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Flexible contact stamp for electrical conductivity measurements of a soft matter

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ABSTRACT

In this communication, a simple homemade four probe conductivity setup has been presented to measure the electrical conductivity of molecularly grafted and passivated solid surfaces. Setup was also extended for the temperature dependent conductivity measurements by designing a small furnace using nichrome heating element. The importance of prepared setup lies in its easy designing ability, portability and reliability to measure the conductivity of soft matters. Setup was designed for four probe conductivity measurements which can be used for two probes conductivity measurements also, depending upon the requirements under investigation. Setup was tested using its four probes for electrochemically grafted indium tin oxide surfaces with thiol containing organic molecules and trichloroethylene passivated Si surface. It was found very sensitive even for observing small changes in current–voltage values whereas recorded curves were quite reproducible.

1. Introduction

Soft functional materials, which include organic semiconductors, polymers, push–pull conjugated molecules, bio-molecules, nanomaterials and their guided assembly on metal and semiconductor surfaces as active interfaces, have received a considerable attention due to their potential importance in modern electronics [1–6]. Molecular electronics is also one of the important categories that is studied under the soft matter, here the suitably designed organic molecules are positioned between the electrodes to constitute molecular junctions [7–9]. The organic molecules as an active component permit an easy miniaturization of molecular junctions to realize the nanoscale devices, wherein individual molecules can be active components [10,11]. Here the main emphasis is to control the junction properties through the size, shape, length, conjugation and dipole moment of molecules to explore new device physics [12,13]. Further, it leads to ultrathin, flexible and low cost devices using simple bench chemistry [14,15]. In literature, a large number of simple, as well as complex techniques have been adopted for the self/guided assembly of organic molecules on different substrates to constitute electronic devices and to modify surface electronic properties [16–19].

The study of electron transport across soft functional materials is fundamentally important input information in the development of their devices. However, the establishment of external contacts on these structures is a challenging task [20,21]. Due to soft and fragile nature of these assemblies, sophisticated methods are required to establish the electrical contacts. In the case of monolayer assembly of organic molecules, several approaches have been already published in the literature describing different methods to form proper contacts. Most popular and common approaches include mercury (Hg)-drop contact(s) [22,23], Hg-column setup [24], lift-off float-on (LOFO) [25,26] nano transfer printing [27], spin coating and stamping of electrically conducting inks [28], modified methods of thermal evaporation [29] and the use of routine conducting pastes of silver and carbon [30]. More advance and expensive techniques using AFM and STM probes are also being used [11,31–33]. But all these techniques do suffer some or the other disadvantages, for example, the Hg reacts with many samples and easily forms an amalgam, LOFO needs a good skill to deposit wrinkle free individual contacts, silver/carbon pastes and their solvents reaction leads to shorting of junctions. Hence, an innovative and simple laboratory setup with gentle electrical contacts, which is reusable, is highly desirable to characterize the soft interfaces. In the present work we report such a setup, which is simple, easy to fabricate, posses multiple strip contacts and is capable of measuring the electrical conductivity of almost all types of thin films including organic monolayers and chemically modified semiconductor surfaces. Further, it is designed to carry out temperature dependent conductivity measurements up to 130 °C in open air conditions.

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2. Experimental procedure

All the chemicals such as ethyl alcohol, trichloroethylene, hydrofluoric acid (HF), and acetone were supplied by sd-fine chemicals, India. Specific thiols such as thioglycolic acid ($HSCH_2CO_2H$), 1-heptanethiol ($CH_3(CH_2)_6SH$) and 1-dodecanethiol ($CH_3(CH_2)_{11}$-SH) were purchased from Sigma–Aldrich. Commercial single crystals of silicon, p-type, (100) orientation, 4 Ω cm resistivity and one side mirror polished and indium tin oxide (ITO) 10 ohm/sq were supplied by Semiconductor Wafers Inc., Taiwan.

These were used as substrates to deposit organic monolayers and for chemical modification. Thioglycolic acid, 1-heptanethiol and 1-dodecanethiol were electro grafted on ITO surface under the anodic condition and silicon surface was modified with hydrofluoric acid (HF) and trichloroethylene (C_2HCl_3). In a typical procedure, ITO was degreased well with soap solution followed by washing with copious amount of triple distilled water then sonication in ethanol solution for more than 15 min. This was anodically polarized in 0.05 M of the above molecular solution in ethanol for the current density 0.025 mA/cm^2 for 60 min. Then the resulting ITO was washed neatly with ethanol and dried in open air condition for charge transport measurements. In the case of silicon, the starting material was etched in dilute HF: H_2O solution for few minutes to remove native oxide. In one case the conductivity was measured for the freshly HF: H_2O etched sample and in the case such freshly etched sample was further treated with trichloroethylene for five minutes in open conditions to study the chemical treatment. The current–voltage measurements on all the above modified samples were measured in open air condition using a separate regulated DC power supply 0–32 V, 1A. The current was measured with Keithley 6512 electrometer and voltage with Keithley 197A digital multimeter. All the measurements were carried out using four probes configuration with appropriate corrections [34]. The thickness of present monolayers over ITO surface is estimated by ellipsometric measurements (using SENTECH SE850). These are carried out at an incident angle of 60° with a source of wavelength 670 nm. The average refractive index of organic monolayers is taken as 1.42 [35], that is commonly used by many researchers.

