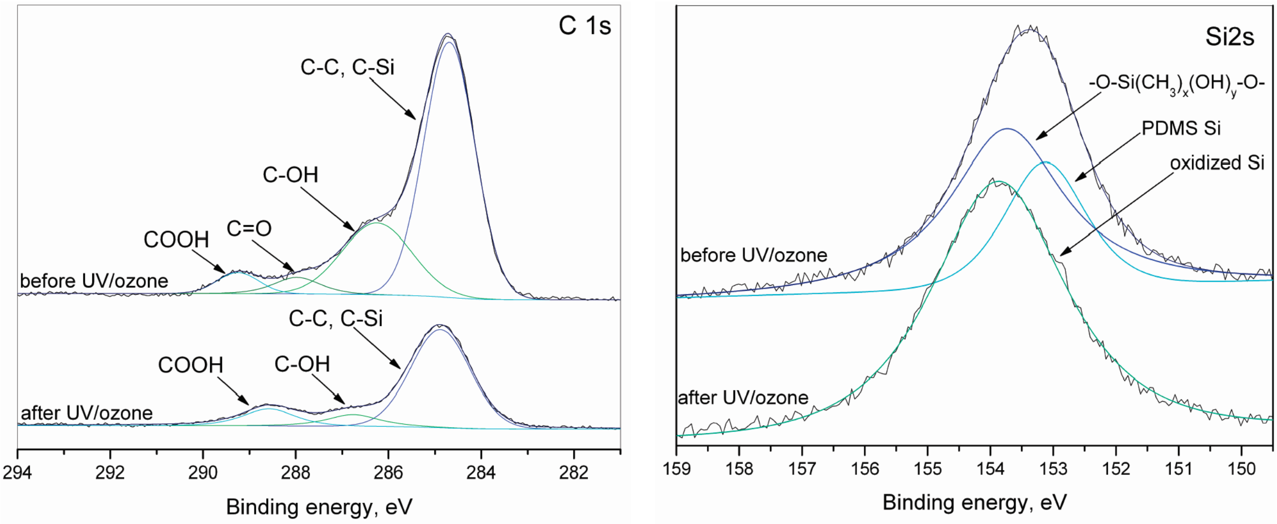

Figure 4. XPS spectra from samples of silver deposited by mTP before and after UV/ozone treatment.

Table 2. Relative Atomic Concentrations of Compounds Present on Silver Surface after mTP from XPS Data

	Ag 3d5/2	Si 2s	C 1s
immediately after mTP	1	0.27	1.16
after UV/ozone exposure	1	0.26	0.49

inevitable presence of Al_2O_3 on the aluminum surface ($W_{Al2O3/DPVA}$ = 307 mJ/m^2), the metal transfer is still energetically favored. Unfortunately, experiments strongly invalidate those theoretical predictions: in practice the only way to carry out transfer of aluminum on the studied substrates without any liquid layer requires heating at 100 °C while applying a considerable pressure of 800 Pa for 3 h. There are obviously some external factors which prevent efficient mTP. One of these factors can be surface roughness that prevents intimate junction between the metal and the substrate. Application of a thin ethanol layer improves the contact and adds a significant capillary component to the adhesion.

Practical Limitations of mTP. As mentioned above, liquid-mediated mTP often results in metal transfer from the raised stamp zones with no direct contact with the substrate because of the stamp sagging. Sagging is much more pronounced in the case of organic substrates such as polymer films compared to inorganic surfaces. This behavior is governed by a strong suction force in the cavities formed upon the stamp contact with the substrate. When the volume of liquid decreases upon drying, the cavity walls experience deformation starting from its center resulting in a suction effect. During the transfer to surfaces like Si or SiO_2, their rigidity precludes their deformation and thus only the stamp is bent, whereas in the case of flexible organic films, both the substrate and the stamp undergo deformation to respond to the cavity shrinking compensation (Figure 3, top). This increases the probability of undesired metal−substrate contact followed by its transfer from the raised stamp regions and thus results in a lost resolution (Figure 3, bottom). To avoid the resolution issues due to the suction-induced sagging, one can make the patterns in PDMS deeper. For water-mediated mTP, optimal pattern depth was found to be >10 μm, which is definitely too high when reproducing nanometer-scale patterns is sought.[30] Optimal pattern depth for efficient ethanol-mediated metal transfer was found around 5 μm.[31]

