Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp1113-1114

Fabrication of Molecular Junctions in Micropores on Photoresist-Free and Ultra-smooth Electrodes using a Two-step Etching Process

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Abstract.
Molecular electronics aims to use molecules as the functional building blocks in electronic circuitry due to low power consumption, complementary functionality to CMOS, and synthetic tailorability to control electronic function at the molecular length-scales. The fabrication of reliable and non-invasive contacts to molecule is still a challenging issues. Here, we report a method to fabricate large-area molecular junctions based on template stripped bottom electrodes without photoresist, and contamination from the fabrications processes, which was confirmed by AFM characterization. The electrical characteristics of micropore device with different length of alkanethiolate SAM shows the consistency in our transport measurements and observed β is similar to the other test beds. We also studied chemical functionality and utilized this method to construct molecular electronic devices which allows large-scale fabrication of the molecular electronic device using carbon paint as a protective layer.

1. Introduction

In molecular electronic device, fabrication process continues to face challenges due to the presence of defects such as surface roughness of electrodes, fabrication contamination (photoresist, organic residues), pinhole formation during top electrode deposition, and self-assembled monolayer (SAM) defects.[1-3] Large-area junctions are usually fabricated by first pre-patterning a bottom electrode, followed by the formation of a SAM layer, and deposition of the top-electrode; these junctions can be obtained in high yields (>90%) with small spreads of data, but usually a certain technique works well for a limited number of chemical structures and reproducibly between different groups is still an issue.[1-4] In general, patterning of the bottom-electrode usually involves photolithography but the role of residual resist is unknown, and bottom-electrodes have been used obtained from direct deposition methods. These methods yield surfaces with a relatively large root-mean-square (rms) surface roughness with residual resist contaminations at which SAMs cannot pack well.[5]

Template-stripping is a method that generates ultra-smooth and clean metal surfaces on demand, support high quality SAMs, and can be incorporated in large-area junctions using the EGaIn techniques,[5, 6] cpAFM based techniques,[7] plasmonic device,[8] and STM.[8] This process, however, requires the use of an adhesive which is not stable in most solvents.

The "EGaIn technique" is a versatile method to form non-invasive contacts to SAMs. EGaIn stands for eutectic mixture of Ga and In (75% Ga and 25% In by wt.) and it is coated with a thin conductive layer of GaO_x (predominantly GaO_x) which gives this material non-Newtonian properties. Therefore, GaO_x/EGaIn can be stabilized in microchannels or through-holes in polydimethylsiloxane (PDMS) or shaped into cone-shaped tips which can be used to contact SAMs. The cone-shaped tip method is a relatively straightforward approach to yield statistically large number of junctions, while junctions with EGaIn stabilized in PDMS make it possible to measure the electrical properties of junctions over a moderate range of temperatures (about 200 – 300 K). In general, all EGaIn based methods give junctions in >90% yields with good reproducibility and are compatible with a large variety of SAMs.

The length and temperature dependent charge transport characteristics of a molecular junction are main tools to understand the mechanism of charge transport across molecular junctions as well as the define junction "quality". The electrical characteristics of the junctions are described by the general tunneling equation (1),

$$J = J_0 e^{(-\beta d)} \qquad (1)$$

Where β (n_c^{-1}) is the tunneling decay coefficient, J_0 (A/cm^2) is the contact resistance and d is the effective distance between the electrodes. Defects in junctions that lower the value of d (or thin-area defects) induce disorder in the SAMs, thereby resulting in high values of J_0, and a small fraction of thin-area defects in the junctions may dominate the electrical characteristics. Defects that increase the value of d (or thick-area defects) cause low values of J_0 and are mainly the result of physisorbed particles. In large area junctions, parasitic capacitance must be regarded as a parameter that limits the usage frequency and switching speed of the device.

Recently, many "testbeds" have been developed and focused on the improving the highly stable, "defect free", cost effective devices that are compatible with molecular functionality, generate high yield of working junctions and allow large scale fabrication with simple fabrication steps. We use carbon paint as a protective layer to protect SAMs from pinhole formation during the deposition of the Au top electrode. Graphite flakes are made of large grains that prevent filaments from entering the micro-pore during the Au deposition. This device allows us to fabricate large-scale fabrication of molecular electronics device.

2. Results and discussion

We report a method to fabricate a molecular tunnel junctions (Fig. 1) based on SAMs in micropores fabricated on ultra-flat template stripped bottom electrodes of Au which have not been exposed to resist during the entire fabrication process (detailed procedure will be presented). The micropores are etched into AlO_x using a two-step

etching process where first a pattern in resist on top of the AlO_x layer was transferred into the AlO_x layer of 35 nm via deep reactive ion etching to yield 10 nm deep pores followed by removal of the resist and a second etch with NH_4F to yield micropores with exposed Au. The quality of junctions was characterized by length and temperature dependent charge transport measurements across a series alkanethiolate SAMs inside the micropores which were contacted via EGaIn stabilized in microchannel aligned over the micropores.