3. Experimental setup

A schematic diagram of our home made conductivity setup is shown in Fig. 1a. A vertical shaft (2) is mounted at the one corner of metallic base plate (7.2 cm × 7.2 cm and 0.9 cm) (14) to support the other arrangement. A thick (1.5 mm) glass plate (13) is fixed on the surface of this base plate to minimize the thermal loss and electrical shorting of conductivity probes. An aluminum block (3) (7 cm × 3.8 cm and 2.3 cm) having two holes at the extreme ends on its length is made. It is fixed through a back screw (4) to the vertical shaft such that the other hole directly projects almost on the centre of base plate. Using the back screw the position of this block can easily be adjusted to the desired height from the base plate. An another light weight shaft (1) made up of aluminum is taken, at the bottom face of this, a flexible layer of polydimethylsiloxane (PDMS) (9) (thickness = 2 mm) is fixed with glue and over which a plastic strip (8) containing flat copper contacts coated with gold are carefully mounted (such polyester strip cables are available commercially in computer market as accessories), these are further extended to make electrical connections with measuring meters. In the present case, there are four flat contacts having length 4.0 mm, breadth 0.56 mm, thickness 0.05 mm and separation between the probes is 0.43 mm. The contacts are physically bonded to the polyester strip and in turn, the strip is attached to PDMS. The expansion of polyester is not much upon heating in the range 25–100 °C and hence, there will not be any displacement in contacts [36]. The soft polymer (PDMS) spacer between aluminum shaft and electrical contacts strip is quite flexible and it gets compressed easily for a small applied load. This is mounted through the second hole in aluminum block and is loaded through a spring (5) as shown in Fig. 1a, the spring pressure can be adjusted by changing the position of a small acrylic base (7) with a screw (6) at the bottom of spring. To reduce the friction between this shaft and hole in the aluminum block, these surfaces were applied with graphite powder as a solid lubricant. This entire assembly acts a flexible contact pad that can be lifted and gently lowered on the desired sample surface (10). An expanded view of this contact assembly is shown in Fig. 1a as an inset. Furthermore, this setup was also extended to measure temperature dependent electrical measurements by making a small furnace using copper cup (11) (diameter = 4.5 cm and height = 2 cm), it is chosen such a way that the sample and contacts lie almost 10 mm below the upper edge of the furnace so that sample and contacts remain in a uniform heating zone. A nichrome heating element (12) is inserted in the copper cup with proper insulation and this miniaturized furnace produces a temperature close to 130 °C for 15 W. A real photograph of this setup is shown in Fig. 1b, it is simple, low cost and quite convenient for measuring the electrical conductivity of soft as well as the normal surfaces of given materials.

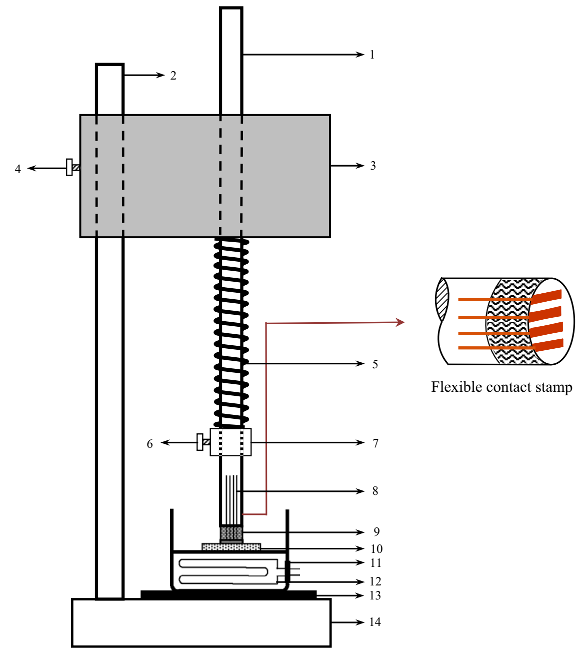

Fig. 1a. Schematic diagram of home made four probe electrical conductivity setup.

The organic molecules such as thioglycolic acid, 1-heptanethiol, and 1-dodecanethiol were electro-grafted on a cleaned ITO surface. A 0.05 mol solution of these molecules was prepared in ethanol and then electro-grafting was carried out by passing a constant current of 25 µA (J = 0.25 A m^{-2}) between ITO anode and platinum cathode for one and half hours. After the completion of reaction, the ITO was thoroughly washed in extra ethanol and dried under open air. ITO surfaces with different organic molecules were subjected to electrical conductivity measurements by the above setup.

Further, to check the reliability of our setup the surface conductivity measurements were also carried out on bare and chemically modified silicon surfaces. Here, the single crystal of silicon (p-type, boron doped, 4 Ω cm resistivity, one side mirror polished supplied by Semiconductor Wafers Inc., Taiwan) is chosen for the work. Bare silicon (as supplied) is left in open air condition for a long time of