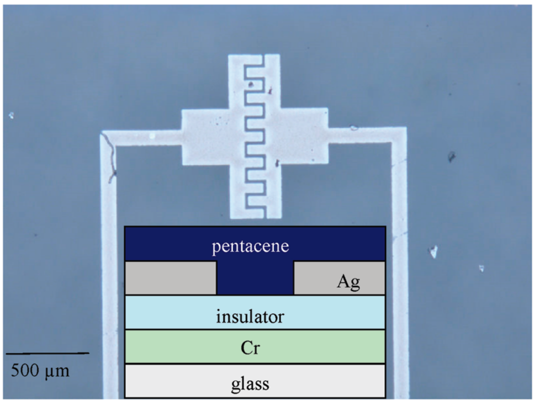

Figure 5. Optical micrograph of typical silver transistor electrodes deposited by mTP onto the insulator layer.

Encouraged by promising results of metal transfer with ethanol, we have attempted to realize it with PDMS stamps metallized directly after the fabrication, without the HIPS treatment. However, the pattern transfer was not successful, aluminum interacts so strongly with the PDMS surface because of its relatively high surface energy, that it makes impossible to separate the metal film afterward even by exerting high temperature and pressure during the transfer.

Ethanol-mediated mTP works best with metals of medium surface energy, such as silver or aluminum. Attempts to transfer metals with lower surface energy, such as gold ($\gamma \approx$ 1000 mJ/m^2), or higher ones, such as chromium (3500 mJ/m^2), did not result in efficient transfer. Gold films adhered too weakly to the stamp and got deformed immediately after the contact with ethanol on the substrate, whereas after the evaporation of chromium, the adhesion at the interface Cr/PDMS was too strong, which rendered mTP difficult and resulted in limited localized transfer of cracked patterns.

Metal transfer from stamps gets considerably less efficient a few days after the metal evaporation. This can be explained in terms of the diffusion of PDMS oligomers with low molecular

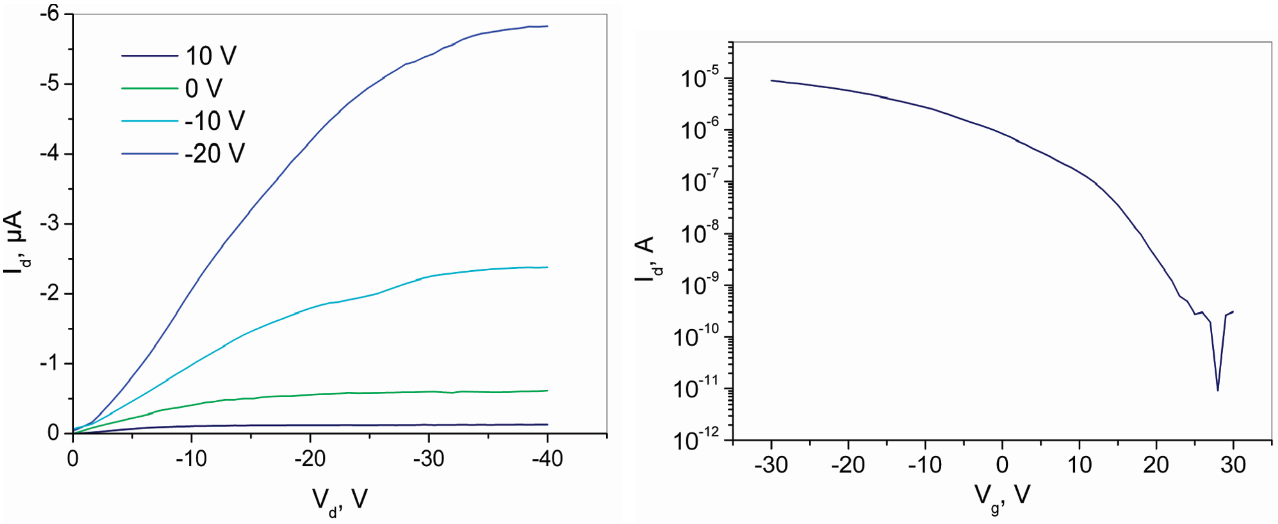

Figure 6. Electrical characteristics of a typical pentacene-based OTFT with silver electrodes deposited by mTP.