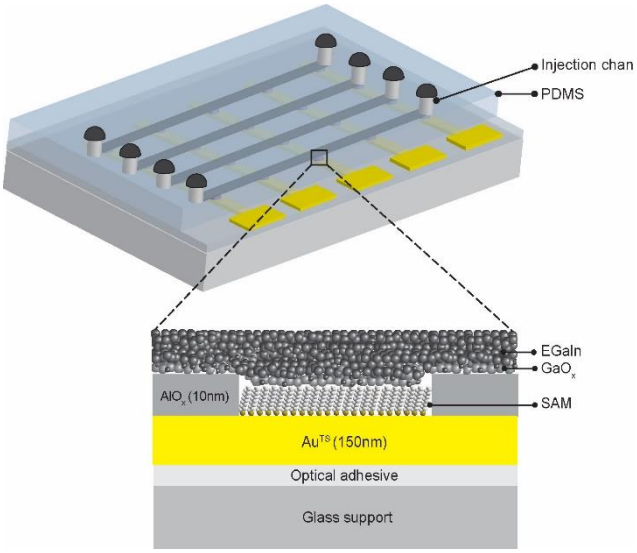

Fig. 1. Schematic illustration of (A) an array of micropore device and cross section view of molecular junctions fabricated using the two step etching, ultra-smooth bottom electrode and EGaIn top-electrode stabilized in a microchannel in a rubber stamp (made of polydimethylsiloxane; PDMS).

The electrical characterization of microprobe device shows *J* values of the n-alkanethiolate decrease exponentially as the number of carbons increases (the distance between top and bottom electrode d), which suggests tunneling is the dominant process for conduction in these working junctions. Based on the general tunneling equation (1), linear fitting of length dependent *J* value yields the tunneling decay coefficient $\beta = 1.02 \pm 0.02$ per carbon and $\log|J_0|$ of 4.20 ± 0.1 A/cm^2. The value of β is very close to the consensus value and $\log|J_0|$ are very close to previously reported values obtained for EGaIn stabilized in a through hole PDMS device and cone shaped EGaIn junctions formed with Au^{TS} substrate, from which we conclude that we formed high quality molecular tunnel junction in micropore device. We used impedance spectroscopy to study the presence of parasitic capacitance and the quality of the micropore device. We also analyzed *I-V* curve using well known models widely used in studies on charge transport through molecular devices. The extracted characteristic parameters from the models are compared with other EGaIn based platforms such as junctions formed with cone shaped EGaIn and EGaIn stabilized in a through hole PDMS device.

We developed a new fabrication method to construct molecular electronic devices which is compatible with ultra-flat, template-stripped bottom-electrodes and allows large-scale fabrication. We use carbon paint as a protective layer to protect SAMs from pinhole formation during the deposition of the Au top electrode. Graphite flakes are made of large grains that prevent filaments from entering the micro-pore during the Au deposition. The electrical characteristics of the device are characterized by length and temperature dependent charge transport through alkanethiolate SAMs formed inside the micropore device. The yield of working junctions in this method was found to be 68%. Charge transport studies were shown to be temperature independent, indicating that through-molecular bond tunnelling dominates. We observed a β of 1.04 ± 0.03 nc^{-1} which is similar to the β observed in junctions formed with EGaIn ($\beta = 1.04 \pm 0.06$ nc^{-1}) and higher than that of PEDOT:PSS ($\beta = 0.66 \pm 0.06$ nc^{-1}) and rGO protection layer ($\beta = 0.66 \pm 0.01$ nc^{-1}) based junctions. We suggested that defects induced by the surface roughness of the bottom electrode were reduced and that carbon paint was used as non-destructive protection layer.

3. Conclusions

The electrical characteristics of the device are characterized by impedance, length, and temperature dependent charge transport through alkanethiolate SAMs formed inside the micropore device. The micropore device provide access to a wide range of molecular system and temperature for charge transport studies as compared to other EGaIn, PDOT:PSS, graphene production layer based platforms. Additionally, the junctions within the device have good stability under continued voltage cycling (>5000 cycles) and bias stressing (up to 2×10^5 s). Therefore, we conclude that micropore device of SAM-based junctions are of good quality and this device can be used to measure detailed charge transport properties of molecules in wide range of temperature. Carbon paint was found to be a viable protection layer in the fabrication of this defect free bottom electrode ME device. The detailed characterization of microprobe device and their chemical functionality as well as utilization of this device for large-scale fabrication of molecular electronic device will be presented.

Acknowledgements

We also acknowledge the Ministry of Education (MOE) for supporting this research under award No. MOE2015-T2-2-134. Prime Minister's Office, Singapore under its Medium sized centre program is also acknowledged for supporting this research.

References

[1] Vilan, A.; Aswal, D.; Cahen, D. *Chemical Reviews* 2017, *117*, 4248-4286.
[2] McCreery, R. *Chemistry of Materials* 2004, *16*, 4477-4496.
[3] Jeong, H.; Kim, D.; Xiang, D.; Lee, T. ACS Nano **2017**, 11, 6511−6548.
[4] Xiang, D.; Wang, X.; Jia, X.; Lee, T.; Guo, X. Molecular-Scale Electronics: From Concept to Function. Chem. Rev. 2016, 116 (7), 4318−4440.
[5] Yuan, L.; Jiang, L.; Zhang, B.; Nijhuis, C. A. *Angew. Chemie - Int. Ed.* **2014**, *53*, 3377–3381.
[6] Kumar, K. S.; Jiang, L.; Nijhuis, C. A. *RSC Adv*. **2017**, 7, 14544–14551.
[7] Castañeda Ocampo, O. E. C.; Gordiichuk, P.; Catarci, S.; Gautier, D. A.; Herrmann, A.; Chiechi, R. C. *J. Am. Chem. Soc*. **2015**,137, 8419−8427.
[8] Yoo, D.; Johnson, T. W.; Cherukulappurath, S.; Norris, D. J.; Oh, S. H. *ACS Nano* **2015**, 9, 10647−10654.
[9] Baserga, A.; Vigano, M.; Casari, C. S.; Turri, S.; Li Bassi, A.; Levi, M.; Bottani, C. E. *Langmuir* **2008**, 24, 13212−13217.