Materials Science in Semiconductor Processing 17 (2014) 168–172

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Functionalization of Si(1 0 0) surface with benzonitrile molecules in an ultra-high-vacuum molecular evaporator

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ARTICLE INFO

Available online 18 October 2013

Keywords:
Organic molecules
Molecular deposition
Semiconductor substrate
Ultra-high-vacuum scanning tunneling microscopy

ABSTRACT

We investigated benzonitrile adsorption on Si(1 0 0) deposited in a home-made molecular source using scanning tunneling microscopy (STM). A high-purity molecular source was constructed for evaporation of organic molecules in the liquid phase. The molecular flux and deposition rate are stable over time and yield good control of the coverage level to less than one monolayer. The method described for creation of a molecular beam can be extended to various molecules in the liquid phase under ambient conditions and substrates. To confirm the reliability of our results, we used benzonitrile molecules on Si (1 0 0) as a substrate that is highly demanding in terms of the vacuum quality (residual gases and impurities) and level. The results were compared with previously obtained results using STM and theoretical methods. This simple molecular source yields enhanced measurement possibilities for different experimental systems without the need for significant investment or system modifications. A simple model is presented to predict the expected coverage and to evaluate device parameters appropriate for the evaporated material.

1. Introduction

Miniaturization of electronic devices has led to the need for greater numbers of smaller structures. Organic molecules are among the smallest structures appropriate for applications in nanoelectronics. It is expected that they could be used as the active part in devices such as single electron transistors [1], organic thin-film transistors [2] and nanoswitches [3]. Therefore, the physical and chemical properties of individual molecules adsorbed on various types of substrate are widely investigated using different surface-sensitive experimental methods, including scanning probe microscopy [4–8].

Ultra-high vacuum (UHV) conditions are necessary to obtain and maintain clean semiconductor substrates for most applications. Creation of a controlled and stable molecular beam is not simple and is strongly dependent on the vacuum quality. For organic compounds that are in the solid state under normal conditions, a thermal evaporator with heated quartz glass (Knudsen cell) [9,10] or ceramic pipes [6,11] are typically used. However, the creation of a stable and pure molecular beam under UHV conditions is a very complex and resource-consuming task for compounds that are in the liquid phase under normal conditions. One possible method is direct solution injection, but the cleanness cannot be monitored as the injection times are very short (in ms range) [12]. This method is only suitable for nonpolar molecules because the electric field due to electrodes on the piezoceramic element of the valve blocks the injection of molecules into the vacuum. Electrospray deposition systems are effective and clean but are expensive and quite large, so they are not easily mountable in existing systems [13]. A common practice is to generate the molecular vapor in an additional vacuum chamber connected to the preparation vessel to minimize contamination of the

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http://dx.doi.org/10.1016/j.mssp.2013.09.006

UHV system. Deposition is achieved by momentary exposure of the substrate to the molecular beam by opening the valve separating the two chambers [11,14].

Our proposed molecular source is a clean, simple, and cost-efficient method for molecules that are in the liquid phase under normal external conditions. The design is quite simple and to the best of our knowledge has not been reported before. Its compatibility with highly polar molecules and the possibility of monitoring cleanness using mass spectroscopy before sample exposure are the main advantages. We demonstrate that surface functionalization using our device gives results consistent with previous experiments [15]. This approach could be useful for the creation of various molecular layers on substrates. The only limitation is the requirement for an initial liquid phase for evaporated molecules.

2. Experimental setup

All experiments were performed in the UHV system at a base pressure of 1×10^{-8} Pa. The main part of the UHV system is equipped with an Omicron scanning probe microscopy head operating at room temperature and an OCI low-energy electron diffraction/Auger electron spectrometer capable of standard sample preparation (sputtering, heating/cooling, metal evaporation). A single DN40 outlet conflat (CF) flange targets the sample stage. This flange is used to attach the molecular chamber via a gate valve. The molecular chamber is mounted after full evacuation and heating of the UHV system and is independently pumped by a combination of rotary and turbomolecular pumps. A cold cathode gauge and a Hiden Analytical mass spectrometer (equipped with a channel electron multiplier detector and an ion counting system) are used to control the pressure and composition of the gas inside this chamber.