weight from the bulk of the stamp onto its surface, gradual replacement of the fluorinated molecules dominating on the surface, and as a result stronger aluminum bonding to a stamp due to its contact with more hydrophilic oligomers. Delamarche et al. observed a similar phenomenon with gold deposited on treated PDMS stamps.[6]

In practice, by the ethanol mediated mTP method we easily obtained patterns with average features in the 20 μm range. As the aim of this study was to demonstrate a new metal deposition process for the fabrication of organic electronic devices, we did not try to decrease that average size since a higher resolution is not required for that application domain. However, current state of the art in stamp-assisted metal-transfer printing gives features in the hundreds-of-nanometers range,[7] and we are convinced our process is able to reach the same target. Indeed, its main practical limitations are the same as for most of metal transfer methods, namely metal plasticity and stamp robustness. Regarding the maximum size of the transferred patterns, our experiments were limited to a few centimeters. Indeed, above this size local surface defects coming both from the substrate (roughness, dust, irregularities) and the metallized stamp (nonuniform evaporation) together with the geometrical control of the deposition become detrimental to the overall quality of the transfer. We expect, however, that this upper limit can be considerably improved if mTP is conducted in the clean room with a dedicated tool that controls precisely the orientation of the stamp with respect to the substrate, and the applied pressure.[32]

Post-transfer Surface Study and Treatment. For the applications of ethanol mediated mTP in the fabrication of organic electronic devices, the state of the surface of the deposited metals is extremely important. Silver and aluminum films were studied by XPS right after the transfer onto a substrate. On the XPS spectrum one can see that traces of silicone compounds are present on the surface of the metals, which show up as C and Si peaks (Figure 4). On the C 1s spectrum one can see the presence of various carbon types, from aliphatic and C−Si to more oxidized states. Si 2p signal typically used for identification of silicon-containing species is masked by the presence of substrate Ag 4s peak, which complicates its interpretation. However, Si 2s peak is well resolved and after decomposition clearly shows the presence of two types of Si atoms at different oxidation states, at 153.2 and at 153.7 eV. They were ascribed to silicones $-O-Si(CH_3)_2-O-$ and to a more oxidized silicon form, respectively. On the basis of this data, the organic contamination on top of the silver has been attributed to residual PDMS oligomers. Similar silicone transfer has been previously described in case of microcontact printing on different surfaces.[33,34] More oxidized silicon compounds with the possible following structure, $-O-Si(CH_3)_x$-$(OH)_y-O-$, are probably products of partial photochemical oxidation of oligosiloxanes during the initial UV/ozone stamp treatment, which corresponds well with previous PDMS photo-oxidation studies.[35]

Fabrication of various transistors with silver electrodes used “as is” after the mTP did not lead to working devices. Indeed, the contamination hinders charge injection from the metal to a semiconductor.

To remove this contamination the electrodes were exposed to UV/ozone treatment typically used to clean various surfaces from organic residues. To estimate the efficiency of this treatment, we compared relative atomic concentrations of contaminants with respect to the metal calculated from XPS studies (Table 2).

As seen from the table, the UV/ozone treatment was particularly efficient for the removal of carbon-containing contaminants, their contribution dropped more than twice, however silicon contamination remained almost constant. It is not surprising taking into account the mechanism of UV/ozone cleaning. It generates extremely reactive oxygen radicals in the vicinity of substrate, which attack and oxidize all species on the surface. Carbon-based molecules are oxidized into alcohols, aldehydes, carboxylates (Figure 4, left) and eventually CO_2 gas, which leaves the surface easily, while silicon-containing compounds are oxidized to nonvolatile compounds, which remain on the surface, as manifested by the complete disappearance of the PDMS signal at 153.2 eV and shift of oxidized oligosiloxanes peak to a 153.9 eV (Figure 4, right). This smaller but wider higher energy peak was identified as a superposition of residual silicones of more oxidized forms, such as $-O-Si(OH)_2-O-$, found also on PDMS surface after UV/ozone exposure.[35,36] Overall, UV/ozone cleaning removes most of organic contamination, which should result in metal surfaces of reasonable quality giving way for the application of mTP deposited electrodes in working devices.

