6 Self-Assembled Monolayers for Molecular Nanoelectronics

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Summary. In this chapter, we describe recent progress related to organic self-assembled monolayers (SAMs), ranging from the basic properties of SAMs to their application in molecular nano-electronics. The molecular arrangements and chemical properties of organosulfur SAMs on Au surface have been characterized using surface sensitive techniques, such as scanning probe microscopy, which have revealed that the organic molecules in the SAM were well ordered and densely packed. Also, nanoscale pattern formation in SAMs has been demonstrated using several self-organized methods, such as fill-in or co-adsorption techniques. The electrical conduction through SAMs was examined by scanning probe microscopy and using other other nanogap electrodes. In some conjugated molecules, a large negative differential resistance and memory device operation were reported. These interesting physical phenomena will provide us with ideas for the realization of nanoscale molecular devices.

6.1 Introduction

Organic molecules can be synthesized with unique properties that could be used to promote their self-assembly with one another and on specific surfaces, and to perform functions that could allow electronic-device operations. New conductive conjugated molecular wires have been found or synthesized for the purpose of constructing molecular devices. Self-assembled monolayers (SAMs) (Fig. 6.1) [1] provide a convenient technique to fix these functionalized organic molecules on suitable metal or semiconductor substrates. In particular, SAMs made from organosulfur compounds on an Au surface have been utilized for demonstration of nanomolecular electronics devices [2,3], because of the ease of formation of Au–S chemical bonds. Also, the fabrication of nanoscale structures using SAMs has attracted much attention; it is possible to form device-like structures such as nanodots [4] and nanowires [5]. For future application in nanoscale molecular devices, it is essential to explore new methods of using self-organization to obtain smaller nanoscale patterns and control the nanoscale structure. Here we describe recent progress in SAMs, mainly in relation to recent work in molecular nanoelectronics.
6.2 Basic Properties of Organosulfur SAMs on Au Surfaces

First, we describe the basic properties of organosulfur SAMs formed on Au surfaces. It is well known that organosulfur compounds react with Au surface. Taniguchi et al. observed the spontaneous formation of pyridine disulfide SAMs on an Au surface in 1982 [2]. Nuzzo and Allara reported the formation of alkanethiol SAMs in 1983 [3]. Typically, alkanethiols or dialkyl disulfides are utilized for organosulfur SAM formation. Dialkyl monosulfides can be also used for the same purposes [6–10]. However, the molecular arrangement and the strength of chemical bonding are different from those of alkanethiol or dialkyl disulfide SAMs. Typically, the Au(111) surface has been used for SAM formation because of the ease of preparation and stability of the crystal face. For other Au crystal faces, some studies have been performed, for example of SAMs on Au(100) [11]. However, the number of such studies is quite small.

(a) Monomer Structure (alkylthiolate)

(b) Dimer Structure (disulfide)