All scanning tunneling microscopy (STM) images were obtained using tungsten tips that were electrochemically etched and sputtered in situ with Ar^+. The bias voltage applied to the sample was kept in the range ± 2.5 V, the tunneling current was varied from 50 to 150 pA, and the typical scanning frequency was 1 Hz.

3. Evaporator design

The UHV molecular source is connected to the molecular chamber using a precision dosing valve. This valve allows control of the quantity of molecules in the chamber during preparation. The molecular source construction is based on the commercial Swagelok high-purity gas transfer system. It consists of 10-cm-long pipe (outer diameter 6 mm), a needle valve and a short pipe welded at the end to create a very small (~ 0.5 cm^3) container for storing the molecular liquid (Fig. 1).

The set-up should be assembled so that the needle valve and the cup point downwards at all times to avoid flooding of the pipe and the needle valve. The length of the pipe is determined by the saturated vapor pressure of the chosen molecule. The lower the saturated vapor pressure, the longer the tube should be to achieve a well-defined and stable molecular beam. Conversely, the tube should be as short as possible because of the reduced pumping speed caused by the dosing valve. A greater Swagelok pipe volume should ensure an appropriate molecular concentration during deposition; however, it should also limit molecular condensation at the dosing valve. All components were alternately cleaned in isopropanol and acetone using an ultrasonic bath and then heated at ~ 420 K under nitrogen for 2 h in an ex situ oven to remove residual chemicals and water. The container was connected to the Swagelok needle valve and filled with benzonitrile liquid; all tasks were performed in a nitrogen atmosphere. The needle valve was closed and connected to the precision dosing valve (leak valve, Fig. 1) using the pipe ending in a DN16 CF flange. Opening of this valve creates a molecular vapor inside the longer pipe of the evaporator; it is opened only for the length of time necessary for the vapor to form. The set-up is compatible with all liquid compounds that do not dissolve the fittings of the leak valve.

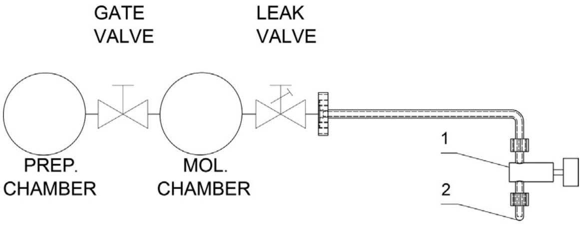

Fig. 1. Schematic of the evaporator design as described in the text. The gate valve is connected to the preparation chamber and directed to the sample in the preparation manipulator. 1, Swagelok needle valve; 2, molecular container (small welded cup).

The molecular chamber must be at as low a pressure as possible. This is achieved by pumping and simultaneous heating of the chamber at 473 K for approximately 48 h. The typical vacuum achieved is better than 1×10^{-7} Pa. The dosing valve is fully open during this procedure and this leads to the best possible cleaning of the evaporator element. When the target vacuum level is achieved, the dosing valve is closed and the line valve is opened for up to 1 min. During this time, a saturated molecular vapor arises in the evaporator tube. The dosing or leak valve is used to control the flow of the molecular vapor to the molecular chamber. The gas is controlled via mass spectrometry monitoring during transfer to the molecular chamber. The pressure in the molecular chamber is $\sim 1 \times 10^{-6}$ Pa before sample exposure. This pressure should be adjusted to obtain the desired deposition rate for a given substrate and deposition molecule.

This device has two key features. The first is the absence of an electric field, which makes it suitable for polar molecules, in contrast to an injection valve, and ensures a soft landing on the substrate. The second is control of the flow rate using a precision valve, which can be important for molecular self-assembly growth.

4. Experimental

An atomically flat Si(1 0 0) surface was obtained by thermal preparation under UHV conditions. Silicon substrates were cut from a commercial wafer and mounted in an Omicron direct heating sample holder for sample annealing under UHV conditions. This holder fits our manipulator system and facilitates sample transfer between the vacuum