OTFT Fabrication. By using ethanol-mediated mTP, we fabricated a series of OTFTs of bottom gate bottom contact configuration with pentacene as an organic semiconductor. The Cr common gate was deposited on the glass substrate followed by the spin-coating of organic polymer insulator and the metal electrodes deposition by mTP (Figure 5). The OTFT fabrication was completed by pentacene evaporation after which several routine electrical measurements were performed. Transistors with DPVA as insulator showed rather low drain currents (I_d) (1×10^{-9} A), relatively high gate currents (I_g) (1×10^{-10} A) and low on/off ratio (113) probably because of leaks through the polymer. Aluminum electrodes also resulted in small I_d due to the passivating Al_2O_3 surface oxide layer. The best OTFTs were obtained with the following structure: glass/Cr/SiN_x/PMMA/Ag/pentacene.

Typical I_d−V_d curves characteristic of pentacene, a *p*-type semiconductor, were obtained under negative gate bias (Figure 6). For the transistors with $W/L = 1000/10$ the drain current was modulated with the gate voltage and reaches saturation. I_d-V_g plot measured in the saturation regime ($I_d = -20$ V) shows a solid on/off ratio of 1×10^5 and the threshold voltage of 12 V. On the basis of these data, a mobility value could be calculated, $\mu = 0.0081$ cm^2/(V s), which corresponds well to the current state of the art for similar transistors.[37] Relatively high values of the drain currents and mobility as well as classical transistor behavior confirm that working OTFTs can be obtained by using ethanol mediated mTP as the electrode deposition technique. The work to adapt this method for the fabrication of other organic electronic devices is underway.

4. CONCLUSIONS

We have developed a new method for metal deposition onto organic surfaces, ethanol-mediated metal transfer printing. The method is fast, robust and works well with silver and even aluminum, which is normally hard to transfer by soft lithography techniques. Because of the capillary forces, ethanol results in a stronger metal−substrate contact and thus more efficient pattern transfer. Metal patterns transferred by mTP can be used as the electrodes for organic electronic devices immediately after their cleaning by UV/ozone. OTFTs with such electrodes demonstrate good performance.

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■ REFERENCES

(1) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823–1848.

(2) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550–575.

(3) Singh, P. K.; Sharma, V.; Tanwar, V. K.; Jain, S. C. *J. Optoelectron. Adv. Mater.* **2007**, *9*, 127–133.

(4) Krevelen, D. W. V. *Properties of Polymers*; Elsevier: Amsterdam, 1997.

(5) Loo, Y.-L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. *Appl. Phys. Lett.* **2002**, *81*, 535–564.

(6) Schmid, H.; Wolf, H.; Allenspach, R.; Riel, H.; Karg, S.; Michel, B.; Delamarche, E. *Adv. Funct. Mater.* **2003**, *13*, 145–153.

(7) Hur, S.-H.; Khang, D.-Y.; Kocabas, C.; Rogers, J. A. *Appl. Phys. Lett.* **2004**, *85*, 5730–5732.

(8) Kang, M.-G.; Guo, L. J. *J. Vac. Sci. Technol., B* **2007**, *25*, 2637–2641.

(9) Kang, M.-G.; Guo, L. J. *J. Vac. Sci. Technol., B* **2008**, *26*, 2421–2425.

(10) Sharpe, R. B. A.; Burdinski, D.; Huskens, J.; Zandvliet, H. J. W.; Reinhoudt, D. N.; Poelsema, B. *J. Am. Chem. Soc.* **2005**, *127*, 10344–10349.

(11) Guerin, D.; Merckling, C.; Lenfant, S.; Wallart, X.; Pleutin, S.; Vuillaume, D. *J. Phys. Chem. C* **2007**, *111*, 7947–7956.

(12) Loo, Y.-L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 7654–7655.

(13) Felmet, K.; Loo, Y.-L.; Sun, Y. *Appl. Phys. Lett.* **2004**, *85*, 3316–3318.

(14) Erbe, A.; Jiang, W.; Bao, Z.; Abusch-Magder, D.; Tennant, D. M.; Garfunkel, E.; Zhitenev, N. *J. Vac. Sci. Technol., B* **2005**, *23*, 3132–3137.

(15) Wang, Z.; Yuan, J.; Zhang, J.; Xing, R.; Yan, D.; Han, Y. *Adv. Mater.* **2003**, *15*, 1009–1012.

(16) Hines, D. R.; Mezhenny, S.; Breban, M.; Williams, E. D.; Ballarotto, V. W.; Esen, G.; Southard, A.; Fuhrer, M. S. *Appl. Phys. Lett.* **2005**, *86*, 163101.

