Towards Molecular Electronics: Using Electroless Deposition to Deposit Nano-objects

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We describe recent developments in our laboratory on the selective deposition of metals and deposition of metallic nanowires using electroless deposition (ELD). This work has important applications in molecular and organic electronics, sensing, biotechnology and photonics. These methods are easily parallelized, afford precise nanoscale placement and are compatible with photolithography. We illustrate our approach by giving two examples: the selective deposition of Cu on –COOH terminated self-assembled monolayer (SAMs), and the *in situ* deposition and precise placement of Ni and Cu nanowires on organic surfaces.

Selective deposition of copper is of particular interest because it is often employed as an interconnect material. Previous studies have demonstrated that Cu can be selectively deposited on –COOH terminated SAMs using ELD. These films nucleated by forming Cu^{2+}-carboxylate complexes with the SAM terminal group. Unfortunately, the deposited films were rough and contained irregular crystallites and the copper penetrated through the film. We have recently demonstrated that copper can be selectively deposited on –COOH terminated SAMs with improved morphology and without penetration of copper through the organic layer. The method employs a Cu(II) seed layer and an additive, adenine or guanine. The efficacy of this method is shown on photopatterned –COOH/–CH_3 SAMs. Copper deposits only atop the –COOH terminated SAM area and not on the –CH_3 terminated SAM. The use of a Cu(II) seed layer increases the Cu ELD rate on both –COOH and –CH_3 terminated SAMs. However, the deposited copper layer only strongly adheres to the –COOH terminated SAMs because the copper layer nucleates at Cu^{2+}-terminal group complexes. In contrast, for –CH_3 terminated SAMs the deposited copper layer can easily be removed because there is no specific surface interaction. The additives adenine and guanine mediate the interaction of Cu^{2+} and the deprotonated –COOH terminated SAMs via the formation of additive–carboxylate complexes. These complexes lead to a significant reduction of copper penetration through the SAM. In the case of adenine, the diffusion of copper through the organic film was eliminated.

We have recently introduced a promising new technique electroless nanowire deposition on micropatterned substrates (ENDOM), by which to direct the growth of metallic nanowires. Our approach for the construction of nanowires begins with a single SAM layer deposited and UV-photopatterned using standard techniques. We then employ seedless, selective ELD to deposit metallic nanowires at the interface of SAMs by careful control of the reaction conditions. A nanowire forms at the junction of two dissimilar SAMs, or other surfaces, if the following conditions are met. First, metal deposition is kinetically favored on one of the materials because of the preferential adsorption of the reducing agent. Second, the transport of the reactants must be slower to the surface with the faster electroless deposition rate.

We illustrate this process by deposition of Ni, Cu, Pd and other nanowires on patterned –OH/–CH_3 SAMs. We exploit the different deposition rates electroless deposition of metals using dimethylamine borane (DMAB) on –CH_3 and –OH terminated SAMs to deposit nanowires. The deposited nanowires are long (centimeters) and uniform in diameter, and can be patterned in continuous paths with arbitrary shapes, such as a right-angled turn. In this paper we discuss the reaction pathways involved in the formation of these nanowires including the nucleation sites and the dependence of the nanowire growth on pH and deposition temperature.

ENDOM is generally applicable to the preparation of metallic, semiconducting, and even insulating nanostructures on many technologically relevant substrates. This is because DMAB is a versatile reducing agent which can be used to deposit a wide range of materials. Furthermore, ENDOM can also be employed using other Lewis acid/base or ionic reducing agents, for example, sodium borohydride,which allows even greater synthetic flexibility. Finally, since this technique does not require expensive lithographic equipment or a clean room, it will enable the development of new methods to create sensors and other nanotechnological devices.