

Nanoscale Engineering of Inorganic-Organic Interfaces: Applications to Molecular Scale Electronics

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Our work focuses on developing novel chemical approaches to forming well-behaved and robust interfaces between small organic molecules and both conducting and insulating inorganic ultrathin films for applications in molecular scale electronics. Much of the success of present day microelectronics is due to the ability to integrate a variety of (mostly) inorganic materials into structures useful for devices. For example, silicon dominates the field not because of its intrinsic electrical properties, but because of the quality of the interfaces it forms (e.g., the Si-SiO₂ interface). The work we are conducting seeks to develop organic-inorganic interfaces possessing equivalent or superior properties, where small organic molecules form the active layers. We believe that the solution lies in the development of chemically based approaches to the formation of the critical interface between the inorganic layers (both metallic and dielectric) and the organic layers. Success in this venture requires the application of sophisticated synthetic organometallic chemistry, surface and interface science, self-assembly and nanofabrication, and “chemically accurate” computer simulation. Our team has also been actively involved in the development of a *Workshop on Research Ethics*. From the experience of both working to develop and attending this workshop the participants have built a better understanding and recognition of responsible research conduct.

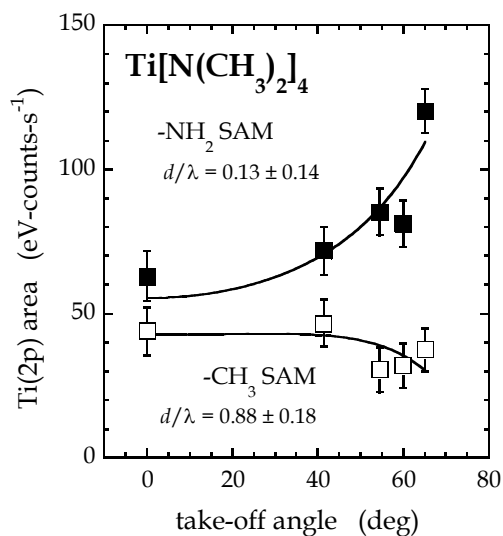


PROGRESS TO DATE

In the first 1-¹/₃ years of our NIRT project we have focused on recruiting graduate students to our Team, initiated our first experiments and computer simulations, and organized and conducted our first *Workshop on Research Ethics*. Briefly we have recruited 4 graduate research assistants to the Team, and plan to recruit an additional member (possibly a postdoc) in the upcoming year. Our first experiments and computer simulations have focused on three areas: (i) examinations of the reactions of transition metal complexes with self-assembled monolayers (SAMs) possessing a variety of organic functional tail groups; (ii) computer simulation of these same classes of reactions, focusing on molecular-level, first principles quantum mechanical total energy calculations; (iii) synthesis of unique transition metal complexes for formation of what we have termed seeded self-assembled monolayer structures; (iv) and examination of alternative methods for the formation of metal-organic interfaces. Progress has been made in all four areas, which we believe will result in new solutions to the “top contact problem” in molecular electronics.

Reactions of transition metal complexes with SAMs

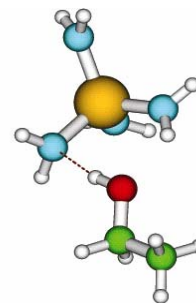
Concerning issue (i) described above, we have examined the reaction of the titanium precursor, tetrakis(dimethylamino)titanium (TDMAT), with model organic surfaces [self-assembled monolayers (SAMs) terminated by $-\text{OH}$, $-\text{NH}_2$ and $-\text{CH}_3$ groups] using X-ray photoelectron spectroscopy (XPS) and molecular beam scattering. Trichlorosilane self-assembled monolayers on SiO_2 have been chosen here to serve as model SAMs for molecular electronics. Briefly, we find that the reaction of TDMAT with these self-assembled monolayers is self-limiting (the desired result). We find that the $-\text{OH}$ and $-\text{NH}_2$ terminated SAMs exhibit high reactivity towards TDMAT, whereas the $-\text{CH}_3$ terminated SAM exhibits much lower reactivity. Angle-resolved XPS results



(figure at right) indicate that the Ti formed on the $-\text{NH}_2$ terminated SAM is essentially at the surface, most likely bound to the SAM via the terminal $-\text{NH}_2$ group. The Ti formed on the $-\text{CH}_3$ terminated SAM however is buried below the surface of the SAM, most likely bound to the underlying SiO_2 surface. Reaction on the $-\text{OH}$ terminated SAM was intermediate—there appeared to be reaction at both the terminal $-\text{OH}$ group and at the SAM/ SiO_2 interface. These results suggest that even for an organometallic species, penetration and reaction at the SAM-substrate interface is possible. The results with the $-\text{NH}_2$ terminated SAMs are most encouraging from the viewpoint of forming top contacts for molecular electronics.