(17) Kim, J.-W.; Yang, K.-Y.; Hong, S.-H.; Lee, H. *Appl. Surf. Sci.* **2008**, *254*, 5607–5611.

(18) Lee, K.; Oh, S.-H.; Kang, N.-G.; Lee, J.-S.; Kim, D.-Y.; Lee, H.; Jung, G. Y. *Langmuir* **2008**, *24*, 8413–8416.

(19) Abu Hatab, N. A.; Oran, J. M.; Sepaniak, M. J. *ACS Nano* **2008**, *2*, 377–385.

(20) Yu, X.; Yu, S.; Wang, Z.; Ma, D.; Han, Y. *Appl. Phys. Lett.* **2006**, *88*, 263517.

(21) Lee, B. H.; Cho, Y. H.; Lee, H.; Lee, K.-D.; Kim, S. H.; Sung, M. M. *Adv. Mater.* **2007**, *19*, 1714–1718.

(22) Oh, K .; Lee, B. H.; Hwang, J. K.; Lee, H.; Lee, K. H.; Im, S.; Sung, M. M. *Small* **2009**, *5*, 558–561.

(23) Chen, L.; Gu, X.; Fasolka, M. J.; Martin, J. W.; Nguyen, T. *Langmuir* **2009**, *25*, 3494–3503.

(24) *Polymer Surfaces and Interfaces*; Feast, W. J.; Munro, H. S., Eds. Wiley: Chichester, U.K., 1987.

(25) Kumar, A.; Biebuyck, H. A.; Whitesides, G. *Langmuir* **1994**, *10*, 1498–1511.

(26) Sheraw, C. D.; Zhou, L.; Huang, J. R.; Gundlach, D. J.; Jackson, T. N.; Kane, M. G.; Hill, I. G.; Hammond, M. S.; Campi, J.; Greening, B. K.; Francl, J.; West, J. *Appl. Phys. Lett.* **2002**, *80*, 1088.

(27) Kinloch, A. J. *J. Mater. Sci.* **1980**, *15*, 2141–2166.

(28) Airoudj, A.; Debarnot, D.; Beche, B.; Boulard, B.; Poncin-Epaillard, F. *Plasma Proc. Polym.* **2008**, *5*, 275–288.

(29) Vitos, L.; Ruban, A. V.; Skriver, H. L.; Kollar, J. *Surf. Sci.* **1998**, *411*, 186–202.

(30) Delamarche, E.; Schmid, H.; Michel, B.; Biebuyck, H. *Adv. Mater.* **1997**, *9*, 741–746.

(31) We have tried the stamps with the three different pattern depths: 1, 3, and 5 μm. For each stamp, we made 2−3 transfer attempts. The best reasonable resolution (ratio of transfer in the low and high regions) was found to be at 5 μm.

(32) Decré, M. M. J.; Schneider, R.; Burdinski, D.; Schellekens, J.; Saalmink, M.; Dona, R. *Mater. Res. Soc. Symp. Proc.* **2004**, *EXS-2*, M4.9.1.

(33) Glasmästar, K.; Gold, J.; Andersson, A.-S.; Sutherland, D. S.; Kasemo, B. *Langmuir* **2003**, *19*, 5475–5483.

(34) Hale, P. S.; Kappen, P.; Prissanaroon, W.; Brack, N.; Pigram, P. J.; Liesegang, J. *Appl. Surf. Sci.* **2007**, *253*, 3746–3750.

(35) Graubner, V.-M.; Jordan, R.; Nuyken, O.; Schnyder, B.; Lippert, T.; Kötz, R.; Wokaun, A. *Macromolecules* **2004**, *37*, 5936–5943.

(36) Fu, Y.-J.; Qui, H.; Liao, K.-S.; Lue, S. J.; Hu, C.-C.; Lee, K.-R.; Lai, J.-Y. *Langmuir* **2010**, *26*, 4392–4399.

(37) Di, C. A.; Yu, G.; Liu, Y. Q.; Xu, X. J.; Wei, D. C.; Song, Y. B.; Sun, Y. M.; Wang, Y.; Zhu, D. B.; Liu, J.; Liu, X. Y.; Wu, D. X. *J. Am. Chem. Soc.* **2006**, *128*, 16418–16419.