Computer simulation of reactions at inorganic-organic interface

Concerning issue (ii) described above we have conducted a number of calculations using the Gaussian suite of programs. Most single point energy calculations were made using density functional theory using, for example, the B3LYP functional and a 6-311+G(2d,p) basis sets. Initially, our model transition metal complex was $\text{Ti}(\text{NH}_2)_4$, but more recently we have modeled $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$. A number of molecules were chosen as attacking ligands: NH_3 , CH_3NH_2 , $\text{NH}(\text{CH}_3)_2$, $\text{CH}_3\text{CH}_2\text{NH}_2$, $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$, CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3SH , $\text{CH}_3\text{CH}_2\text{SH}$. Briefly, these calculations indicate that reactions with the $-\text{OH}$ containing molecules should be fast and proceed with virtually no activation barrier (transition state for the $\text{Ti}(\text{NH}_2)_4 + \text{CH}_3\text{CH}_2\text{OH}$ reaction is shown at right). Reactions with the $-\text{NH}_2$ groups are predicted to be activated, however, the barriers are sensitive to nearby $-\text{NH}_2$ groups, and this “excess” $-\text{NH}_2$ can catalyze these reactions by lowering the barrier.



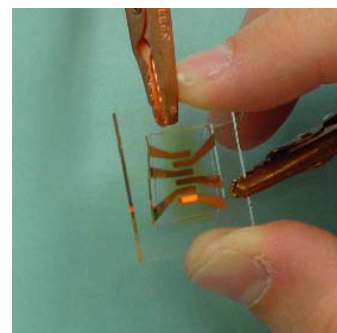
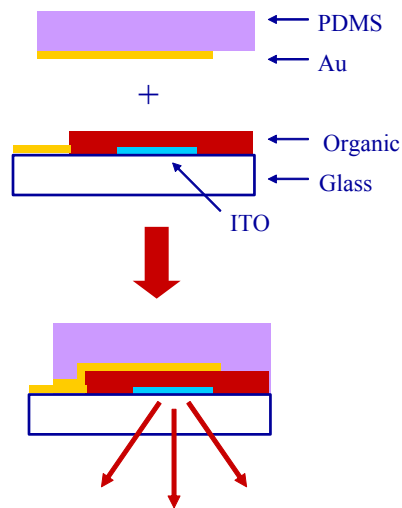
Synthesis of unique transition metal complexes

We have developed a general procedure for the synthesis of a π -conjugated organic linker that will bind to a noble metal surface via a thiophene group at one terminus, and can be covalently attached to an early transition metal via an amide bond derived from an amine. Using established coupling reactions, including a final connection derived from a Pd/Cu catalyzed procedure, this convergent synthesis has thus far yielded (2-thiophenyl)CC(*p*-C₆H₄)CC(*p*-

C_6H_4NHR) [$R = H$ (AH_2), iPr (AH^iPr)], and lends itself to further modification of R . Using $M(NMe_2)_4$ ($M = Ti, Zr$) as a precursor, aminolysis reactions have been used to prepare coordination compounds bearing A . 1H NMR spectral evidence suggests that for $M = Zr$, the complex $AZr(NMe_2)_3$ may be cleanly prepared, but that the sterics and solubility of the amine greatly affect the ease of attachment.

Alternative methods for the formation of metal-organic interfaces

In addition to examining methods to form inorganic-organic interfaces that make use of transition metal complexes and self-assembled monolayers (SAMs) possessing a variety of organic functional tail groups, we are also examining alternative, less chemically-inspired approaches. Examination of these techniques for metallization can provide “standards” against which our novel approaches can be benchmarked. In this spirit, we are examining the use of a “lamination” technique for the formation of contacts between Au electrodes and organic thin films. The technique involves first the deposition of a thin film of Au on an elastomer [typically poly(dimethyl siloxane), PDMS] and, second, subsequent lamination with an organic thin film. We have used this technique to form Au electrodes on organic electroluminescent devices. We chose this type of organic thin film for our first demonstration because it enables an easy check for contact uniformity: Observation of the emission (see figure at right) shows that the lamination is uniform over an area of 3 mm^2 . The current density and efficiency measured for the device was found to be consistent with the formation of an ohmic contact at the Au/organic interface.



Workshop on Research Ethics

Our major outreach activity was associated with our *Workshop on Research Ethics*, that was held June 2-3, 2003 at Cornell University. This Workshop involved the P.I. and all 4 co-P.I.'s in the NIRT, 5 other senior participants, and 11 graduate students/postdoctoral research associates. The 5 senior participants included Prof. Paul McEuen (who played a key role in “blowing the whistle” in the Bell Labs/Schön case), Dr. Phil Szuromi, a Senior Editor from *Science* magazine (also with connections to the Schön case), Prof. Michele Moody-Adams, Director of the Ethics and Public Life Program at Cornell, Dr. Kathy Vaeth, a Research Scientist at Kodak, and Mr. Ernie Davis, a staff member at the Cornell Research Foundation. A number of topics were discussed at our 2-day Workshop, and we will be developing a report of our findings, which we plan to include on our NIRT web page that we are developing. The Bell Labs/ Schön case was used as an example of what can go wrong, and a number of scenarios sparked discussion concerning issues such as the integrity of research, credit in research and publications, confidentiality and proposal/manuscript review, and intellectual property.

References

[1] For further information about this project contact Prof. James R. Engstrom (jre7@cornell.edu).